

Synthesis and Swelling Behavior of pH-Responsive Polyurethane/Poly[2-(diethylamino)ethyl methacrylate] Hybrid Materials

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ABSTRACT: Polyurethane (PU)/poly[2-(diethylamino)ethyl methacrylate] hybrids, having a chemical bond between the PU and acrylic moieties and with different compositions, were prepared by the dispersion polymerization of 2-(diethylamino)ethyl methacrylate (DEA) in the presence of preformed PU chains with polymerizable terminal vinyl groups. The PU dispersion was synthesized according to a prepolymer mixing process by the polyaddition of isophorone diisocyanate, poly(propylene glycol), 2-hydroxyethyl methacrylate, and dimethylol propionic acid (DMPA). Then, it was dispersed in water by the prior neutralization of the carboxylic acid groups of DMPA with triethylamine, chain-extended with ethylenediamine. The effect of the DEA content on the swelling properties (water uptake and dynamic swelling degree) at different pHs and at 37°C was determined. The samples were also characterized by Fourier transform infrared spectroscopy and modulated differential scanning calorimetry. The experimental results indicate a higher water uptake when the DEA content was increased on the hybrid materials and a significant change in the kinetics of swelling at pH 4 compared to those at pH 7. The water content of the hydrogels depended on the DEA content, and it was inversely proportional to the pH value. The pure PU film did not show important changes over the pH range examined in this study. The synthesized hybrids were useful as drug-delivery, pH-sensitive matrices. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2013**, *000*, 39799.

KEYWORDS: drug-delivery systems; PUs; stimuli-sensitive polymers; swelling

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INTRODUCTION

The combination of polymers as materials for controlled drug-delivery applications may offer significant advantages because it allows the adjustment of the mechanical properties of the material, the desired drug-release pattern, and the drug-release mechanism of the drug. For example, Siddaramaiah et al.¹ proposed the use of chitosan and hydroxypropyl methylcellulose blends in different compositions for the delivery of propranolol HCl, and Abd El-Bary et al.² used a blend of chitosan with different proportions of poly(vinyl alcohol) to study drug delivery with brilliant blue dye as the model drug.

Different polymeric materials have been used in drug delivery, including chemically or physically crosslinked hydrogels, because of their biocompatibility.^{3,4} Even a blend of hydrogels was also used as a drug-delivery system to incorporate theophylline as a model drug.⁵

On the other hand, stimuli-sensitive polymers are very attractive materials for application in biomaterials science and technology because they are capable of changing their structure and physical properties in response to external stimuli, such as pH, ionic strength, temperature, or specific chemical compounds. The utilization of a stimuli-sensitive hydrogel would be of special interest

for new drug-delivery systems and, in particular, pH-sensitive hydrogels.⁶

To change the environmental response behavior of hydrogels, a significant number of ionic (acidic or basic) monomers can be incorporated into the chemical structure. Ionic monomers, such as *N*-(3-aminopropyl)methacrylamide, 2-(dimethylamino)ethyl methacrylate, methacrylic acid, and 2-aminoethyl methacrylate, and neutral hydrophobic monomers, such as butyl methacrylate, allyl diglycol carbonate, diallyl phthalate, and methyl methacrylate, have been used.^{7–9} Cationic monomers, such as tertiary amine methacrylates, 2-(diethylamino)ethyl methacrylate (DEA), and 2-(diisopropylamino)ethyl methacrylate, have also been used to prepare pH-sensitive hydrogels.¹⁰ Pure poly[2-(diethylamino)ethyl methacrylate] (PDEA) homopolymer was used in particular for preparing pH-sensitive polymers for drug-delivery applications.¹¹ A blend of polyurethane (PU) and PDEA was also proposed as a drug-delivery matrix.¹² However, PDEA as a pure polymer is not mechanically suitable, so in a first attempt to modify and improve the mechanical properties, it was combined (blended) with a low-glass-transition temperature (low- T_g) PU that showed outstanding mechanical properties. However, the desired final properties of the material can sometimes be difficult to achieve by blending, and in some applications, more homogeneous systems that are not phase-separated may be more adequate. In view of this situation, we proposed the use of a hybrid acrylic/PU system, where the acrylic component is a stimuli-sensitive polymer, and there is a chemical bond between the acrylic and the PU component, to prevent, in that way, phase separation. Several articles have been published dealing with hybrid acrylic/PU systems,¹³ but to our knowledge, no hybrid acrylic/PU blend with tertiary amine methacrylates have been reported. Pan and Chen¹⁴ used 2-(dimethylamino)ethyl methacrylate in the formulation of PU/acrylate hybrid emulsions as a reactive neutralizer rather than in a polymer composition, and no swelling studies were performed as we did in this study. By introducing the DEA monomer into the PU network, we expected to induce a stimuli-sensitive behavior. Because the pK_a of PDEA is known to be close to a neutral pH (7.0–7.3)¹⁰ and the PU properties are almost independent over the pH range examined in this study (see later discussion), we expected an interesting pH-dependence behavior of the swelling properties of the PUs containing DEA as a comonomer.

Herein, we describe the synthesis and characterization of a PU based on isophorone diisocyanate (IPDI) and poly(propylene glycol) 1000 (PPG1000) with different amounts of DEA monomer (from 10 to 50 wt %) and slightly crosslinked with poly(propylene glycol) diacrylate with Fourier transform infrared (FTIR) spectroscopy, modulated differential scanning calorimetry (MDSC), ultraviolet–visible (UV–vis) spectroscopy, and dynamic and equilibrium swelling degree (ESD) measurements of water. In our previous article,¹² we reported that the ESD of a 50 wt % blend of PDEA and PU at pH 6 was 54%, and at pH 2, the value was 180%. However, when hybrids of the same composition were prepared, the swelling degree increased to more than 200% at pH 6 and 300% at pH 4. Furthermore, by changing the DEA content, we could change the ESD as required. In this study, the influence of the DEA content on the

swelling behavior and pH sensitivity was evaluated at human body temperature (37°C).

EXPERIMENTAL

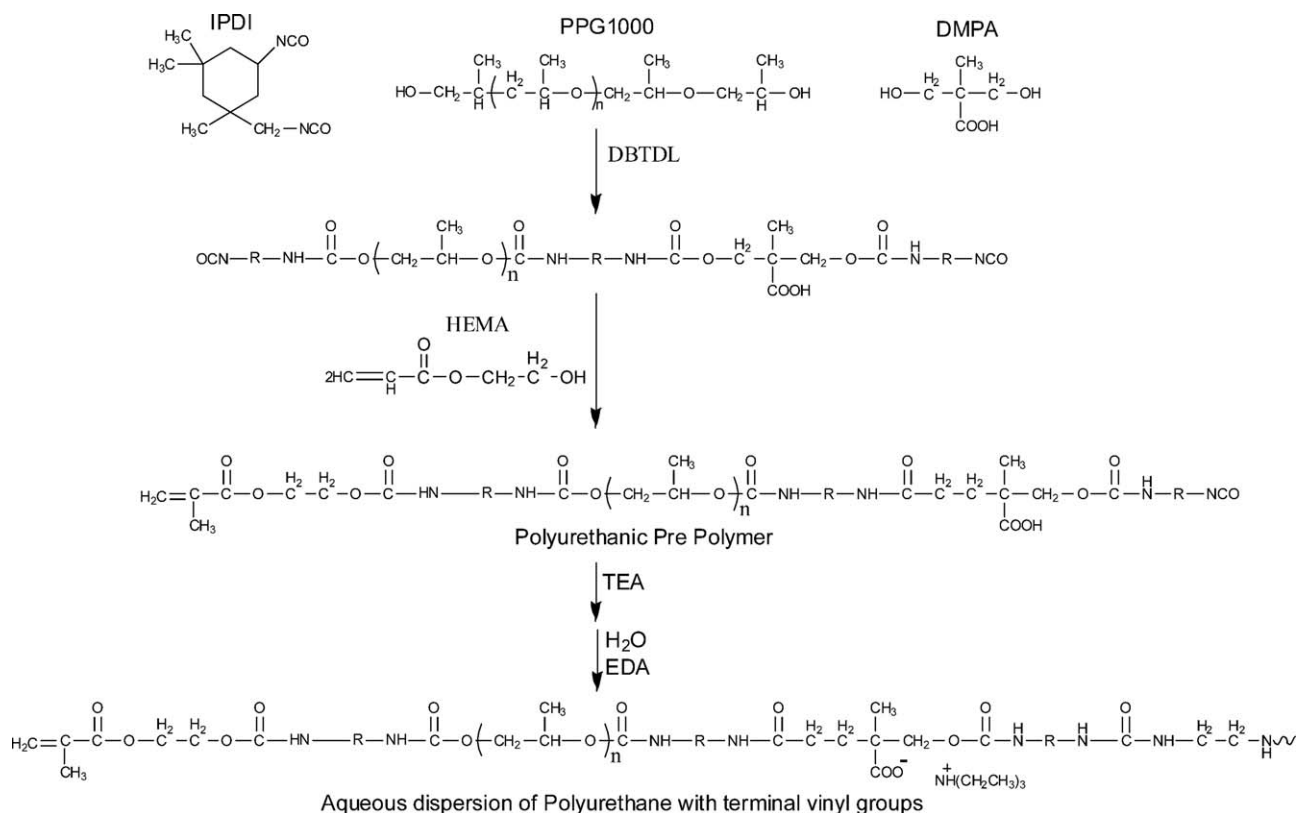
Materials

DEA (Scientific Polymers Products), IPDI (Aldrich), 2-hydroxyl ethylmethacrylate (HEMA; Aldrich), poly(propylene glycol) diacrylate (PPGDA; Aldrich), ammonium persulfate (APS; Fisher Scientific), ethylenediamine (EDA; Aldrich), dibutyltin dilaurate (DBTDL; Aldrich), and sodium dodecyl sulfate (Anedra) were analytical grade and were used as received. Monomethoxy-capped poly(ethylene glycol) methacrylate (PEGMA) macromonomer (number-average molecular weight = 2000; weight-average molecular weight/number-average molecular weight = 1.10) was supplied by Cognis Performance Chemicals (Hythe, United Kingdom) as a 50 wt % aqueous solution. PPG1000 (Voranol 2110) was technical grade, and triethylamine (TEA) was provided by ADELFA S.A. The DEA monomer was treated with basic alumina to remove the inhibitor. Poly(propylene glycol) was dried and degassed at 80°C at 1–2 mmHg before used. Dimethylol propionic acid (DMPA; Aldrich) was dried at 100°C for 2 h in an oven. TEA was also dried before use. The buffer solutions for fixing the medium pHs were prepared from standard chemicals.

Polymer Synthesis

Synthesis of the PU Dispersion. A 1000-mL, six-necked separable flask with a mechanical stirrer, thermocouple, condenser, sampling tube, inlet system for gases, and pump feed inlet was used as a reactor. PPG1000 and DMPA were charged into the dried flask. During stirring, the mixture was heated to 90°C, homogenized, and bubbled with dry air for approximately 60 min; this was followed by an increase in the temperature to 98°C and the addition of a mixture of IPDI and DBTDL catalyst. The mixture was allowed to remain at this temperature for approximately 2 h. The prepolymer was cooled to 45°C, and HEMA dissolved in acetone was added slowly and allowed to react for approximately 90 min. Then, the temperature was raised to 60°C and kept constant until the isocyanate (NCO) content reached the desired value (ca. for 90 min). The free NCO content was determined with the conventional dibutylamine back-titration method.¹⁵ When the theoretical NCO value (ca. 4.7%) was obtained, the mixture was cooled to 55°C, and TEA (in acetone) was fed in slowly over 50 min. After neutralization, the temperature was lowered to room temperature. An aqueous dispersion of PU was obtained by the addition of the PU prepolymer to water containing the appropriate amount of EDA to perform the chain-extension reaction. The dispersion was performed at about 300 rpm in an ordinary glass reactor at 30°C for 45 min. The resulting product was a stable dispersion with solid content of about 30 wt %. A typical base formulation used in this study is given in Table I, and the synthesis of the PU dispersion is illustrated in Scheme 1.

Synthesis of the PDEA Dispersion. The polymerization of PDEA was carried out in a 100-mL, round-bottomed flask fitted with a nitrogen gas inlet, water condenser, and overhead mechanical stirrer operating at 250 rpm. For batch reactions with the APS initiator, the required amount of water and sodium dodecyl sulfate (1.0 wt % based on the DEA monomer)



Scheme 1. Synthesis of the vinyl-terminated PU dispersion.

and a mixture of DEA and PPGDA crosslinker (2.0 wt % based on the DEA monomer) was added to the flask, and the solution was stirred for 30 min under a nitrogen flow at 60°C. The polymerization began with the addition of a previously degassed aqueous solution of the initiator (1.0 wt % based on the DEA monomer). The reactive macromonomer stabilizer (10.0 wt % based on the DEA monomer) was added to the aqueous solution before the addition of the monomer and crosslinker. The reaction solution turned milky white within 5 min and was stirred for 16–20 h at 60°C under a nitrogen atmosphere

Table I. Recipe for the Synthesis of the PU Dispersion

Component	Weight (g)	Moles
Prepolymer reaction		
IPDI	102.2	0.46
PPG1000	140.4	0.28
DMPA	14.0	0.10
HEMA/acetone	12.03/10.0	0.09/0.17
DBTDL	0.406	7.54×10^{-4}
Neutralization reaction		
TEA/acetone	53/10	0.52/0.17
Dispersion and chain-extension reaction		
EDA	5.108	0.08
Water	695.26	38.61

The recipe is for the preparation of 1000 g of a 30 wt % dispersion.

(Table II). For more experimental details on the PDEA synthesis and characterization, see ref. 10.

Synthesis of the PU/PDEA Hybrid Dispersions. The resulting PU dispersion was divided into several parts, and we added different amounts of DEA, PPGDA as the crosslinking agent, and PEGMA as the steric stabilizer. The polymerization of the PU-DEA/PPGDA/PEGMA mixtures was performed in batch mode with a glass reactor (1000 mL) with a water jacket for temperature control. The mixture was degassed with nitrogen gas and then dispersion-polymerized at 80°C with APS (0.015 wt % on the DEA monomer base) as the initiator. The polymerization led to the formation of PU/DEA hybrids having a chemical bond between the PU and DEA moieties. The resulting product was a stable dispersion with a solid content of approximately 30 wt %. A shorthand notation is used in this article to describe the hybrid systems. Thus, H90/10 denotes a hybrid system prepared containing 90 wt % PU and 10 wt % DEA monomer. A typical base formulation used in this article is given in Table III,

Table II. Recipe for the Synthesis of the PDEA Dispersion

Component	Weight (g)	mol
DEA	100	0.54
PEGMA	19.52	0.068
PPGDA	2	0.013
Water	878.48	48.80

The recipe is for the preparation of 1000 g of a 13 wt % dispersion.

Table III. Typical Recipe for the Preparation of 100 g of the PU and Hybrid Dispersions

System	DEA content (wt %)	PU dispersion (g) ^a	DEA/PPGDA/PEGMA monomer (g)	Water (g)
PU	0	94.84	—	5.16
H90/10	10	85.46	2.82/0.05/0.51	11.42
H80/20	20	76.07	5.64/0.10/1.02	17.69
H70/30	30	66.67	8.46/0.15/1.52	23.95
H60/40	40	57.28	11.28/0.20/2.03	30.22
H50/50	50	47.89	14.10/0.25/2.54	36.49

^a30 wt % aqueous dispersion.

and the synthesis of the PU/DEA hybrids is illustrated in Scheme 2.

Synthesis of the PU Polymerized Dispersion. The PU polymerized (PU) dispersion was prepared in the same way as the hybrids systems without the addition of the DEA monomer, and it was used as a reference material for comparison with the hybrid systems (see Table III and Scheme 3).

After polymerization, films were prepared by the casting of the aqueous dispersions on Petri dishes. After drying, the films were cut into circular pieces (ca. 25 mm in diameter) with a cork borer, dried, and cured at 60°C for 48 h and then stored in desiccators with silica gel until they were ready to be used for the experiments

Measurements

FTIR Spectroscopy. The FTIR spectra were measured in transmission mode with an FTIR Nicolet 380 spectrometer from Thermo Scientific. Samples were either in freestanding films or were powder-mixed with KBr and formed into disks by pressing.

The FTIR spectra were obtained by the recording of 64 scans between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹. Spectra processing was performed with EZ Omnic software.

MDSC. The *T_g* of the polymeric materials was measured with a modulated differential scanning calorimeter (modulated DSC Q 200, TA Instruments). Nitrogen was used as a purge gas at a

flow rate of 30 mL/min. An empty hermetic aluminum pan was used as a reference, and the heating/cooling rate was 2.5°C/min. It was modulated by a sinusoid with amplitude of 1°C and a period of 60 s. The temperature range was -100 to 120°C. All *T_g*'s were determined from the inflection point in the reversing heat-flow signal with TA Instruments Analyzer software.

Light Transmission of Films. The UV-vis spectra were determined on dried free standing films and were normalized by the thickness of films. The transmittance from 200 to 800 nm was measured with a Nicolet Genesis 10 spectrophotometer.

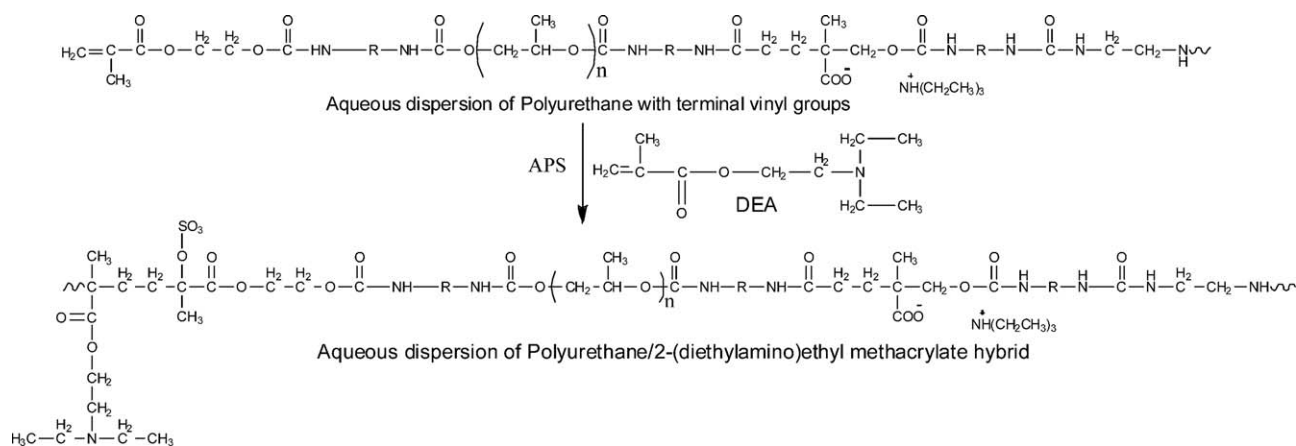
Swelling Degree. The ESD of the films were determined by the immersion of the samples (the disk was 25.0 mm in diameter and had a thickness ranging from 150 to 300 μm) in a phosphate buffer solution (ca. 0.1M) of desired pH (ranging from 5.0 to 8.0) and at a temperature of 37°C until it reached the swelling equilibrium. A buffer solution of sodium dihydrogen phosphate/phosphoric acid (ca. 0.1M) was used for pH 4.

The equilibrium swelling degree (*Q_∞*) was calculated with the following equation:

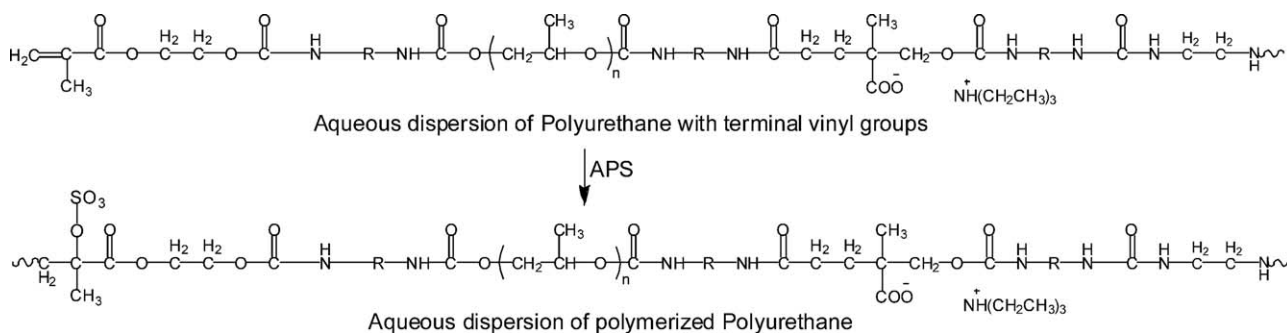
$$Q_{\infty} = \frac{(W_{s,\infty} - W_d) \times 100}{W_d} \quad (1)$$

where *W_{s,∞}* is the weight of the swollen film at equilibrium and *W_d* is the weight of the dry film.

Dynamic Swelling Degree. For the determination of the dynamic swelling degree, dry samples were immersed in buffer



Scheme 2. Synthesis of the PU/DEA hybrid dispersions.



Scheme 3. Synthesis of the aqueous dispersion of the polymerized PU.

solution of the desired pH (4.0 and 7.0) at 37°C. At regular periods of time, the samples were removed from the aqueous solution, blotted with filter paper to remove the surface liquid, weighed, and returned to the same container until weight stabilization was observed.

The degree of swelling at time t (Q_t) was calculated with the following equation:

$$Q_t = \frac{(W_{s,t} - W_d) \times 100}{W_d} \quad (2)$$

where $W_{s,t}$ is the weight of the swollen film at time t .

RESULTS AND DISCUSSION

Characterization of the PU/PDEA Hybrid Systems

Figure 1 shows the FTIR spectra of the pure PU and hybrid systems. The PU spectra showed typical bands corresponding to the hard segments, where the absorption around 3337 cm^{-1} arose from the hydrogen-bonding N—H stretching vibration, and the free N—H stretching vibration appeared as a shoulder at about 3460 cm^{-1} . The absorption at 1534 cm^{-1} was assigned to a combination of C—N stretching and NH bending, the amide II band. A broad band at 1712 cm^{-1} was assigned to free C=O and H-bonded C=O stretching (main contribution from urethane groups), and the other at 1655 cm^{-1} was assigned to

disordered urea C=O. This band was weak or not observed in our previous work on PUs.¹³ In those studies, we used hydrazine as a chain extender; however, because of regulatory issues, we replaced the chain extender by EDA, and as a consequence, a high proportion of urea groups was formed.¹⁶ A signal centered at 1305 cm^{-1} (a combination of NH bending and C—N stretching), absorption at 1242 cm^{-1} (combination of NH bending and C—N stretching, amide IV band), and a band at 1110 cm^{-1} (C—O—C stretching vibration of the polyetherdiol) were observed. Typical bands corresponding to soft segments were also observed at 1373 cm^{-1} (bending of methyl groups), at 1457 cm^{-1} (antisymmetrical methyl bending and methylene scissoring), and from 2960 to 2875 cm^{-1} (saturated C—H stretching vibration bands).¹⁷ The spectrum of PDEA showed a band at 1729 cm^{-1} , assigned to carbonyl (C=O) stretching vibration of the acrylic ester groups, and a band at 1150 cm^{-1} corresponding to the C—O stretching vibration.

A close examination in the C—H stretching region also showed the contribution of the DEA moieties at 2807 cm^{-1} for the —CH₂— groups close to the nitrogen atom.

A shift to higher wave numbers in the NH stretching bands was observed with increasing DEA content; this arose from breaking hydrogen-bonding interactions. The presence of different amounts of DEA moieties changed the distribution of hydrogen-bonding interactions. A low DEA content (<20 wt %) did not seem to be enough to modify this interaction, but a DEA content of 30 wt % and higher shifted the maximum NH absorption band to higher wave numbers (3450–3340- cm^{-1} region), characteristic of NH free stretching vibration.

A close examination of the spectra showed that the maximum of the C=O band in the hybrids shifted slightly to higher wave numbers (1726 cm^{-1} in the 60/40 system); this was probably a contribution from the urethane and acrylic component. On the other hand, the C=O of the urea band was almost nonshifted.

In the low wave-number region, increased intensities were observed at 1469 and 1385 cm^{-1} ; these corresponded to the asymmetric angular deformation (δ_a) and symmetric angular deformation (δ_s) of the CH₃ group of the DEA moiety. The contribution from the methylene groups adjacent to the N atom of the DEA moiety was observed at 1452 cm^{-1} and corresponded to the scissoring mode of CH₂. A clear band at 750 cm^{-1} was also observed when the DEA content was increased; this was due to the rocking of CH₂ groups.

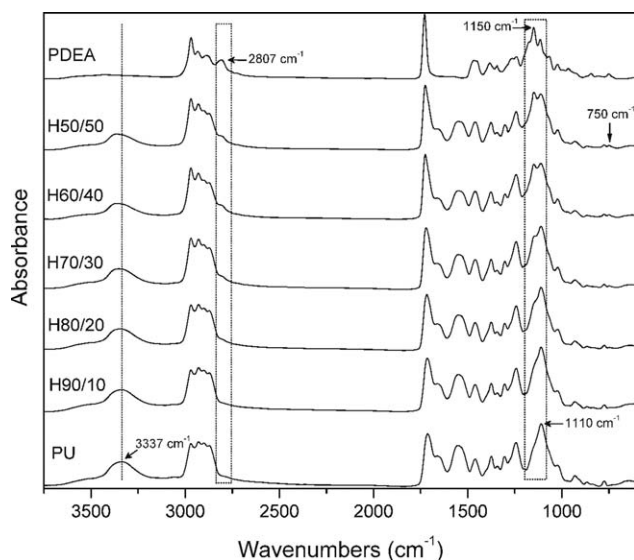


Figure 1. Survey FTIR spectra of the PU, hybrid systems, and PDEA.

The overall behavior observed here was similar to those reported for PU/acrylic systems the acrylic content was increased.¹³ The observed changes were attributed to the breaking of the hydrogen-bonding interactions in PU and the formation of new H bonds with the acrylic component.¹³ However, it is well known that the strength of the hydrogen bonds between urea groups is stronger than those between urethane groups because the polarity of the urea groups is stronger than those of the urethane groups.¹⁸ When DEA was included, the most affected hydrogen bonds with carbonyl groups were probably those from the urethane and ether groups.

Characterization by MDSC

The MDSC curves (reversing heat flux) for the PU polymer and hybrids systems with different amounts of DEA are shown in Figure 2.

The pure PU curve showed the glass-transition temperature of the soft segments (T_{gs}) at -33.88°C .¹³ As expected, the T_{gs} for the hybrid systems increased when the DEA content was increased, as the T_g of PDEA was -19.8°C .¹⁹ The observed values were -33.65 , -33.62 , -33.58 , -33.43 , and -31.69°C for H90/10, H80/20, H70/30, H60/40 and H50/50, respectively.

For a binary miscible mixtures of polymers, the dependence of T_g on the composition can be presented by several equations; the Fox equation [eq. (3)] and Gordon–Taylor equations [eq. (4)]:²⁰

$$\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} \quad (3)$$

$$T_g = \frac{x_1 T_{g1} + k_{GT} x_2 T_{g2}}{x_1 + k_{GT} x_2} \quad (4)$$

where x_i ($i = 1, 2$) is the weight fraction of component i , T_{gi} ($i = 1, 2$) is the glass-transition temperature of component i , T_g is the glass-transition temperature of a mixture, and k_{GT} is a constant that is characteristic of the particular system. In this case, the agreement between the experimental data and the description via the Gordon–Taylor equation was satisfactory;

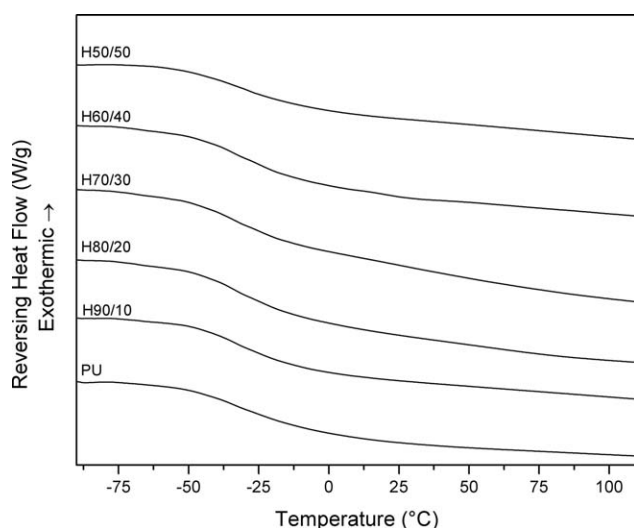


Figure 2. MDSC curves for the PU and hybrid systems.

indicating a random distribution of PDEA on the PU polymer ($k_{GT} = 0.13$).

UV–Vis Spectroscopy and Light Transmission of the Films

UV–vis spectroscopy is a common technique for characterizing materials. The carbonyl absorption band is sensitive to the chemical environment, so information about active centers in the polymer network can be obtained.

For some applications, such as therapeutic contact lenses, ocular drug delivery, and the monitoring of wound healing (for making it easy to see the instruments in the working area during application), transparency is an important issue, and therefore, the behavior in the visible region of the spectrum is important.

The transmission of films in the range 400–800 nm was higher than 60% for film thicknesses of about 150–300 μm for different DEA contents. Interesting differences in the UV–vis spectra were observed when the composition was varied from 10 to 50 wt % DEA (Figure 3).

Pure PU displayed an important absorption around 220 nm because of the electronic transitions of the urethane carbonyl group. The absorption in the 200–250-nm region increased when the DEA content was increased. This electronic absorption came from the $\sigma \rightarrow \pi^*$ transition of the carbonyl groups of the ester of the DEA moiety. The band at 295 nm was not observed in the UV spectrum of PDEA without PEGMA (not shown here), so it was assigned to the ester group of the PEGMA moiety. The increasing intensity of absorbance was related first to the increasing amount of DEA monomer but also indicated the loss of local symmetry around the carbonyl groups.

Anyway, with increasing DEA content, the optical transmissions of the films were high enough when the optical clarity was a significant concern.

Swelling Degree

Several characteristics in hydrogels, such as the permeability and mechanical, surface, and others properties are influenced by the swelling degree.²¹ The swelling degree is also modified by the chemical structure of the polymer network, the crosslinking density, the type of ionic groups in the polymers, the pK_a of the

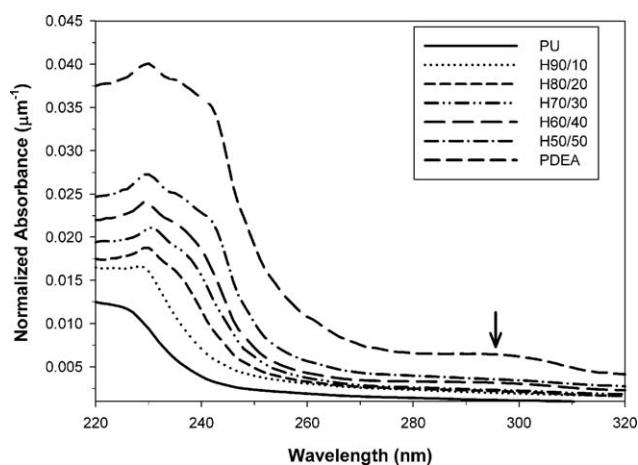


Figure 3. Electronic spectra of the PU/DEA films with different DEA contents. The arrow indicates a wavelength discussed in the text.

ionizable groups, and factors from the solution, such as the ionic strength, pH, and temperature.^{22,23} The effect of the composition and pH on the swelling degree of the PU/DEA films at 37°C is discussed in this section.

Figure 4 shows the variation of ESD for the hydrogels as a function of the PU/DEA ratio from pH 4.0 to pH 8.0. At low pH, an increase in the DEA content caused an increase in ESD; this was attributed to the protonation of amino groups and an increase in the electrostatic repulsive force between ionized groups. The increase in the network space, in turn, allowed water to get into the matrix.^{24,25}

The ESD at pH values between 4.0 and 7.0 for the pure PU was similar (~15 wt %), and it increased when the pH was increased to 8.0 because of the ionization of carboxylic groups from the DMPA moiety.

The critical pH for this swollen-to-nonswollen transition was around pH 6.5–7.0; this corresponded approximately to the known pK_a of 7.0–7.3 for the linear PDEA homopolymer.²⁶ When the pH of the solution was lower than 7.0, the number of ionic groups increased, and the effect on the osmotic swelling force by the presence of ions was greater. Interesting enough was the behavior at pH values lower than 5. The pK_a of DMPA was 4.41,²⁷ which was lower than the pK_a of PDEA (7.0–7.3),²⁶ so the carboxylic groups were in the nonionized molecular form. This caused a decrease in ionic groups and, therefore, a decrease of the swelling degree. In this way, the reduced swelling at pH 4 could be explained by a reduced charge of the hydrogel by the formation of —COOH groups. Also, the formation of hydrogen bonds among the —NHCO and —COOH groups of PU/PDEA^{28,29} gave a more compact network structure, which restricted the movement and relaxation of the chains within the hydrogel and reduced the swelling capacity. Also, the increasing ionic strength (from 0.116 to 0.172) when we moved from pH 5 to pH 4 resulted in a smaller swelling effect as a consequence of the screening of electrostatic repulsions between the protonated amino groups.

By increasing the DEA content, the amount of crosslinking monomer (PPGDA) also increased. It is well known that hydrogels with

a higher crosslinking degree have a tighter structure and less swelling compared to hydrogels with a lower crosslinking degree. However, the crosslinking monomer (PPGDA) in the hybrid PU/PDEA systems was included at 2.0 wt % on the basis of DEA monomer, and it represented less than 1 wt % of the final film in a narrow range, so the effect on ESD could be neglected compared to the changes produced by the increase of DEA monomer on the composition.

The characteristics of these hybrids hydrogels allowed the system to control the drug release when the surrounding medium changes.³⁰

Dynamic Swelling

As shown in the previous section, the ESD depends on the solution pH. At pH 7.0, the maximum ESD values were 60% for 50/50 PU/DEA, 50% for 60/40 PU/DEA, 45% for 70/30 PU/DEA, and lower than 40% for the remaining compositions (Figure 4). The solution pH also modified the swelling dynamics. Figure 5(a) shows the curves obtained at pH 4.0 for different DEA contents, and Figure 5(b) shows the corresponding curves at pH 7.0. For the pure PU sample, the dynamic swelling curves were similar at both pH values, and for the 90/10

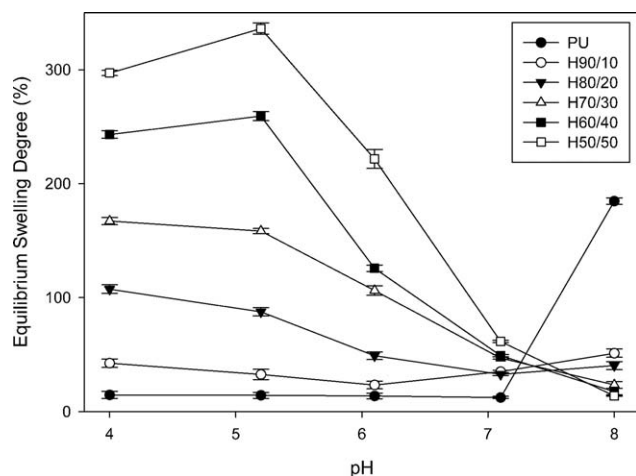
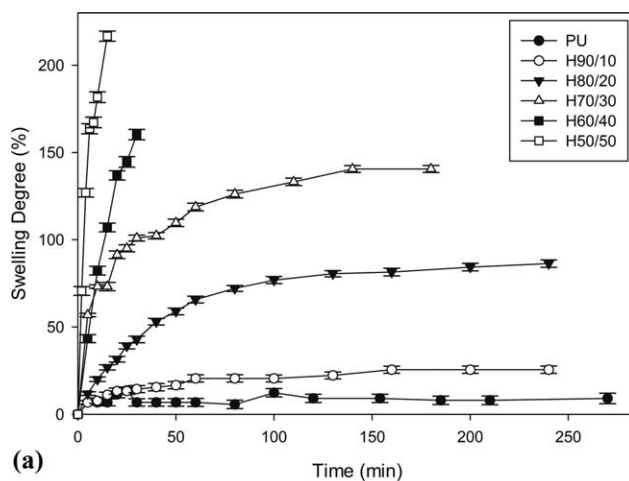
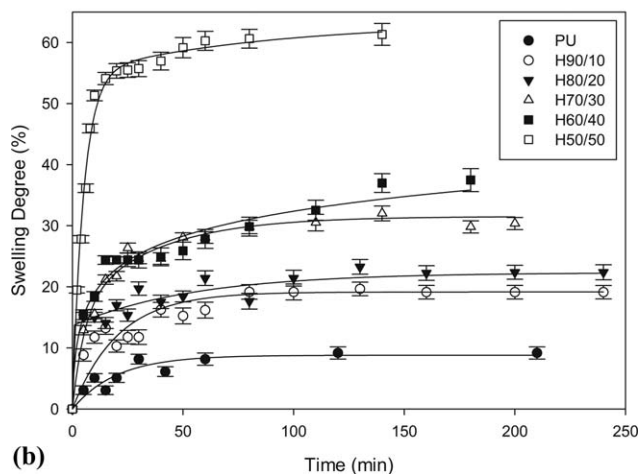


Figure 4. ESD (Q_{∞}) values for different PU/DEA ratios at different pHs (from 4.0 to 8.0) at 37°C.



(a)



(b)

Figure 5. Curves of dynamic swelling for PU and PU/DEA (90/10, 80/20, 70/30, 60/40, and 50/50) at pH (a) 4.0 and (b) 7.0.

PU/DEA, the observed curves were slightly different. However, for the 80/20 PU/DEA, the differences became larger, and the swelling process was faster when the pH was changed from 7 to 4.

However, there were no differences in the overall kinetic behavior between the swelling solutions with different pHs, except for the maximum swelling degree.

For pure PU, the sensitive behavior was only observed at pHs higher than 7.0 as a consequence of the full ionization of carboxylic groups from the DMPA moiety.

CONCLUSIONS

Hybrid polymers of PU and DEA with good film-forming abilities and swelling capacity and potentially useful for drug-delivery applications were prepared and characterized. The incorporation of the DEA monomer modified the interactions between PU chains, as revealed by FTIR analysis, and caused the water ESD and the kinetics process to become pH-dependent. These differences were more significant when the DEA content was increased. Levels of water content in the studied hybrid polymers were adequate for drug-delivery applications, and their release behavior with Rhodamine 6G as a model drug is under investigation, and the results will be published in due course. The morphology of these hybrid polymers will also be the subject of future research.

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