

Gradient Interpenetrating Polymer Networks. II. Polyacrylamide Gradients in Poly(ether Urethane)

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Synopsis

The surface of poly(ether urethane) is modified by preparing gradient interpenetrating polymer networks (IPNs) with polyacrylamide hydrogels. Several experimental methods are used for preparing the gradient IPNs. Attenuated total reflection Fourier transform infrared (ATR-FTIR) is used as the main characterization technique.

INTRODUCTION

A method for preparing interpenetrating polymer networks (IPNs) from poly(ether urethane)s and polyacrylamide was discussed in Paper I of this series.¹ The method used was similar to that of Predecki,² who bonded poly(hydroxyethyl methacrylate) to silicon rubber by impregnating the monomer, crosslinker, and initiator in the rubber, followed by thermal initiation. We have shown that in distinction from that work, due to the special morphological properties of poly(ether urethane), the acrylamide monomer can be "directed" mainly to the soft phase of the poly(ether urethane) matrix. The physical crosslinks of the poly(ether urethane) thermoplastic elastomer are mostly preserved during impregnation and the ensuing polymerization. As mentioned in Paper I of this series,¹ the IPNs obtained could be categorized as pseudo-IPNs in view of the presence of chemical crosslinks in the polyacrylamide and physical rather than chemical crosslinks in the poly(ether urethane). In the present study we have concentrated on preparing gradients of polyacrylamide restricted to the surface of the poly(ether urethane). The idea of gradient structure was mentioned by Ferry³ in a discussion of gradients in the degree of crosslinking of a chemically homogeneous gel and their use for achieving unidirectional gradients in physical properties. Shen and Bever⁴ have differentiated between gradients in single phase and in heterophase systems; polymer mixtures were included in the latter. They remarked that the most intimate polymer mixture from the molecular point of view can be obtained by preparing interpenetrating polymer networks. Shen and Bever describe also the potential uses of gradient polymers based on their chemical, mechanical, and transport properties. In the present work the surface of poly(ether urethane) is modified by preparing gradient IPNs with polyacrylamide hydrogels. The method is not restricted to physically crosslinked polyurethane elastomers, which can be processed and shaped into different products. Moreover, the method could be applied in principle also to other

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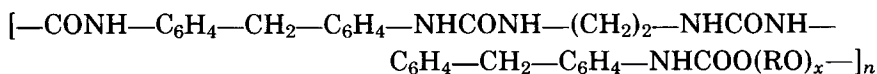
physically crosslinked elastomers. The choice of polyacrylamide hydrogels in this work was based on biomedical considerations; it was suggested in the literature⁵ that hydrogel surfaces in contact with blood remained clean and hence could be blood compatible.

Several different experimental methods for preparing gradient IPNs are discussed below. The main characterization technique chosen was attenuated total reflection Fourier transform infrared (ATR-FTIR).

EXPERIMENTAL

Materials

Poly(ether urethane) obtained from SRI International, Menlo Park, Calif., designated 3-2000-1-E by SRI⁶ (abbreviated PEU 3-2000 in this work), with the repeat unit



was prepared in a two-step process from diphenylmethane-4,4'-diisocyanate and polypropylene glycol with $(\text{RO})_x$ of average molecular weight 2000, using 1,2-diamino ethane as the extender (density: 1.071; molecular weight by GPC, using polystyrene standards: 100,000).

PEU 3-2000 films were cast from 15% w/w solutions in dimethylformamide on glass, dried at 75°C in a draft oven and extracted with ethanol and water consecutively. Sheet dimensions were 25 × 15 cm², with a fairly homogeneous thickness ranging for different sheets between 200–600 μm. These were cut with a scalpel knife into samples of usually 2.5 × 2.5 cm². Polymerization reagents included: acrylamide (Polysciences, Inc.) ultra pure grade, recrystallized three times from acetone; methylene bisacrylamide (MBA) (Polysciences, Inc.), recrystallized twice from methanol; azobisisobutyronitrile (AIBN) (Polysciences, Inc.) recrystallized twice from methanol; tetraethyleneglycol dimethacrylate (TEGDMA) (Polysciences, Inc.) used as received; poly(ethylene glycol 200) diacrylate (PEGDA) (Polysciences, Inc.) used as received and *n*-hexane and ethanol (Fisher Scientific Co.), analytical grade, used as received.

Preparation of Gradient IPNs

The methods used for the preparation of gradient IPNs were similar to those described in Paper I of this series.¹ Triplicate samples of poly(ether urethane) (PEU) film were shaken in a 1% Sparkleen detergent solution (Fisher Scientific Co.) for 30 min, and then washed with distilled water and dried. The samples were swollen in ethanolic solutions of acrylamide, initiator (AIBN), and cross-linker. The swollen samples were hung on nichrome hooks suspended from a glass stand located inside a 3-L glass reactor equipped with a condenser. Polymerization was induced by heating in refluxing *n*-hexane vapor (69°C). The polymerized IPNs were swollen in ethanol for several hours to extract unreacted monomeric species and decomposition products of the initiator. They were then immersed in distilled deionized water for 24 h to leach linear polyacrylamide

(PAM). Finally, the IPNs were dried under vacuum (1 Torr) at room temperature to constant weight. The swelling solution was 3*M* acrylamide in ethanol in most experiments, and the weight loss of PEU 3-2000 in this solution due to extraction¹ was 3.5–5% in 16 h at 30°C, depending on film thickness. The weight fraction of PAM in the IPN was calculated as: $W_{\text{PAM}}/(W_{\text{PAM}} + W_{\text{PEU}})$, and the water uptake capability of the PAM in the IPN was defined as $W_{\text{H}_2\text{O}}/W_{\text{PAM}}$, where W_{PAM} and W_{PEU} are the weights of polyacrylamide and poly(ether urethane) in the dry IPN, and the $W_{\text{H}_2\text{O}}$ is the weight of water in an IPN swollen at 30°C for 24 h. The calculation of the weight fractions defined above was described before.¹ Use of the following three methods to promote gradient formation in the IPN was studied. Each method involved some modification of the general method described above.

(a) Polymerization after short swelling times—in this method the PEU film samples were exposed to the swelling solution for a short period relative to the time needed for equilibrium swelling. Typical swelling times were between 5 and 30 min.

(b) Use of higher molecular weight crosslinking agent—in this method the relatively low molecular weight crosslinker MBA was replaced by TEGDMA. The higher molecular weight crosslinker was expected to penetrate the PEU film slower than MBA.

(c) Polymerization after differential diffusion of crosslinking agent—in this method the PEU specimens were first swollen to equilibrium in a solution in which only the monomer and initiator were dissolved, followed by a short immersion period in a solution with the crosslinker. In this way the crosslinker penetration was limited to layers relatively close to the specimen surface.

ATR-FTIR Spectroscopy

Attenuated total reflection infrared Fourier transform (ATR-FTIR) spectroscopy was used to characterize the composition of the IPNs. The instrumentation used consisted of a Digilab FTS-14 Fourier Transform Interferometer equipped with a Nova data processor which averaged 100 scans and analyzed the data.⁷ The crystal used was KRS-5 with 45° face angles, 2 mm thickness and a surface of 52 × 20 mm².

The ATR-FTIR method is well documented⁸ and will not be reproduced here. IPNs consisted of PAM and PEU, the PAM having a characteristic absorption at 1660 cm⁻¹ and the PEU having a characteristic absorption at 925 cm⁻¹. The absorption bands could be used to provide a measure of the composition of the IPN near the surface (to a depth of a few microns—see below).

Based on the Beer–Lambert relation and assuming that the instrument baseline is wavelength independent (this condition can be relaxed if necessary), one has the relation

$$\frac{A_2}{A_3} = \frac{1 - \exp[-(\mu_2^A c_A + \mu_2^U c_U)]}{1 - \exp[-(\mu_3^A c_A + \mu_3^U c_U)]} \quad (1)$$

where A_2 and A_3 are the measured absorbances at λ_2 and λ_3 of the ATR beam which penetrated to a depth d_p (see below) of the IPN. c_A and c_U are the con-

centration of PAM and PEU averaged over the IPN thickness from the surface to a depth d_p . $\mu_2^A, \mu_2^U, \mu_3^A, \mu_3^U$ are the effective extinction coefficients (including depth of penetration) at λ_2 and λ_3 for PAM (A) and PEU (U). Since $\mu_3^A \sim 0$ (i.e. extinction coefficient of PAM at 925 cm^{-1} is very close to zero), and all absorptions are fairly weak (so that all $\mu c \ll 1$), eq. (1) can be reduced to the linear relation

$$A_2/A_3 = \mu_2^U/\mu_3^U + \mu_2^A c_A/\mu_3^U c_U \quad (2)$$

where μ_2^U/μ_3^U and μ_2^A/μ_3^U can be evaluated by analysis of the spectra of known compositions. Use of the relation

$$c_A/c_U = \rho_A \phi_A / \rho_U (1 - \phi_A)$$

with

$$\phi_A = w_A \rho_U / [\rho_A + (\rho_U - \rho_A) w_A]$$

where ρ , ϕ , and w 's are densities, volume fractions, and weight fractions respectively, leads to a more useful form of eq. (2):

$$A_{1660}/A_{925} = k_1 + k_2 w_A / (1 - w_A) \quad (3)$$

where k_1 and k_2 are constants to be evaluated from the spectra of samples with known w_A (see below). The depth of penetration d_p of the specimen sampled by ATR-F'TIR calculated from the relation⁸:

$$d_p = \lambda / 2\pi (n_x^2 \sin^2 \theta' - n^2)^{1/2} \quad (4)$$

where n_x and n are the refractive indices of the prism (for KRS-5, $n_x = 2.4$) and the polymer, respectively, λ is the wavelength of the absorption band in vacuum, and θ' is the angle of incidence of the ray with the sample on the crystal (usually different from the angle θ of the ray with the prism, due to refraction effects that can be taken into account). The penetration depth is greater at longer wavelengths than at smaller angles of incidence (provided the angle of incidence is not below θ_c , the critical angle of incidence). In the present experiments, the angle θ was varied over the range 38.8° , 45° , and 53.8° , so that the depth of penetration was 8.5 ± 2.0 , 1.21 ± 0.02 , and $0.78 \pm 0.01\ \mu\text{m}$, respectively (in these calculations $n = 1.50 \pm 0.002$ for the polymer).

Electron Microscopy and Contact Angle Measurements

Scanning electron micrographs were taken on a Jelco-50A. Transmission electron micrographs were taken on a Phillips 200 Electron Microscope. Samples were stained by osmium tetroxide following Kato's procedure,⁹ and then embedded in epoxy resin¹⁰ which was cured at 60°C for 16–20 h.

Sections of 200–1000 Å thickness were microtomed at room temperature using a MT-2 Sorvall Microtome.

Contact angle measurements were carried out by Dr. Andrade¹¹ at the University of Utah. IPNs swollen in doubly distilled water for 96 h with two complete water changes during this period. All contact angles were measured on duplicate samples, immersed in doubly distilled water, using three air bubbles and three *n*-octane bubbles on each surface.

RESULTS

Preparation of Gradient IPNs

All IPNs prepared in Paper I were polymerized after equilibrium swelling.¹ As reported there, the swelling kinetics of PEU 3-2000 was fitted by the equation

$$W_t - W_0 = (W_\infty - W_0)(1 - e^{-kt}) \quad (5)$$

where W_0 , W_t , and W_∞ are the weights of a polymer specimen before swelling, swollen for a time t , and swollen to equilibrium, respectively. Here we report studies of three different methods for inducing gradient formation in the IPNs. In each case, ethanol was chosen as the swelling solvent since it was shown¹ that, with this solvent, acrylamide can be introduced into the PEU matrix with small distortion of the specimen.

The first method involved short immersion times of the specimen in the reactant solution (acrylamide, initiator, and crosslinker) followed by polymerization. It was shown in Paper I that the swelling rate in a 3M solution of acrylamide in ethanol was considerably slower than in pure ethanol ($k^{-1} = 76$ and 33 min, respectively), whereas the degree of swelling was higher in the solution than in the solvent [$(W_\infty - W_0)/W_0 = 2.14$ and 0.83, respectively]. The weight fraction of polyacrylamide (PAM) in the IPNs ($w = W_{\text{PAM}}/W_{\text{IPN}}$) obtained by this method from PEU 3-2000 could be fitted by the equation

$$w_t = w_\infty(1 - e^{-ct}) \quad (6)$$

where w_t and w_∞ are the PAM weight fraction in the IPN obtained by polymerization after swelling for time t and after equilibrium swelling, respectively. The time constant was $c^{-1} = 80$ min (in comparison with $k^{-1} = 76$ min) when the swelling solution concentration was 3M acrylamide in ethanol.

There was also good correlation between $W_\infty = 0.31$ obtained by polymerization after equilibrium swelling, and the acrylamide monomer equilibrium uptake (before polymerization) $W_{\text{AM}}/(W_{\text{AM}} + W_0) = 0.37$, where W_{AM} is the acrylamide component of $W_\infty - W_0$. The gradient IPNs prepared by this method had smooth and soft surfaces. The water uptake capability of the hydrogel in these

TABLE I
Effect of Time of Swelling on Polyacrylamide Gradient IPNs with PEU 3-2000^a

Time of swelling ^b (min)	$W_t^c = W_{\text{PAM}}/W_{\text{IPN}}$	$W_{\text{H}_2\text{O}}/W_{\text{PAM}}$
10	0.029	3.60
30	0.082	2.90
45	0.109	1.96
60	0.168	1.94
120	0.244	1.91
960	0.305	1.90

^a PEU sheets 1 mm thick.

^b Time of swelling in 3M acrylamide in ethanol with 1 mol % of crosslinker (MBA) and initiator (AIBN), respectively.

^c Polyacrylamide fraction in the gradient IPN.

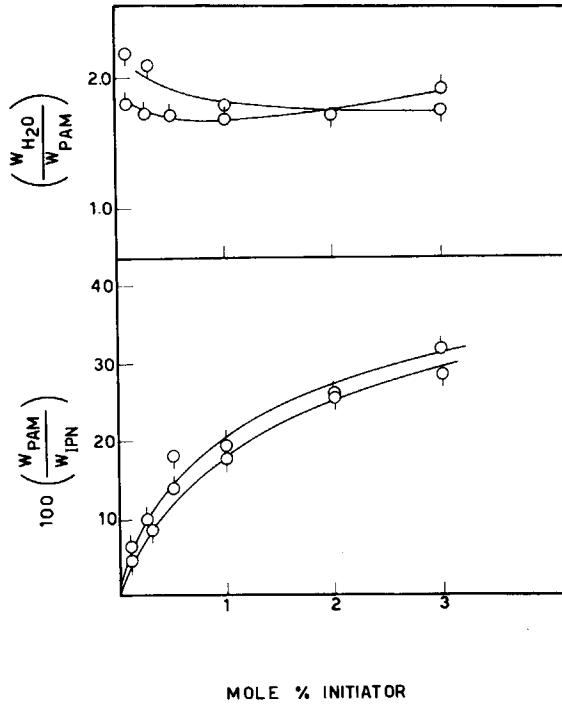


Fig. 1. Effect of initiator (AIBN) concentration on polyacrylamide fraction and water uptake of IPNs polymerized after equilibrium swelling of PEU 3-2000 films (thickness = 0.25 mm) with different crosslinkers: (○) 0.03M TEGDMA, 3M acrylamide/ethanol; (◻) 0.03M MBA, 3M acrylamide/ethanol.

specimens was higher, the shorter the time of swelling of the PEU sheet in the monomer solution, as seen in Table I.

The second method for inducing gradient formation was the use of higher molecular weight crosslinkers during equilibrium swelling of the specimen. The

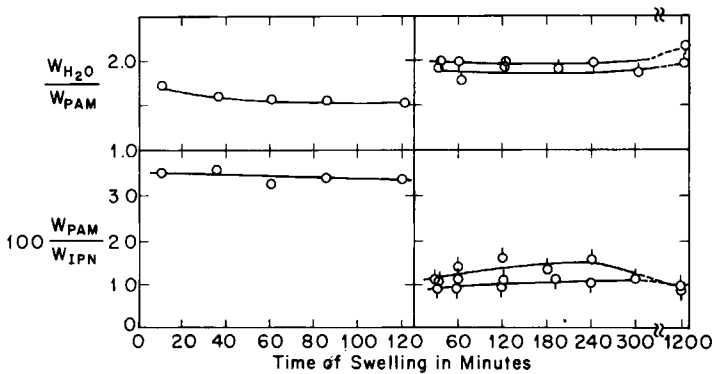


Fig. 2. Effect of time of exposure to the crosslinker solution (after initial equilibrium swelling in monomer and initiator solution) on polyacrylamide fraction and water uptake capability in IPNs prepared from PEU 3-2000 (thickness = 0.25 mm) with different crosslinkers: (○) 0.1M PEGDA, 3M acrylamide, 0.09M AIBN in ethanol; (◻) 0.03M MBA, 3M acrylamide, 0.006M AIBN in ethanol; (◊) 0.03M TEGDMA, 3M acrylamide, 0.006M AIBN in ethanol.

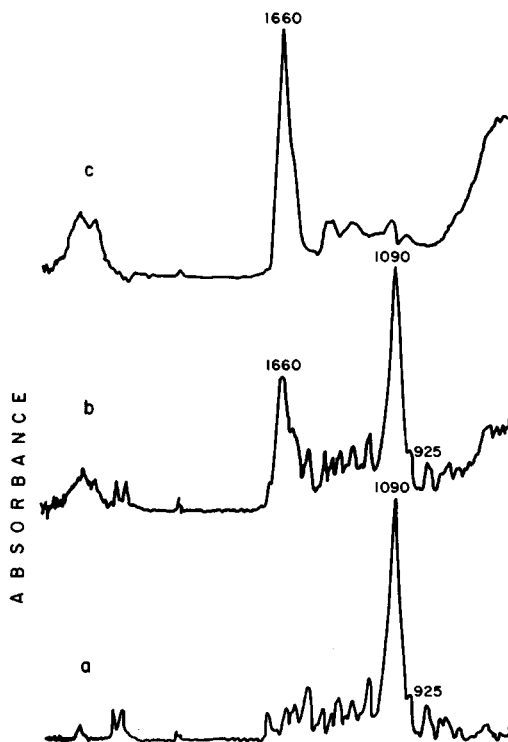


Fig. 3. ATR-IR spectra: (a) PEU 3-2000; (b) IPN; (c) difference spectrum, (b) - (a); θ (angle of incidence) = 60° .

weight fractions obtained with MBA and TEGDMA are shown in Figure 1. The difference between the properties of IPNs prepared with each of these crosslinkers was small, though in all cases the IPNs obtained with TEGDMA had a slightly higher $W_{\text{PAM}}/W_{\text{IPN}}$ than the IPNs obtained with MBA.

The third method for inducing gradient formation in the IPNs was differential diffusion of the crosslinker. The weight fractions of PAM in IPNs prepared in this manner are shown in Figure 2, and do not appear to depend on the duration of swelling in the crosslinker solution.

Characterization of the IPNs by ATR-FTIR

Spectra for PEU, for an IPN with PAM, and the difference between the two are given in Figure 3. The difference spectrum, which was normalized to 925 cm^{-1} , a wavelength for which the extinction coefficient of PEU is much greater than for PAM, reveals the presence of PAM.

Subtraction of one spectrum from the other is possible since the depth of penetration of the ATR-IR beam is identical for both samples. Spectra obtained with an IPN at two different angles θ are given in Figure 4 along with the difference spectrum. The difference spectrum has the typical PAM absorption band at 1660 cm^{-1} , showing that the PAM concentration was dependent upon depth, as the depth of penetration for spectra taken at $\theta = 60^\circ$ and $\theta = 45^\circ$ differ

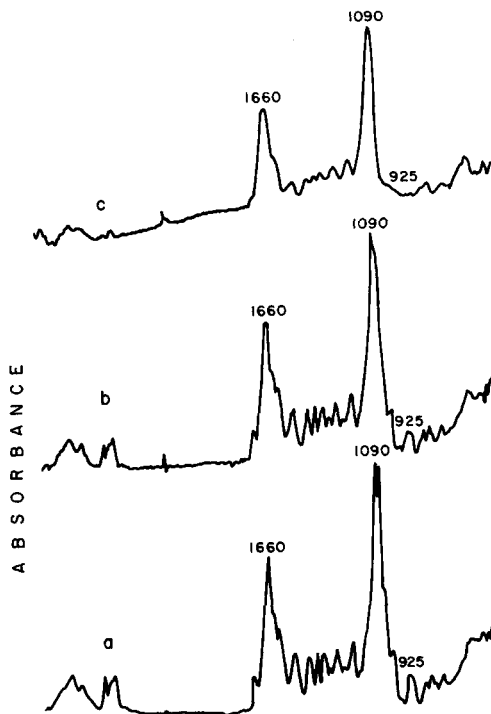


Fig. 4. ATR-IR spectra of an IPN of PAM and PEU 3-2000: (a) θ (angle of incidence) = 45° ; (b) $\theta = 60^\circ$; (c) difference spectrum, (b) - (a).

by about 0.4μ (see Experimental). These data show that the PAM concentration is highest close to the surface of the specimen. It should be noted that the absorption band at 1090 cm^{-1} , which is characteristic for PEU, has not been completely eliminated in the difference spectrum. This points to the care that must be taken when comparing spectra taken at different angles, owing to optical effects⁸ that cause the bands to distort and shift to longer wavelength as θ approaches θ_c (the critical angle). This effect can be clearly seen in Figure 5, in which spectra for PEU are given for two angles of incidence. The difference spectrum does not vanish at 1090 cm^{-1} , owing to the distortion and shift (10 cm^{-1}) of the absorption peak at an angle of 30° .

The ratio A_{1660}/A_{925} vs. the angle of incidence serves as a measure of PAM concentration as a function of depth from the surface for comparison of the PAM gradients in IPNs prepared by different methods. The profiles of the PAM concentration in IPNs prepared by polymerization after short swelling periods and after equilibrium swelling are given in Figure 6(B). The plots show that in both sets of IPNs a gradient is present with the PAM concentration decreasing from the surface inwards. The PAM concentration profiles of IPNs prepared by differential diffusion of crosslinker are given in Figure 6(A). The IPNs prepared with MBA as crosslinker and with a very low concentration of initiator had a considerably smaller gradient of PAM than that found for the IPN prepared with PEGDA, and a much higher initiator concentration. The IPN composites prepared with PEGDA exhibited the steepest gradients and the

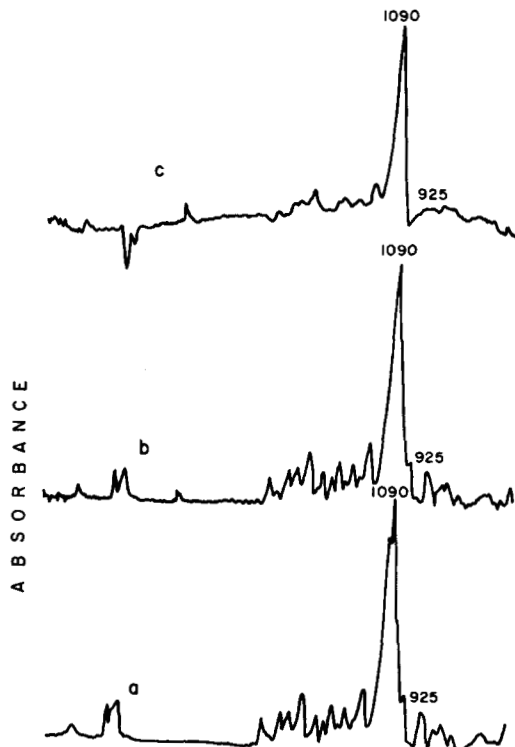


Fig. 5. ATR-IR spectra of PEU 3-2000: (a) θ (angle of incidence) = 45°; (b) θ = 60°; (c) difference spectrum, (b) - (a).

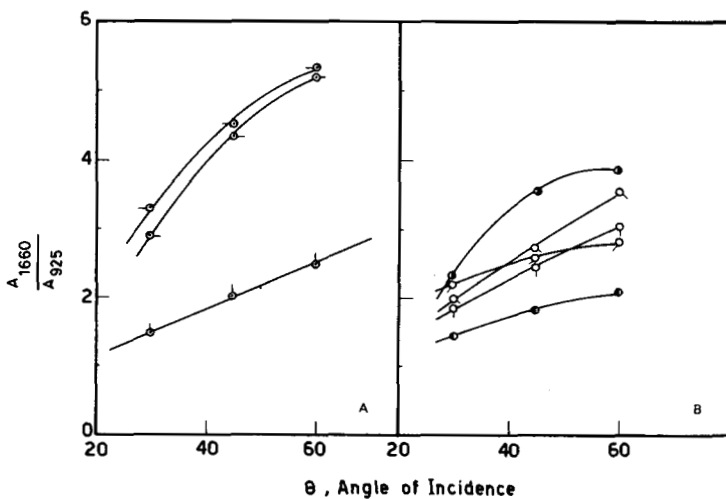


Fig. 6. A_{1660}/A_{925} (ratio of absorbances at 1660 and 925 cm^{-1}) as a function of θ (angles of incidence) for IPN of PEU 3-2000 and polyacrylamide. (A): (\circ , \square , \triangle) $W_{\text{PAM}}/W_{\text{IPN}} = 0.341, 0.355, 0.088$, respectively; these IPNs were polymerized after equilibrium swelling of monomer and initiator followed by partial diffusion of crosslinker (see Table III); (B): (\circ , \square , \triangle , \bullet) $W_{\text{PAM}}/W_{\text{IPN}} = 0.244, 0.168, 0.029$, respectively; these IPNs were polymerized after partial swelling (see Table III); (\bullet , \bullet) $W_{\text{PAM}}/W_{\text{IPN}} = 0.316, 0.284$, respectively. These IPNs were polymerized after equilibrium swelling (see Table III).

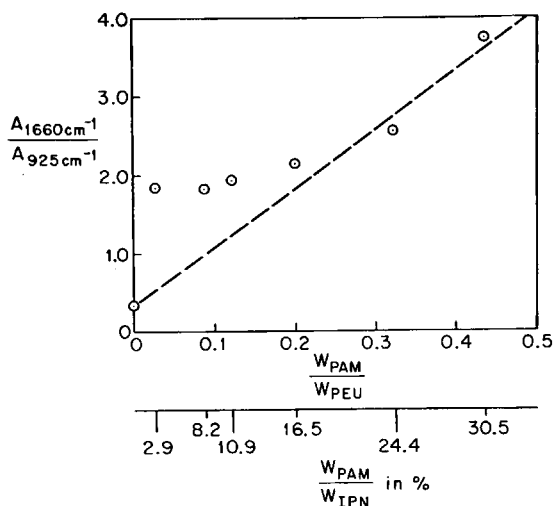


Fig. 7. A_{1660}/A_{925} (ratio of absorbances at 1660 and 925 cm^{-1}) for θ (angle of incidence) = 45° , as a function of polyacrylamide weight fraction in IPNs prepared from PEU 3-2000 after short swelling times [the line is based on eq. (3), $k_1 = 0.35$ and $k_2 = 3.35$].

largest absorbance ratio among the data given in Figure 6. Data obtained with an angle of incidence of 45° from samples prepared with short swelling times (Table I) are plotted in Figure 7 vs. the overall gravimetric PAM content.

The constants k_1 and k_2 in eq. (3) were evaluated with the spectrum of PEU 3-2000 ($W_A = 0$), which gave $k_1 = 0.35$, and ATR-FTIR of IPNs of PAM and PEU 3-2000, which gave $k_2 = 3.35$.

Electron Microscopy and Contact Angles

The scanning electron micrograph (SEM) of a cross section of an IPN composite of PEU 3-2000 and PAM prepared by polymerization after short swelling

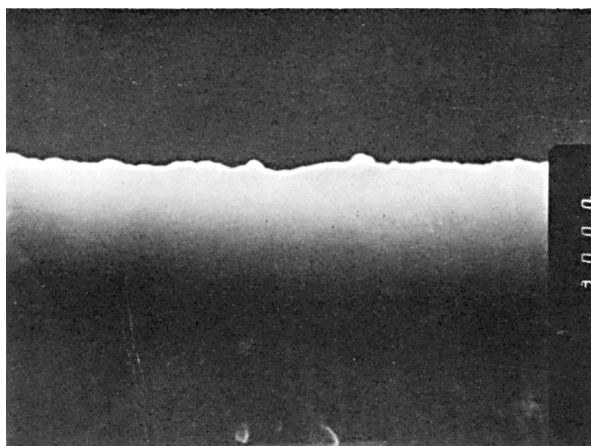


Fig. 8. Scanning electron micrograph (original magnification, 3000 \times) of cross section of IPN of PEU 3-2000 and PAM with $W_{PAM}/W_{IPN} = 0.16$, polymerized after short swelling time (20 min) in 3M AM, 0.03M AIBN and MBA, respectively, in ethanol.

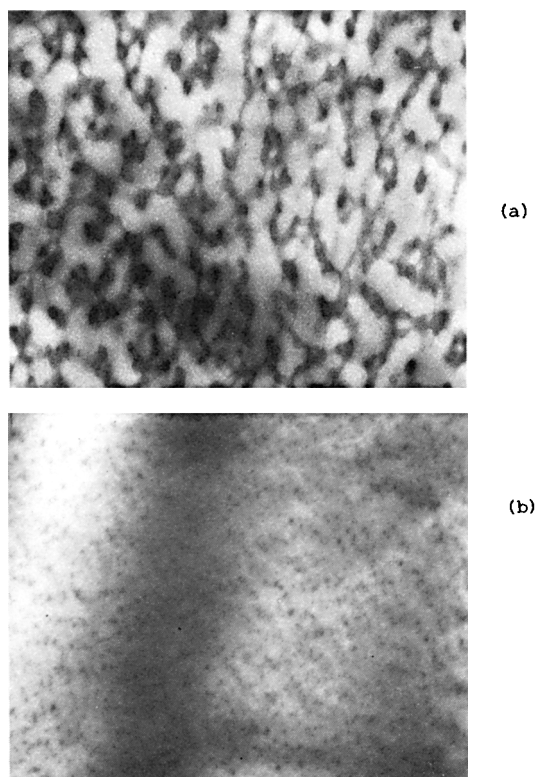


Fig. 9. Transmission electron micrographs (original magnification, 100,000 \times) of IPNs of PEU 3-2000 and PAM: (a) $W_{\text{PAM}}/W_{\text{IPN}} = 0.34$ polymerized after equilibrium swelling in same solution as Figure 8; (b) $W_{\text{PAM}}/W_{\text{IPN}} = 0.13$ polymerized after short swelling time in same solution as in (a).

time (20 min) in 3M acrylamide in ethanol with 0.03 AIBN and MBA is shown in Figure 8. The micrograph reveals the presence of a layer near and including the surface, differing in composition from the bulk. This layer is probably the PAM hydrogel, the concentration of which appears to decrease gradually from the surface inwards. Similar patterns were obtained for composites prepared by grafting PEU-2000 with PAM by the ceric ion¹² and by the atomic hydrogen¹³ techniques. The SEMS of the other gradient IPN composites prepared here had the same features. Figures 9(a) and 9(b) show transmission electron micrographs (TEM) of two gradient IPN composites, one with $W_{\text{PAM}}/W_{\text{IPN}} = 0.34$ prepared by polymerization after equilibrium swelling, and another with $W_{\text{PAM}}/W_{\text{IPN}} = 0.13$ prepared by polymerization after short swelling time (20 min). The distinct dark domains are attributed to the PAM network (see Paper I of this work). The size of the domains increased with increasing overall concentration of the PAM in the IPN.

The results of contact angle measurements are shown in Table II. It can be clearly seen that the surface properties of the IPNs were distinctly different from those of the poly(ether urethane). It is interesting to observe that subjecting PEU 3-2000 to a 3M solution of acrylamide in ethanol, results in some extraction¹ and also in changes of surface properties.

TABLE II
Contact Angle Measurements of the IPNs

Description	Contact angle (deg) ^a			γ_c^b	γ_{sw}^c
	H ₂ O	Air	Octane		
PEU, extracted ^d	—	46 ± 2	70 ± 3	37	12
PEU-2000	—	36 ± 1	56 ± 3	32	6
PAM/PEU = 19.2%	64	20 ± 2	14 ± 2	19	0
PAM/PEU = 18.2%	65	13 ± 2	16 ± 1	21	0

^a See measurement method in Ref. 11.

^b γ_c = critical surface tension (dyn/cm).

^c γ_{sw} = interfacial free energy (dyn/cm).

^d PEU-2000 extracted with a 3M ethanolic solution of acrylamide and ethanol, respectively, followed by vacuum drying.

DISCUSSION

The ATR-FTIR data in Figures 6 and 7, as well as the SEM and TEM micrographs, show that the IPNs prepared by all three methods discussed above have gradients of polyacrylamide close to the surface. In particular, the absorbance determined by the ATR experiment gives the average cumulative composition \bar{w}_l from the surface to a depth l determined by eq. (4); the value of \bar{w}_l may be estimated from the absorbance by use of eq. (3). Thus the data in Figure 6 are analyzed below in terms of w_l as a function of l . Before this analysis is given, it may be remarked that the data in Figure 7 for IPNs prepared after various times of monomer contact as shown in Table I provide qualitative evidence that the features of the gradient can be varied by the swelling treatment. The data in Figure 7 (obtained for $l = 1.2 \mu\text{m}$) show that the IPNs prepared after short contact with the monomer solution, and, consequently, low overall PAM content, have relatively high absorbance down to a depth of $1.2 \mu\text{m}$. That is, the PAM concentration near the surface is nearly independent of the overall PAM.

To facilitate further discussion, it is convenient to represent the composition gradient observed in the IPNs by a simple model in which the weight fraction w_l of hydrogel at depth l from the surface is approximated by the relation

$$w_l = w_0 + (w_s - w_0)e^{-l/\Lambda} \quad (7)$$

Here w_s is the weight fraction of hydrogel in a layer of infinitesimal thickness at the surface of IPN and w_0 is the fraction of hydrogel far to the interior of the IPN, in a region where l is much greater than the length Λ over which the composition decays from w_s . The \bar{w}_l give by the ATR experiment is

$$\bar{w}_l = \frac{1}{l} \int_0^l w_u du \quad (8)$$

so that, with eq. (7) for w_l ,

$$\bar{w}_l = w_0 + (w_s - w_0) \frac{1 - e^{-l/\Lambda}}{l/\Lambda} \quad (9)$$

Analysis of experimental data with eq. (9) permits representation of the data

TABLE III
Parameters Describing PAM Gradients for Several Interpenetrating Network Polymers^a

Description of swelling prior to polymerization	Contact time	Initiator (AIBN) concn (mol/L)	Crosslinker concn (mol/L)	W_0^b	W_s^c	Λ^d (μm)
Equilibrium swelling	20 h ^e	0.09	0.03 MBA	0.316	0.53	2.7
	20 h	0.006	0.3 TEGDMA	0.284	0.37	1.0
Partial swelling	10 min ^e	0.09	0.03 MBA	0.029	0.49	6.8
	60 min	0.09	0.03 MBA	0.168	0.43	11.8
	120 min	0.09	0.03 MBA	0.244	0.51	2.4
Equilibrium swelling of monomer and initiator followed by partial diffusion of crosslinker	10 min ^f	0.09	0.1 PEGDA	0.355	0.60	3.6
	85 min	0.09	0.1 PEGDA	0.341	0.61	5.1
	35 min	0.006	0.3 MBA	0.088	0.40	5.0

^a All swelling solutions 3M acrylamide in ethanol with initiator and crosslinker as needed, swelling followed by polymerization (see Experimental).

^b Weight fraction of hydrogel far to the interior of the IPN.

^c Weight fraction of hydrogel in a layer of infinitesimal thickness at the surface of the IPN.

^d Length over which the composition decays from W_s to W_0 .

^e Contact times of PEU with swelling solution.

^f Contact times of PEU with swelling solution after 20 h contact of PEU with the latter without crosslinking agent.

by w_s and Λ , with w_0 approximated by the overall gravimetric composition. This representation is useful for comparative purposes, even if eq. (9) is not precisely correct.

Comparison of eq. (9) with the data in Table III is given in Figure 10; values of w_s and Λ were obtained by fitting experimental data with eq. (9). The plots in Figure 10 have been separated into: (A) polymers obtained after short time swelling; (B) polymers obtained after equilibrium swelling; (C) polymers obtained after differential diffusion of crosslinker. As shown in Figure 10, the IPN materials obtained by polymerization after partial swelling resulting in low w_0 show considerable gradient of composition from the surface; indeed, w_s may be near the value obtained after equilibrium swelling even though w_0 is very much less as shown qualitatively by the data in Figure 7. Hence, the partial swelling method affords IPNs, where the hydrogel tends to be close to the surface of the specimen. Since Λ is in excess of 10 μm for these asymmetric materials, it is evident that the hydrogel is well anchored in the matrix.

The data in Figure 10 also show that gradients are present in samples polymerized after equilibrium swelling. Thus, two samples of equilibrium swollen IPNs gave an overall PAM level ($W_{\text{PAM}}/W_{\text{IPN}}$) of 0.316 and 0.284 by gravimetric analysis, yet had a surface concentration w_s of 0.53 and 0.37, respectively.

The mechanisms responsible for small Λ values (ca. 1 μm) in equilibrium swollen samples and large Λ values (ca. 10 μm) in short time swollen samples appear to involve separate processes. Namely, the diffusion of monomer into the swelling sample and the exudation of monomer out of the contracting sample during the initial contact between the swollen matrix and the *n*-hexane vapor.

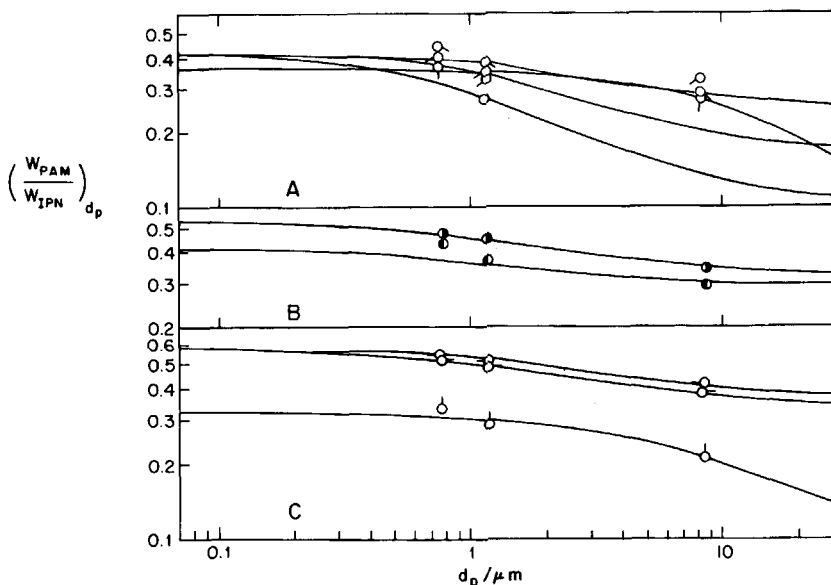


Fig. 10. Weight fraction of polyacrylamide in the IPN as a function of depth from the surface (note: Weight fraction data based on ATR measurements; d_p is calculated with eq. (4); experimental points notation same as in Fig. 6: (A) polymers obtained after short time swelling; (B) polymers obtained after equilibrium swelling; (C) polymers obtained after equilibrium swelling of monomer and initiator followed by partial diffusion of crosslinker.

For short time swollen samples, diffusion dominates, but for samples swollen for long periods, exudation must dominate.

The data in Table I indicate that the shorter the swelling time prior to polymerization, the higher the water uptake per unit weight of PAM (W_{H_2O}/W_{PAM}). Thus, the PAM confined to the surface is able to swell more effectively than that in the interior of the material. This is consistent with the observations¹ that PEU surfaces are richer in polyether blocks than the bulk, thus exhibiting a smaller degree of physical crosslinking. The same behavior could also be caused by decreased swelling of PAM in the far interior of IPNS, which has a larger overall PEU content, resulting, for example, in PAM being isolated in domains not accessible to water.

The results for IPNs prepared using either (1) differential diffusion of the crosslinker (Fig. 10) or (2) equilibrium swelling in the presence of a crosslinker with high molecular weight (Fig. 1) show that these methods gave essentially the same products as did the method of homogeneous swelling. Originally, it was hoped to enhance gradient formation through localization of the crosslinker in layers close to the surface. Localization of crosslinker in the first method above was achieved through brief diffusion times and in the second method through lowering of the diffusion constant of the crosslinker. It should be noted that in Paper I of this series¹ it was shown that the rates of diffusion of monomer and solvent were quite different. It was conceived that a similar diffusion rate difference between monomer and crosslinker could be conducive for gradient formation. In order to promote the desired diffusion rate difference, a crosslinker with higher molecular weight than MBA was chosen (PEDGA), without mea-

suring actual diffusion rates. The PAM formed in the rest of the matrix was expected to be uncrosslinked and consequently leachable with water. As discussed previously,¹ PAM will crosslink under certain circumstances, even in the absence of a difunctional crosslinker. Moreover, even in the absence of such a crosslinking reaction for the monomer in the interior without crosslinker, water-soluble PAM molecules could be "trapped" by the IPN layer at the surface. The time needed for water-soluble PAM molecules to diffuse through the IPN gradient, consisting of chemically crosslinked PAM and physically crosslinked PEU, could be longer than the 24 h allowed for water extraction (see Experimental).

The difference observed in Figure 2 between the results with PEGDA and the results with MBA or TEGDMA is due to the difference in initiator concentrations used. Thus, in the experiment with PEGDA, the level of initiator was 15-fold higher than in the other experiments, resulting in much faster initiation with consequential retention of more monomer in the IPN matrix and higher $W_{\text{PAM}}/W_{\text{IPN}}$. The lower water uptake per unit weight of PAM for the IPNs prepared with PEGDA is also attributable to the high initiator level, which can increase the rate of hydrogen abstraction from the PAM chain, thus increasing the degree of crosslinking and reducing the swellability of the PAM in water.

Consistent with the spectroscopic data, the surface of all IPNs prepared, including gradient IPNs with low overall PAM concentration, were slippery when swollen with water. Indeed, this simple "tactile test" provided a convenient qualitative means to substantiate the conclusion about high PAM content at the surface based on extrapolation of the ATR data (Fig. 10). Quantitative evidence of high surface PAM is provided by the contact angle data in Table II, which show that the surface properties are those of PAM.

The formation of gradient IPNs by control of the duration of the exposure to monomer solution prior to polymerization relies on maintenance of the monomer concentration gradient induced in the host during the short term swelling for a long enough period that the gradient can be made permanent by polymerization. To this end, swelling solvents, such as ethanol, that lead to a low overall swelling rate [eq. (5)] are beneficial (comparative swelling data for several solvent systems are given in Paper I). Monomer exudation that appears to occur on contact with the hexane vapor used to heat the monomer-swollen PEU may also be effective in maintaining high PAM content at the surface. Indeed, in some experiments with heating effected by other means, the surface of water-swollen IPNs did not feel slippery, even though spectroscopic data revealed the presence of appreciable PAM (to appear).

CONCLUSION

Poly(etherurethane) may be treated by short term exposure to solutions of acrylamide to produce IPNs with high PAM content near the surface and extending into the host polymer to depths of about 10 μm , with little or no PAM in the far interior of the host polymer. Long term exposures to the monomer solution produce an IPN more nearly homogeneous in PAM content, but somewhat enriched in PAM near the surface, presumably owing to exudation of monomer during the polymerization process, which involves contact with vapor of an organic solvent (hexane). The former procedure offers a means to effect

surface modification of PEU without substantial effect on its mechanical properties. Exposure to monomer solution for durations that result in only 1–2% monomer uptake or overall PAM in the resultant IPN, nevertheless, produce materials with high (ca. 30–50%) PAM near the surface and surfaces that have the slippery feel of IPNs with much higher PAM content. Owing to the nature of the IPN, the PAM hydrogel is well anchored in the host, and is not readily removed by superficial abrasion.

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