

Surface studies of partially fluorinated polymethacrylates by XPS and LEIS: the outermost atomic layer of polymer films

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4 Conclusion

The viscoelastic properties of polyester/melamine paint systems with different molecular weights and different T_g of polyester resin and different weight ratios of polyester/melamine were studied and the relationship between the viscoelastic properties of free paint films and the drawing resistance of PCM was investigated.

It was clarified that the drawing resistance of PCM relates to the rubbery modulus, steady state compliance, creep viscosity and permanent strain. The PCM with paints having low rubbery modulus, high steady state compliance, low creep viscosity and large permanent strain had good drawing resistance. From the rheological aspect of the paint films, good drawing resistance is expected in the paint systems having the coarse network structure and plastic properties.

These viscoelastic properties are dominated by the molecular weight and T_g of polyester resins and inclusion of melamine resin in paint films. The paint films with a high molecular weight and low T_g of polyester resin, but which are glassy in a drawing process, have good drawing resistance. In addition, the paint films having a low crosslinking density also have good drawing resistance.

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Surface studies of partially fluorinated polymethacrylates by XPS and LEIS: The outermost atomic layer of polymer films

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Summary

Copolymers of 1,1-dihydroperfluoroheptyl methacrylate (FHMA) and methyl methacrylate (MMA) together with the homopolymers PFHMA and PMMA were prepared and investigated with respect to both their molecular and macroscopic surface properties.

Introduction of FHMA entities in PMMA decreases the surface energy to a large extent. Angle resolved XPS measurements show an increased average fluorine concentration in a surface layer thickness of a few nanometers, compared to the fluorine concentration in the bulk. This observation is confirmed by static LEIS experiments from which it is clearly shown there is a much stronger enrichment of fluorine atoms in the outermost atomic layer.

Introduction

The applications of fluorinated materials are wide-spread in systems where water and oil repellency, low coefficient of friction and nonwettability, nonstick surfaces are required. In general, these materials are characterized by a low surface energy. The surface energy (γ) of a material is expressed by Macleod's relation:¹

$$\gamma = \gamma^0 \rho^\beta$$

where γ^0 is a temperature-independent constant, ρ the specific gravity of the material and β the Macleod exponent, which is between 3 and 4.5 for polymers.

Perfluoroalkyl polymethacrylates are known for having low-energy surfaces, due to the migration of the fluoroalkyl side chains to the air-coating interface.^{2,3,4,5} Although it is obvious that surface energies are determined by the compositions and the structures present in the top layer, no detailed information is available about the effective thickness of the surface layer, which determines the macroscopic surface energy. The answer to this question can be helpful for the development of tailor-made surfaces. This idea is depicted in the coating design triangle (Figure 1); knowledge of the relationship between the chemical structure and the surface composition of a material allows us to design the desired surface properties.

The goal of this study is to investigate the correlation between the surface energy and the surface composition of random perfluorinated polymethacrylates. Techniques that have been used in the surface characterization are: contact angle measurements, X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS).

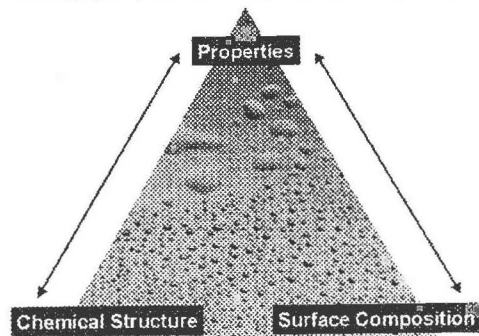


Figure 1. Coating design triangle

This study is a part of the research on self-stratifying coatings in our laboratory.^{6,7} Self-stratification takes place when a single coating separates into a multi-layered system during film formation. The driving mechanism for stratification is believed to be surface energy differences. Self-stratifying coatings offer two principal advantages. The first is the economic advantage of effectively applying two coatings in one operation. Secondly, the intercoat adhesion is supposed to be improved.

Results and Discussion

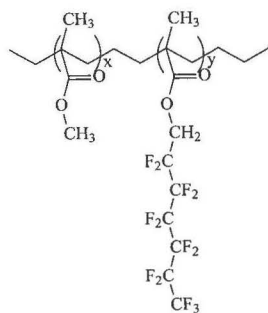


Figure 2. Chemical structure of the copolymers synthesized

As model systems, random copolymers of 1,1-dihydroperfluoroheptyl methacrylate (FHMA) and methyl methacrylate (MMA) were used. Preparation of these polymers took place in BuOAc under 'starved conditions' as described previously.⁸ A monomer mixture with initiator (2 mol% of AIBN) was added slowly at 80 °C to a BuOAc solution. After complete addition of the monomers the polymerization was quenched by the addition of methanol to avoid any further polymerization. The general structure of the polymers obtained is given in Figure 2. Six different polymers were synthesized, homopolymers of both FHMA (sample 6) and MMA (sample 1) and copolymers with 2.4 (sample 2), 6.7 (sample

3), 14.7 (sample 4), and 31.7 (sample 5) mol% of FHMA. The chemical compositions were determined by proton NMR and elemental analysis (fluorine and carbon). Both data sets are in good agreement with each other.

The molecular weights of the polymers were all adjusted to be around 16,000 and the polydispersities were kept around 1.5. This low polydispersity could be obtained by precipitating the polymer twice in methanol to remove low molecular weight species.

Contact angle measurements were carried out, using the sessile drop technique, to study the influence of the incorporation of the FHMA monomer on the wetting and the surface energy of the copolymer. Distilled water and methylene iodide were used as wetting liquids. The surface tensions of these two liquids are given in Table 1.

Table 1. Surface tensions of liquids at 20 °C for the harmonic-mean methods

Liquid	γ (mN/m)	γ^d (mN/m)	γ^p (mN/m)
Water	72.8	22.1	50.7
Methylene iodide	50.8	44.1	6.7

Figure 3a shows a low contact angle, which corresponds to a high wettability, whereas Figure 3b shows a high contact angle corresponding to a poor wettability.

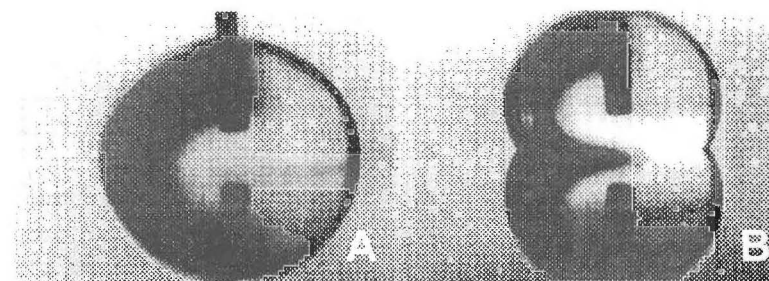


Figure 3. Wetting behavior of water on PMMA (a) and PFHMA (b)

The measured contact angles (θ) were used to calculate the surface energy of the copolymer, applying the harmonic mean method proposed by Wu¹. Combining the harmonic mean equation with the Young's equation gives:

$$\gamma_l(1 + \cos\theta) = 4 \left(\frac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} \right) \quad (1)$$

where γ^d and γ^p are the contributions from dispersion interaction and polar interaction, respectively, and θ represents the contact angle of a droplet of the wetting liquid on the polymer surface. The subscripts l and s refer to the liquid and solid state, respectively. Substituting the contact angle data of the two wetting liquids into equation 1, two equations are obtained with γ^d and γ^p as unknown parameters. After solving these two equations, the polar and the dispersion contributions of the surface energy of the polymers are obtained.

Figure 4 shows the total surface energies of different copolymers synthesized. Incorporation of perfluoroalkyl side chains into a polymer chain lowers the polymer surface energy significantly, resulting in a reduction of the surface energy by a factor of two at an incorporation of 10 mol% of FHMA. Similar trends have been observed for copolymers of styrene and fluoroalkyl-substituted styrene.⁹ The steep drop in the surface energy is not due to a preferential adsorption of polymer chains containing extra FHMA units, as all copolymer chains have the same composition arising from the polymerization technique applied.

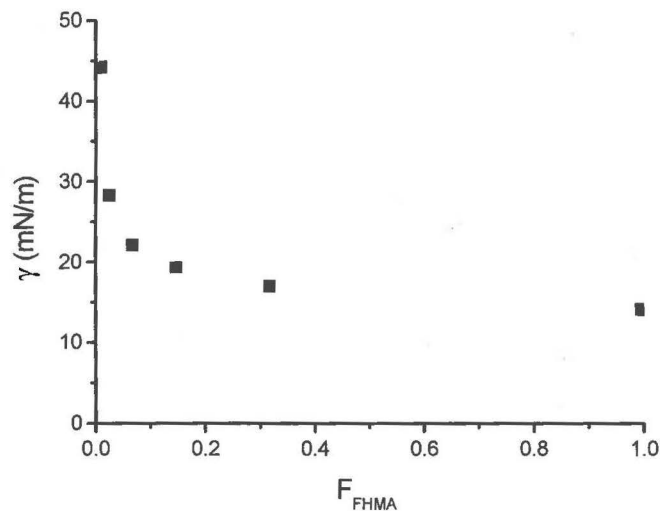


Figure 4. Surface energy (mN/m) of MMA-FHMA copolymers as a function of the molar fraction of FHMA.

In order to determine the surface composition, XPS measurements were conducted on thin films of the random copolymers. In these XPS measurements, we focused on electrons from the 1s-orbital of carbon (C_{1s}). In order to obtain quantitative data, all C_{1s} spectra were fitted with five peaks that represent to the aliphatic part (1), RCH_2O (2), $R'COO$ (3),

$-CF_2-$ (4) and $-CF_3$ (5) as shown in Figure 5. The areas of all peaks were calculated using a Gaussian-Lorentzian fitting procedure.

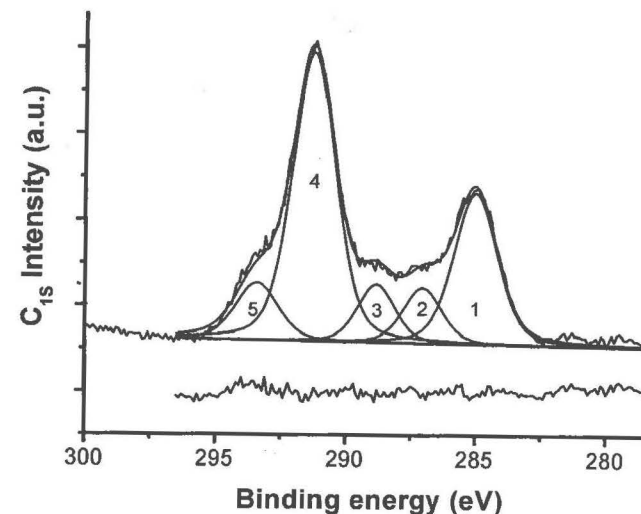


Figure 5. A typical XPS spectrum of the C_{1s} region of the partially fluorinated copolymer showing the carbon atoms at different environments. The peaks were assigned to the aliphatic part (1), RCH_2O (2), $R'COO$ (3), $-CF_2-$ (4) and $-CF_3$ (5).

Angle resolved XPS analysis (at $\theta = 0^\circ$ and 60°) on the films was applied to study the preferential orientation of the fluorinated side chain towards the air-coating interface in more detail and to gain a better understanding of the surface composition versus the surface energy of the samples. The sampling depth (d) of an XPS analysis is defined by:

$$d = 3 \lambda \cos \theta \quad (2)$$

where λ is the inelastic mean free path of the electrons, and θ is the angle between the emitted photoelectrons to the analyzer and the surface normal. The sampling depth (at 3λ) is between 6 and 10 nm, depending on the kinetic energy of the ejected electrons. The value 3λ is taken because 95 % of detected electrons originate from this depth or less.¹⁰ On the basis of curve-fitting data, the molar amount of FHMA can be calculated from the relative intensities of the CF_3 and the CF_2 peaks with respect to the intensities of the C-O and the C=O peaks (theoretical ratio for PFHMA; $CF_3 : CF_2 : C-O : C=O$ is 1:5:1:1).

These results together with the bulk composition as calculated from elemental analysis are given in Table 4. From these data it can be seen that the amount of fluorine is higher than the calculated (bulk) amount. Moreover the data found by XPS-60 are even higher than those of XPS-0. It is therefore evident that there is a preferential enrichment of the perfluorinated side chains in the surface.

Table 4. XPS results for the different copolymers of MMA-FHMA at different depths.

Sample #	Theory ^a	Experimental ^b	
	Amount (mol%) of fluorine	Amount (mol%) of fluorine; XPS-60	Amount (mol%) of fluorine; XPS-0
1	0	0	0
2	0	6	3
3	5	14	7
4	13	25	15
5	26	39	28
6	50	60	55

^a bulk composition as calculated by element analysis of fluorine.

^b XPS-0/60 refers to the emission angle (0°/60°) relative to the surface normal

Figure 6 shows 2D topographic images of film surfaces as obtained by AFM with scanning areas of 2 μm x 2 μm for PMMA (a), for the copolymer with 31.7 mol% of FHMA (b) and for PFHMA (c). The arithmetic mean roughness obtained for PMMA, the copolymer with 31.7 mol% of FHMA and for PFHMA is 0.28 nm, 0.26 nm, and 0.35 nm, respectively.

This means that the influence of surface roughness on the contact angle measurements and the XPS data can be excluded.

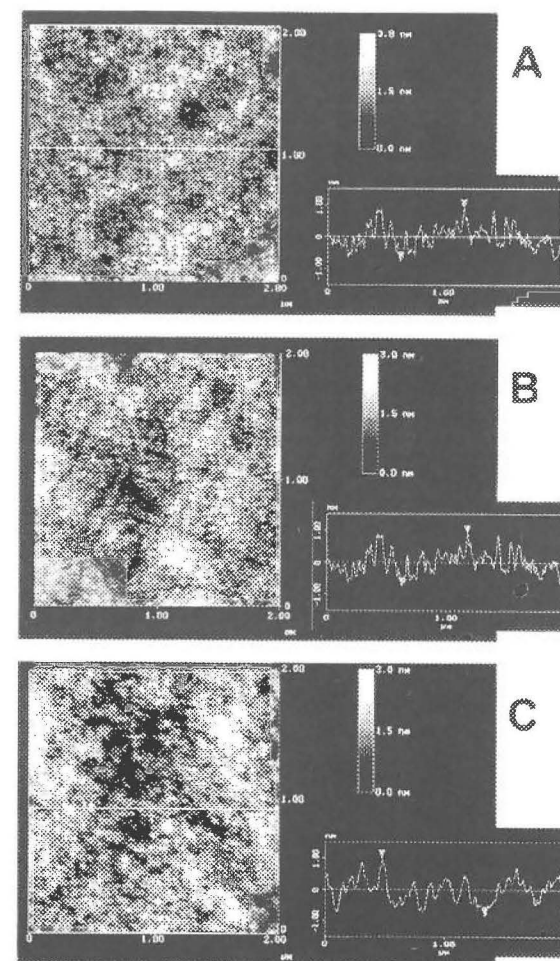


Figure 6. 2D topographic images with a scanning size of 2 μm x 2 μm (a) PMMA, mean roughness of 0.28 nm; (b) copolymer with 31.7 mol% FHMA, mean roughness of 0.26 nm; (c) PFHMA, mean roughness of 0.35 nm.

It is thought that the outermost atoms in the surface predominantly determine the wettability. For example, Mach et al.¹¹ found a dramatic effect in the surface energy by replacing a terminal fluorine atom with a hydrogen atom in a perfluorinated side chain of a liquid-crystalline compound. In order to study the composition in the outermost atomic surface layer low-energy ion scattering measurements were carried out for the perfluorinated polymers used in the preceding experiments.

During such a LEIS experiment, noble gas ions are bombard to the sample and the back-scattered ions are detected. The energy of a back-scattered ion is characteristic for the mass of the target atom as given by:

$$E_1 = \frac{M_1^2}{(M_1 + M_2)^2} \left[\cos \theta + \left(\frac{M_2^2}{M_1^2} - \sin^2 \theta \right)^{1/2} \right]^2 E_0$$

where E_0 is the energy of the ion before the collision, M_1 the mass of the impinging ion, M_2 the mass of the surface atom, and θ the scattering angle. The information depth of LEIS is limited to one atomic layer because the low-energy inert gas ions have a high neutralization probability. This results in a negligible scattered-ion yield from target atoms below the surface.

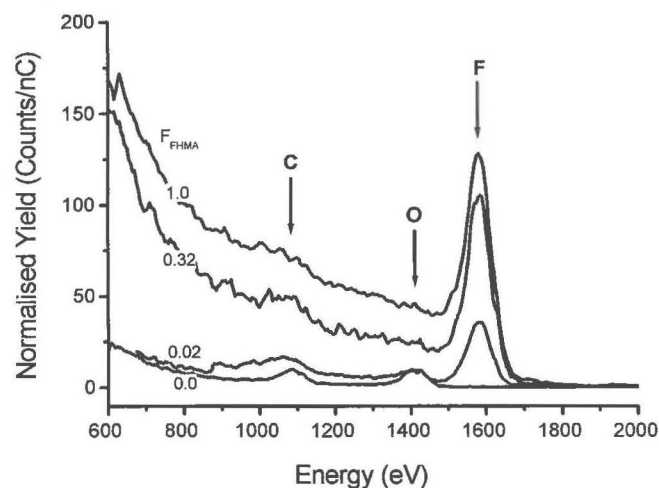


Figure 7. LEIS energy spectra of partially fluorinated copolymers; samples 1, 2, 5 and 6.

The energy spectra of the LEIS measurements with four polymer films are shown in Figure 7. These energy spectra can directly be interpreted as mass spectra of the surface atoms.

The LEIS measurements resulted in three peaks in the energy spectra, representing carbon, oxygen and fluorine. The intensity of the fluorine peak increases with increasing FHMA content in the copolymer, showing already at an incorporation of 2.4 mol% of FHMA a large fluorine peak. On the other hand, the oxygen and to a less extent also the carbon peak vanishes with increasing FHMA content.

By plotting the fluorine atomic concentration of the first atomic layer, $[F]_{LEIS}$ vs. the surface energy of the polymer film, an almost linear correlation is found (Figure 8).

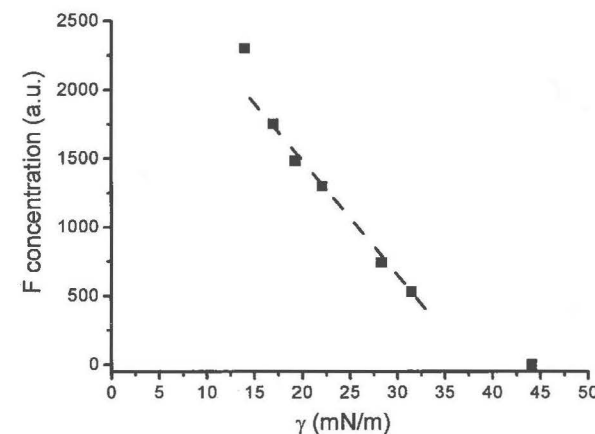


Figure 8. Correlation between the surface energy γ and $[F]_{LEIS}$

Conclusion

Fluorine containing materials have many properties like water and oil repellency, low coefficient of friction and non-wettable surfaces that are desirable for coatings. In this respect the methacrylic polymers containing fluorinated monomers are interesting candidates. It is demonstrated that a small molar fraction of perfluoroalkyl groups reduces the surface energy of the polymer significantly. The enrichment in fluorine in the surface region is observed by angle resolved XPS. LEIS experiments show a much stronger enrichment in fluorine in the first atomic layer (for instance, for sample two this is by a factor of 8).¹²

Studies on related polymer systems are underway to correlate the structural characteristics of the upper surface layer with macroscopic properties, such as surface energy.

Experimental

Polymer preparation. Methyl methacrylate (MMA, Aldrich), 1,1 dihydroperfluoroheptyl methacrylate (FHMA, ACR Technologies B.V.) were used without further purification. Polymerizations were carried out in solution as described elsewhere⁸ using azobisisobutyronitrile (AIBN, Merck) as initiator.

Film preparation. Thin polymer films were prepared by spin coating (5000 rpm/60 s) of polymer solutions in toluene or Freon 113. After spin coating the polymer films were annealed for two hours at 125 °C.

Contact angle measurements. Advancing contact angles were obtained by means of the sessile drop method on a Krüss G10 apparatus. The complete profile of the sessile droplet was fitted by the tangent method to a general conic section equation. The derivative of this equation at the baseline gives the slope at the three-phase contact point and thus the contact angle

X-ray photoelectron spectroscopy. The XPS measurements were performed on a VG Ionex system equipped with a Clam II analyzer and a monochromatic Mg K α X-ray source. All C_{1s} peaks corresponding to hydrocarbons were calibrated at a binding energy of 285.0 eV to correct for the energy shift caused by charging.

Low energy ion scattering. The static LEIS measurements were performed in the Calipso LEIS-setup.¹³ In order to obtain a high sensitivity to light elements, a 3 keV ⁴He⁺ ion beam was used. Special care was taken to ensure that the measurements were performed in a static mode. A detailed description of the experimental condition is given elsewhere.¹⁴

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Halogen-free Flame Retardant Radiation Curable Coatings

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Summary

Radiation-curing technology is widely used in the field of protective coatings, electronics, adhesives and inks. It combines several advantages such as high cure speed, low energy consumption and is environmental friendly since radiation-curing formulations are solvent free.

Due to the continuous trend in more stringent safety regulations, search for polymers with flame retardant (FR) properties is important. In the case of coatings (radiation curable or conventional), their flammability can contribute to the fire propagation. In some wood and cable coating applications, significant level of fire-retardancy are required and coatings with FR properties have been developed.

In conventional plastics, additives such as chlorinated/brominated aromatics, antimony halides, organophosphorus compounds etc. and their combination are commonly used to impart FR. However, the additive approach suffers from several drawbacks like low compatibility with the polymer matrix, negative impact on the physical and mechanical properties of the material and additive loss by migration. Moreover in the case of UV-curable coating, pigmented additives will reduce the UV reactivity of the resin and additive migration leads to a blooming of the surface. Finally, halogen based fire retardant systems show undesirable negative side effects so that an urgent need is now to be satisfied for halogen free fire retardant systems.

In order to avoid such drawbacks, UCB Chemicals has developed oligomers and monomers containing halogen-free FR moieties covalently bound to the polymer backbone. ³¹P-NMR and ¹H-NMR spectroscopies were used to characterize the structure of the new compounds. Thermogravimetric analysis, Limiting Oxygen Index (LOI), cone calorimeter and flame propagation tests were used to assess the flame-retardant properties of these resins.

