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Structure-Property Relationships of Coatings Based on Perfluoropolyether Macromers

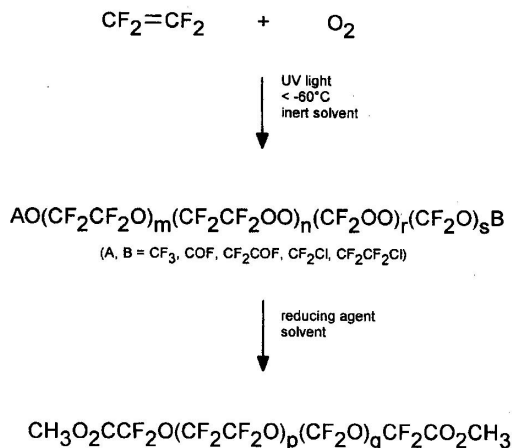
STEFANO TURRI, MASSIMO SCICCHITANO, ROBERTA MARCHETTI, ALDO SANCUNETI, and STEFANO RADICE

9.1. INTRODUCTION

Linear perfluoropolyethers (PFPE) having a random copolymeric composition and reactive end groups can be manufactured by photocopolymerization of tetrafluoroethylene with oxygen at very low temperatures,^{1,2} as shown in Scheme 1. The final product of the multistep process shown in the scheme is a diester oligomer having a molecular weight from 1000 to 2000, known as Fomblin[®] ZDEAL, which is the starting material for the preparation of resins (commercial name Fluorobase[®] Z) presented in this chapter. Alternatively, when appropriate thermal and photochemical treatments are applied to the polyperoxidic intermediate, completely perfluorinated copolyethers (known as Fomblin[®] Z perfluorocopolyethers) can be obtained. Typical features of a random perfluoropolyether chain and corresponding polymers are an extremely low glass transition temperature

STEFANO TURRI, MASSIMO SCICCHITANO, ROBERTA MARCHETTI, ALDO SANCUNETI, and STEFANO RADICE • Centro Ricerche & Sviluppo. Ausimont S.p.A.. 20021. Bollate. Milan. Italy.

Fluoropolymers 2: Properties. edited by Hougham *et al.* Plenum Press. New York. 1999.



Scheme 1

(generally below -100°), a solubility parameter around $10 \text{ (J/m}^3)^{1/2}$, a refractive index of about 1.3, and a surface energy of less than 20 mN/m , as well as excellent thermal and oxidative stability and chemical inertness.²

While perfluorinated polyethers find many applications as inert and lubricant fluids in various sectors such as vacuum, aerospace, electronics, and cosmetics, the functionalized derivatives are today increasingly used as specialty additives and intermediates for the preparation of partially fluorinated polymeric materials. In this last general case, the difficulties in applying conventional organic chemistry to PFPE functional derivatives³ can be overcome by adopting specific methodologies and selecting proper molecular weights for the fluorinated oligomers.

The use of functionalized fluoropolyether oligomers as coating resins offers many advantages in regard to the polyphasic structure of the final cross-linked polymers (mechanical properties), their peculiar surface composition and properties (low energy, stain-resistant surfaces), and the high fluorine content of the protective film (chemical resistance and durability characteristics). Moreover, in many cases the intrinsically low viscosity of PFPE resins and their concentrated solutions makes it feasible to obtain paint compositions that can be applied even with a very limited quantity of solvent (so-called “high-solid” coatings⁴), with consequent reduced volatile organic compound (VOC) emission into the atmosphere.

In this review, all these properties of new Fluorobase[®] Z (in the following simply noted as FBZ) fluoropolyether coatings will be described, with a focus on the existing correlations with the structure of the material.

9.2. THE RESINS

The oligomeric diester ZDEAL can be chemically reduced to its corresponding macrodiol. Molecular weight and molecular-weight distribution of the latter is controlled by both the process synthesis conditions and by thin-layer distillation or solubility fractionation. Some recent works reported studies on fundamental physical properties of the diolic homologous series of perfluorocopolyethers, such as glass transition, viscosity, and density-specific volume.⁵⁻⁸ A molecular weight around 1000 gives the minimum contribution to viscosity, as well as the best compatibility and miscibility with conventional, "hydrogenated" solvents. For that reason, a grade having such a molecular weight represents the best candidate for obtaining new high-solid, highly fluorinated coatings.

The structures of the FBZ resins described in this chapter are shown in Figure 9.1, and the main characteristics of FBZ resins are listed in Table 9.1. FBZ1030 and 1031 are dihydroxy-terminated fluoropolyether resins that have slightly different molecular weights and molecular-weight distributions because of their different technological fields of application. For both, a number average molecular weight around 1000, with elimination of molecular weights higher than 2000-3000 represents an optimized compromise in terms of reduced viscosity, improved reactivity at low temperatures, compatibility with organic molecules and hardeners, and better mechanical and optical properties in the final cross-linked coating. Z1031 resin is characterized by the absence of low oligomers and is specifically designed for high-temperature curing. The low surface tension of both resins assures good wettability of most substrates.

Some other physical properties such as viscosity and glass transition of the hydroxy-terminated Z resins are most influenced by cohesive interactions among the end groups, such as hydrogen bonding. Accordingly, interactions with solvents^{9,10} and cross-linkers are also ruled by that last "end copolymer effect"⁵: hydroxy FBZ resins can be diluted with high-solubility-parameter solvents such as alcohols, ketones, or esters, but are completely immiscible with, e.g., hydrocarbons, aromatics, and chloroform. Proton-acceptor solvents having, e.g., carbonylic

Table 9.1. Characteristics of FBZ Resins

Resin	OH equivalent weight	NCO content (% w/w)	Solid content (%)	η_{20° (mPa.s)	T_g ($^\circ\text{C}$)	Density 20° (g/ml)	γ_{25° (mN-m)
Z1030	450-550	—	100	100-160	-100	1.80	21.5
Z1031	600-650	—	100	100-160	-105	1.80	21.5
Z1072	—	5-5.5	60	160-220	-90/-35	1.11	23-24
Z1073	—	3-3.5	60	330-550	-90/+45	1.15	23-24

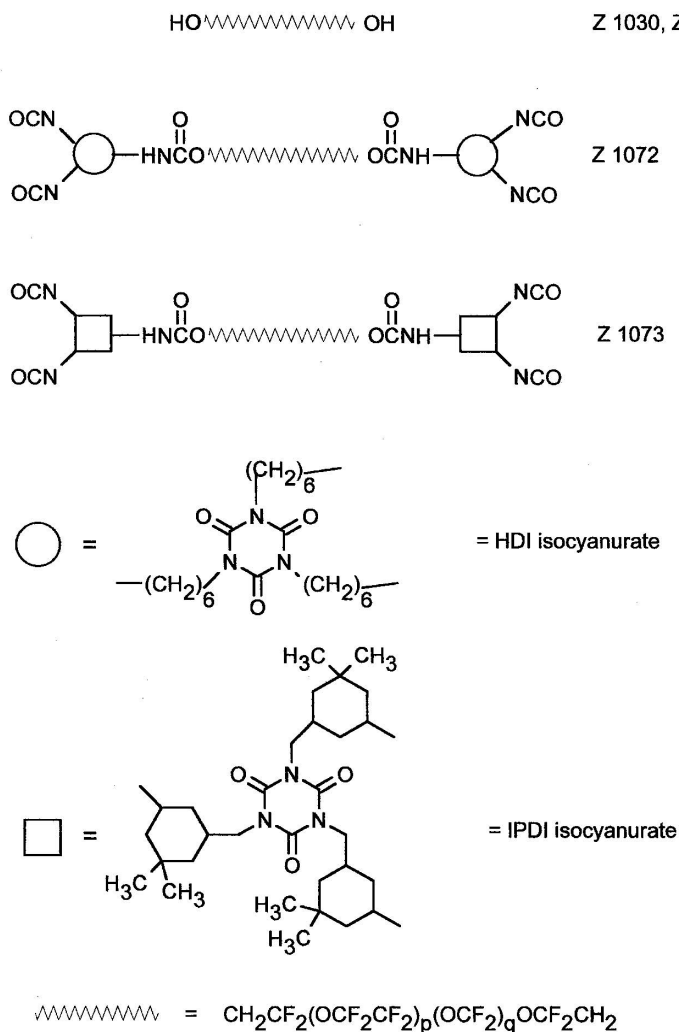


Figure 9.1. Schematized structures of FBZ resins.

groups show a higher viscosity-reducing power^{4,9,10} as they are able to disrupt the intermolecular association that characterizes the bulk state of PFPE functional oligomers. Figure 9.2 shows the isothermal viscosity of a standard FBZ1030 sample in several different polarity solvents (butyl acetate, *n*-butanol, hexafluorobenzene). It is worth noting that the fluorinated solvent, which is known^{11,12} to be a thermodynamically “good” solvent of the PFPE chain, shows a limited viscosity-reducing power, closer to the trend theoretically predicted by log–linear additive mixture laws.

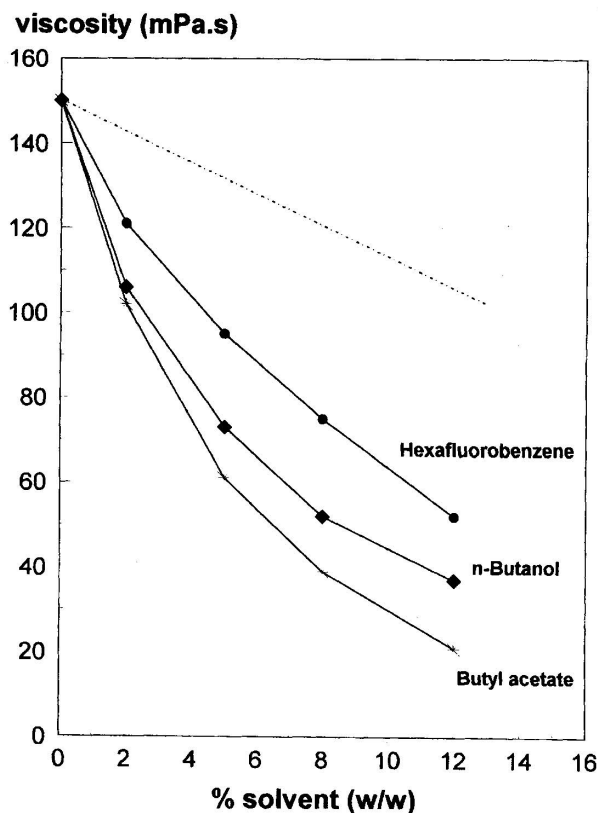
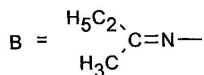
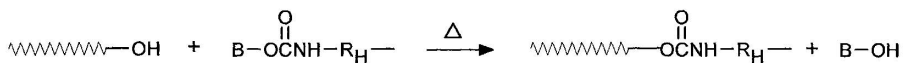


Figure 9.2. Viscosity-concentration relationships for FBZ1030 in butyl acetate, *n*-butanol, and hexafluorobenzene ($T = 20^{\circ}\text{C}$).

The miscibility of FBZ resins with the main classes of conventional polyisocyanate cross-linkers was also tested, and it was found¹³ that they can be blended and formulated with some blocked NCO hardeners as the ketoxime-blocked isocyanurates, in order to obtain monocomponent or “one pack” (1K) high-solid polyurethane coatings¹⁴ as shown in Scheme 2. Such formulations are



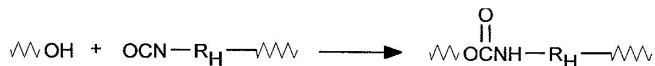
Scheme 2

unreactive at ambient temperature, since the isocyanate group is masked by a mobile blocking agent; therefore temperatures as high as 150°C or more and typical urethanation catalysts (e.g., dialkyltindicarboxylates) are generally needed for a sufficiently rapid curing. In such coating compositions hydrocarbons, which are nonsolvent of FBZ1031, can also be used as diluents to obtain macroscopically clear formulations owing to the favorable interactions between the resin and the cross-linker.

In order to obtain polyurethane coatings for applications at ambient temperature, i.e., bicomponent or “two-pack” compositions,¹⁴ one must use polymnctional cross-linkers with free NCO functions. However, compatibility of Z1030 with classical cyclic trimers of aliphatic diisocyanates is poor, likely owing to the lower polarity of the unblocked cross-linker. Therefore, some new partially fluorinated prepolymers based on the addition of Z1030 onto the cyclic trimers of hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) have been synthesized and developed (FBZ1072 and Z1073 resins). These polyisocyanate resins are obtained as clear solutions in butyl acetate or butyl acetate/hydrocarbon mixtures (solid content 60%) after prepolymerization of about one-third of the NCO groups with Z1030. These new resins possess some very attractive features: they are substantially monomer-free polyisocyanic resins, quite compatible with Z1030, able to give reduced “tack-free time” and excellent film-forming properties at the same time.

As shown by differential scanning calorimetry (DSC) analysis, the dry Z1072 and Z1073 resins are typically biphasic because of the strong difference in the solubility parameters of PFPE and polyisocyanic macromers^{2,15}; the higher T_g values are around -35 and +45°C for the HDI- and IPDI-based adducts, respectively, in agreement with the different physical states of the two isocyanate trimers. Formulations of Z1072 and Z1073 resins with Z1030 give polyurethane cross-linked coatings according to the base reaction of Scheme 3.

These formulations can be applied by using twin-feed spraying equipment in order to manage the extremely reduced pot-life typical of high-solid two-pack polyurethanes for ambient-temperature curing. The extent of cross-linking can be easily checked by IR spectroscopy monitoring the disappearance of the NCO band at about 2260 cm^{-1} , as shown for example in Figure 9.3. A complete curing of Z1030/1072 coating at ambient temperature is generally reached within 8 h with conventional tin catalysts such as dibutyltindilaurate (DBTDL) or dibutyltindiacetate (DBTDA). The relatively long tack-free time of this coating is caused by low T_g of the “hydrogenated” phase. The tack-free time is of much shorter



Scheme 3

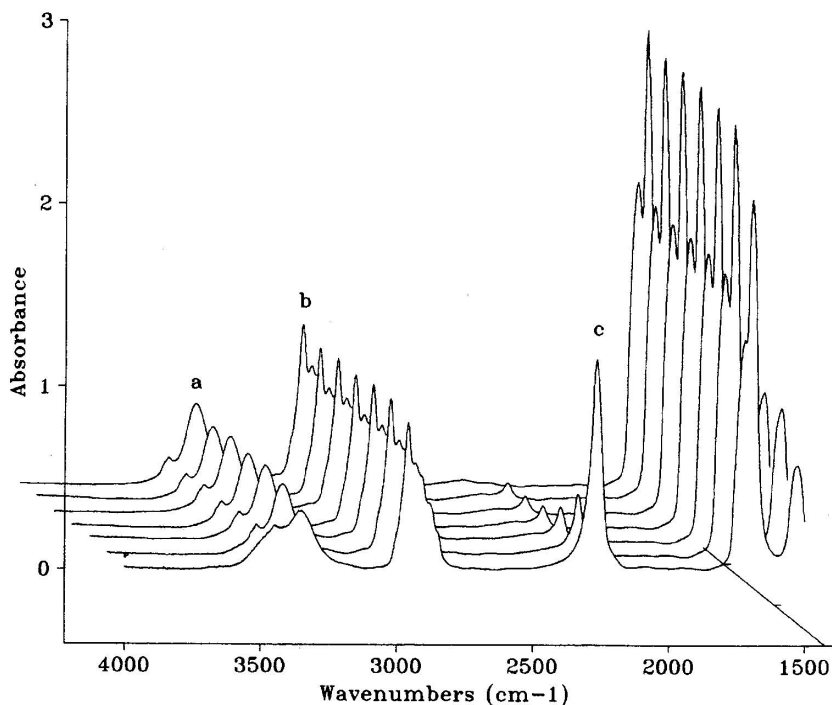
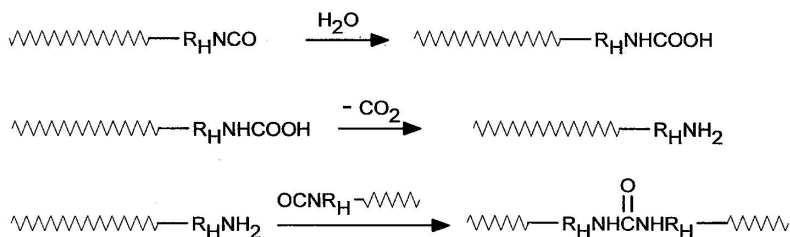


Figure 9.3. Cross-linking kinetics of a Z1030/1073 coating monitored by FTIR spectroscopy: (a) O—H and N—H; (b) CH₂, CH₃; (c) NCO.

duration for the Z1030/1073 system, owing to the faster physical drying of the high- T_g IPDI cyclic trimer, but curing time is longer because of the lower reactivity of IPDI isocyanic functions; in any case, at 30°C, NCO disappears in a few days.

FBZ1072 and Z1073 resins are NCO-ended prepolymers that are also suitable for moisture-curing (MC) applications,¹⁴ giving polyurea-urethane cross-linked films as shown in Scheme 4. In this way, monocomponent coatings for low-temperature curing are available. Curing of Z1072 in normal environmental humidity conditions reveals a rather fast cross-linking owing to the high reactivity of the HDI-type ends. Z1073 achieves faster physical drying because of its higher T_g , but it has a lower reactivity with water, and reaction temperatures as high as 50–60°C are needed for a complete curing within a reasonable time.

Table 9.2 summarizes some technological characteristics of typical one-pack and two-pack FBZ formulations, as well as the curing conditions. Viscosity is sufficiently low and suitable for spray or roll applications. In most cases, high-solid coatings can be obtained. The materials described herein include the bicomponent polyurethanes obtained by addition of Z1030 to Z1072 or Z1073



Scheme 4

Table 9.2. Characteristics of FBZ Formulations and Curing Conditions

Type	Solid (%)	Solvent	Catalyst (DBTDL)	Tack-free time	η (mPa.s)	Curing conditions
Z1030/1072 (NCO/OH=1)	75	Butyl acetate	0.3% (on NCO)	50 min	270 (20°C) 70 (50°C)	50°C 60 min
Z1030/1073 (NCO/OH=1)	72	Butyl acetate	0.3% (on NCO)	20 min	520 (20°C) 110 (50°C)	50°C 60 min
Z1072-MC	60	Butyl acetate hydrocarbons	0.5% (on NCO)	60 min	180 (20°C) 70 (50°C)	50°C 24h
Z1073-MC	60	Butyl acetate hydrocarbons	0.5% (on NCO)	10 min	350 (20°C) 90 (50°C)	50°C 72h
Z1031-H (NCO/OH=1.05)	90	Hydrocarbons	0.5% (on solid)	—	1640 (20°C) 210 (50°C)	150°C 30 min
Z1031-I (NCO/OH=1.05)	83	Butyl acetate hydrocarbons	0.5% (on solid)	—	1050 (20°C) 140 (50°C)	150°C 30 min

(Z1030/1072 and Z1030/1073 coatings); the polyurea–urethanes obtained by moisture-curing the last two resins, indicated as Z1072-MC and Z1073-MC, respectively; and the monocomponent polyurethanes obtained by polycondensation of Z1031 with the blocked cyclic trimers of HDI (Z1031-H) and IPDI (Z1031-I). The stoichiometric ratios used were typically NCO/OH = 1 for bicomponent polyurethanes and NCO/OH = 1.05 for the monocomponent ones. It is worth noting that it is expected that the final chemical constitution of the Z1031-H and Z1030/1072 polyurethanes will be exactly the same, as will that of the Z1031-I and Z1030/1073 films, notwithstanding the different mechanisms for cross-linking in 1K and 2K formulations.

9.3. THERMAL AND MECHANICAL PROPERTIES OF Z COATINGS

Composition, thermal transitions by DSC, and the results of stress–strain curves at ambient temperatures are given in Table 9.3, while the DSC traces and tensile curves are shown in Figures 9.4–9.6. The composition data in Table 9.3 have been calculated for standard Z1030 and Z1031 samples having number average molecular weights of 950 and 1200, respectively. The average composition of polyurethanes and polyurea–urethanes is rather diversified in terms of volume/weight fraction of PFPE phase and cross-link density, the latter parameter being estimated by the average molecular weight between chemical cross-links M_c . The 1K polyurethanes, although having substantially the same chemical structure as 2K films, have a higher fluorine content and M_c because of the higher molecular weight of the Z1031 macromer.

The thermal analysis results (Figure 9.4) indicate that most of the materials show a clear phase segregation with two, distinct glass transition temperatures, indicated in Table 9.3 as T_{gF} and T_{gH} , respectively. The T_{gF} value is around $-80/ -90^\circ\text{C}$ close to, although somewhat higher than, that of the polyhydroxy

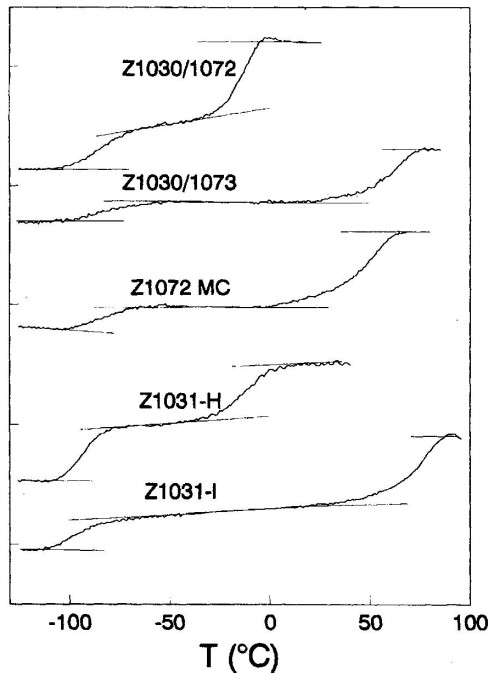


Figure 9.4. Thermal transitions by DSC of some Z coatings.

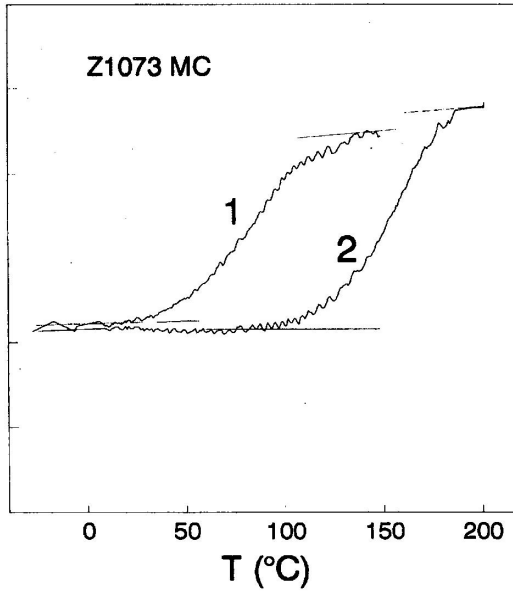


Figure 9.5. DSC trace of Z1073-MC coating: (1) first scan; (2) second scan.

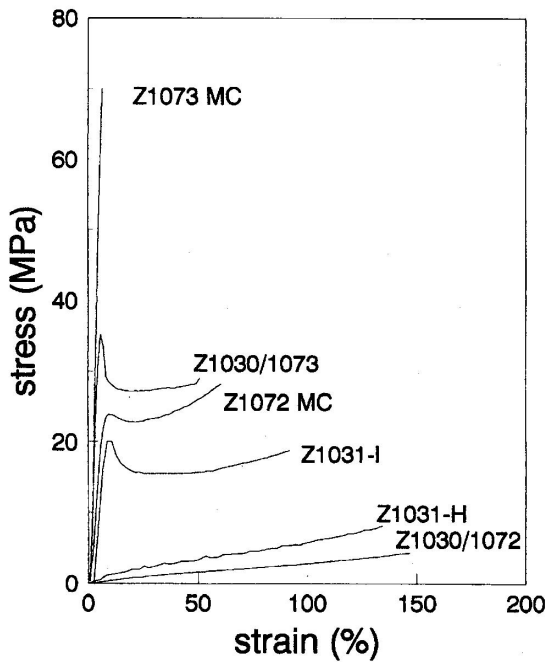


Figure 9.6. Tensile curves of Z coatings ($T = 23^\circ\text{C}$, 100 mm/min).

Table 9.3. Composition, Thermal Transitions and Mechanical Properties of Z Coatings

Property	Z1030/1072	Z1030/1073	Z1072MC	Z1073MC	Z1031-H	Z1031-I
Composition ^a	0.60	0.55	0.31	0.33	0.65	0.60
% Fluorine	42	39	25	26	45	42
M_c^b	2000	2160	1000	1300	2290	2450
Density (g/ml)	1.52	1.51	1.32	1.36	1.55	1.54
T_{gF} (°C)	-85	-85	-80	n.d.	-90	-90
T_{gH} (°C)	-15	+60	+45	+80	-10	+70
E (MPa)	8	1000	600	(+130) 1700	10	500
σ_y (MPa)	—	36	25	—	—	20
ϵ_y (%)	—	6	8	—	—	6
σ_T (MPa)	5	30	28	70	8	19
ϵ_T (%)	150	50	60	5	120	80
Persoz hardness (ASTM D4366)	60	240	180	270	50	160
Coefficient of friction (ASTM D1894)	> 1	0.2-0.3	0.1-0.25	0.2-0.35	> 1	0.1-0.3
Taber abrasion (mg/kcycle) (ASTM D-1044)	< 3	28	8	18	< 3	30
Impact (kg-cm)(AICC16)	55	40	50	10	55	50
T-bend (AICC12)	0-T	1-T	0-T	> 5-T	0-T	0-T
Conic mandrel (ISO 6860)	< 3.13 mm	< 3.13 mm	< 3.13 mm	—	< 3.13 mm	< 3.13 mm

^a Volume fraction of PFPE phase.

^b Number average molecular weight between cross-links.

FBZ precursor and can therefore be attributed to the segregated PFPE moiety. This kind of behavior is quite general for copolymers containing PFPE macromers¹⁶ and also in the Z1072 and Z1073 resins themselves. The driving force is the relevant difference in solubility parameters between fluorinated and nonfluorinated macromers, since the cohesive energy density (CED) of the perfluorocopolyethers is one of the smallest known.²

The T_{gH} attributed to the “hydrogenated” phase, ranges from -15 to $+130^\circ\text{C}$ depending on the type of polyisocyanate and the cross-link density. Some useful generalizations can be made: as a rule, the IPDI trimer promotes higher T_{gH} values than the HDI trimer (the glass temperatures of the two polyisocyanic macromers are around $+60$ and -50°C respectively) in both 1K and 2K polyurethanes. For IPDI- and HDI-containing materials, still higher glass transition temperatures are present in the MC films than in the 2K or 1K polyurethanes owing to the higher content of hydrogen bonding caused by the urea linkages. T_{gF} is apparently absent in Z1073-MC coatings (Figure 9.5), which are characterized by a higher cross-link density and a very high glass transition T_{gH} ($+130^\circ$ as second scan). Since formation of a single homogeneous phase is unlikely, the phenomenon may be related to a relatively low sensitivity of the analytical method or to some constraint effect exerted by the hard phase boundaries on the PFPE moiety, as is known in other polyphasic systems.¹⁷ In this latter case, the typical chain flexibility of the PFPE would be very limited.

Figure 9.5 also shows an example of the dependence of the coating T_g on the curing conditions; in fact, the second scan T_g evaluation of Z1073-MC film (given in Table 9.3 in brackets) is much higher than the first scan measurement. The practical consequence is that Z1073 resin should be preferentially cured in bicomponent formulations or in a mixture with the more reactive and softer Z1072 for MC applications, in order to achieve a sufficient degree of cross-linking at low temperatures in a shorter time. The Z1030/1073 coating, on the other hand, can cross-link even at low temperatures when properly catalyzed, likely owing to the high molecular mobility of the $-\text{CF}_2\text{CH}_2\text{OH}$ chain ends at ambient temperature.

Mechanical properties of Z coatings are exceptionally diversified, as is clearly shown in Figure 9.6. From an analysis of Table 9.3 data and Figures 9.6 and 9.7, a first comparison can be made of structure, thermal transitions, and mechanical behavior among coatings having similar chemical constitution, but obtained from quite different cross-linking conditions and mechanisms, such as the mono- and bicomponent polyurethanes based on the Z1031 and Z1030 resins, respectively. Figure 9.7 compares the IR spectra of 1K and 2K polyurethanes. The spectra are dominated by the strong absorptions at $1300\text{--}1000\text{ cm}^{-1}$, typical of highly fluorinated molecules, and mainly the result of asymmetric and symmetric CF_2 stretchings, C—O—C asymmetric stretching, and cooperative motions. In the carbonylic region, the main band at 1690 cm^{-1} , due primarily to the isocyanurate

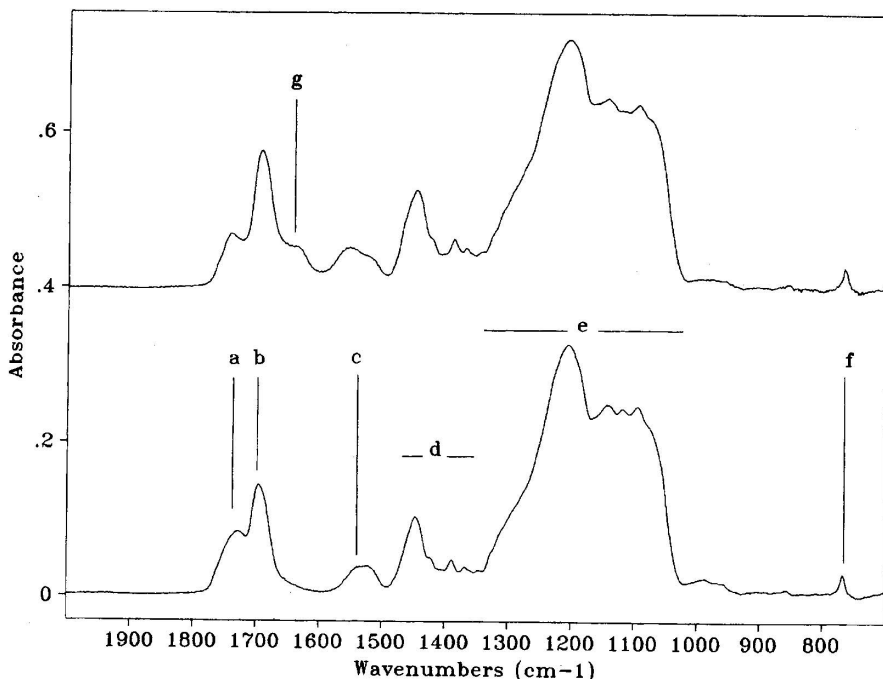


Figure 9.7. Comparison between IR spectra of Z1031-I (upper) and Z1030/1073 (lower) coatings: (a) carbonyl of urethane groups; (b) carbonyl of isocyanurate ring and urethane by-products; (c) NH urethane and urethane by-products; (d) CH_2 , CH_3 ; (e) CF_2 , COC, backbone; (f) isocyanurate ring; (g) carbonyl of ureas and urethane by-products).

$\text{C}=\text{O}$ groups, is always accompanied by another band at about 1730 cm^{-1} , attributed to urethane carbonyl groups of fluorinated alcohols. In the 1K film there is also a third band at 1640 cm^{-1} , mostly absent in the 2K polyurethane, which may be assigned to urea groups or urethane by-products such as allophanates and biurets,¹⁸ promoted by the high curing temperature. Other differences between 1K and 2K polyurethane IR spectra can be seen in the band pattern at 1540 cm^{-1} , attributed to $\text{N}-\text{H}$ deformations. The main effect of that difference in chemical structure is a slight increase of T_{gH} values in monocomponent polyurethanes, as shown in Figure 9.4 and Table 9.3. 1K and 2K coatings show qualitatively similar mechanical properties as shown in Figure 9.6, although the Z1031-I film has an elastic modulus clearly lower than that of the corresponding 2K material, likely owing to the lower cross-link density of the former.

In general, the position of thermal transitions markedly affects the mechanical behavior of polymeric coatings.¹⁹ 1K and 2K polyurethanes based on the IPDI macromer behave as “toughened plastics,” since the ambient temperature T is

such that $T_{g_F} < T < T_{g_H}$, with the rubbery and glassy domains being present simultaneously. The former moiety thus imparts high deformability ($\epsilon_r = 50\text{--}80\%$) and flexibility while the latter confers hardness. Both materials are characterized by a clear yielding occurring at $\sigma_y = 20\text{--}36$ MPa and $\epsilon_y = 6\%$.

Polyurethanes based on the HDI cyclic trimer show a rubberlike mechanical behavior. In fact, the Z1030/1072 and Z1031-H films show a low elastic modulus E , no yielding, and an ultimate, widely reversible, deformation beyond 100–150%, likely underestimated owing to the difficulty in assessing the ultimate properties of self-supported thin films.

Mechanical behavior of the Z1072-MC coating shows only a small decrease in the stress after yield. Yielding phenomena seem generally less evident in films containing the HDI trimer. On the other hand, those latter materials are significantly softer because of their lower T_g . Finally, the Z1073-MC coating is a rather hard and brittle material, showing a roughly constant $d\sigma/d\epsilon$ value close to 1.5 GPa. The results of DSC analyses (apparent absence of a mobile fluorinated phase) are consistent with the small elongation-at-break ϵ reported (5–6%).

Table 9.3 also lists the results of some technological mechanical tests. In coating technology, surface hardness is often estimated with several tests based on indentation methods, scratch, and damping of pendulum oscillations.¹⁹ Correlation with the elastic modulus of the material is often overlapped by factors such as surface roughness, friction, and sample thickness. The Persoz pendulum hardness data given in Table 9.3 are in any case qualitatively in agreement with the $\sigma\text{--}\epsilon$ curves shown in Figure 9.6. All the materials, except for the brittle Z1073 MC film, show good results in conventional postcure formability tests (impact, conic mandrel, T-bending), confirming such a positive feature of PFPE-containing coatings. However, the performances in such tests are heavily influenced by adhesion, which for PFPE-containing coatings, is generally good on organic primers such as epoxy, polyester, and polyurethane but rather poor on inorganic substrates such as steel, untreated aluminum, and glass.

Coefficients of friction (COF) range from 0.1 to 0.3 for most materials. As the actual value of the coefficient of friction is heavily influenced by many experimental variables (surface roughness, coating thickness, applied load, speed), the COF values in Table 9.3 vary over a broad range, being clearly much higher for materials that have thermal transitions above the test temperature and thus behave as rubbers. The COF, as well as other physical parameters such as hardness, surface roughness, and elasticity of the material, generally affect the abrasion resistance of the coating. The work-to-break (the integrated area of the $\sigma\text{--}\epsilon$ curves) was also correlated with abrasion resistance of polymeric coatings.¹⁹ Polyurethanes are widely known as abrasion-resistant polymers; the behavior reported for FBZ coatings is generally good, and it is outstanding especially for Z1031-H and Z1030/Z1072 films, which are characterized by the lowest modulus and the highest COF. Their elastomeric behavior (high deformability, widely

reversible) seems to be a very important factor in determining such a performance. However, a slightly higher wear index characterizes coatings based on Z1030 or Z1031 and IPDI macromers, which are those that show a rather marked yielding.

Both the excellent formability and abrasion resistance should be correlated with the particular biphasic morphology of PFPE-containing coatings owing to the high flexibility of the segregated fluorinated phase.

9.4. OPTICAL AND SURFACE PROPERTIES OF Z COATINGS

Table 9.4 lists some optical and surface characteristics of FBZ coatings described in this chapter. All the materials are completely transparent without any detectable hazing effect even when rather thick, which means that only segregated microdomains (of the order of 100 Å) are formed during cross-linking.

Perfluorocopolyethers are among the polymers that have the lowest known refractive index.²⁰ Refractive indexes of coatings described in the present chapter scale regularly with the volume fraction of PFPE phase (Figure 9.8a). Since the difference in the refractive indexes of the constituent species of the coating is about 0.2, the dependence of n on the PFPE-phase volume fraction can be calculated using the Gladstone–Dale equation²¹ and the additivity of the refractive indexes of the two phases. The linear regression to the pure PFPE component, as shown by the straight line in Figure 9.8a, extrapolates nicely to 1.3, corresponding to the value found experimentally for Z1030 resin. Interestingly, the coatings with a higher fluorine content have $n_{25^\circ\text{C}}$ values lower than 1.4. The value obtained for the urethane hard phase (1.53) is also in broad agreement with the values calculated for HDI and IPDI trimers from the group contribution method.²²

The rather low refractive index n of PFPE-containing coatings also markedly affects the specular gloss value, as shown clearly in Figure 9.8b, since the specular reflectance R_s increases with n according to the Fresnel equation.²³ Typical gloss values of Z coatings range from 75 to 87 at 60°, and appear to be inversely

Table 9.4. Some Optical and Surface Properties of Z Coatings

Property	Z1030/1072	Z1030/1073	Z1072MC	Z1073MC	Z1031-H	Z1031-I
Transmittance (ASTM D4061)	> 95%	> 95%	> 95%	> 95%	> 95%	> 95%
Gloss (60°) (ASTM D523)	78	80	87	85	75	78
$n_{25^\circ\text{C}}$ (ASTM D452)	1.393	1.412	1.467	1.455	1.386	1.399
θ_a (25°C)	110–105°	115–110°	116–113°	119–114°	114–107°	117–109°
θ_r (25°C)	75–70°	70–67°	73–70°	72–67°	70–66°	78–70°

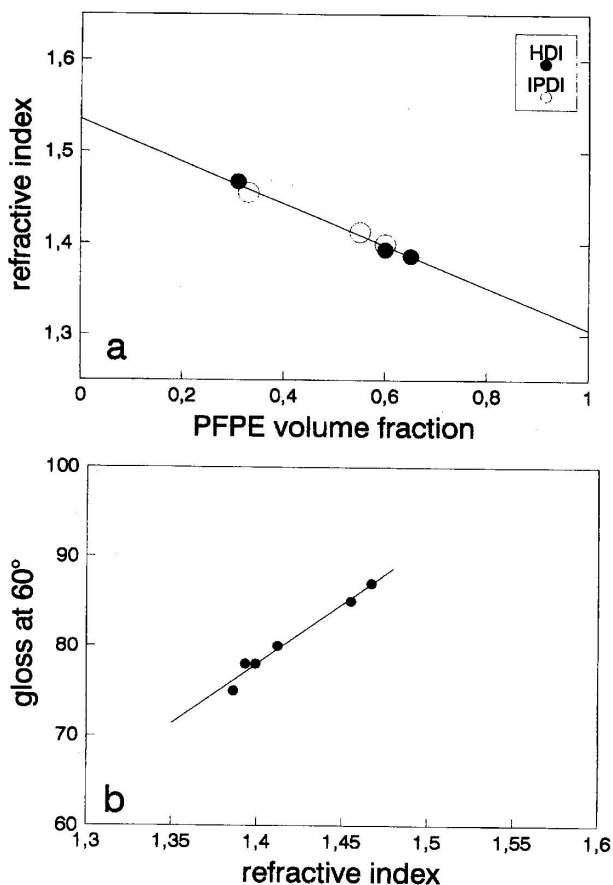


Figure 9.8. Gladstone–Dale plot of refractive indexes of Z-coatings (a) and correlation between gloss and refractive index of Z coatings (b).

proportional to the fluorine content. Filmability of Z formulations is excellent, owing to the low T_g and surface tension of the fluorinated macromer, and very regular film surfaces are generally obtained. Under such a condition, the use of gloss for comparing the surface finishing of PFPE-containing and conventional nonfluorinated coatings has to take into account the intrinsically lower specular reflectance of the former materials, due to their lower refractive index.

Contact-angle measurements between liquids and polymer solids can be used for an approximate evaluation of the surface energy and wettability characteristics of the material. It is known²⁴ that advancing and receding contact angles with water (θ_a and θ_r) indicate the low- and high-energy zones of heterophasic polymer surfaces. Accordingly, it was found that θ_a measurements of Z coatings in water

generally range from 119° to 105° , while receding angles θ_r go from within 66° to 78° . Thus a relatively large thermodynamic hysteresis is always observed during such dynamic measurements. These results are indicative of predominantly fluorinated, low-energy polyphasic surfaces and seem to be independent of the chemical structure of the coating, at least within possible experimental error. Actually, it is worth noting that MC coatings perform substantially like those of 2K or 1K, notwithstanding that the fluorine content of the urea-cured material is much lower (see Table 9.3).

Further information is given by X-ray photoelectron spectroscopy (XPS), which allows a quantitative determination of elements present in the polymeric surface.²⁴ Figures 9.9, 9.10, and 9.11 show the survey spectra of three coatings based on the IPDI cross-linker. Spectra were recorded at take-off angles of 10° and 90° , corresponding to a sampling depth of about 1–3 nm and 7–10 nm, respectively, and are displayed as recorded, without correction due to surface charging present during the experiments (the BE scale must be shifted about 2.6 eV toward lower energy). Spectra obtained at the lower angle are therefore indicative of the very top layer of the surface, and appear very similar for all of the polymeric films. Survey spectra clearly reveal the presence of F, C, O, and N. The comparison of 10° and 90° spectra shows that the intensity ratio between F 1s/N1s signals is always higher at 10° , suggesting a preferential stratification of the fluorinated components near the polymer–air interface. This interpretation is in agreement with the results of contact-angle measurements, and is supported by the analysis of high-resolution C1s XPS spectra, as shown, e.g., in Figure 9.12 for the bicomponent polyurethane. In fact, the intensity of higher-energy doublet signals at 292 and 291 eV, which may be assigned^{25,26} to $-\text{CF}_2-$ and $-\text{CF}_2\text{O}-$ groups, decreases significantly with respect to bands characteristic of nonfluorinated carbons (287 eV and the complex band at 282 eV), passing from 10° to 90° spectra. Similar considerations could be extended to the high-resolution O1s binding energy spectra, as the signal attributed to CF_2O groups (533 eV) is more intense in the more surface-indicative spectrum.

Finally there is a calculation of the atomic abundance of the surface layer on the basis of XPS data, after correction and normalization of the spectra, as summarized in Table 9.5 for two materials having quite different average compositions, such as the Z1030/1073 and Z1073-MC coatings. Fluorine abundance measured from XPS data is always much higher than that predicted by the average bulk composition of the coatings. In particular, the fluorine abundance at 10° is 49.7% for the bicomponent polyurethane and 46.0% for the moisture-cured material. On the other hand, the nitrogen abundance, indicative of the urethane moiety, is always lower than the corresponding calculated bulk value.

Analogous considerations also hold for the other PFPE-containing coatings described, so that one can conclude that the surfaces of such partially fluorinated

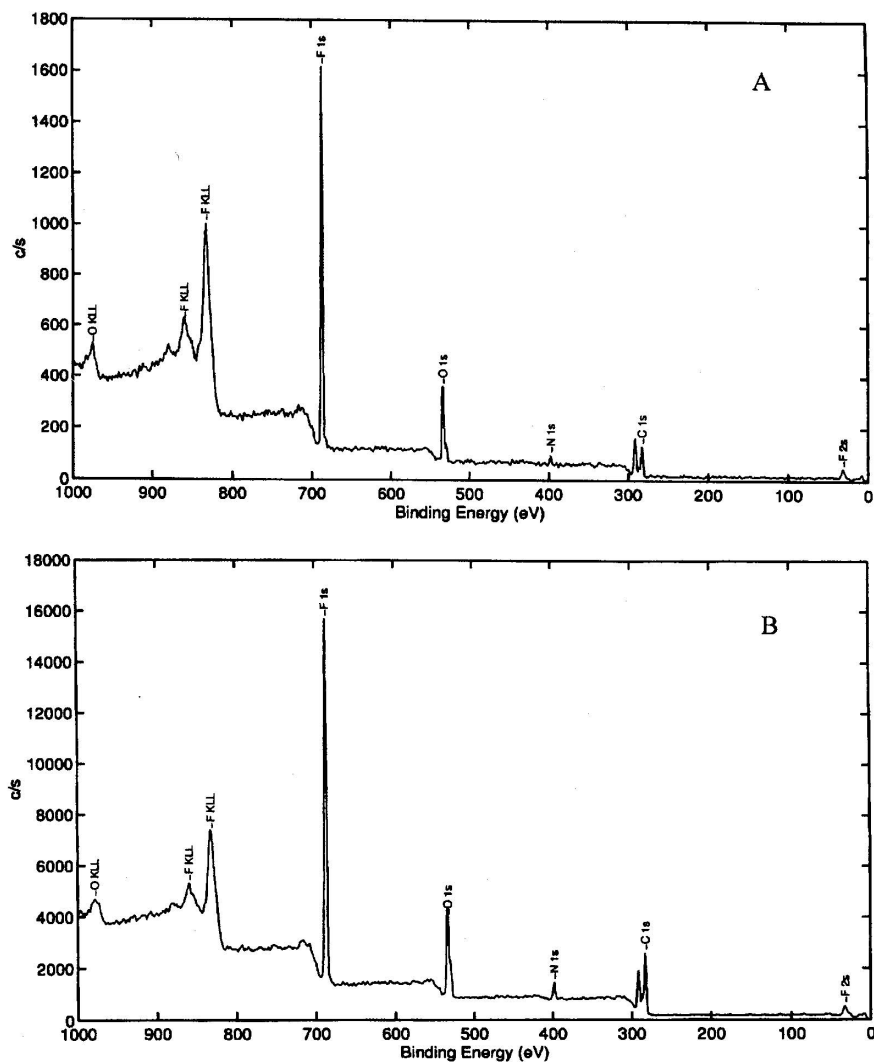


Figure 9.9. XPS survey spectra of Z1030/Z1073 coating at take-off angles 10° (a) and 90° (b).

polymeric films are predominantly fluorinated, with a minor effect of the polymer chemical structure and its average bulk composition. It is likely that the biphasicity of materials, with the presence of mobile PFPE chains, facilitates fluorine enrichment of the surface.

Important practical aspects related to the surface composition and morphology of Z coatings are their release properties with various adhesives and antigraffiti and easy cleanability performances in regard to many chemicals,

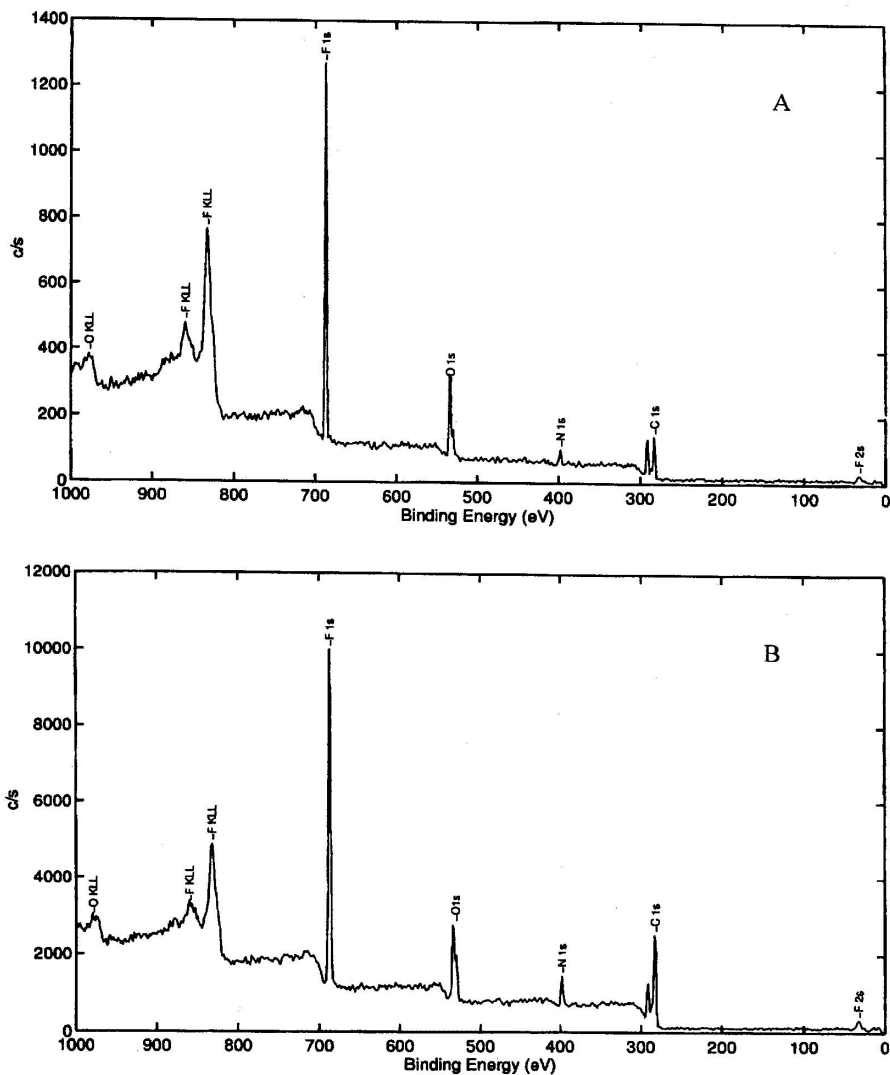


Figure 9.10. XPS survey spectra of Z1073-MC coating at take-off angles 10° (a) and 90° (b).

including markers, paints, and urban dust. In particular, outstanding antistaining performances were observed with Z-coatings during both accelerated lab-scale tests (dipping in a stirred carbon black/iron oxide slurry followed by washing with water) and natural outdoor exposure after artificial staining. Stain-resistant coatings are becoming an increasingly interesting item especially for architectural

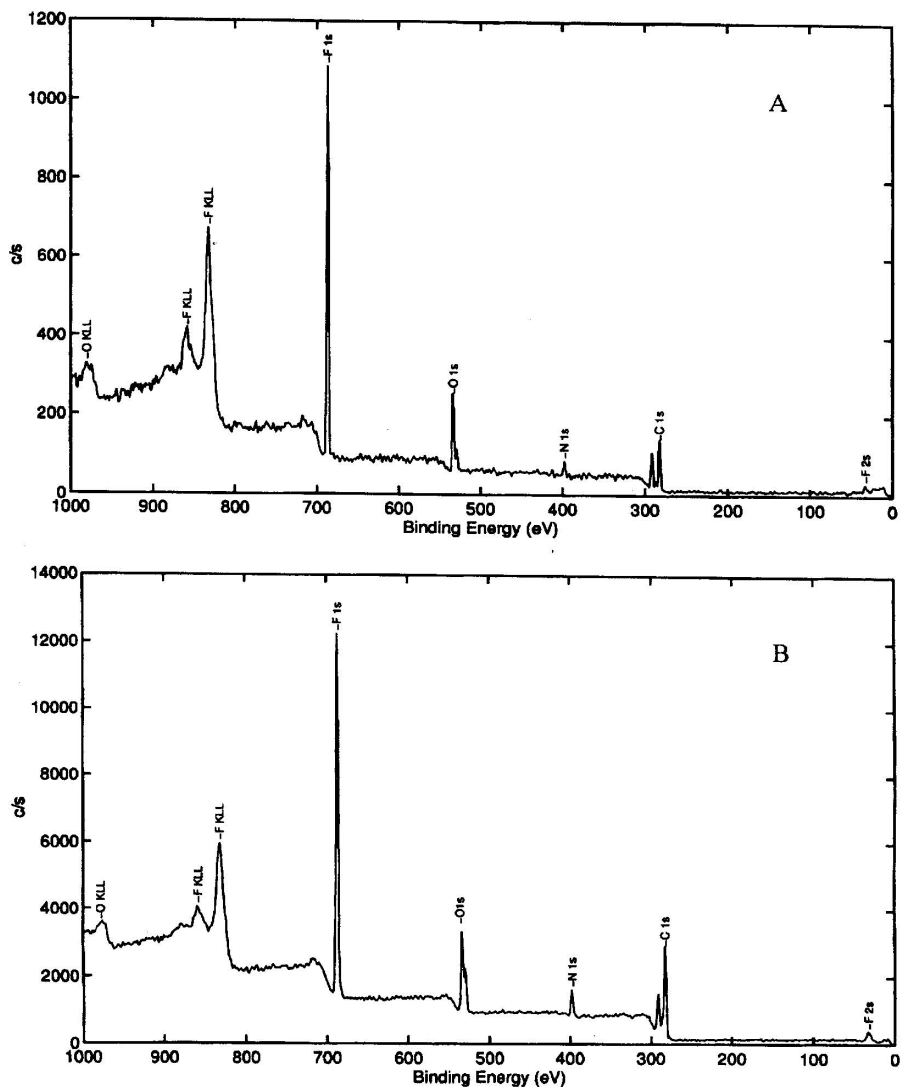


Figure 9.11. XPS survey spectra of Z1031-I coating at take-off angles 10° (a) and 90° (b).

applications in heavily polluted urban areas. Hydrophilic/lipophobic coatings and low-gloss treatments have been described,^{27,28} but PFPE-containing coatings appear to be promising candidates for obtaining stain-resistant, high-gloss, and low-surface-energy paints.

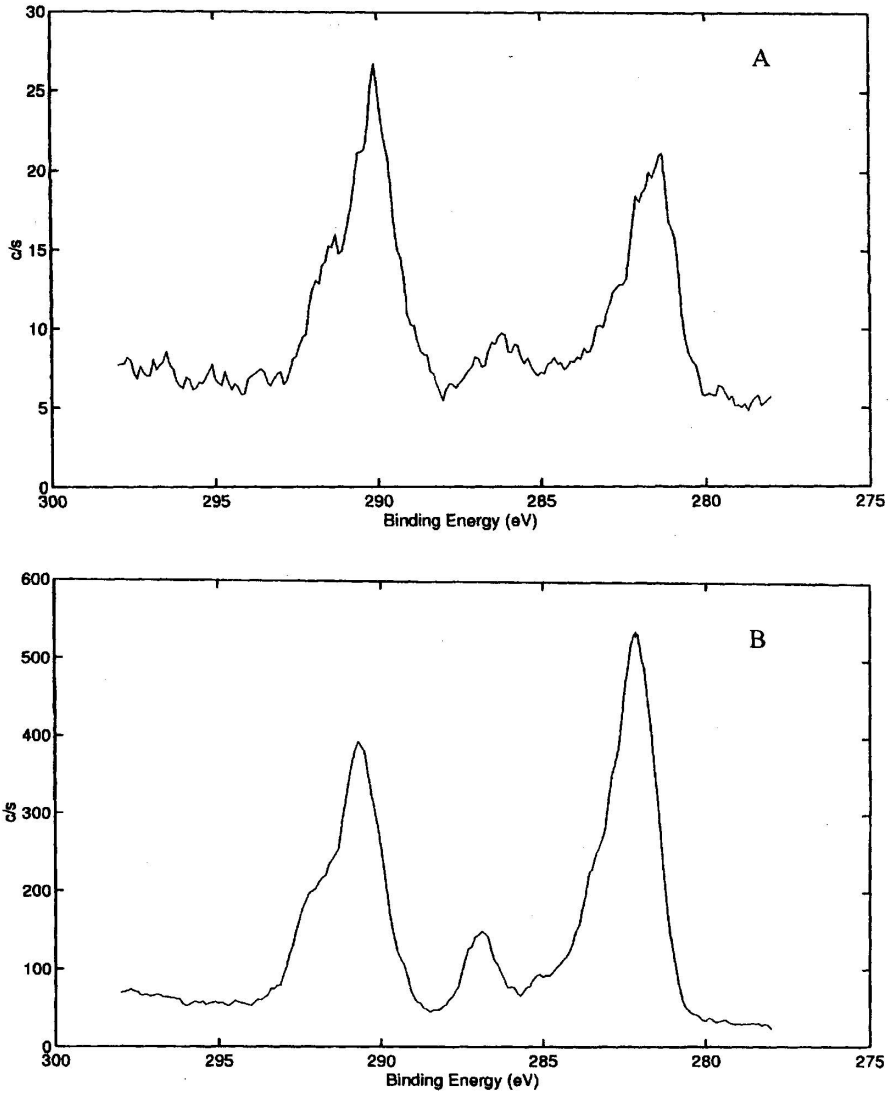


Figure 9.12. High-resolution C1s XPS spectra of Z1030/1073 coating at take-off angles 10° (a) and 90° (b) (BE scale uncorrected).

9.5. CHEMICAL RESISTANCE

Chemical resistance of protective coatings is one of the major concerns especially when stability to fuels, resistance to acid rains and protection of the coated substrate from corrosion are required.²⁹ Chemical resistance has been

Table 9.5. Atomic Abundance of C, F, O, N in Z1030/1073 and Z1073-MC Coatings

Coating	Abundance			
	C (%)	F (%)	O (%)	N (%)
Z1030/1073 calc. (bulk)	46.1	32.3	17.0	4.6
Z1030/1073 XPS (10°)	31.0	49.7	16.6	2.7
X1030/1073 XPS (90°)	38.2	40.3	17.6	3.9
Z1073-MC calc. (bulk)	57.8	22.0	12.3	7.9
Z1073-MC XPS (10°)	32.4	46.0	17.4	4.3
Z1073-MC XPS (90°)	43.1	34.2	16.5	6.3

evaluated by the usual spot tests (ASTM D-1308) on 50- μm films exposed to drops of different solubility parameter solvents and aqueous acids and bases. The principal results have been correlated in Table 9.6.

The effects have been evaluated in terms of visual inspection or decrease in hardness of the exposed zone after a standard period of time, i.e., 24 h for the organic solvents and 3–4 weeks for the aqueous solutions, apart from other conditions as noted in the Table 9.6.

Table 9.6. Chemical Resistance of Z Coatings: Solvents and Aqueous Acids and Bases ($T = 23^\circ\text{C}$)^a

Compound	Chemical resistance					
	Z1030/1072	Z1030/.1073	Z1072MC	Z1073MC	Z1031-H	Z1031-I
Xylene	N	N	N	N	N	N
Chloroform	N	N	W	N	N	N
Methylethyl ketone	N	N	W	N	N	N
Ethanol	N	N	N	N	N	N
Acetic acid	N	N	N	S	N	N
H ₂ SO ₄ 10%	N	N	N	N	N ^b	N ^b
HCl 10%	W ^b	W ^b	W ^c	N	N ^b	N ^b
NaOH 10%	N	N	N	N	N ^b	N ^b

^aN=no effect; W=weak effect; S=strong effect.

^bAfter 3 weeks.

^cAfter 1 week.

All the materials showed generally good stability. Most chemicals caused no detectable effect or only very limited swelling or blistering (weak effect). In no case was there a loss of film continuity after exposure. In general, the 1K and 2K coatings offer superior performances owing to their higher fluorine content (above 40%). The position of thermal transitions (T_g above or below room temperature) has a minor effect on the chemical resistance behavior. Coatings obtained by high-temperature curing with blocked isocyanates show results comparable to bicomponent formulations, confirming that composition, or fluorine content, is the predominant factor. The weight increase of the films after dipping (7 days, 23°C) in water and hydrocarbons was also measured and resulted in less than 0.5% with water and from about 0.5 to 2% in *n*-octane for polyurethanes and polyurea–urethanes, respectively, making PFPE-containing films very interesting protective coatings, since their barrier properties remain unchanged even after long exposure times.

9.6. WEATHERABILITY

The durability of protective coatings for outdoor uses is mainly a function of their stability against solar light and rain, and many attributes have been reported on in order to define general criteria and testing methods for predicting the material lifetime in applications.³⁰ Photooxidation of PFPE functionalized derivatives, which are precursors of Fluorobase Z resins described in this work, has been investigated recently.³¹ Both the OH-bearing oligomers and some of their urethane end-capped model compounds have been exposed to UV light ($\lambda > 300$ nm) without any additive and were found to be extremely stable. In particular, neither the PFPE chain nor the $-\text{CH}_2\text{OH}$ ends undergoes any photochemical degradation even after prolonged exposure. The use of PFPE macromers and the selection of aliphatic polyisocyanates such as HDI and IPDI trimers as cross-linkers should confer a high UV stability on the resulting polyurethanes. In fact, accelerated weathering tests including light and vapor exposure cycles (QUV-B tests, ASTM D2244 and D253, 4 h + 4 h/60°C + 40°C) have been carried out on monocomponent and bicomponent polyurethanes, as well as on MC typical formulations using conventional hindered tertiary amines (HALS) and UV absorbers as additives. The results of these tests showed a gloss retention as high as 90% or more after 4000h of UV exposure, with a yellowing index $\Delta E = 1-3$, more marked for the MC coating. These preliminary results are significantly positive, and could be further improved with the selection of proper stabilizers.

9.7. CONCLUSIONS

Fluorinated cross-linked polyurethanes can be obtained by the right combination of fluoropolyether macromers with the cyclic trimers of HDI and IPDI.

They are characterized by general excellent surface properties (easy cleanability and antigraffiti performance), good weatherability, and chemical resistance. Mechanical properties can be tuned by the proper selection of the polyisocyanate or blending (formulation) of the single resins: typically the IPDI macromer gives harder coatings with very short tack-free time, while the HDI-based materials have a better abrasion resistance and cross-linkability at low temperatures. Many desirable mechanical and surface properties of Fluorobase 2 coatings can be correlated with their peculiar polyphasic nature. Particularly, the high molecular mobility of the fluoropolyether chains linked to polar functions and their enrichment in the top layer of the coating surface may be one of the reasons for the excellent stain resistance.

Applications can be found in any sector where high durability and protection capability are required.

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