Evaluating the Behavior of Castor-Oil-Based Polyurethanes in Acidic Environments on the Basis of the Sorption Behavior and Analysis with Electron Ionization Mass Spectroscopy and Neutron Activation Analysis

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ABSTRACT: Castor-oil-based polyurethanes (COPUs) were fabricated from 2,4-toluene diisocyanate and hexamethylene diisocyanate. Immersion weight-gain methods at different temperatures were used to measure the sorption and diffusion of acidic solutions into the polyurethane. It was evident from this study that these COPUs can indeed be used in acid conditions as they exhibited a low absorption of diffusing solutions ($<1\%$) with the apparent activation energies of diffusion and permeation estimated to be 85 and 18 kJ/mol, respectively. Neutron activation analysis confirmed the possibility of the clustering of the acidic diffusing solutions because the acid/water molar values within the polymer matrix were significantly larger than those expected of the bulk solution. Mass spectroscopy indicated that any degradation that may have occurred may have been the result of fracture at the ester bond in the castor oil segment of the polyurethane. Tensile tests showed that the modulus of the saturated polymers remained above the values of the unsaturated ones. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3403–3412, 2011

Key words: coatings; diffusion; mass spectrometry; polyurethanes

INTRODUCTION

There has been active research performed at the Royal Military College of Canada since 1997 to identify suitable materials for the fabrication of containers for the storage of Canada's used nuclear fuel. In June 2007, a final decision was made to use oxygen-free, phosphorus-doped copper (OFP-Cu) for the storage of Canada's used nuclear fuel to be contained within a deep geological repository (DGR).[1,2] As such, the focus of this study shifted from the fabrication of a container to a polymer coating. We proposed that the coating provide additional protection to the copper container during the most critical initial oxidizing periods in the DGR. The OFP-Cu would be most susceptible to corrosion during the initial warm, oxidizing stages of containment within the first 100 years of residence within the DGR.[3] Within the DGR, the environment is expected to evolve with time, varying from warm, oxidizing conditions to a cool, anoxic, long-term benign period.

The predicted peak temperature within the DGR is 97°C.[4] Furthermore, the DGR is expected to gradually resaturate with groundwater over time in an environment in which oxygen is limited. Depending on the area of burial, the pH of the groundwater is expected to vary from 6.8 to 8.4 and is determined by the amount of calcite present in the groundwater.[5] The purpose of introducing this additional barrier is to reduce the contact of the OFP-Cu with the surrounding groundwater and, thereby, increase the longevity of the container and, thus, the isolation of the used nuclear fuel.

Polyurethane is the material of choice for coating the metal container because polyurethanes exhibit a microphase property derived from the combination of hard and soft segments from its polyurethane and polyol components, respectively. As such, polyurethanes are able to demonstrate a wide variety of properties ranging from very flexible to hard and brittle films.[6] Castor oil is used as the polyol component as it is derived from a natural source and provides an alternative to conventional petroleum-based derived polyols. Castor oil derived from a plant-based renewable resource is a good option for the preparation of polymers. Additionally, the long-chain component of the castor oil adds flexibility and may help to minimize the effects of degradation, an issue that may occur within the DGR. In addition,

polyurethanes have been used in harsh environments, such as those in the aerospace and the pipeline industry, and have exhibited a good track record as a coating material.[7]

Polyurethanes are known to be susceptible to acid hydrolysis of the ester bond. Therefore, although the testing site in the Canadian Shield indicated a pH range between 6.8 and 8.4,[5] in this study, we investigated the effects of more acidic pH solutions. We hypothesized that if the castor-oil-based polyurethanes (COPUs) could maintain their mechanical integrity in the most acidic pH solutions, they will sufficiently function at pH values between 6.8 and 8.4. In addition, a specific final site for the DGR is yet to be determined; thus, the final site may have more aggressive groundwater conditions. Therefore, it is best to investigate the most critical conditions to which the coatings may be subjected. It was postulated on the basis of other work[8] that the acid hydrolysis of polyurethane would be lower in the more crosslinked polyurethanes than in an uncrosslinked one, perhaps because the diffusing ends of the COPU fragments separated by hydrolysis have a propensity to undergo recombination due to the caged network structure, which thereby reduces the degradation rate. To date, there have been few studies related to the sorption and diffusion properties of polyurethanes and even fewer for COPUs.[9–12] In the experimental studies that have been published, the main focus has been on the diffusion of organic solvents into COPUs. The differences between the hydrophilicity of organic solvents and that of the polar acidic solutions used in this study were indeed a good incentive to carry out further study on the topic of sorption and diffusion properties of COPUs.

The goal of this study was to investigate the diffusion and sorption properties of COPUs in low acidic concentration environments over temperatures ranging from 25 to 70°C. Because one of the major anions found in the groundwater is chlorine, a series of hydrochloric acid solutions (HCl) and distilled water solutions were used to provide the various pHs. Neutron activation analysis (NAA) is an effective tool that was used in this study to analyze the actual amount of chorine ions that were within the polyurethane samples. NAA was used to compare the actual quantities of chlorine in the samples to those which were expected from the surrounding bulk solution. There are only two naturally occurring isotopes in chlorine, from which the radioisotopes ^{36}Cl and ^{38}Cl are produced; ^{38}Cl is used for NAA.[13] For the samples that had reached saturation, the analysis of the sorption curves allowed for the calculation of the apparent activation energy for sorption and permeation. After saturation, electron ionization mass spectroscopy (EIMS) allowed for deductions to be made about the transport of small molecular particles from within the polymer to the external surrounding solution.

EXPERIMENTAL

Materials

The castor oil, hexamethylene diisocyanate (HMDI), and 2,4-toluene diisocyanate (TDI) were obtained from Sigma-Aldrich Co., Inc., and were used as received. The equivalent weight per hydroxyl group for castor oil was 345 g and those per NCO group for HMDI and TDI were 84 and 87 g, respectively. Double-distilled water and HCl solutions were used for the diffusion studies. The HCl solutions of various molality, 0.1 and 0.001M, were prepared from 12 and 0.1M stock solutions, respectively. The 12M stock solution was supplied by Caledon Laboratory Chemicals (Georgetown, Ontario, Canada).

Sample preparation

We prepared the samples by simultaneously introducing a predetermined amount of castor oil and isocyanate corresponding to a fixed NCO/OH ratio of 1.5 into a round-bottom flask. The round-bottom flask was then affixed to a rotary evaporator attached to an aspirator pump, which provided a 30-mmHg vacuum. The mixture was stirred vigorously (100 rpm), and heated to approximately 65°C for at least 1 h to form the urethane prepolymer. After mixing, the blend was poured into rectangular molds. The molds were degassed under reduced pressure, 76 mmHg (10.13 kPa), and heated to 65°C for 30 min. Then, the blends were cured in the molds at 100°C for 9.5 h. Once cured, the polyurethane samples were cut into the tensile dumbbell shape prescribed by ASTM D 638-96[14] with a D-412-C die (± 0.002″) provided by Benz Materials Testing Instruments, (Providence, Rhode Island, New York) and rectangular shaped samples with dimensions of 12 cm × 1 cm × 2.5 mm were also produced. In this article, the COPUs based on HMDI and TDI are called COPUH and COPUT, respectively.

Diffusion experiments

The weight gain method based on ASTM D 570-95[15] was used to analyze the diffusion properties of the polyurethane samples in this study. Rectangular bars (12 cm × 1 cm × 2.5 mm) were used for the COPUs diffusion tests. Five samples were placed in each of the 100-mL test tubes. The test tubes were then filled with the diffusing solution and lowered through an insulating top into a water bath. To ensure minimal heat loss and maximum insulation,

in addition to the insulating top, the water bath was surrounded by flexible foam sheets, which maintained the system at the experimental temperature ($\pm 1°$C). The samples were periodically removed from the test tubes, then dried with absorbent paper, and weighed on an analytical balance (± 0.05 mg). The specimens were immediately returned to the diffusing solution and the temperature-controlled bath. The samples spent less than 1 min outside the temperature-controlled bath to minimize errors due to solvent evaporation. Weighing of the samples was continued until the attainment of equilibrium sorption or until an accumulated time of 1.44×10^6 s (1200 s$^{1/2}$) had passed.

Neutron activation analysis (NAA)

The SLOWPOKE-2 nuclear reactor at the Royal Military College of Canada was used to generate the NAA data. At the Royal Military College of Canada, NAA is based on the absorption of slow (thermal) neutrons into the target nuclei. One makes the quantitative assessment of the content of an element within a sample by comparing the intensity of key γ photopeaks to those of standard samples irradiated and counted usually under the same conditions as those for the unknown sample. A simple rule of three is then used to determine the mass of the element of the unknown sample, which is commonly done in the parts per million range, or even in the parts per billion range, with an accuracy of usually better than 1%.[16] Errors commonly associated with NAA are due to counting statistics and calibration errors in the detection of the γ photons.

To run the NAA, the samples were placed in low-density polyethylene containers. The containers entered the SLOWPOKE-2 pool type reactor via low-density polyethylene tubes through a "rabbit" system, which was operated with compressed air. The software used to analyze the results was the Java version of École Polytechnique's Activation Analysis Program for the SLOWPOKE-2 Facility at École Polytechnique in Montreal.

Characteristic γ rays were counted from those emitted by the resulting radioactive isotopes (radioisotopes).[13] NAA was performed on fully saturated polyurethane samples. The quantity of chlorine determined by NAA was compared to a chlorine standard, which allowed for the calculation of the percentage chlorine content. Natural chlorine can be found in two radioisotopes: ^{35}Cl (75.78%) and ^{37}Cl (24.22%), with the percentages representing the natural atomic composition.[13] The capture of thermal neutrons provided by the SLOWPOKE-2, whose population consisted of mainly thermal neutrons (~ 90%), into the nucleus of ^{35}Cl and ^{37}Cl led to the formation of radioisotopes. The isotopes formed

were ^{36}Cl and ^{38}Cl, and their respective half lives are 301,000 years and 37.2 min, respectively.[13]

For NAA, the radioisotope that was used was ^{38}Cl, which has a half-life of 37.2 min. This ^{38}Cl decays rapidly into stable 38Ar by β decay but also includes the emission of γ photons with an energy spectrum displaying several energies. The energies of interest to this study were 1642 and 2167 keV, the most important being the one from the 1642-keV peak (this photon was emitted 100% of the time).[13] The high energy of the main γ photon emitted made its detection easy and the measurement unambiguous because few radioisotopes have γ energies with comparable intensities within their γ spectra.

Electronic ionization mass spectroscopy (EIMS)

The saturated solutions collected once the castor oil samples were saturated were analyzed with EIMS. A few milliliters of each of the solutions was placed into glass vials and sent to Queen's University to be analyzed. The spectra were acquired with a VWaters/Micromass gas chromatography/time-of-flight instrument from Applied Biosystems at Queen's University (Kingston, Ontario). The VWaters/Micromass gas chromatography/time-of-flight instrument was operated in the reflectron mode. The accelerating voltage was 2600 kV. The samples were injected into the instrument and heated until they became volatile. Spectra were recorded with a standard ionization energy of 70 eV.

Tensile testing

An Instron model 4206 universal testing instrument was used to measure the tensile properties of polymers on the basis of the procedure set by ASTM D 638-96.[14] The polymer test specimens were made in the form of standard dumbbell-shaped type IV bars. Measurements were taken with 50-N and 5-kN load cells at crosshead speeds of 10.0 and 20.0 mm/min for COPUH and COPUT correspondingly. Tests were run until break occurred or until the maximum displacement was reached, and the modulus was then determined. To keep the undetermined error to a minimum, five samples were tested for each data set.

RESULTS AND DISCUSSION

Diffusion/sorption

The extent of sorption and the manner by which solvents are absorbed and retained are dependent on the nature of the polymer and can be related to the polymer structure. Because of the very long chain of the polyol component contributed by the castor oil
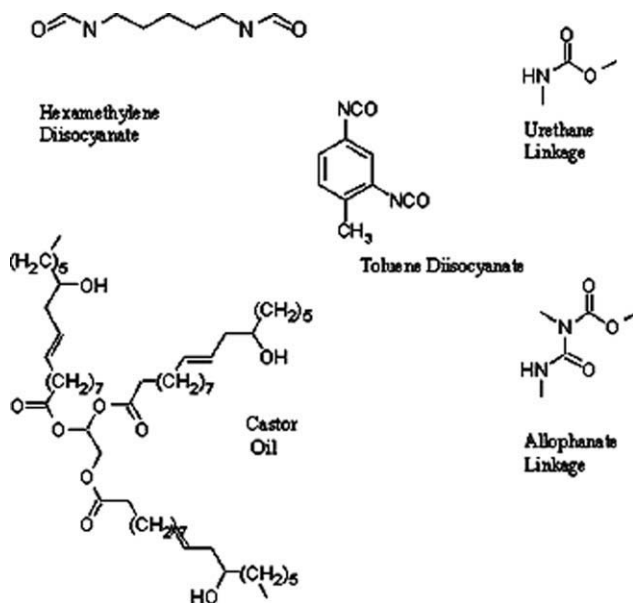
Figure 1 Components of the COPUs.

(Fig. 1), both the aliphatic and the aromatic polyurethanes exhibited very hydrophobic properties and, thus, resulted in the limited sorption of the aqueous solutions (<1%). Notwithstanding, these polymers were able to absorb enough aqueous solution over an acceptable experimental timescale for several conclusions to be drawn about their behavior, as discussed in upcoming paragraphs.

Sorption curves are expressed as the percentage of penetrant uptake (Q_t) versus the square root of time ($t^{1/2}$) at 25, 50, and 70°C at each of three pHs, 1, 3, and 5.5, and are displayed in Figures 2 and 3. Q_t of the soaked polymer is calculated as follows:

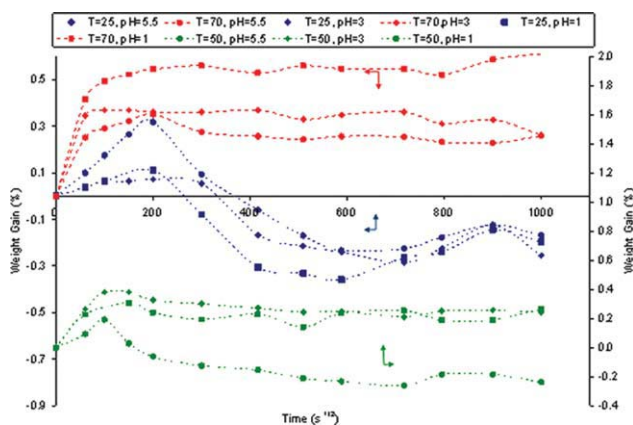$$Q_t = \frac{M_t - M_i}{M_i} \times 100 \qquad (1)$$

Figure 2 Sorption curves of the COPUH polyurethanes at 25, 50, and 70°C and at pHs 1, 3, and 5.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
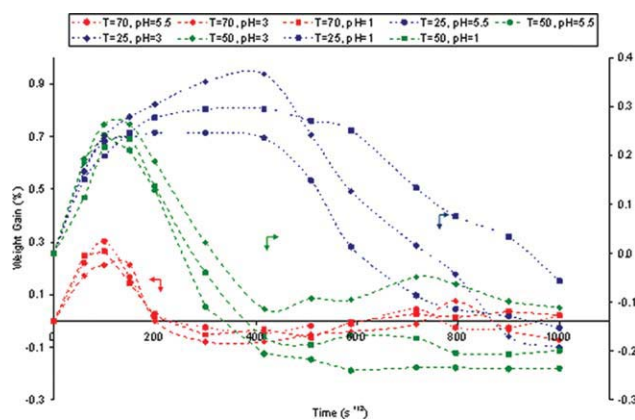
Figure 3 Sorption curves of the COPUT polyurethanes at 25, 50, and 70°C and at pHs 1, 3, and 5.5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where M_i is the initial weight of the polymer and M_t is the weight of the polymer at time $t^{1/2}$.

As shown in Figures 2 and 3, the hard-segment isocyanate component was a crucial factor in the overall sorption and diffusion properties of the COPUs. There was a definite distinction between the sorption behavior of the COPUHs and COPUTs. Equilibrium saturation occurred when the sorption curves reached a maximum sorption value and maintained a plateau at that given value over time. The COPUT graphs illustrated in Figure 3 show sorption curves that never attained equilibrium saturation. Rather, all of the curves increased from the starting unsaturated value to a maximum sorption value, and then, these curves decreased back toward the original unsaturated polymer weight. In the case of the COPUHs in Figure 2, at 70°C with pHs of 1, 3, and 5.5 and at 50°C with pHs of 1 and 3, equilibrium saturation was obtained. At all of other temperatures and pHs, the behavior of the COPUHs were similar to that of COPUT.

The differences in the behavior of aromatic and aliphatic polyurethanes can adequately be attributed to the time-dependant response of the polymers' chain relaxation in relation to the rapid solvent diffusion.[17,18] Therefore, in terms of the polymer, the release of stress and the diffusion of the solvent within a polymer is a function of the transposition of holes within the polymer. The formation of holes is determined by several factors, which include the polymer packing and side-group complexity, polarity, crystallinity, orientation, fillers, and plasticization.[19] Hence, the effect of the choice of the isocyanate is related to the ability of the polymer to form holes in which the solvent may diffuse into. Therefore, the limitations of the more rigidly ordered structure of the aromatic group result in less variation in the amount and size of holes through which

a solvent may pass; this results in a relatively standard amount of solution sorbed. The more flexible aliphatic group can form different sized holes and allows for a greater range of sorption, depending on the temperature and pH.

In this study, the apparent coefficients were only calculated for the castor oil polyurethanes that exhibited equilibrium (plateau regions) over an extended period of time. The values of the apparent diffusion coefficient [D (cm^2/s)] were calculated on the basis of the initial linear portions of the sorption curves [i.e., the initial gradient (θ)] of Figures 2 and 3 and with Fick's equation [eq. (2)]. Therefore, at these initial stages (<200 s$^{1/2}$), with solution diffusing into the polymer, it was unlikely that the polymer had swollen to the extent that any small particles, which were already present in the polymer, may have diffused out into the solution at this stage. As such, the calculations performed with the initial straight-line portions of the curves were indeed valid and did not account for the simultaneous weight loss.

The fractional sorption is typically linear with $t^{1/2}$ for at least a portion of the total sorption (desorption) for systems obeying Fickian transport kinetics.[20] On the basis of eq. (2), D was obtained from θ for a graph of M_t/M_∞ (where M_∞ is the mass uptake at equilibrium) as a function of $t^{1/2}$:

$$D = \pi \left[\frac{h\theta}{4M_\infty} \right]^2 \qquad (2)$$

where h is the thickness of the polymer and θ is defined as $M_t/t^{1/2}$. The permeability coefficient [P (cm^2/s)] may be expressed as a product of D (cm^2/s) and the solubility coefficient [S (g/g)]. Hence, P is equal to $D \times S$. The penetrant solubility in this study was determined from the plateau regions as the amount of solvent sorbed per gram of polyurethane:

$$S = \frac{M_\infty}{M_i} \qquad (3)$$

The calculated values of S, D, and P under the working temperatures are given in Table I.

The trends for the diffusive data given in Table I show an increase in these values with increasing temperature for COPUH only. The changes in free volume, which directly affected the size of the holes in the polymer and, therefore, the amount of solvent that could be absorbed, depended on the segmental motion of the polymer chains, which created these voids. Increasing the temperature increased the segmental motion by increasing the vibrational and rotational energy of polymer segments. Hence, the sorption, diffusion,

TABLE I
S, D, and P Values for the COPU Penetrant Systems at Various Temperatures

Sample	Temperature (°C)	pH for HCl								
		1			3			5.5		
		$S \times 10^2$ (g/g)	$D \times 10^6$ (cm^2/s)	$P \times 10^7$ (cm^2/s)	$S \times 10^2$ (g/g)	$D \times 10^6$ (cm^2/s)	$P \times 10^7$ (cm^2/s)	$S \times 10^2$ (g/g)	$D \times 10^6$ (cm^2/s)	$P \times 10^7$ (cm^2/s)
COPUH	25	–	–	–	0.02	0.85	0.16	–	–	–
COPUH	50	0.09	2.13	1.89	0.08	3.13	2.43	–	–	–
COPUH	70	0.17	1.97	3.35	0.15	3.03	4.55	0.07	3.31	2.42
COPUT	25	0.11	0.88	0.99	–	–	–	0.06	1.6	0.89

TABLE II
E_D, E_P, and ΔH_S for COPUH in an HCl
Solution (pH 3)

Activation parameter	Value
E_D (kJ/mol)	85
E_P (kJ/mol)	18
ΔH_S (kJ/mol)	−67

and permeability values increased with increasing temperature.

At a given temperature, for example, 70°C, on the basis of the data in Table I, from the more acidic pH of 1 to the less acidic pH of 5.5, D increased. The diffusivity was related to the free volume within the polymer. The decrease in the diffusivity with acidity may have implied that the more dissociated ions may have increased the hydrogen bonding within the polymer sample and/or underwent clustering. The increased hydrogen bonding may have resulted in smaller holes and less free volume within the structure and, therefore, allowed less solubility and diffusivity. Instead of having a 1 : 1 relation between the number of holes within the polymer and the number of solvents sorbed into each hole, in the case of acid diffusion into the COPUs, more than one solvent molecule attached itself to a hole; this resulted in clustering. Clustering may have occurred as the dissociated ions formed multiple hydrogen bonds to the polar groups (hydroxyl, carboxyl, amide) in the polymer; this resulted in an $X : 1$ ratio (where X is any whole number greater than 1). The results of the NAA agreed with this and are discussed later.

Arrhenius activation parameters were calculated for the COPUH polymers submerged in pH 3 HCl on the basis of the Arrhenius relation:

$$X = X_o \exp\left(\frac{-E_\chi}{RT}\right) \qquad (4)$$

where X and X_o are the diffusivity or permeability at time t and infinite time, respectively; E_x is the activation energy for the diffusivity or permeability process (kJ/mol); R is the molar gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (K). In addition to the Arrhenius activation parameters, the heat of solution (ΔH_S) was also calculated ($\Delta H_S = E_P - E_D$, where E_D is the activation energy for diffusion and E_P is the activation energy for permeation), and these values are given in Table II for COPUH in a pH 3 HCl solution.

The diffusivity values determined and stated in Table I were explained in terms of the acidity and affinity of the hydrogen ions in the HCl and distilled water series. Kumar et al.[21] noted that the D values for HMDI-based COPUs in water were 1.63×10^{-5}

cm^2/s at 30°C, 2.63×10^{-5} at 50°C, and 1.28×10^{-4} at 70°C. The D values for TDI-based COPUs in water reported by Kumar et al.[21] were 1.41×10^{-5} cm^2/s at 30°C, 1.88×10^{-5} at 50°C, and 6.75×10^{-5} at 70°C. Similar to this study, the aromatic TDI structure formed a more structured matrix, which reduced the ability of water molecules to move along the polymer segments and, hence, the lower diffusivities. The diffusivities values in Kumar et al.'s study were higher for the sorption of water molecules into the polyurethanes than in this study, and this was attributed to a lower NCO/OH or hard-segment ratio.[22]

Table II reveals two points: (1) the values for E_D and E_P were positive, with $E_D > E_P$, and (2) ΔH_S was negative. The positive values of E_D and E_P indicated that the diffusion and permeation process of the acidic HCl solvent into the COPU required a significant amount of energy. This is clearly reported in Table I, which shows that with increasing temperature, the rates of diffusion and permeation increased. The high activation energy also in part may have been due to the restriction of the pore size and free volume in the polymer samples. ΔH_S is governed by endothermic contributions from Henry's law mode, which states that the sorption course proceeds through the creation of new sites or pores in the polymer with the exothermic contributions from hole-filling Langmuir activities.[10]

Several of the polymers in Figures 3 and 4 showed a decrease in mass uptake in the later diffusion time periods. The loss of mass was attributed to the loss
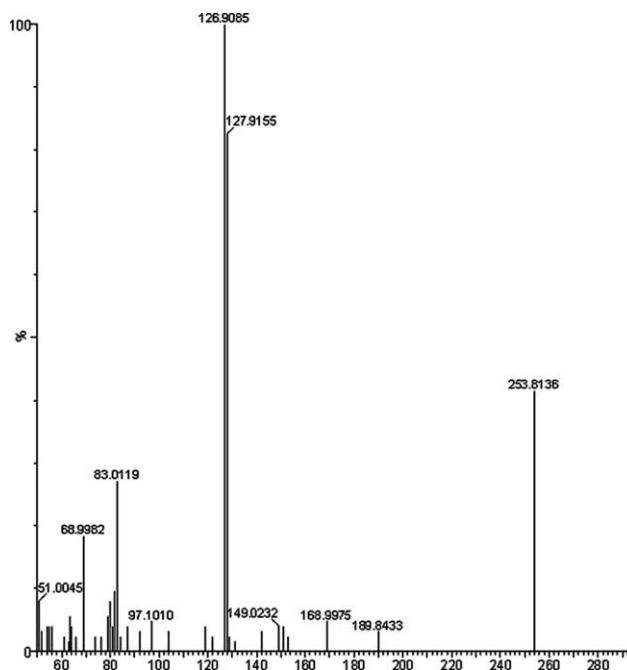
Figure 4 Mass spectroscopy derived from solutions of COPUHs saturated in a pH 1 HCl solution at 70°C.
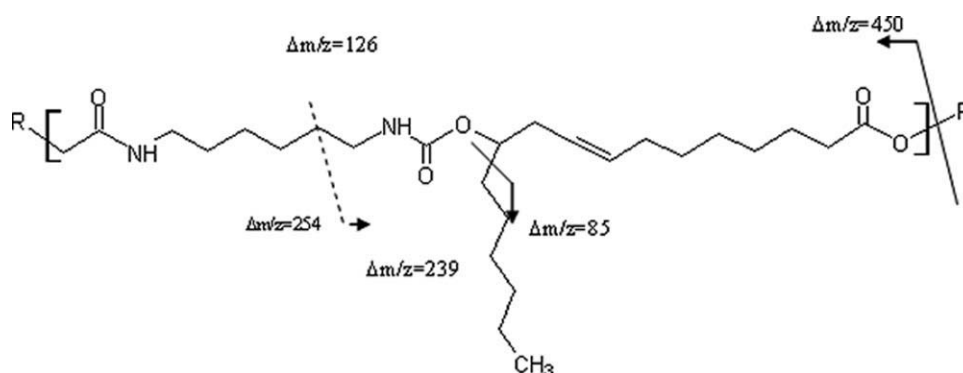
Figure 5 Proposed fragmentation pattern of the COPUs

of low molecular mass components. These low molecular mass components were able to diffuse out of the polymer matrix after a path was formed in the now swollen polymer by the diffusing solution. This loss may have been due to a combination of factors, which may have included the formation of more energetically favorable smaller molecules or simply the release of indigenous materials that were already present in the polymer. EIMS was used to investigate the low-mass components that diffused out of the polymer into the bulk solution.

EIMS

We used mass spectroscopy in this study to look at the composition of the material remaining in the solvent after the saturated polymer sample was removed. The idea was that any fragmentation that may have occurred would have diffused out of the polymer sample into the surrounding solvent. We found that the mass spectra for both the COPUH and COPUT had several overlapping peaks, regardless of what temperature was used or in what solution the sample had been saturated. This led to the conclusion that all activity occurred at the urethane linkage attached to the soft segment, which was derived from the castor oil component of the polyurethane. At pH = 1 and at 70°C, it was expected that acid hydrolysis would be at its most rampant, as this was the most acidic pH and highest temperature used in this study; thus, Figure 4 was chosen as the representative spectrum.

On the basis of the fragmentation pattern in Figure 5, it seemed that some acid hydrolysis occurred at the ester bond in the castor oil ($m/z = 450$) to give the starting fragment. The fragment at $m/z = 450$ is not shown as this fragment was presumably quickly broken. With EIMS, cleavage is favored at alkyl-substituted carbons, so the more substituted the carbon is, the more likely it is to cleave. This is a result of the increased stability of carbocations in the following order: $CH_3^+ < R'CH_2^+ < R'_2CH^+$

$< R'_3C^+$. Customarily, the largest substituent at a branch is eliminated most readily as a radical because it is thought that the long-chain radical can achieve some stability by delocalization of the lone electron. The largest substituent lost, as shown in Figure 5, was a fragment at $m/z = 85$. The remaining section underwent fragmentation next to the nitrogen heteroatom and the α CH$_2$ adjacent to the nitrogen atom to give fragments at m/z values of 111, 126, 239, and 254.

The fragment at $m/z = 126$ then underwent a McLafferty rearrangement with the result being the elimination of a stable neutral olefin product at $m/z = 83$ (Fig. 6). In addition to the McLafferty rearrangement, the spectrum of the long-chain amide fragments was such that it gave a series of hydrocarbon clusters at intervals of 14 mass units. The retention of charge remained on the alkyl fragment ($m/z = 27, 41, 55, 69, 83,$ or 111). In each cluster, there was a prominent peak at $C_nH_{2n-1}NO$.

NAA

NAA was used to determine the concentration of chlorine once the samples were fully saturated. Table III reports the results obtained for the castor oil polyurethane samples at the fully saturated stage of the diffusion process. A pH of 5.5 was obtained from doubly distilled water, and as expected, NAA revealed no chlorine content in the samples saturated in these solutions. As such, only the samples saturated at pHs of 1 and 3 were considered in NAA. Measurements of the dry sample indicated
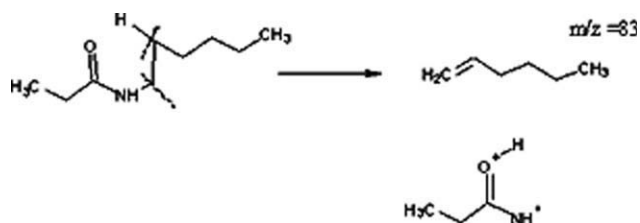

**Figure 6** McLafferty rearrangement.

TABLE III
NAA Results (% mass)

Sample	Temperature (°C)	pH 1		pH 3	
		Diffusing acid (%)	Acid/water molar ratio (%)	Diffusing acid (%)	Acid/water molar ratio (%)
COPUH	25	0.012	4.14	0.011	1.113
COPUH	50	0.029	3.41	0.01	0.905
COPUH	70	0.034	2.23	0.01	0.89
COPUT	25	0.002	0.24	0.001	0.125
COPUT	50	0.002	0.31	0.004	0.509
COPUT	70	0.009	1.17	0.002	0.337

that there were low levels of chlorine present within the polymer matrix, 0.0062% for the COPUH polymers and 0.0007% for the COPUT polymers.

In Table III, one can discern the effect of temperature and pH on the chlorine content present within the polymers. It was expected that on the basis of the initial molarities of the initial acid and water ratios, regardless of temperature and polymer type, this acid/water molar ratio would remain constant at 0.18% for the pH 1 solution and 0.0018% for the pH 3 solution. However, this was not found to be the case. Using the elemental mass composition of chlorine found in the polymer samples by NAA, we performed a quantity analysis to deduce what differences occurred within the polymer versus that of the bulk solution in which they were saturated. We assumed from eq. (5) that once dissolved in water, each molecule of HCl fully dissociated into one solvated proton and a chlorine ion. For all intents and purposes, we assumed that the right-hand side of eq. (5) could be considered as one acid molecule, which consisted of a single unit of two ions because of the necessity for charge neutrality, with a molecular mass of 54.5 g/mol:

$$\text{HCL} \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{O}^+ + \text{Cl}^- \tag{5}$$
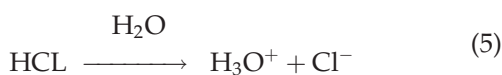
The Cl^- amounts derived from NAA were related to the mass percentage of Cl^- in the diffusing acid solution (65.1%) because we assumed that all of the chlorine present was contained in the diffusing solution. The mass percentage value of chlorine was used to calculate the actual percentage of diffusing acid into the polymer, and the molar ratio of acid/water inside the polymer versus the bulk solution are reported in Table IV.

It is evident from the values in Table IV that the actual acid/water ratios were several orders of magnitude greater than those of the expected bulk solution ratios. The greater acid/water molar ratio indicated that there were more protonated HCl units within the polymer than water. The increase in acid concentration may have been due to a higher attrac-

tion of urethane groups in the polyurethane to the protons in the diffusing acid solution than to those of water. From the results in Table IV, we concluded that there was indeed some clustering of the diffusing acid unit within the polymer sample. In an ideal situation, the holes in the polymer molecules would exclude their own volume to one diffusing molecule but otherwise would not affect the distribution of the remaining diffusing solution.[21] Because the diffusing acid/water ratio was so much greater inside the polymer than in the bulk solution, clustering may have been the reason.

H bonding and polymer structure have been shown to be important aspects of water clustering. The tendency for water to cluster has been shown to be highly dependent on the local structure of the hydrogen-bonding site, which varies as a result of interweaving of molecules and the formation of hard and soft segments.[23] In the case of COPUs, the more flexible aliphatic-based polyurethanes, as discussed previously, may have formed bigger holes, which allowed for greater diffusion within the polymer, greater clustering, and therefore, higher acid/water ratios than the corresponding aromatic-based ones.

The clustering ability of the solvent depended on both the polymer and the solvent. In other experimental literature, it has been shown that clustering can be investigated by light-scattering techniques, and in the case of high water absorption levels, a translucent hue evolved in the polymer samples. The hue indicated the presence of two distinct

TABLE IV
Actual Acid/Water Ratios and Diffusing Acid Contents in the COPU Samples

Sample	Temperature (°C)	Chlorine content (%)	
		pH 1	pH 3
COPUH	25	0.0079	0.0069
COPUH	50	0.0187	0.0066
COPUH	70	0.0224	0.0063
COPUT	25	0.0014	0.0009
COPUT	50	0.0014	0.0026
COPUT	70	0.0059	0.0014
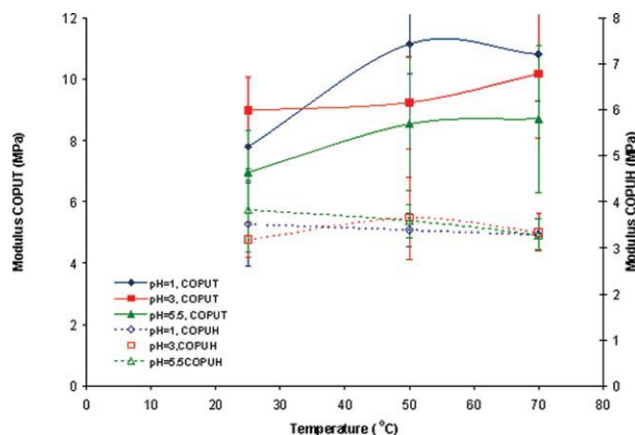
Figure 7 Modulus as a function of temperature for the various COPUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phases with different refractive indices.[21] The translucent hue discussed in past articles was clearly observed in these experiments.

Tensile testing

The unique design of polyurethane is made up of hard and soft segments. Its resistance to deformation and its flexibility are dependent on the nature of these hard and soft segments. In this study, the isocyanate component was the only factor that differed in the composition of the two polyurethane samples. Clearly, as shown in Figure 7, the aromatic-based diisocyanates produced stronger or harder to deform samples; this was due to the rigid aromatic structure, whereas the aliphatic-based polyurethane produced more flexible, easier to deform samples.

When the COPU samples were placed in the HCl solvents, as shown in Figure 7, the modulus values increased and remained above those of the unsaturated polymer, regardless of polymer type and experimental parameters. The unsaturated modulus values for the aromatic and aliphatic COPUs, respectively, were 1.71 ± 0.65 and 1.55 ± 0.30 MPa. It was thought that the diffusing solutions within the polymer resulted in hydrogen bonding, which in turn, caused an increase in the saturated polymer modulus values.

CONCLUSIONS

In this study, we investigated the sorption and the diffusion properties of COPUs, which differed only in isocyanate structure. In general, differences in the sorption properties between the aromatic versus the aliphatic-based polyurethane were shown to be a result of the ability to form free-volume spaces or holes within the matrix.

The absorption of diffusing liquid was minimal, regardless of pH and temperature (<1%). NAA, through comparisons of the acid/molar ratio within the polymer to that of the bulk solution, exposed a greater absorption of acid than expected. The increased acid uptake was attributed to clustering and to the greater attraction of the urethane group to the hydrogens associated with the acid unit than those of water. The clustering, which resulted in increased hydrogen bonding, also explained the increase in the modulus values of the saturated polymers compared to the unsaturated ones.

The apparent E_D and E_P values were calculated to be 85 and 18 kJ/mol, respectively. The large positive values of E_D and E_P indicated that the diffusion process into these COPU was not an energetically favored reaction. The hydrophobic nature of the castor oil soft segments of these polyurethanes ensured very little hydrophilic sorption through the polymer, as represented by the very small diffusion and permeation values. Thus, any degradation that occurred was limited and, from EIMS, would have occurred because of the fracturing of the ester bond in the castor oil segment of the polyurethane bonds.

This study showed that these polymers could be used in the saturation conditions expected in a DGR.

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