

Surface Properties of a Segmented Polyurethane Containing Amphiphilic Polymers as Additives

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SYNOPSIS

Two different types of amphiphilic polymers were used as surface-modifying additives to a polyetherurethane, Pellethane 2363-75D, which has T_g close to room temperature. The additives used were a segmented polyetherurethane designated Pol C, and Pluronic PE6800 and PE9400, i.e., triblock copolymers of propylene oxide and ethylene oxide. Pol C was prepared from poly(ethylene glycol), methylene diphenylene diisocyanate, and a fatty acid monoglyceride. The properties of the blends were investigated in their unhydrated state and after water immersion at 23°C and 80°C. Surface composition, water absorption, and leakage of additives to the aqueous phase have been studied. From ESCA and contact angle measurements it was concluded that Pol C was enriched in the surface layer of the matrix material after water immersion at 80°C. The Pluronic showed less effects on the surface properties of the matrix material, probably because of their high water solubility. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

As compared to metals and ceramics, polymers are quite mobile on the molecular scale, and can molecularly reorganize in a relatively short time,¹⁻⁷ the time scale depending on if the material is in its glassy or rubbery state. Rearrangements of segments of the polymeric chain can be environmentally induced,^{1,3,5-13} that is, the interface between a polymer and its environment will rearrange in the direction of a minimum free surface energy.^{1,2,5-8,10,12,14} The rearrangement will be restricted to the surface regions^{5-8,10} of the material, i.e., the interphase between the bulk and the environment.

The properties of segmented polyurethanes are governed by their microphase separated structures^{1,10,11} as well as their contents of hydrophilic and hydrophobic segments.^{8,9,15} The microphase separation is a consequence of a positive free energy of mixing of the hard and soft segments of the polyurethane.^{10,16} Below a critical volume fraction the hard segments, i.e., the urethane blocks, are dispersed in a soft polyether or polyester matrix.

Environmental changes may induce surface rearrangements of the hard and the soft blocks relative to one another, provided they differ in their surface free energies.^{1,8,9,15}

Surfaces of polyurethanes as well as other polymers have been investigated regarding their surface mobility in contact with water and other solvents.^{2,4-8,10-15,17} From these investigations it can be concluded that polymer surfaces become more hydrophilic when contacted with water, that is, the most hydrophilic segments or groups in the polymer will orient themselves towards the aqueous phase when the environment changes from air to water. It has also been shown that when the environment changes back again from hydrophilic to hydrophobic, the hydrophilic segments of the polymer will disappear and the hydrophobic segments reappear at the surface. The relaxation time for the rearrangement will be different for polymers with different degrees of chain mobility.⁴

In previous communications we have reported on the use of a highly amphiphilic polyurethane for surface modification of a commercial polyetherurethane, Pellethane 2363-80AE (Pel 80AE).¹⁹⁻²¹ The glass transition temperature of Pel 80AE is -47°C, as measured by DSC, which indicates that at room temperature the chain mobility of the matrix allows

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drawn up in the syringe to obtain the receding contact angles. Both angles were later evaluated from printouts of the video screen. The reproducibility of the measured angles depended on the sample. On each sample 3–7 measurements were made on the air-facing side of the film.

The time dependence of the surface properties for the different materials was investigated. Films of the materials were immersed in water (24°C and 80°C) for different time periods, and the contact angles were measured after different drying times. The first 5 min of drying was done in a desiccator under reduced pressure, followed by drying in air at room temperature.

ESCA

The air-facing side of dry polymer films was analyzed by Electron Spectroscopy for Chemical Analysis (ESCA) using an AEI ES200B spectrometer. Excitation x-ray source was Al-K (1486.6 eV). High resolution spectra of C1s, O1s, and N1s were run. The different band areas were normalized by using Scofield section factors, C1s = 1.00, O1s = 2.93, and N1s = 1.8.²²

Spectra for water-immersed films (24 h at 80°C) were recorded after drying of the wet films at 60°C for 1 h and at 60°C in vacuum for 24 h.

Surface Tension Measurement

Films were cast on contact angle plates (film area about 12 cm²) as described above, and immersed in 100 mL ultrapure water at 23°C and 80°C. The surface tension of the water was measured at different times during 24 h using the surface balance method (Lecomte du Noüy Tensiometer, Krüss, Germany).

Water Absorption, Desorption, and Solubility of Films

Films with an area of approximately 30 cm² (0.5 g) were prepared as described under “film preparation.” The films were weighed and immersed in water (500 mL) for 24 h at 23°C and 80°C, respectively. Water absorption, *Abs*, was calculated as:

$$Abs = \frac{m_{wet} - m_{dry,final}}{m_{dry,final}}$$

where m_{wet} denotes the mass in gram of the wet film and $m_{dry,final}$ the weight of the dry film after water immersion. The wet films were wiped dry with tissue paper and weighed immediately. The desorption rate of water at room temperature was determined by

weighing the films at different times during 24 h after water immersion. The films were then further dried at 60°C for 48 h and allowed to remain at room temperature for additional 4 h before the final weighing.

The water solubility, *WS*, of the polymers was calculated as:

$$WS = \frac{m_{dry} - m_{dry,final}}{m_{dry}}$$

where m_{dry} was the weight of the dry film before immersion in water.

DSC

Differential scanning calorimetry was performed using a Mettler TA 3000 system equipped with a low temperature cell. Mettler Graphware TA 72 was used for T_g evaluation. DSC traces were run under nitrogen purge between –150 and 250°C with a heating rate of 20°C/min. The evaluation was made on the second run of the sample after a controlled cooling (20°C/min).

RESULTS AND DISCUSSION

Two different types of amphiphilic polymers, Polymer C and Pluronic, were used as surface-modifying additives to a polyetherurethane, Pellethane 2363–75D (PEL). Similarly to Pellethane 2363–80AE, PEL is reported to be based on MDI, PTMG, and 1,4-butanediol,¹⁸ although the exact composition is not disclosed. The differences in physical and mechanical properties are presumably due to variations in short/long-chain PTMG ratios. Some selected data for the polymers used are given in Table I. The amphiphilic polyetherurethane Polymer C was prepared from PEG, MDI, and a fatty acid monoglyceride, AH90, according to Figure 1. We have previously reported that Polymer C effectively changes the surface characteristics of Pellethane 2363–80AE when used as an additive in amounts of 1–5% (w/w).¹⁹ Pluronics are triblock copolymers of propylene oxide and ethylene oxide manufactured by BASF (Fig. 1), and have been shown to adsorb from aqueous solutions to polyethylene and polystyrene surfaces to give protein-repellant coatings.^{23–27} The hydrophobic PPG center blocks are believed to adsorb at the polymer surface through hydrophobic interactions, while the hydrophilic PEG blocks orient themselves towards the aqueous phase, thus minimizing the free energy of the interface.^{23,28}

Table I Physical Data for the Materials Used

	PEL	Pol C	PE68	PE94
T_g (DSC) (°C)	20	-34	—	—
T_m (DSC) (°C)	180	—	54	34
Solubility in water*	<i>i</i> [#]	<i>i</i>	<i>s</i>	<i>s</i>
cmc [†] (g/L)/(dyne/cm)	—	—	0.005/58	0.009/47
Water contact angles [‡] $\theta_{ADV}/\theta_{REC}$	76/58	130/5	—	—
Intrinsic viscosity, $[\eta]$ [§] (dL/g)	0.82	0.27	0.26	0.16

* *s* = soluble, *i* = insoluble.

[†] cmc = critical micelle concentration.

[‡] Standard deviation about 2°.

[§] PEL and Pol C dissolved in DMF, PE68 and PE94 dissolved in chloroform.

[#] Solubility 0.2%, see text and Figure 5 for discussion.

As noted in the Introduction, the glass transition temperature of the matrix polymer should have a great influence on the mobility of the amphiphilic additives and the responses of the modified surfaces to environmental changes. The matrix polyurethane chosen in the present investigation had a structure similar to Pellethane 2363-80AE but a significantly higher T_g , which made it possible to study surface restructuring by means of contact angles measurements and ESCA.

Water Contact Angles

Films of the different polymer materials were prepared through solution casting, and contact angles with water were determined for the air-facing sides of the films. As shown in Tables I and II, the advancing and receding contact angles for the matrix polymer PEL were found to be 76° and 58°, respectively. The use of the amphiphilic polyurethane Pol C as an additive at the level of 5% w/w decreased the receding angle by 10°, while the advancing angle remained essentially unchanged. Similar amounts of the triblock copolymers PE94 and PE68 gave greater effects, both contact angles decreasing by 10–15°.

As we have shown in a previous communication, the use of Pol C as an additive greatly affected the surface properties of Pellethane 2363-80AE as shown by changes in the contact angles. It was found that at the 5% level the air-facing side of the surface seemed to be saturated and dominated by the additive.¹⁹ In the present case the contact angle data implied that Pol C did not show any particular enrichment at the surface. The matrix polymer, Pel-

lethane 75D, has a glass transition temperature of 20°C, as compared to -47°C for Pel 80AE. Consequently, the segmental mobility of the matrix is much lower than for Pellethane 2363-80AE at room temperature, and migration of the amphiphilic polymer to the surface would be a very slow process. However, an increase in the temperature to well above T_g should allow the amphiphile to migrate to the surface because of the increased segmental mobility.

Preliminary tests indicated that on subjecting films prepared from PEL-C to temperatures of 80°C in the dry state increased the amounts of Pol C at the surface, as shown by a change in the contact angles (Table II). However, after treatment of the films with water at 80°C for 24 h, very large effects on the wetting behavior of the surfaces were observed. It appears that a combination of high segmental mobilities (high temperature), highly polar surroundings, and hydration of the material would be ideal for surface restructuring. Presumably the polar PEG segments have a greater effect in reducing the free energy of the water/polymer interface than the aliphatic chains for the corresponding free energy reduction of the air/polymer interface in the dry state. The driving force for migration of the amphiphilic polymer would consequently be greater in the first case.

The time and temperature dependence for the contact angles were studied in a series of experiments. Because it could be anticipated that the contact angles would be influenced by the water contents of the films, the drying kinetics were first investigated. At room temperature the drying was rapid—after 7 h only 0.4% water remained in films

Table II Water Contact Angles for Polymers After Different Treatments

Condition	PEL	PEL-C	PEL-PE68	PEL-PE94
	$\theta_{ADV}/\theta_{REC}$	$\theta_{ADV}/\theta_{REC}$	$\theta_{ADV}/\theta_{REC}$	$\theta_{ADV}/\theta_{REC}$
Untreated Films	76/58	78/48	66/43	63/40
Oven at 80°C 24 h	75/55	74/38	59/22	54/29
H ₂ O, 24 h, room temp. Dried 24 h	73/59	86/44	70/47	68/46
H ₂ O, 24 h, room temp. Dried 8 days	76/59	86/46	68/46	65/40
H ₂ O, 24 h, 80°C Dried 24 h	71/55	111/5	68/38	65/36
H ₂ O, 24 h, 80°C Dried 8 days	71/53	113/5	68/39	64/39

Concentration of amphiphilic polymers, 5% w/w. Standard deviation, 3°.

hydrated for 24 h at 23°C (Fig. 2). Similar results were obtained after hydration at 80°C. The behavior of the contact angles were parallel to the drying, i.e., after 5 h drying time the contact angles did not change appreciably.

Contact angles were measured for films immersed in water for different time periods at 23°C and 80°C, and the results are given in Figures 3(A) and (B), respectively. All films were dried for 24 h at room temperature prior to measurement. At 23°C only a small gradual increase of the contact angle hysteresis

was noted for PEL-C [Fig. 3(A)]. For PEL-PE94, the advancing as well as the receding contact angles showed a small decrease at short immersion times, but they returned to their original values at longer immersion. At 80°C, very large effects were observed [Fig. 3(B)]. In contrast to the situation at 23°C, the unmodified PEL polymer was affected by the water immersion, the receding contact angles decreasing by 10° after 24 h immersion time. However, the largest effects were seen for PEL-C surfaces, as noted above. After 5 h immersion time at 80°C, the

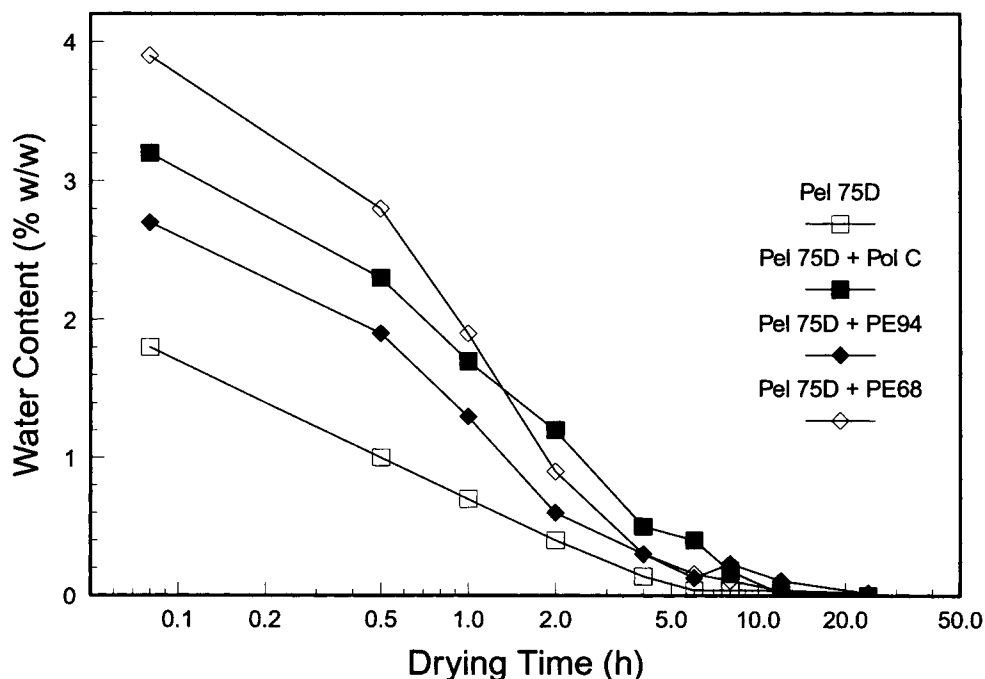


Figure 2 Desorption time for polymer films after immersion in water for 24 h at 23°C. Matrix concentration of additives, 5% w/w.

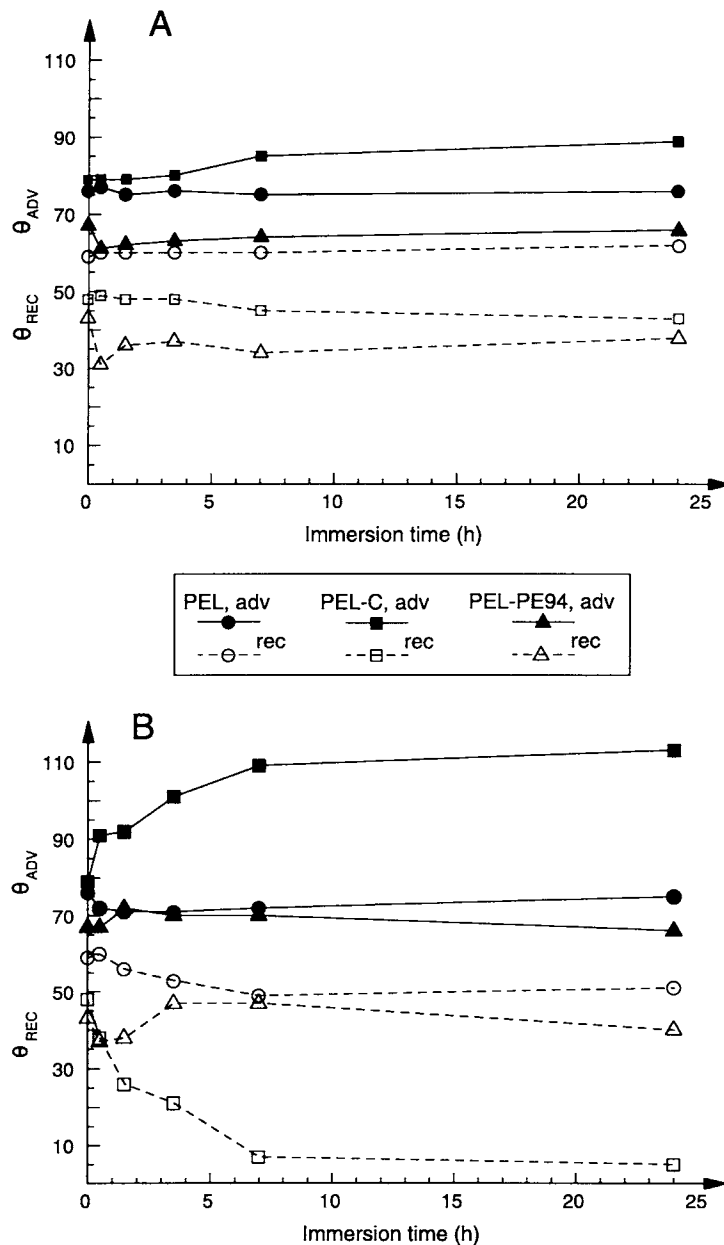


Figure 3 Water contact angles for films dried 24 h after water immersion at (A) 23°C and (B) 80°C. Matrix concentration of additives, 5% w/w.

advancing angle had increased to more than 100°, and the receding angle decreased to approximately 5°. It seems likely that the reason for the large hysteresis is a rearrangement of the polymer surface on contact with water, i.e., the most hydrophilic polymer segments will become exposed to the water in order to minimize the interfacial free energy. This effect was not particularly dependent on the drying time, i.e., the restructured surfaces were quite stable.

It can be noted that PEL-PE94 at hydration at

80°C showed a behavior similar to that observed at 23°C. After a large initial decrease in the receding angles the surface regained its original wetting behavior at prolonged immersion. The high water solubility of PE94 may be a reason for this response. At short immersion times the block copolymer will be enriched at the surface of the blend, but at longer times it may leach out to give a lower equilibrium surface concentration. This is in contrast to Pol C, which has a low water solubility and, consequently,

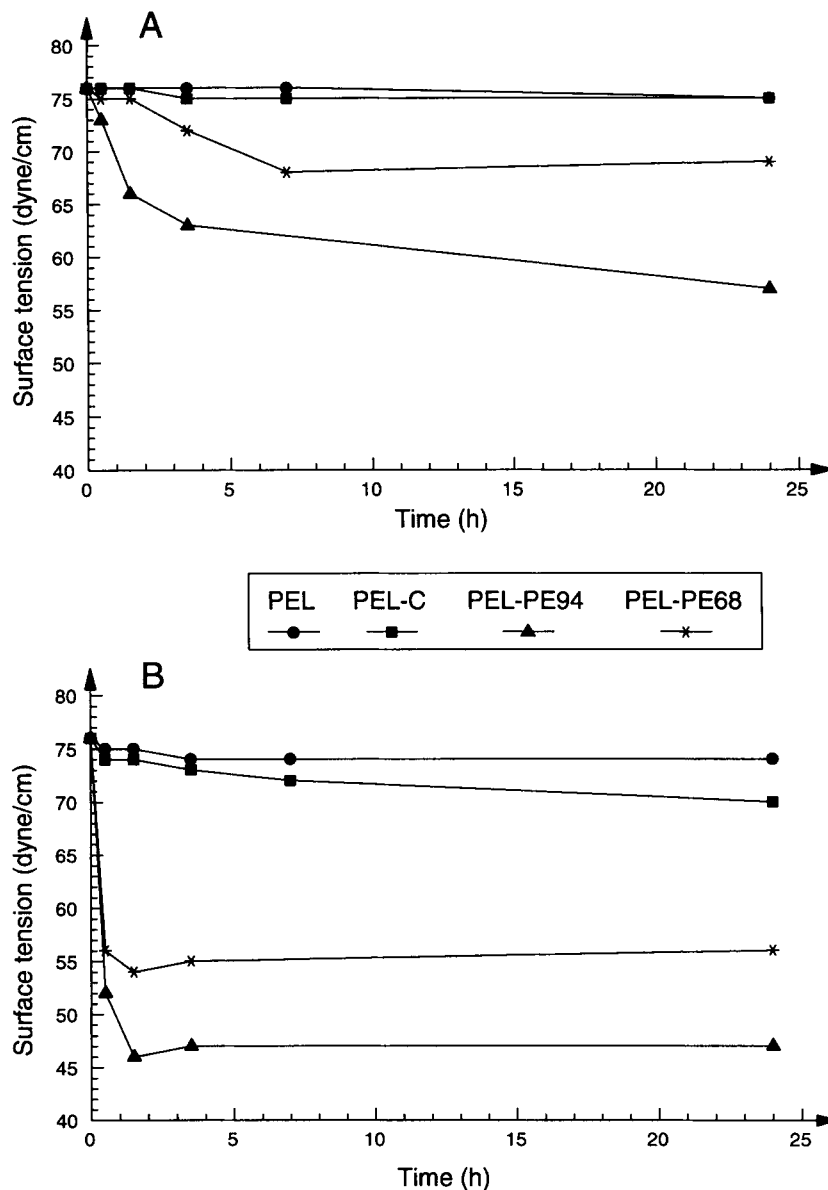


Figure 4 Surface tension values for water leachates of films at (A) 23°C and (B) 80°C. Matrix concentration of additives, 5% w/w.

may accumulate in a high concentration at the polymer/water interface. The properties of the interface will be dominated by the amphiphilic polymer. The solubility of the amphiphilic polymers may, thus, be an additional factor governing their migration and surface enrichment.

Solubility and Water Absorption

In order to investigate the leaching of surface active substances from the blends in contact with water, films of the different materials were immersed in

water and the surface tension of the leachates was measured. The results are presented in Figures 4(A) and (B). For PEL and PEL-C, the surface tension values remained unchanged for 24 h at 23°C [Fig. 4(A)], but at 80°C the surface tension decreased slightly, PEL-C showing the largest decrease (6 dyne/cm) after 24 h [Fig. 4(B)].

The Pluronic modified materials behaved similarly at both temperatures, i.e., surface active substances were leaching out. At 23°C the leaching rate was higher for PEL-PE94 than for PEL-PE68, and the surface tension reached a lower value. At 80°C,

however, there was a rapid decrease of the surface tension for both Pluronic blends, and the final values were lower than those observed at 23°C. The surface tensions observed for PEL-PE68 and PEL-PE94, 55 and 47 dyne/cm, respectively, correspond closely to the surface tensions at the critical micelle concentration (cmc) for pure PE68 and PE94 (Table I). The matrix material is well above its glass transition temperature at 80°C and allows rapid diffusion of the relatively low molecular weight Pluronic molecules. On contact with water at 80°C, PE68 and PE94 may leach out from the blends in amounts large enough to reach cmc in the leachate.

Leaching of substances from the blends should be accompanied by a weight loss on prolonged contact with water. With the method used for analyzing the water solubility, all four materials showed similar weight losses on the order of 0.2–0.3% at 23°C (Fig. 5), including PEL which had been thoroughly extracted with ethanol before use as a matrix material. However, because Pluronics are highly surface active, only very small amounts of these polymers are needed to decrease the surface tension to the values observed in Figure 4, that is, less than 0.5 mg/100 mL (cmc, Table I). Weight differences of this magnitude were within the limits of error for the method of analysis.

At 80°C the Pluronics blends showed weight losses of more than 1% on water immersion, and these values were substantially larger than the corresponding values found for PEL and PEL-C, as can be seen in Figure 5. The amounts of the Pluronics extracted by the aqueous phase were clearly sufficient for reaching cmc, as noted above.

Extraction of the amphiphilic polymers into the

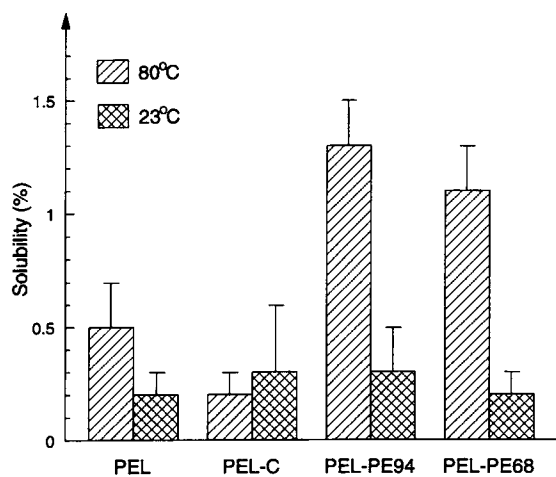


Figure 5 Water solubility of films at 23°C and 80°C. Matrix concentration of additives, 5% w/w.

aqueous phase will depend on the relative solubilities of the polymers in the matrix and in the aqueous phase. An equilibrium will eventually be reached between amphiphilic molecules dissolved in the polymer matrix and in the aqueous solution, respectively, and molecules adsorbed at the interface. Structural differences between the matrix polymers may introduce differences in the matrix solubilities of the amphiphilic polymers, which would lead to differences in the equilibrium distribution of the amphiphile between the matrix and the aqueous solution.

If the solubility of the amphiphile is exceeded in any of the phases, a phase separation will occur with formation of micelles in the aqueous phase and reversed micelles in the polymer phase. Micelle formation in, for example, the aqueous phase, limits the free energy of the dissolved molecules to a value corresponding to cmc, and the extraction of the amphiphile into the solution may continue as long as a reservoir of the amphiphile is present in the polymer matrix. The kinetics of the dissolution will be governed by the mobility of the polymer matrix, i.e., the glass transition temperature, the size and shape of the polymeric amphiphile, the surface excess, and the rate of desorption of the polymer chains from the surface. It follows that a high molecular weight amphiphile should be favorable because of very slow diffusion and desorption rates. The observed difference between the Pluronics and Polymer C is probably a consequence of differences in solubilities in the aqueous medium, because the additives are of approximately the same sizes, as estimated from their intrinsic viscosities (Table I).

The water absorption of the four materials is given in Figure 6. PEL-PE68 has the largest water absorption, which presumably is a consequence of the high PEG content of this polymer. On increasing the temperature from 23°C to 80°C, the absorption was found to decrease for all materials. Schneider et al.¹⁷ has reported a similar phenomenon for polyurethanes having polyethylene oxide/polypropylene oxide block copolymers as the soft segments. The reduction of the water absorption at higher temperatures is probably an effect of the higher densities of the materials at 80°C than at 23°C. All four materials shrink about 5% when contacted with water at 80°C. The shrinkage cannot be correlated to any weight loss—the materials have just become more dense. For the three PEG-containing materials there may be an additional explanation for the lower water absorption at 80°C than at 23°C—the PEG chains become more hydrophobic at elevated temperatures.²⁹

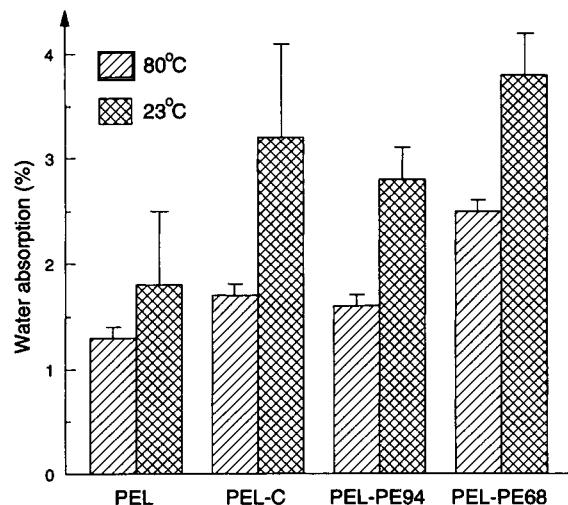


Figure 6 Water absorption of films at 23°C and 80°C. Matrix concentration of additives, 5% w/w.

ESCA Analyses

The accumulation of the amphiphilic polymers at the Pellethane surface after hydration should give rise to differences in surface-sensitive spectra, e.g., ATR-IR and ESCA spectra. Analysis of the materials with ATR-IR gave no measurable differences between hydrated and unhydrated materials. However, as can be seen in Figures 7(A-C) and Table III, ESCA C1s spectra showed significant differences, except for the unmodified matrix material PEL. The surfaces of hydrated and unhydrated PEL-PE68 materials gave similar ESCA spectra [Fig. 7(A)], but as compared to the hydrated matrix material, larger amounts of ether carbons were found, indicating the presence of the block copolymer at the surface.

According to the ESCA C1s spectra, slightly larger amounts of ether carbons were found at the surface of unhydrated PEL-PE94 as compared to

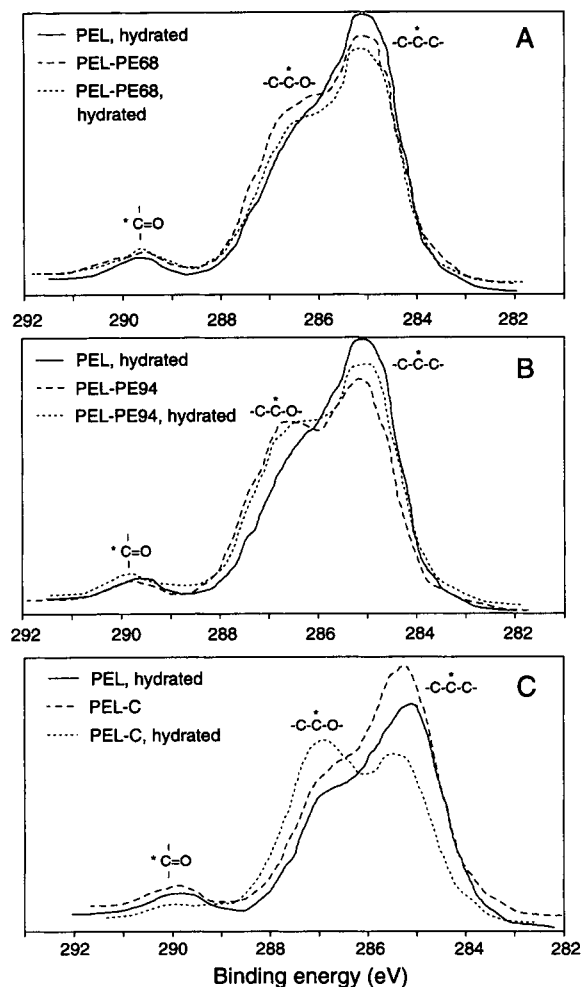


Figure 7 C1s ESCA spectra of hydrated and unhydrated films: (A) PEL-PE68, (B) PEL-PE94, and (C) PEL-C. Matrix concentration of additives, 5% w/w.

the hydrated material [Fig. 7(B)], both materials having significantly more ether carbons present at the surface than hydrated PEL. The spectra are

Table III Data from ESCA Analyses of Hydrated and Unhydrated Films of PEL and PEL-C

Polymer	C, %*	O, %*	N, %*	C/O	C/N
PEL	83.6	13.1	3.3	6.4	25.6
PEL Hydrated film [†]	83.5	12.9	3.6	6.5	23.0
PEL-C	83.3	13.0	3.6	6.4	22.9
PEL-C Hydrated film [†]	80.5	17.0	2.5	4.7	32.5
PEL-C Calculated [‡]	82.9	13.6	3.5		

The PEL-C films contain 5% w/w of Polymer C.

* Atomic %.

[†] Films immersed in water at 80°C for 24 h and dried for 24 h (see text).

[‡] Values calculated under the assumption that the additive was homogeneously distributed throughout the matrix polymer.

similar to those of PEL-PE68, but the surface accumulation of the amphiphile seems to be slightly higher for PEL-PE94, presumably because of the more hydrophobic character of Pluronic PE9400. The reduction of ether carbon after hydration may be explained by leaching of PE94 during the hydration procedure.

The relative intensities of the C1s peaks in the spectra of hydrated PEL and unhydrated PEL-C were almost identical [Fig. 7(C) and Table III], with the aliphatic carbons dominating over the ether carbons. After hydration at 80°C for 24 h, the appearance of the C1s ESCA spectrum of PEL-C became quite different. As shown in Figure 7(C), the ether carbon peak increased to be significantly larger than the aliphatic carbon peak. Also, the relative amounts of nitrogen and oxygen at the surface changed (Table III). The theoretical amounts of C, N, and O for PEL-C, given in Table III as a comparison, were calculated under the assumption that the amphiphilic Polymer C was evenly distributed in the matrix polymer. As evident from the table, the calculated values and the values for unhydrated PEL-C are similar, while the values measured for hydrated PEL-C differ considerably. The oxygen content in the surface has increased while C and N have decreased, which would be the effects of PEG enrichment at the surface.

CONCLUSIONS

It is obvious, from contact angle measurements as well as from ESCA spectra that the amphiphilic polyurethane, Polymer C, is enriched in the surface layers of films prepared from blends of Polymer C and PEL after water immersion at 80°C. This temperature is well above T_g of PEL, and, consequently, diffusion and molecular rearrangements will readily take place. However, on decreasing the temperature the matrix as well as the additive will be locked into the hydrated configuration. Pluronics PE6800 and PE9400 showed less effects on the surface properties of PEL when blended into the PEL matrix as additives, presumably because of their high water solubility.

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