Waterborne Anionomeric Polyurethane–Ureas from Functionalized Fluoropolyethers

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ABSTRACT: A family of anionomeric segmented polyurethane–ureas made from α-ω dimethylol-terminated perfluoropolyethers (M_n = 1000–2000), isophorone diisocyanate, dimethylol propionic acid, and ethylenediamine was obtained in form of stable aqueous dispersions. The dispersions were characterized by viscometry and dynamic laser light scattering. The main compositive parameters explored were the amount of COOH groups and the length of the fluorinated macromer. The new polyurethane–ureas were characterized by dynamic mechanical analysis obtaining information on modulus, thermal transition, and phase segregation. Surface properties and chemical resistance were estimated through measurements of static contact angles and spot tests with different solvents. Although surface hydrophobicity was not affected by composition, water-sorption behavior was sensitive to the ionic character (COOH level) of the polymer. Diffusion and permeability coefficients of polymer films, having different carboxyl contents, were estimated. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 136–144, 2004

Key words: dispersions; anionomers; diffusion; mechanical properties; water sorption

INTRODUCTION

In the last 15 years, a profusion of scientific papers have been published about the preparation and properties of polyurethane materials from functional perfluoropolyethers (PFPE). Examples are based on thermoset and thermoplastic elastomers,[1–3] protective coatings[4,5] and fiber-reinforced composites.[6] The field of coatings is particularly interesting because many fluorine-related properties like friction, cleanability, hydrophobicity, and release are fully exploited by application of fluoropolymers as thin films. Although PFPE coatings can be applied as solvent-borne systems,[4,5] or by expansion from supercritical CO_2,[7] the development of waterborne PFPE coatings is a relatively new approach, present in the patent databases but so far not described in the scientific literature. In particular, PFPE water-based polyurethanes may find several applications as, for example, in low environmental impact heavy duty paints; water- and oil-repellent sizings for textiles, leather, and paper; and antigraffiti systems.[8,9]

Therefore, in this article a series of model segmented anionomeric waterborne polyurethane–ureas (WPUs), containing PFPE blocks of different molecular weights, were prepared and characterized. Characterization will be focused mainly on the determination of bulk viscoelastic and transport properties, as well as on the assessment of surface characteristics of films.

EXPERIMENTAL

Materials

Three perfluoropolyether samples (Fomblin® ZDOL, from Solvay-Solexis, Bollate, Italy) were used in this work, whose chemical structure is represented as follows:

$$HOCH_2CF_2(OCF_2CF_2)_p(OCF_2)_qOCF_2CH_2OH$$
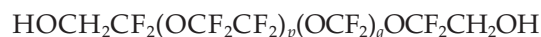
The molecular as well as some physicochemical properties are summarized in Table I.

Other monomers [isophorone diisocyanate (IPDI), dimethylolpropionic acid (DMPA), ethylenediamine (EDA)] and chemicals [trietylamine (TEA), dibutyl tin dilaurate (DBTDL), *N*-methyl pyrrolidone (NMP)] were supplied from Aldrich (Milwaukee, WI). NMP and TEA were stored over dry molecular sieves before use, whereas DMPA was dried *in vacuo* at 80°C for 4 h.

Polymer synthesis and dispersion in water

The polymerization process was carried out in two steps, consisting of an NCO-terminated prepolymer formation, followed by dispersion in water and chain

TABLE I
Characterization of PFPE Starting Samples

Sample	M_n (NMR)	C_2/C_1 (NMR)	M_w/M_n (GPC)	Viscosity$_{30°C}$ (mPa s^{-1})	T_g (°C)
A	1000	1.2	1.2	65	−105
B	1500	2.1	1.4	95	−98
C	2000	1.2	1.7	80	−114

extension according to the prepolymer mixing method.[10] A three-neck glass reactor, equipped with a condenser, a thermometer, and a mechanical stirrer, was used for the prepolymer synthesis. The perfluoropolyether ZDOL, IPDI, and solid DMPA were charged to the reactor and kept under moderate stirring and N$_2$ atmosphere. Typically, the molar amount of IPDI was two times that of DMPA + ZDOL, whereas the molar ratio between ZDOL and DMPA was calculated in such a way that the ionomer content of the final polymer [COOH], expressed in eq/kg, varied from 0.20 to 0.50 (corresponding to a DMPA level of 2.7–6.7% on the dry polymer). Triethylamine (1 : 1 to COOH equivalents of DMPA), diluted in dry NMP (solvent was calculated as 10% w/w on the prepolymer), was added dropwise by cooling, then the reaction mixture was kept under stirring at ambient temperature for 90 min, until the prepolymer reached the theoretical residual isocyanate value (backtitration according to ASTM D2572).

The concentrated (90% solid in NMP) prepolymer solution was then poured into a second vessel, agitated with a turbine impeller, cooled at 15°C, and containing water in an amount sufficient to reach a final solid of 30 ± 1% w/w. Once the prepolymer was dispersed, the chain extender EDA (stoichiometric ratio NH$_2$/NCO = 0.98/1) was added and the polymerization was controlled by IR spectroscopy until no more NCO bands were detected.

Molecular characterization

^{19}F-NMR spectroscopy was used to check the conversion of ZDOL in the prepolymerisation step, monitoring the shift of the pair of signals of –CF$_2$CH$_2$OH (−81.3; −83.3 ppm) to –CF$_2$CH$_2$OCONH– (−70.5; −80.5 ppm), as previously reported for similar systems.[11] NMR spectra were obtained from neat samples with a Varian Unity 300 MHz instrument (Varian Associates, Palo Alto, CA) at ambient temperature (1000 scans). Chemical shifts were referred to standard CFCl$_3$, as determined in separate experiments.

FTIR spectroscopy was used to check the end of the polymerization process, by monitoring the disappearance of NCO band at 2260 cm^{-1}. Two drops of aqueous dispersions were smeared between CaF$_2$ disks, and transmission IR spectra were obtained with a

Perkin–Elmer spectrometer (16 scans, resolution 4 cm^{-1}; FT model 1600, Perkin Elmer Cetus Instruments, Norwalk, CT).

Molecular weights of the final polymers were estimated by intrinsic viscosity measurements. The aqueous dispersion was coagulated under stirring by addition of diluted HCl. The precipitated polymer was dried *in vacuo* at 70°C (constant weight), then it was dissolved in a solvent mixture containing trifluorotoluene/trifluoroethanol 8/2. Intrinsic viscosities were measured with calibrated glass capillary viscometers at 30°C.

Particle size measurements

Average particle dimensions and polydispersity of the final polyurethane dispersion were measured by dynamic laser light scattering. Experiments were performed at 20°C, scattering angle 90°, using a BI-200SM goniometer and a BI-2030AT digital correlator (Brookhaven Instruments Corp., Holtsville, NY), with a Spectra-Physics 2000 argon-ion laser (Spectra-Physics, Mountain View, CA) operating at 514.5 nm. Diffusion coefficients (D) as well as polydispersity index were calculated through the cumulant analysis by expanding the logarithmic correlation function in power series. Therefore, the radius R of the particles was estimated from D by means of the well-known Stokes–Einstein relationship, $D = k_B T/6\pi\eta_0 R$.

Rheological measurements

Viscosity measurements were obtained with a Brookfield model DVII rheometer (Brookfield Engineering Laboratories, Middleboro, MA) at 20°C.

Dynamic mechanical analysis

WPU films were obtained by casting the aqueous dispersions in PTFE molds and by drying them according to the following program: 24 h at ambient temperature, 24 h at 50°C, and 1 h at 100°C in air-forced oven. Circular specimens (thickness 300 ± 50 μm, diameter 0.5 cm) were obtained and tested in shear-sandwich mode with a Mettler DMA/SDTA861[e] dynamic-mechanical analyzer (Mettler Instrumente, Greifensee, Switzerland), in dynamic scans from −150 to +150°C;
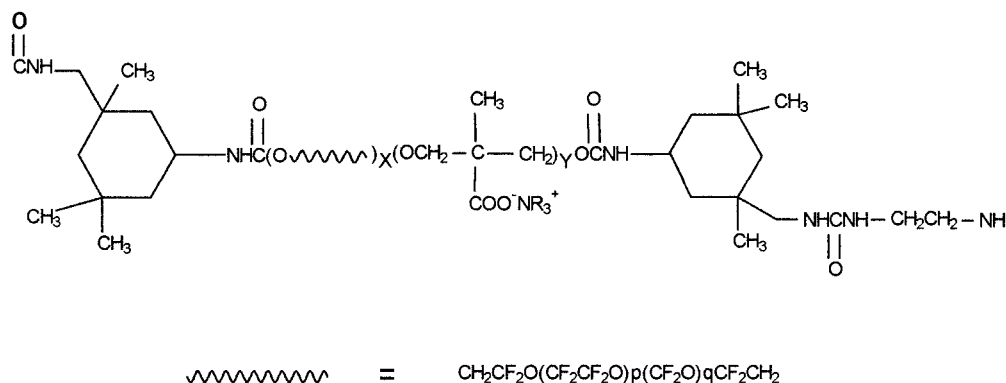
Figure 1 Chemical structure of the repeat unit of WPU anionomer containing the perfluoropolyether segment.

at successive frequencies of 1, 10, 100, and 1000 Hz; deformation < 0.5%. Samples were reclamped at −150°C to counteract the thermal shrinkage.

Water adsorption

WPU square specimens (20 × 20 × 0.3 mm), obtained as described above, were immersed in water at 25°C and weighed every day until they reached a constant value.

Tensiometry

Surface tensions of pure perfluoropolyether samples, as well as of aqueous 30% solid polyurethane dispersions, were measured according to the pendant-drop method with a Krüss G10 instrument (Krüss, Hamburg, Germany). From the equilibrium drop data the surface tension γ was calculated according to the equation, $\gamma = \Delta\rho g d_e^2 / H$, where $\Delta\rho$ is the difference between the density of the two phases, g is the gravitational constant (=9.81 m/s^2), d_e is the maximum drop diameter, and H is a tabulated geometrical value. Glass panels were bar coated with the polyurethane aqueous dispersions, and dried in an oven at 100°C for 5 min. Static contact angles against droplets of bidistilled water and high-purity n-alkane series (from n-hexadecane to n-octane) were measured at 23°C according to the sessile-drop method. The contact angle θ was calculated from the photographic image according to the relation, $\theta = 2tg^{-1}(2h/d)$, were h is the maximum height and d is the diameter of the droplet on the surface. The results were expressed as an average of five independent measurements.

Chemical resistance

Chemical resistance was evaluated by spot tests according to ASTM D1308. A 10-μm-thick film applied on glass panels, and oven-dried at 100°C for 5 min, was exposed to droplets of different test liquids for 24 h at room temperature, in a closed box kept in equilibrium with the solvent vapor. The drops were then removed by wiping, and chemical resistance was visually determined by evaluating the changes in film integrity, haze, or hardness of the surface exposed. A visual scale was used to compare test liquids and materials: 10 (no effect), 8 (light haze), 6 (softening), 4 (cracks), 2 (heavily damaged), 0 (film completely destroyed).

RESULTS AND DISCUSSION

The simplified structure of the final polymer is shown in Figure 1, whereas composition and characteristics of a series of selected polyurethane–urea (WPU) dispersions are reported in Table II. The aqueous dispersions were all characterized by a solid content of 30 ± 1%, viscosity was always <10 mPa s^{-1}, and polymer intrinsic viscosity ranged between 9.0 and 12.5 mL/g. The rather high variability of pH values shown in Table II, from different dispersion runs, is likely attributed to the fact that some excess of diamine chain extender may be present when a stoichiometric ratio NH$_2$/NCO close to 1 is used, as discussed in another article.[12] Changes of pH showed little effect on the reproducibility of the other characteristics of the dispersions, such as viscosity and particle size. The main compositive variables considered in the WPU series were the PFPE segment molecular weight and the DMPA content in the polymer. Given that in all synthesized prepolymers the NCO mol values are two times the sum of DMPA + ZDOL mol values, there is clear indication that a change in DMPA content also influences the fluorine content in the polymer. In Figure 2 the calculated numerical relations between DMPA and F content in the considered polymer series are shown. The dashed line obeys the general equation (DMPA %) = 13.416 × [COOH (eq/kg)].

From examination of Table II data, an effect of COOH concentration on polymer particle size can be postulated. Smaller polymer particles are obtained at

TABLE II
Characteristics of Selected Dispersions of PFPE Containing Polyurethane–Urea Anionomers (Solid 30 ± 1%)

Run	[COOH] (eq/kg)	ZDOL sample	pH	Particle diameter (nm) and polydispersity index	Stability
1	0.15	B	8.0–10.2	—	Fast settling
2	0.20	B	8.0–9.5	150 ± 20 (0.11)	6 months, redispersible
3	0.25	B	9.0–10.5	80 ± 10 (0.06)	>12 months
4	0.30	B	8.5–11.1	65 ± 10 (0.15)	>12 months
5	0.35	B	7.9–9.5	70 ± 15 (0.13)	>12 months
6	0.40	B	8.6–10.0	75 ± 15 (0.13)	>12 months
7	0.50	B	7.8–9.3	50 ± 10 (0.19)	>12 months
8	0.20	A	8.2–9.5	170 ± 20 (0.13)	>12 months, partial settling
9	0.30	A	8.3–10.4	60 ± 10 (0.12)	>12 months
10	0.20	C	8.6–9.5	170 ± 20 (0.20)	>12 months
11	0.30	C	8.0–10.3	70 ± 10 (0.10)	>12 months

higher COOH content. It is actually known that, for conventional waterborne polyurethanes, a higher hydrophilic character of the polymer allows the attainment of finer dispersed particles.[10,13] On the contrary, in our case, the decrease of the ionic character below 0.20 eq/kg (= DMPA 2.7%) caused a rapid settling of the dispersion, so that the attainment of stable dispersions with particles > 170 nm was not feasible. In fact, typical DMPA values as high as 2.5–5.0%, frequently about 3.5%, are reported in the literature for anionomer dispersions based on different macroglycols, such as polytetramethyleneglycole,[14] polypropyleneglycole,[15] polycarbonates,[16] polycaprolactones,[17] and polyesters.[18] In most cases, aqueous polyurethane dispersions, with particle diameters in the range 100–400 nm, were obtained. Much finer polymer dispersions (diameters 36, 62, and 81 nm) were measured by Hourston et al.[14,19] with a series of chemically different polyurethane anionomers based on aliphatic diisocyanates. In that case, however, a DMPA content as high as 4.9% in the polymer was indicated.

On the other hand, the effect of the PFPE segment molecular weight on particle size is controversial,

whereas in the literature[20,21] it is generally reported that smaller particles can be produced by dispersion of polyurethanes with longer (more flexible) soft segments because, in that case, it is easier to obtain a core–shell type particle morphology with hydrophilic parts oriented at the polymer–water interface.

Surface tensions of perfluoropolyether oligomers and of some their WPU dispersions are reported in Table III, showing no apparent effect of composition. In contrast to the behavior of PFPE precursors, the aqueous dispersions are high surface tensions liquids that need substrates, such as glass and chromated aluminum, to show good film-forming characteristics. The films applied and obtained after oven drying were macroscopically transparent, homogeneous, and glossy in the range of thickness explored (5–20 μm). However, it is well known that copolymers from functional perfluoropolyethers may form apparently homogeneous materials, but phase segregation if often present on a submicron- or nanoscale.[1,3,5] This is attributed to the extremely low solubility parameter of the perfluoropolyether chain [~ 10.5 (J/mL)$^{0.5}$; see Marchionni et al.[22]], which is lower than that of any other known polymer species and particularly much lower than solubility parameters of urethanes [~24–26 (J/mL)$^{0.5}$, as can be estimated by group contribution calculations[23]]. Therefore the PFPE segment, al-
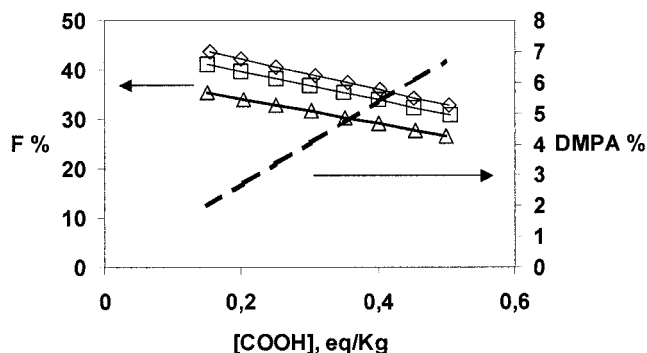

Figure 2 Numerical correlations between COOH concentration and fluorine content in the series of polyurethane–ureas from perfluoropolyethers ($\triangle$, WPU 1000; $\square$, WPU 1500; $\diamond$, WPU 2000; dashed line for relation to DMPA %).

TABLE III
Surface Tensions of ZDOL Samples and Some of Their WPU Dispersions (COOH = 0.30 eq/kg)

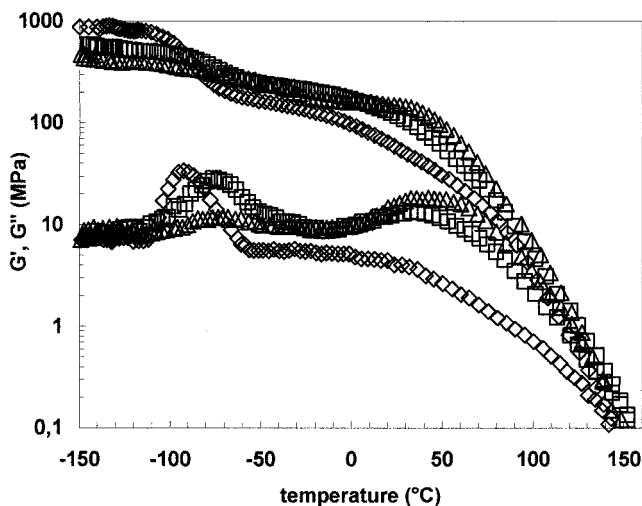| Sample	Surface tension$_{23°C}$ (mN/m)
ZDOL sample A	17.2 ± 0.2
ZDOL sample B	16.4 ± 0.1
ZDOL sample C	15.9 ± 0.1
WPU dispersion run 10	58.7 ± 0.1
WPU dispersion run 4	61.4 ± 0.1
WPU dispersion run 8	60.5 ± 0.2

Figure 3 Dynamic mechanical spectra (storage and loss modulus versus T, $\nu = 1$ Hz) of some polyurethane–ureas from perfluoropolyethers ($\triangle$, WPU 1000; $\square$, WPU 1500; $\diamond$, WPU 2000; dashed line for relation to DMPA %).

though chemically linked to the hydrogenated moiety, is not really mixed into it, and polyphasicity can be generally observed by both electron microscopy and detection of thermal transition corresponding to molecular motions of the pure phases (DSC, DMA).

Because the thermal behavior of WPU polymers was scarcely detected by DSC, as in other cases involving copolymers with PFPE segments of low molecular weight,[24] main investigations were carried out by DMA. The dynamic mechanical spectra of some selected films are shown in Figures 3 and 4. By observing Figure 3 data, the effect of PFPE segment molecular weight on the dynamic properties of WPU waterborne series is confirmed. All the materials have a G' value of about 0.5–0.8 GPa in the glassy state, followed by a relaxation peak (maxima of G'') between -100 and $-60°C$. The intensity of such relaxation is most significant for the ZDOL 2000–based material, for which G' passes from 0.8 GPa at $-140°C$ to 100 MPa at $-60°C$. To study the frequency dependency of this low T transition, Figure 4 shows, as an example, the behavior of the tan $\delta = G''/G'$ behavior of the ZDOL 2000 polymer obtained with a frequency series experiment. It can be observed that the maximum of damping peak is shifted at higher temperatures by increasing, by a factor of 10, the frequency of measurement f. Moreover, the apparent coefficient $dT_{max}/d(\log f)$ is about 7°. All the other WPU polymers tested showed the same behavior. Actually, it is known that for a factor of 10 increase in frequency the maximum of the damping peak is shifted from T_1 to T_2 according to an Arrhenius-type relation:

$$(1/T_1 - 1/T_2) = 2.303(R/\Delta E) \qquad (1)$$

where R is the gas constant and ΔE is the energy of activation, of the order of 10^5 cal/mol for the main T_g, whereas for secondary transitions it is of the order of 10^3–10^4 cal/mol. It is known that in amorphous polymers[25] the T_g value is shifted by about 5–7°C for a factor of 10 increase in frequency. These observations agree very well with the results found for WPU polymers, and therefore the thermal transition at about $-90°C$ should be regarded as an α-transition, in particular attributed to the T_g of the segregated PFPE phase, as already established for other PFPE polyurethane systems.[1,3,5]

For the other WPU materials, containing lower molecular weight PFPE macromers, the decrease of G' after the α-relaxation is less evident. They are quite stiff materials at ambient temperature, where G' is of the order of 1–3 × 10^2 MPa. Moreover, it is clear that the maximum G'' or tan δ peak shifts at higher temperatures by decreasing the length of the perfluoropolyether (in agreement with the T_g values reported in Table I for the ZDOL precursors) and the peak progressively broadens, with the result that it is very difficult to evaluate numerically the T_g of the polymer from ZDOL 1000. The physical meaning of this phenomenon is that a much wider distribution of relaxation times is achieved, and this may be attributed to a stronger interaction between the fluorinated and urea–urethane phases, like a partial miscibility, or to a constraint exerted by the hard phase domains, as typical in thermoplastic polyurethanes.[26] After the low-temperature α-relaxation, a poorly defined rubbery plateau appears, with G' slightly decreasing with T. The length of such a plateau again seems to be inversely related to the PFPE molecular weight, which is shortest with the soft ZDOL 2000–based film. The T_g of the hard, urea–urethane moiety can be estimated by the maxima of the G'' curves, and it is about 42 and 32°C for the ZDOL 1000 and ZDOL 1500 films, respectively, whereas no clear maximum is apparent with the ZDOL 2000–containing polymer. By observing the
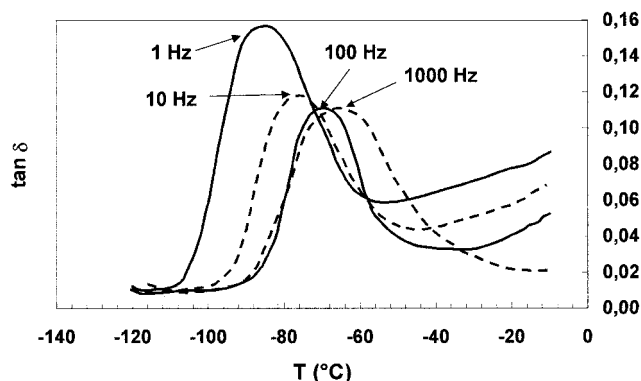

Figure 4 Low-temperature dissipation factor of WPU 2000 at different frequencies of measurements.
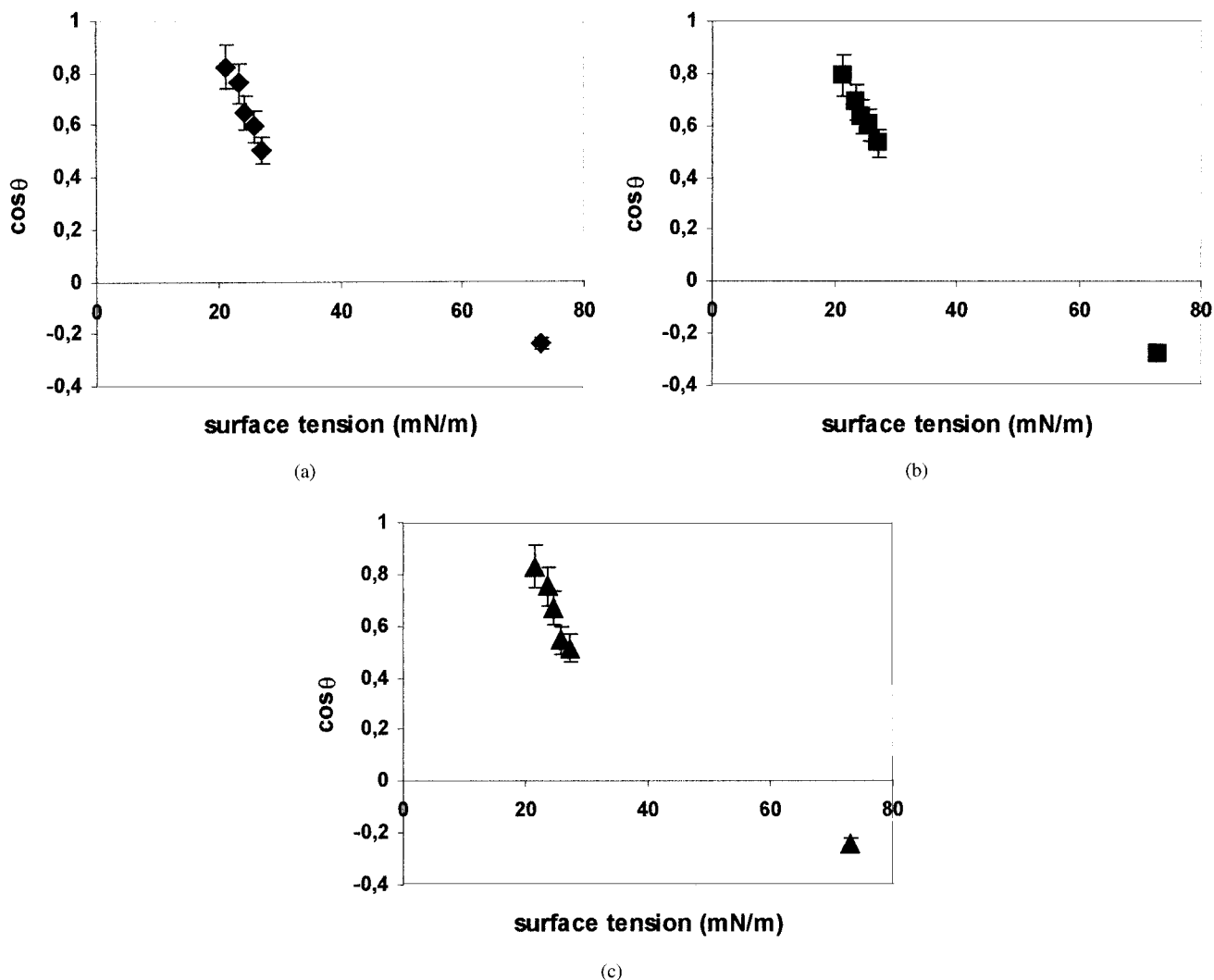
Figure 5 Zisman plots of WPU films: (a) ◆, WPU 1000; (b) ■, WPU 2000; (c) ▲, PU 1500.

G' behavior, another inflection may be estimated at temperatures > 100°C (softening), even if no clear evidence of peaks is present in the corresponding G'' or tan δ– T curves. It is then worth stressing that a rather high value of elastic modulus at ambient temperature was found for the fluorinated WPU series ($\approx 10^2$ MPa), in spite of the intrinsically soft nature of the PFPE chain. A similar effect was also reported for polydimethylsiloxane-containing polyurethane ionomers,[27] and was attributed to the very low polarity of the soft segment, which allows a very efficient phase separation of the hard moiety (no hydrogen-bonding interactions between phases).

In conclusion, the PFPE-containing polyurethane–ureas of the present work show a biphasic morphology. A simple calculation of composition can be done by assuming additivity of volumes with densities of 1.8 g/mL for ZDOL and 1.1 g/mL for the hard phase: the results confirm that the WPU 2000 film likely has the perfluoropolyether as a continuous phase (volume fraction of PFPE $\Phi = 0.58$), whereas the opposite holds for WPU 1000 polyurethanes ($\Phi = 0.45$). The material obtained from ZDOL 1500 is an intermediate case ($\Phi = 0.52$). These considerations, if confirmed by proper morphological analyses such as electron micrography, would contribute to better understanding the behavior of such a class of materials.

Surface properties of the new waterborne PFPE polyurethanes were investigated through static contact angle θ measurements. The results are shown in Figure 5(a)–(c), reporting the data according to the classical Zisman plot (cos θ versus surface tension γ of the test liquid) for a wide range of WPU films characterized both by different PFPE segment lengths (1000–2000), and DMPA levels (0.2–0.40 eq/kg). Films characterized by extreme COOH values (0.15 and 0.50 eq/kg) showed poor film-forming properties and were not considered further. The contact angle data against hydrocarbon droplets allow calculation of apparent critical surface tensions γ_c, as low as 16.5–19.0

TABLE IV
Chemical Resistance of Some WPU Films from ZDOL of Different Molecular Weights and Ionic Character

Film	Polymer/Solvent							
	H_2O	EtOH	MEK	$CHCl_3$	CF_3CH_2OH	THF	Toluene	n-Decane
WPU 1000								
0.2 eq/kg	10	8	4	10	2	4	10	10
WPU 1500								
0.2 eq/kg	10	8	4	10	2	4	10	10
WPU 1500								
0.4 eq/kg	10	6	4	10	2	4	10	10
WPU 2000								
0.2 eq/kg	10	6	4	10	2	4	10	10

mN/m at 23°C, with a slight effect of PFPE molecular weight. High mean square coefficients of linear regression ($R^2 > 0.98$) could be calculated only by excluding data concerning contact angle against water (always >100°, thus showing negative cos θ values). Actually this procedure can be justified by considering that the Zisman model holds when only apolar, "dispersive" components of interfacial energy are considered. The obtained γ_c values are indicative of the formation of predominantly fluorinated surfaces. For a comparison, a value of 18.5 mN/m is reported for PTFE in the literature.[28] Scattering of single experimental points (shown in the figures) is about ±8–12% for hydrocarbons, and standard deviation of such measurements largely overlapped eventual effects of polymer COOH content, which therefore can be considered a compositive parameter of minor importance for this property. All results obtained would suggest an efficient mechanism of particle coalescence during film formation, with orientation of the lower surface energy PFPE chains at the film/air interface, as has already been established for PFPE solvent-borne films.[29] Another consideration should be addressed to the particular meaning of the measurements carried out. In fact static contact angles are certainly representative of the phenomenology of the contact between solid and liquid phases, but they cannot be considered as true "equilibrium" measurements if a polyphasic surface is concerned,[30] as in the case under study. Polyurethane systems based on PFPE are characterized by a rather high contact angle hysteresis,[5] which could also explain the relatively wide data scattering.

Surface chemical resistance of the WPU films was evaluated by spot test with a series of different solubility parameter solvents, as reported in the experimental section. The results are shown in Table IV. It is clear that PFPE molecular weight and COOH content have a minor effect on the chemical resistance, which is excellent with both low (toluene, n-decane) and very high (water) solubility parameter liquids, and with solvents having hydrogen bonding donor character ($CHCl_3$). On the other hand, greater film damage was observed with medium solubility parameter solvents

like ethanol, methyl ethyl ketone, and THF. Even with carboxyl concentration as high as 0.40 eq/kg, water resistance is high. This would confirm that the ionic groups are very likely not oriented air side, but rather substrate side.

The effect of ionic character can be conveniently studied by observing the water-sorption curves of WPU films over a prolonged exposure time (1000 h). The results are shown in Figure 6 for three materials belonging to the WPU 1500 series, having different DMPA contents. For each material, data were obtained by measuring water uptake of two separately prepared specimens, and this would explain in part the scattering of data. The data were represented by plotting mass gain % versus $t^{0.5}/l$, where l is the sample thickness. The water uptake after 900–1000 h is practically constant and it was used to estimate the equilibrium solubility coefficient S, as indicated in Figure 6. The first clear observation is that largely different water uptake levels are reached, in which the film with the highest COOH level is the most hydrophilic. In that case the sorption curves also show a sigmoidal, nonlinear shape, suggesting a deviation from the Fickian diffusion mechanism. Actually, it is
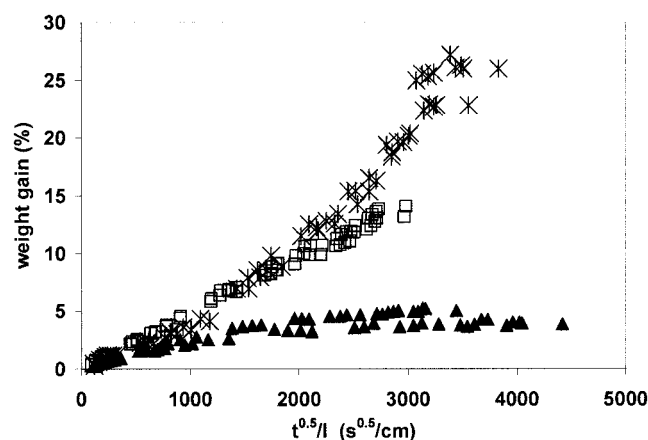

Figure 6 Water-sorption behavior of WPU 1500 films with different COOH contents (∗, COOH 0.35 eq/kg; □, COOH 0.20 eq/kg; ▲, COOH 0.25 eq/kg).

TABLE V
Parameters of Least-Squares Linear Regression of Water
Sorption Data in WPU Films from ZDOL 1500 According
to the Relation log $M_{(t)}/M_{(\infty)}$ Versus Time (t)

Polymer (COOH)	n	Correlation coefficient (R^2)
WPU 1500		
0.20 eq/kg	0.50 ± 0.05	>0.99
0.35 eq/kg	1.2 ± 0.1	0.97
0.25 eq/kg	0.7 ± 0.1	0.93–0.97

known[31] that a high segmental mobility (as in the case of rubbers) is needed to have Fickian diffusion, where the rate of diffusion is much lower than the chain relaxation time. In general terms the sorption data follow the empirical equation

$$M_{(t)} = Kt^n \tag{2}$$

where $M_{(t)}$ is the mass of fluid adsorbed at time t, and $n = 0.5$ if the ideal Fickian mode is obeyed. Rates of diffusion faster than or comparable to segmental relaxation times lead to higher n values, indicative of non-Fickian, or "anomalous" diffusion modes.[31] This behavior is often interpreted in terms of interaction between the permeant and the polymeric glass, with formation of a boundary between the outer swollen shell and the inner glassy core of the polymer. WPU sorption data were elaborated according to eq. (2), and the results of the least-squares linear regression [log $M_{(t)}$ versus t] are collected in Table V. It is confirmed that only the polymer with lowest COOH value adequately fits the Fickian model. This may be related to minimized interactions of water and COOH groups of the polymer. The general equation of diffusion can be simplified if the sorption process is considered in the early stages, and approximated values of diffusion coefficients (independent of concentration) can be estimated by the initial rates of the sorption curves according to the following equation[32]:

$$M_{(t)}/M_{(\infty)} = 4/\pi^{0.5}(Dt/l^2)^{0.5} \tag{3}$$

Therefore from the slope m of the straight line, represented in the plot $M_{(t)}/M_{(\infty)}$ against $t^{0.5}/l$, the diffusion coefficient can be calculated as

$$D = (\pi/16)m^2 \tag{4}$$

Figure 7 shows the initial sorption data [$M_{(t)} < 0.4$] of the film showing Fickian behavior, arranged according to eq. (3), whereas numerical results of all the obtained diffusion coefficients D, as well as the corresponding permeability coefficients P, calculated according to $P = DS$, are summarized in Table VI, along with indication of the standard error [confidence interval (CI) = 95%]. For comparison, the D values obtained (of the order of 10^{-9} cm^2/s) are typical of diffusion of water in glassy polymers,[33] whereas for a family of segmented, nonionomeric thermoplastic polyurethanes containing hydrogenated polyether or polyester type macroglycols, water sorption diffusion coefficients D as high as 10^{-7} cm^2/s were reported.[34]

A final remark concerns the transport behavior of WPU film with COOH = 0.25 eq/kg, which apparently leads to an extremely low water uptake. This result is not easily justified, although it was confirmed in two separate experiments. One possible explanation is that the considered sorption curve approached only a "quasi-equilibrium" state, and much more prolonged exposure times would be necessary to reach the final true equilibrium, as typical of two-stage sorption processes.

CONCLUSIONS

In this work the effect of perfluoropolyether segment molecular weight and COOH content on the properties of a family of waterborne fluorinated anionomers was amply clarified. In spite of the intrinsic softness of perfluoropolyethers, relatively high modulus films can be obtained because of the efficient phase segregation of the hard urethane–urea domains. Mechanical properties are influenced by composition, given that higher elastic moduli are achieved by lowering the molecular weight of the PFPE or by increasing the COOH content (and thus the fraction of the hard phase). On the other hand, surface-related properties, like wettability and chemical resistance by spot tests, are only marginally influenced by composition. In other words, the PFPE-containing waterborne polyurethane–urea anionomers behave like substantially perfluorinated surfaces, opening the possibility to exploit these performances by designing polymers with

TABLE VI
Solubility (S), Diffusion (D), and Permeability (P) Coefficients of Water in WPU 1500 Films at +23°C

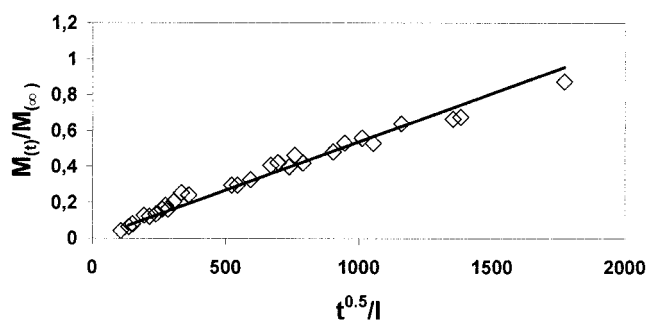| Polymer (COOH)	S (g/g)	D (cm^2/s)	P (cm^2/s)
WPU 1500			
0.20 eq/kg	0.14 ($\pm$0.01)	5.7 ($\pm$0.7) $\times 10^{-8}$	7.9 ($\pm$1.0) $\times 10^{-9}$
0.35 eq/kg	0.25 ($\pm$0.02)	3.9 ($\pm$0.7) $\times 10^{-9}$	9.8 ($\pm$1.6) $\times 10^{-10}$
0.25 eq/kg	0.04 ($\pm$0.01)	6.8 ($\pm$1.2) $\times 10^{-8}$	3.1 ($\pm$0.5) $\times 10^{-9}$

Figure 7 Extrapolation of diffusion coefficient D from initial water sorption data of WPU 1500 film (COOH = 0.2 eq/kg).

a tailored amount of fluorine in water-based formulations. The study of water-sorption behavior is particularly interesting; in contrast to surface behavior the presence of COOH groups in the polymer has a significant effect on bulk hydrophobicity, resulting in largely differentiated solubility coefficients, whereas diffusivity—more related to free volume and molecular relaxation considerations—seems clearly smaller than values known for nonfluorinated, segmented polyurethanes.

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