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ORIGINAL PAPER

Study of metal protective hydrophobic coatings from waterborne polyurethane ionomers

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Abstract A series of waterborne coatings obtained from aqueous dispersions of fluorinated polyurethane ionomers were characterized by Differential Scanning Calorimetry (DSC), Contact Angle measurements (CA), and Electrochemical Impedance Spectroscopy (EIS) with evaluation of water uptake and barrier properties at prolonged exposure. All the considered materials showed two glass transition temperatures and the formation of highly hydrophobic surfaces with CA values against water well above 100°. On the other hand the compositive parameters of the polymers—presence and concentration of cationic as well as anionic groups, linear or crosslinked molecular structure—showed a significant effect on the electrochemical behaviour. In particular it resulted that less water absorption is shown by coatings with lower ionic character, while crosslinked anionomer structures show excellent long-term barrier properties. The research offers useful indication towards the design of a new class of hydrophobic barrier coatings from aqueous dispersions.

Keywords Polyurethane · Ionomer · EIS · Contact angle · Barrier properties

1 Introduction

Waterborne polyurethanes represent an important class of coating resins characterized by good appearance, adhesion, abrasion resistance and durability [1]. Their surface properties like hydrophobicity and cleanability can be improved by introducing low surface tension fluorinated monomers or macromers, like in case of fluorinated polyether containing polyurethanes [2–4]. In these products it was observed that water permeability, barrier properties and durability are largely affected by phase segregation phenomena involving the apolar fluoroether segments and polar urethane moieties [2]. More recently waterborne versions of fluoroether containing polyurethanes have been described [5, 6]; they are based on the introduction within the polymer chain of ionic groups which act as internal emulsifiers allowing the formation of stable and environmentally friendly aqueous dispersions.

In this work a series of different waterborne polyurethane ionomers based on the presence of fluoroether segments were considered and comparatively evaluated in terms of surface wettability and electrochemical behaviour. The structures concerned differ each other in the nature of the ionic group (cationic or anionic), in the ionic group content (low or high), in the molecular architecture (linear or crosslinked), and in the crosslinking strategy adopted (monocomponent self-crosslinked, or bicomponents with external crosslinkers). Their chemico-physical properties were evaluated through Differential Scanning Calorimetry (DSC), Contact Angle (CA) measurements and Electrochemical Impedance Spectroscopy (EIS).

2 Experimental

2.1 Materials

Some characteristics of the six base aqueous ionomer dispersions (30% solid) are summarised in Table 1.

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Table 1 Some characteristics of fluorinated polyurethane ionomer dispersions

Type	Name	Ionic content (eq/Kg)	pH	Viscosity 20 °C mPa s	Particle size[a] (nm)
Cationic ($-NR_3^+X^-$) low ionic group content	C22	0.20–0.25	3.8	200	70 ± 20
Cationic ($-NR_3^+X^-$) low ionic group content silanol end groups	C22-SIL	0.20–0.25	3.5	200	n.d.
Cationic ($-NR_3^+X^-$) high ionic group content	C42	0.40–0.50	4.2	200	40 ± 10
Anionic ($-COO^-M^+$) low ionic group content	A21	0.20–0.25	8.2	<10	180 ± 30
Anionic ($-COO^-M^+$) low ionic group content silanol end groups	A21-SIL	0.20–0.25	8.0	40	n.d.
Anionic ($-COO^-M^+$) high ionic group content	A49	0.40–0.50	7.2	150	30 ± 10

[a] By dynamic light scattering

Aqueous dispersions from polymers containing a higher ionic group concentration tend to be more viscous and clearer; this corresponds to the formation of smaller and more stable polymer particles (as supported by Light Scattering data of Table 1). On the other hand lower ionic group concentration polymers form milky-white dispersions. An ionic group content as low as 0.20–0.22 eq/Kg is the least value needed to form stable dispersions without settling problems.

All the polymers were prepared starting from a fluorinated polyether diol with number average molecular weight 1,500 and having the following structure:

$$HOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)qCF_2CH_2OH$$

In a typical preparation procedure a NCO terminated prepolymer was formed by reaction of such fluorinated polyether with an excess of isophorone diisocyanate (IPDI) using a stoichiometric ratio NCO/OH = 2. Then the prepolymer was diluted with N-methyl pyrrolidone (NMP, 10% by weight on the solid polymer) and finally various types of chain extenders were added up to a complete consumption of isocyanate. Back titration with dibutylamine/HCl according to ASTM D2572, and FTIR spectroscopy were used to monitor the extent of reaction. The exact molar composition of all the polymers considered is shown in Table 1 making reference for all products to 1 mole of fluorinated polyether diol. The following reagents were used: N-methyl diethanolamine (NMDEA), 1-4 butanediol (BD), dimethylolpropionic acid (DMPA), 1-4 cyclohexanedimethanol (CHDM), γ-propylamino triethoxysilane (APTES), all purchased by Aldrich.

Stoichiometric amounts of acetic acid and triethylamine were used for the salification of cationic and anionic polyurethanes respectively; after salification the aqueous dispersione were obtained by simple adding deionized water under vigorous mechanical stirring up to a solid concentration as high as 30%. More details are given in references (Table 2) [5, 6].

Thin films (thickness about 8–10 microns) were obtained by bar-coating the dispersions on chromated aluminium Q-panels and drying in oven at 150°/5 min.

The denotation of the films used in this work is self-explanatory. The samples are named with three alphanumeric groups separated by a dash. The first letter stands for “film”. The second group indicates the original PU ionomeric dispersion and the last group the crosslinking process adopted (if any).

Coatings indicated as F-C22, F-C24, F-A21 and F-A49 consist of linear, unreactive polymers and therefore form substantially thermoplastic films. Products indicated with the suffix—SIL consist of the low charge cationic and anionic polyurethanes modified by introduction of trialkoxysilil end groups [7]. Such groups during dispersion in water are hydrolyzed so generating silanol end groups of

Table 2 Molar composition of fluorinated polyurethane ionomers

Type	Name	Isocyanatate	Ionic chain extender	Non-ionic chain extender	Amino-silane
Cationic ($-NR_3^+X^-$) low ionic group content	C22	IPDI 2 moles	NMDEA 0.5 moles	BD 0.5 moles	–
Cationic ($-NR_3^+X^-$) low ionic group content silanol end groups	C22-SIL	IPDI 2 moles	NMDEA 0.45 moles	BD 0.45 moles	APTES 0.1 moles
Cationic ($-NR_3^+X^-$) high ionic group content	C42	IPDI 2 moles	NMDEA 1 mole	–	–
Anionic ($-COO^-M^+$) low ionic group content	A21	IPDI 2 moles	DMPA 0.5 moles	CHDM 0.5 moles	–
Anionic ($-COO^-M^+$) low ionic group content silanol end groups	A21-SIL	IPDI 2 moles	DMPA 0.45 moles	CHDM 0.45 moles	APTES 0.1 moles
Anionic ($-COO^-M^+$) high ionic group content	A49	IPDI 2 moles	DMPA 1 mole	–	–

the type –Si(–OH)$_3$, which during the drying step of the coating can give crosslinking and grafting to the substrate through a polycondensation sol-gel type mechanism [8]. Anionomers can be also crosslinked with conventional external crosslinkers (bicomponent formulations), due to the presence of –COOH groups [9]. Therefore, the anionic dispersion with high ionic group content A49 was also formulated with an external crosslinkers, namely haxamethoxy-methylmelamine (MEL), and applied in the same way.

2.2 Testing procedures

Thermal transitions of dried films were investigated by DSC. Static contact angles against water were measured with the sessile drop method. Chemical resistance was evaluated by conventional MEK test according to ASTM D4752. The evaluation of water uptake and barrier properties of the coatings was carried out by EIS measurements exposing the coated metal to a NaCl 3% aqueous solution [10, 11].

2.3 Differential scanning calorimetry measurements

DSC thermograms were recorded using a Perkin–Elmer Pyris 1 instrument in a helium atmosphere. Indium (melting point 156.6 °C) and n-hexane (melting point −95 °C) were used to calibrate the apparatus. The glass transition temperatures were taken as the midpoint of thermal transitions determined in heating scans at a rate of 20°/min. Samples of weight 15–20 mg were cooled to –170 °C at a rate of 80°/min, then heated at 120 °C. In order to evaluate phase segregation, as well as annealing and hysteresis effects, cycles were chosen including cooling rates of 80°/min and 20°/min and heating to 120 and 150 °C.

In order to achieve a better physical contact of the coating to the measuring cell, about 20 mg samples of prepolymers were also directly coated, crosslinked and annealed at 120 °C for 96 h on standard aluminum pans. The following measurements have shown an improved stability and reproducibility. All the experiments were repeated twice, and the estimated accuracy in determination of Tg is about 3 °C.

2.4 Static contact angles against water with the sessile drop method

Surface energy is a direct manifestation of intermolecular forces. The molecules at the surface of a solid are influenced by unbalanced forces and, therefore, possess additional energy, in contrast with the molecules inside the solid.

Contact angle measurements was used to evaluate the wettability and energy of the coated surface. A drop of bidistilled water was placed on the sample surface and the angle between the baseline of the drop and the tangent at the drop boundary was measured using a microscope optical system with a back light (OCA 20 instrument, Dataphysics).

2.5 Electrochemical Impedance Spectroscopy measurements

The voltage perturbation was applied to an aluminum panel coated with the fluorinated polyurethane coatings (working electrode, WE) through a platinum electrode (counter electrode, CE) at ambient temperature, at the open-circuit potential [12], using a Metrohm AUTOLAB PGSTAT30 [4].

Data collected in the frequency range between 1 and 40 kHz were used to evaluate the dielectric constants of the coatings [13, 14]. On the other hand, the barrier behaviour of the different coatings during long term exposure to the aggressive solution was evaluated through the analysis of the impedance data collected at frequencies ranging from 50 to 100 kHz at voltage amplitudes of 10 mV. Three samples for each coating were analysed. Once verified good agreement between the data of the different samples of the same coating, the best one was considered to show the results.

3 Results and discussion

3.1 Thermal transitions and surface properties

Table 3 reports the glass transition temperatures measured for all the polymer films.

From an examination of Table 3 data, it appears that all the coatings are amorphous and biphasic (two different Tg indicated) due to the thermodynamic segregation of fluoroether and urethane parts; such a phenomenology is well known and already observed and reported for solventborne fluoroether polyurethane coatings [2].

Table 3 Characteristics and some physical properties of coatings from polyurethane ionomers

	Tg_1 (°C)	Tg_2 (°C)	Contact angle (°)	MEK test
F-C22	−85	+21	105	<10
F-C42	−90	+13	103	<10
F-C22-SIL	−85	+28	108	70
F-A21	−86	+34	108	<10
F-A21-SIL	−86	+35	103	80
F-A49	−86	+32	107	<10
F-A49-MEL	−86	Nd	109	>100

The efficiency of crosslinking was investigated by MEK test. As expected all linear polymers do not resist rubbing test, while coatings both self-crosslinking (sililated) and with external crosslinker (polyaziridine and melamine) show a much improved chemical resistance. Crosslinking in such a case occurs by hydrolysis of ethoxy silane end groups of polymer (see Table 2) followed by polycondensation during the drying step of the coating.

It is worth noticing that all coatings considered show the formation of a hydrophobic surface with CA against water routinely >100°, irrespective of chemical composition, ionic group character and molecular structure. This would suggest that predominantly low surface tension fluorinated surfaces are formed during the film-forming process from the aqueous dispersion, conforming the observations already reported for solventborne polyurethanes.

3.2 EIS study of the water uptake

According to Brasher–Kingsbury's equation

$$v(t) = \log[C_c(t)/C_c(0)]/\log \varepsilon_{H_2O}$$

the volume fraction of water (v) in organic polymers can be calculated from the coating capacitance, which can be estimated through EIS measurements [4]. The volume fraction of electrolyte absorbed by the coatings is reported in Fig. 1.

The curves are characterized by two regimes. In the first very short regime, water is transported in the coating with a linear relationship between v and $t^{0.5}$; this behaviour occurs because there is no chemical interaction between coating and penetrating water and the conditions of Fick's law are met. In the second regime a decrease of the rate of water permeation until saturation of the coating (v constant with time) can be observed. The initial v/t trend of the curves can be considered as a measure of the rate of water penetration into the coating, being a higher slope indicative of a greater rate of water uptake of the film; it is therefore related to the kinetic of permeation. On the other hand, the asymptotic values of the v/t trends are representative of the saturation of the coatings, and it can be related to the thermodynamic coefficient of solubility of water in the film.

After 350 min of exposure all the materials reached a nearly constant value of v (Fig. 1). It was about 1% and 0.5% for the two high ionic content polymer films and the two low ionic content films, respectively. This behaviour is explained by the higher affinity of water for the coating characterised by the higher ionic group content.

On the other hand both the coatings containing silanol end groups show the lowest initial slopes of v(t) curves, probably related to the decrease in free volume derived by the molecular rearrangement of the resins.

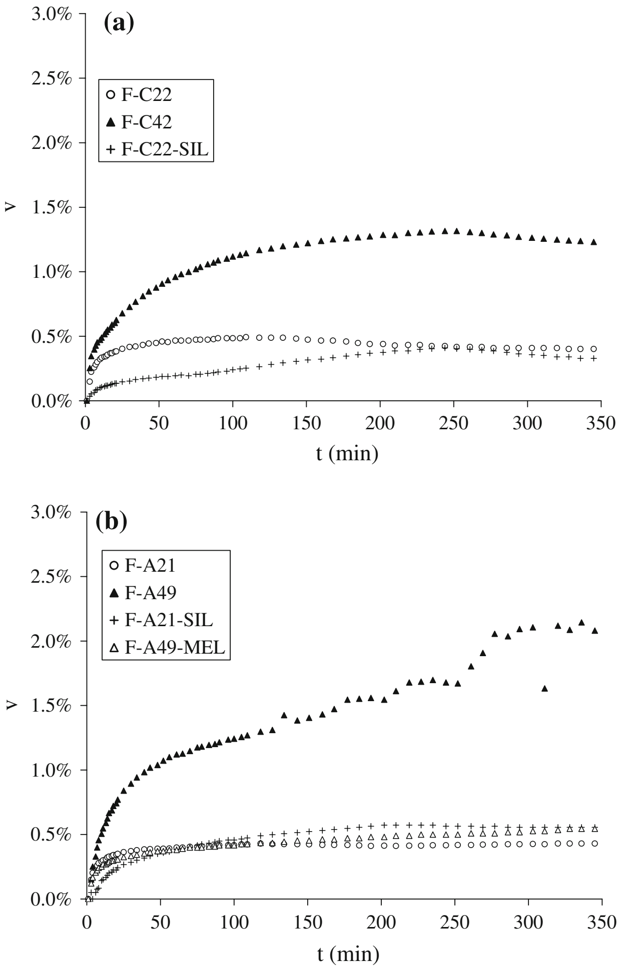


Fig. 1 Kinetic of water uptake for ionomeric coatings: **a** from cationic dispersions; **b** from anionic dispersions

For the anionic coatings the saturation value for F-A49-MEL is remarkably lower than for F-A49; it is explained by the reduction of the ionic groups consumed in the crosslinking process.

In conclusion, it can be observed that high ionic content polymer films tend to show high affinity towards water, notwithstanding their high surface hydrophobicity. A lower ionic character of the coating and the chemical crosslinking can significantly reduce water sorption.

3.3 EIS study of long term exposure

The long term performance of the coatings was evaluated by investigating the impedance spectra as a function of time, from initial to 16 weeks exposure to the electrolyte.

Figure 2 shows the electrochemical data obtained for the 3 cationic films. As known, a perfect dielectric should be represented by a straight line of slope—1 in the log Z versus log f plot with the phase shift $|\theta| = 90°$ and constant at all the frequencies, while real coatings present defects (holes, ionic impurities) which act as conductive paths. In this case a deflection of the log Z-log f plot or a decrease of phase shift in the θ-log f plot appear. In general terms, coatings with better barrier properties show minimal deflection from the ideal behaviour at low frequencies [12].

By inspection of Fig. 2 it appears that the initial water uptake of coatings F-C22 and F-C42 causes a decrease in the impedance modulus. After 4 weeks of exposure the appearance of a new frequency time constant at low frequencies can be related to the accumulation of water into the metal/coating interface. At longer times of exposure there is a further decrease of the barrier properties, expecially for F-C42, where the plateau at low frequencies, indicative of a resistive behaviour, is easily visible at 16 weeks. On the other hand the self-crosslinked film F-C22-SIL shows a long lasting capacitive behaviour.

Similar considerations can be made for the corresponding films obtained from the anionic dispersions (Fig. 3); taking into account the coatings with linear molecular architecture, F-A21 and F-A49, an evident

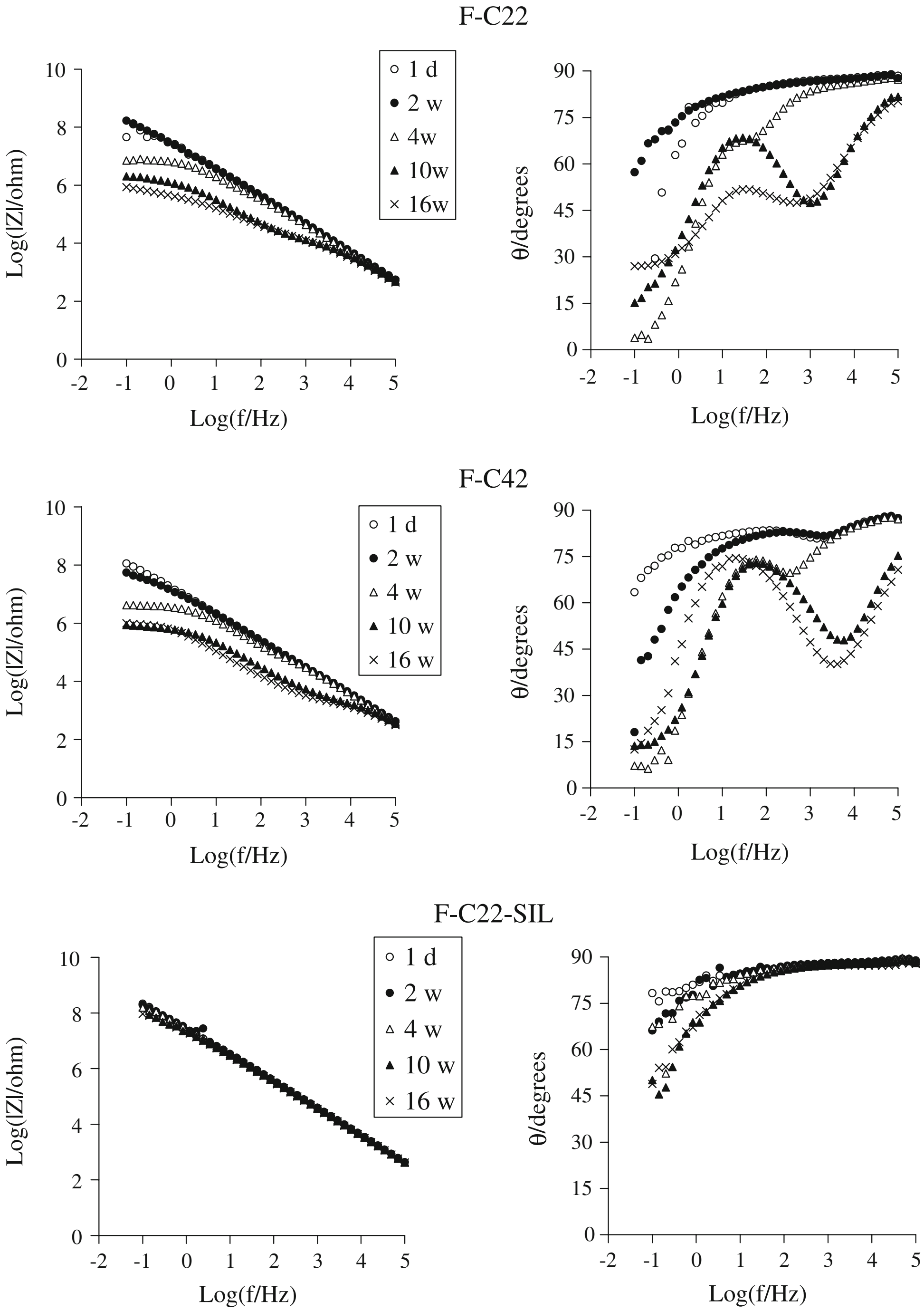
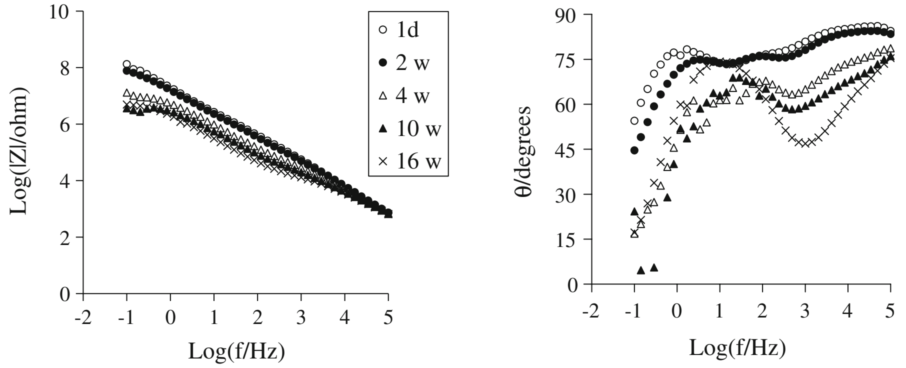
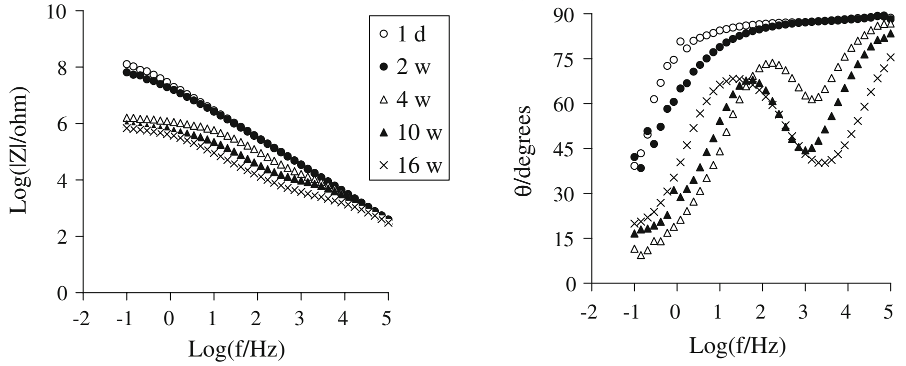
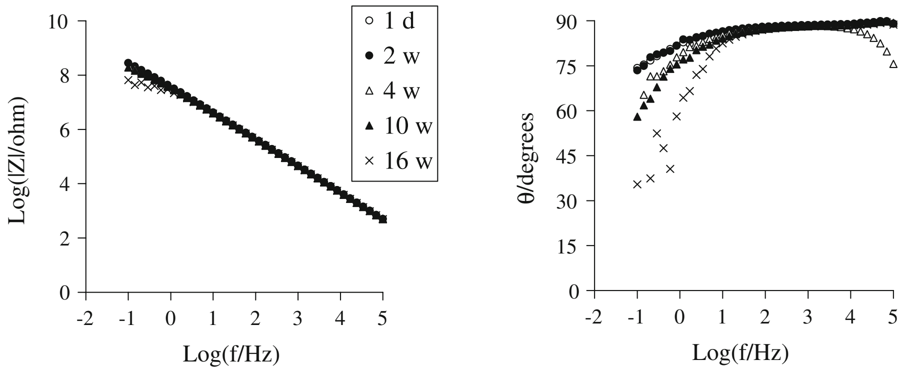


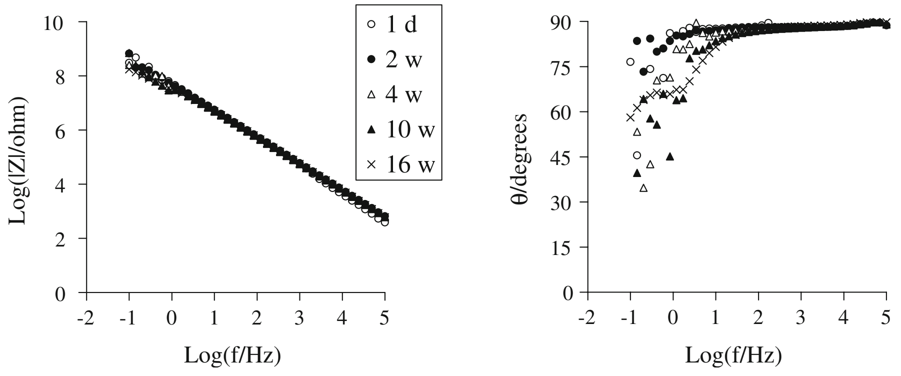
Fig. 2 Impedance spectra for the films obtained from cationic dispersions

Fig. 3 Impedance spectra for the films obtained from anionic dispersions


F-A21


F-A49


F-A21-SIL


F-A49-MEL

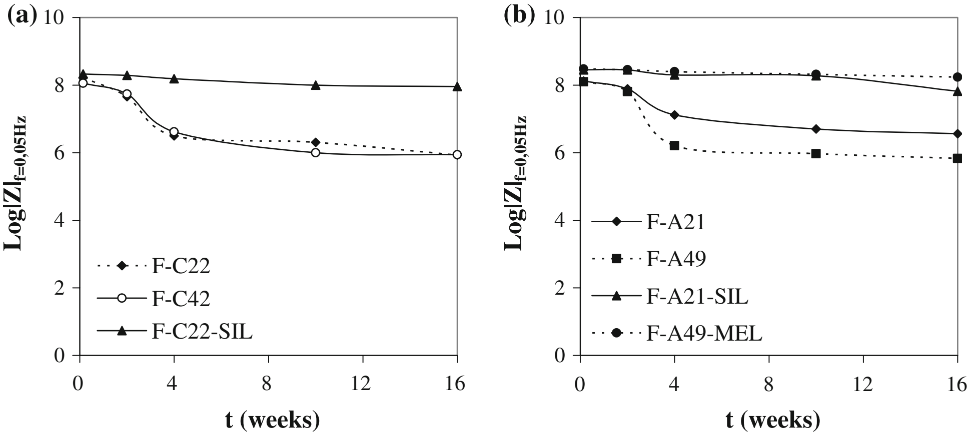


Fig. 4 Evolution of the low frequency impedance modulus with exposure time for films obtained from: **a** cationic dispersions, **b** anionic dispersions

decrease of the barrier properties occurred after 4 weeks, with the appearance of a phase angle maxima in the mid frequency section of the θ curve, but larger changes in the impedance spectra characterise F-A49, whose impedance modulus at low frequencies reached about 10^6 Ω. Only slight variations of the impedance response of the two films were detected after longer exposure time. Again the silanol based structure F-A21-SIL showed highly capacitive spectra, typical of very protective coatings, for the whole period of testing. The same behaviour is shown by the sample crosslinked with melamine.

Extracting the impedance values at low frequency as a function of time, the data reported in Fig. 4 can be obtained.

It is worth noticing that all the crosslinked coatings show high, nearly constant impedance values ($>10^8$ Ω) for the whole period of exposure to the electrolyte, indicating their long lasting barrier properties [15, 16].

On the other hand, the coatings characterized by the linear molecular architecture show starting values of $\mathrm{Log}|Z|_{f=0.05\ \mathrm{Hz}}$ lower than those of the crosslinked films, with a remarkable decrease of the impedance values after 4 weeks of exposure to the aggressive solution, which remain about constant (around 10^6 Ω) for the following period of testing.

4 Conclusions

It has been shown that ionomeric fluoroether containing polyurethanes show high surface hydrophobicity and low water uptake once applied on a metallic substrate. This would indicate a preferential stratification of lower surface tension components at the polymer-air interface, with ionic groups interacting with the metallic substrate. Chemical crosslinking does not affect the water sorption behaviour, but it improves the barrier properties of the protective coating at prolonged water exposure. This effect is particularly evident in self-crosslinking silanol based structures, and it could be related to the ability of silanol groups to form strong linkages with the metal surfaces (mainly with the oxide layer) giving good adhesion and stable interfaces.

References

1. Dieterich D (1981) Progr Org Coat 9:281
2. Simeone G, Turri S, Scicchitano M et al (1996) Angew Makromol Chem 236:111
3. Barbucci A, Delucchi M, Goretta L et al (1998) Progr Org Coat 33:145
4. Delucchi M, Turri S, Barbucci A et al (2002) J Polym Sci Part B: Polym Phys 40:52
5. Canteri R, Speranza G, Anderle M et al (2003) Surf Interface Anal 35:318–326
6. Trombetta T, Iengo P, Turri S (2005) J Appl Polym Sci 98:1364
7. Trombetta T (2005) EP 1559733
8. Cuney S, Gerard JF, Dumon M et al (1997) J Appl Polym Sci 65:2373
9. Coogan RG (1997) Progr Org Coat 32:51
10. Walter W (1986) Corros Sci 26:681
11. Touhsaent E, Leidheser H (1972) Corrosion 28:435
12. Ross MacDonald J, Johnson WB (1987) In: Ross MacDonald J (ed) Impedance spectroscopy. Wiley-Interscience, New York
13. Mansfeld F (1995) J Appl Electrochem 25:187
14. Bierwagen G, Allahar K, Hinderliter B et al (2008) Progr Org Coat 63:250
15. Bard AJ, Faulkner LR (1980) In: Electrochemical methods. Wiley, New York
16. Lobnig RE, Villalba W, Goll K et al (2006) Progr Org Coat 55:363