

Fluorine Modification of ORMOCER (ORGANICALLY MODIFIED CERAMICS)-Coating Materials

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Abstract

Fluorine modified ORMOCER (ORGANICALLY MODIFIED CERAMICS) coating materials have been synthesized from 3-methacryloxypropyltrimethoxysilane, zirconium-n-propoxide, methacrylic acid and various amounts of 1H,1H,2H,2H-perfluorooctyltriethoxysilane. The $\approx 5 \mu\text{m}$ thick films showed a good adhesion to glass surfaces and good abrasion resistance. Evaluation of contact angle measurements has shown that these transparent materials exhibit a low surface free energy similar to perfluorinated polymers.

1. INTRODUCTION

Perfluorinated polymers are well known for their low surface free energy [1] which leads to an antiadhesive behavior of polar and non polar substances on these surfaces. Their good weathering stability [2, 3], due to the stability of the carbon-fluorine bond, is an important feature necessary for outdoor applications. Polymer surfaces in general are soft and show a poor abrasion resistance if they are not reinforced by fillers. However, filling of polymers with inorganic particles leads to non-transparent composites not suitable for transparent coatings. Therefore, investigations were carried out to develop transparent fluorine containing coating materials with antiadhesion properties similar to perfluorinated polymers and increased abrasion resistance.

Various techniques such as physical vapor deposition of PTFE (polytetrafluoroethylene) [4], vacuum coating with polyfluoroalkylalkoxysilanes [5], addition of fluorotensides [6] or immersion of substrates in solutions of perfluorocompounds [7] have been investigated. But all of these investigations did not lead to coatings with sufficient transparency and abrasion resistance.

An alternative route was investigated in [8] by use of sol-gel techniques. Composites from tetraethoxysilane and PVDF-polytetrafluoroethylene copolymer have been synthesized. They are opaque or translucent due to a phase separation between the organic copolymer and the SiO_2 -phases.

Polymers based on 1H,1H-perfluorooctylmethacrylate, showing

a low surface energy of 11.2 mJ/m^2 [9], are used for oil, water and mud repellent coatings on textiles. This indicates that surfaces with a low surface energy and antiadhesion properties can be obtained from partially fluorinated systems, too. According to [10], the surface free energy depends on the surface fluorine concentration which not necessarily has to be the same as the bulk concentration. Therefore, the question arises whether it is possible to transfer antiadhesive effects into ORMOCERs known for their high abrasion resistance [11] by introducing perfluorinated organic groups.

In general, ORMOCERs are synthesized by the sol-gel process, using organoalkoxysilanes, alkoxysilanes and metalalkoxides (or the corresponding halides) as precursors, as described elsewhere [12 - 15]. One advantage of this process is that the precursors can be mixed on a molecular level, and phase separation can be avoided by carefully controlling the reaction conditions during synthesis. For instance, the preparation of UV curable transparent coatings with high abrasion resistance and high transparency has been reported [16, 17].

From this point of view, the goal of this study was to develop a new ORMOCER coating which combines a high abrasion resistance and good transparency with a low surface free energy as a third function of the material. Therefore, the incorporation of a partially fluorinated organoalkoxysilane into ORMOCER matrices described in [16, 17] was studied.

2. Experimental

The coating materials were prepared by reacting one mole 3-methacryloxypropyl trimethoxysilane (MPTS), purified by vacuumdistillation, with 1.5 mol H_2O dissolved in methanol at $50 \text{ }^\circ\text{C}$ for one hour. Subsequently the reaction mixture was cooled down to $-10 \text{ }^\circ\text{C}$, and a solution of 0.1 mole zirconium n-propoxide in 1-propanol, complexed with 0.1 mole methacrylic acid was added. The mixture was stirred for 90 minutes followed by the addition of water (0.15 mol). After a reaction time of 12 hours at room temperature various amounts (0.01 to 0.12 mol per mol MPTS) of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FTS) were added and stirred for additional two hours. For UV curing experiments, one weight percent of a photoinitiator (Irgacure 184, Ciba Geigy) was added.

Coating experiments were carried out with glass plates as substrates using a dip coating technique (substrates for evaluation of contact angles) as well as a squeegee method. The coatings were cured by UV light and then thermally treated at $130 \text{ }^\circ\text{C}$ for one hour. The coating thickness was determined with a 3D-profilometer. The advancing contact angles of the coatings were measured at $20 \text{ }^\circ\text{C}$ with a Wilhelmy balance apparatus (tensiometer, Krüss K12C) by measuring the force during dipping a flat substrate in a test liquid. With known substrate geometry and surface tension of the liquid the contact angle is a function of the force during dipping[1,

18]. For the evaluation of the dispersive and polar parts of the surface free energy, H₂O (bidistilled), glycerol, 1-octanol and hexadecane were used as test liquids. The surface tension of each liquid was measured and found to be in the range cited in the literature [19 - 21].

Adhesion was proved, according to [22, 23], using a cross cut test in combination with a tape test (0 is the best and 5 the worst value). A combination of taber abrader test (100 revolutions) and haze measurement (percentage of scattered light compared to the non-abraded surface) was used for determination of abrasion resistance [24].

3. Evaluation of Surface Properties

The surface free energies γ_s were calculated using the Young equation $\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos \theta$ [25], where γ_{sl} is the solid/liquid interfacial surface energy, γ_l stands for the surface energy of the liquid and θ is the contact angle.

In order to calculate the unknown interfacial surface energy γ_{sl} , the well established model of Wu [26] was used, assuming that each surface energy is the sum of a polar part and of a dispersive one, which are tabulated for different liquids in [19 - 21].

4. Results and Discussion

4.1. Preparation of the Coating Material

The composition described in [16] (UV-curable ORMOCER based on 3-methacryloxypropyltrimethoxysilane and zirconiumpropoxide complexed with methacrylic acid) was used as a starting point. Since organoalkoxysilanes with fluorine in the α - and β -positions to silicon hydrolyze very easily at the $-C-Si\equiv$ bond [27], fluoropropylalkoxysilane was used as fluorine carrier.

Simple mixing of the precursors followed by hydrolysis leads to phase separation. Therefore, a special procedure as indicated in the experimental part had to be developed.

Liquids showing no phase separation could be obtained by hydrolyzing the mixture of MPTS and Zr(OPr)₄ (complexed with methacrylic acid) with a half of the concentration of water necessary for a complete hydrolysis of all the present alkoxy groups. It was found out that a critical residual water content of about ≤ 0.3 weight % in the hydrolyzed mixture was suitable for avoiding phase separation after addition of the fluorine compound; the H₂O content was determined by Karl-Fischer-Titration.

4.2 Properties of Coatings

Crackfree coatings with thicknesses of about $5 \pm 1 \mu\text{m}$ were obtained after UV and thermal curing. The coatings have a good adhesion to glass substrates, shown by values for crosscut/tape test between 0 and 1 [22 - 23]. Taber abrader tests show

that the fluorine-free ORMOCER has a slightly higher abrasion resistance (Δ haze = 2 %) than the fluorine modified coatings (Δ haze = 4 %).

The transparency of the coatings was determined by UV-Vis-spectroscopy. The transmittance of a coated glass slide in the visible region was measured to be above 95 percent. Scattering and decreased transmittance caused by phase separations in the coating were not detected.

The next interesting question was the wetting behaviour of the coatings. Therefore, contact angles were measured with a standard set of liquids (polar to nonpolar). In figure 1, the contact angles of the test liquids on coatings with increasing FTS content are shown in comparison to float glass and PTFE.

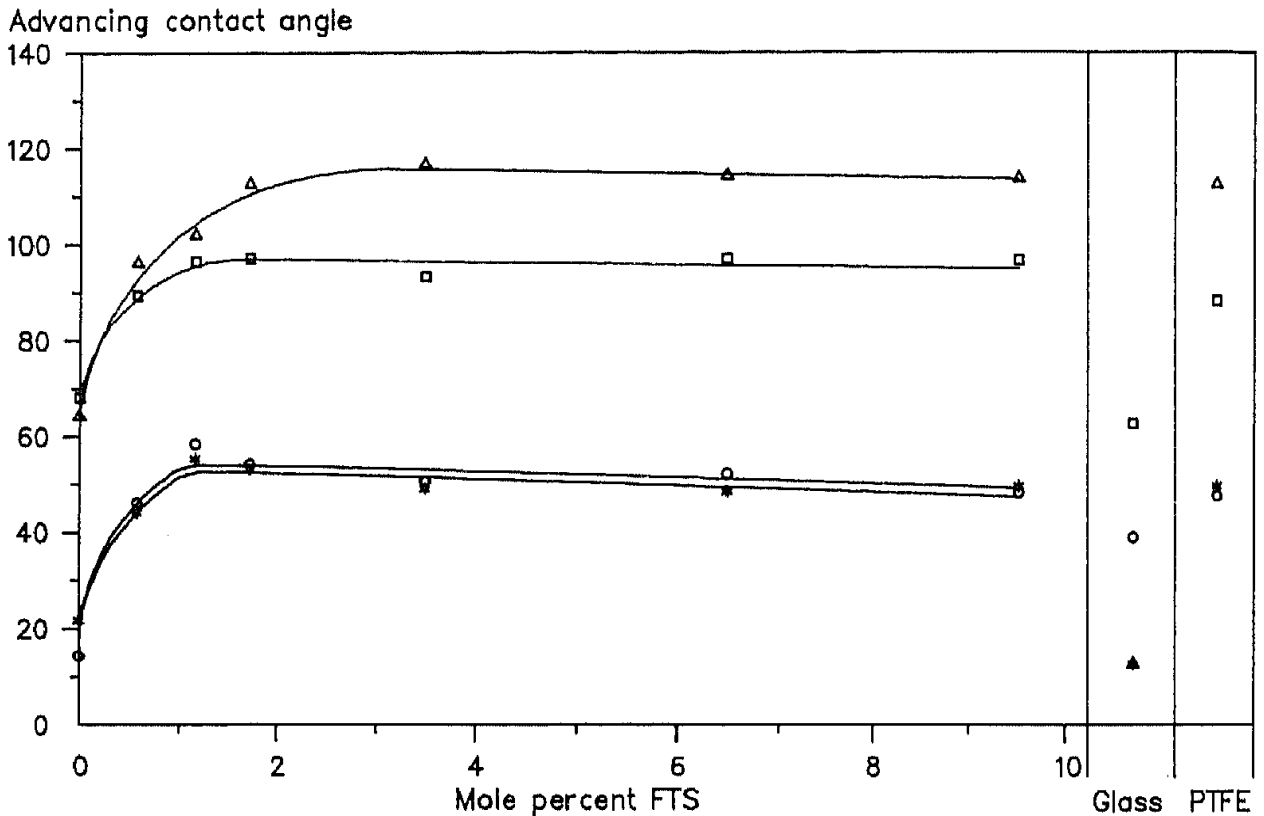


Figure 1: Contact angles of ORMOCER coatings depending on used test liquid and FTS concentration in comparison to float glass and PTFE; Δ Water, \square Glycerol, \circ n-Octanol, $*$ Hexadecane.

The unmodified ORMOCER coating has a higher contact angle for water (64°) and a lower value for octanol (14°) due to the more non polar behavior when compared to the glass surface (water 14° , octanol 37°).

With increasing FTS contents (0 - 1.7 mol-%), a strong increase of all contact angles of the used test liquids is observed. The incorporation of only 1.7 mol-% FTS in the ORMOCER results in a set of contact angle values for the test

liquids comparable to those of PTFE. For example, the values for the coating were 113° for water and 54° for octanol, compared to 110° (water) and 54° (octanol) for PTFE.

It is of significance that with FTS contents of about 2 mole-%, the contact angles reach the maximum plateau, indicating an enrichment of the fluorine-containing groups at the surface. XPS spectra of the surface and of the bulk (fig. 2) show that the fluorine content is far higher at the surface than in the bulk.

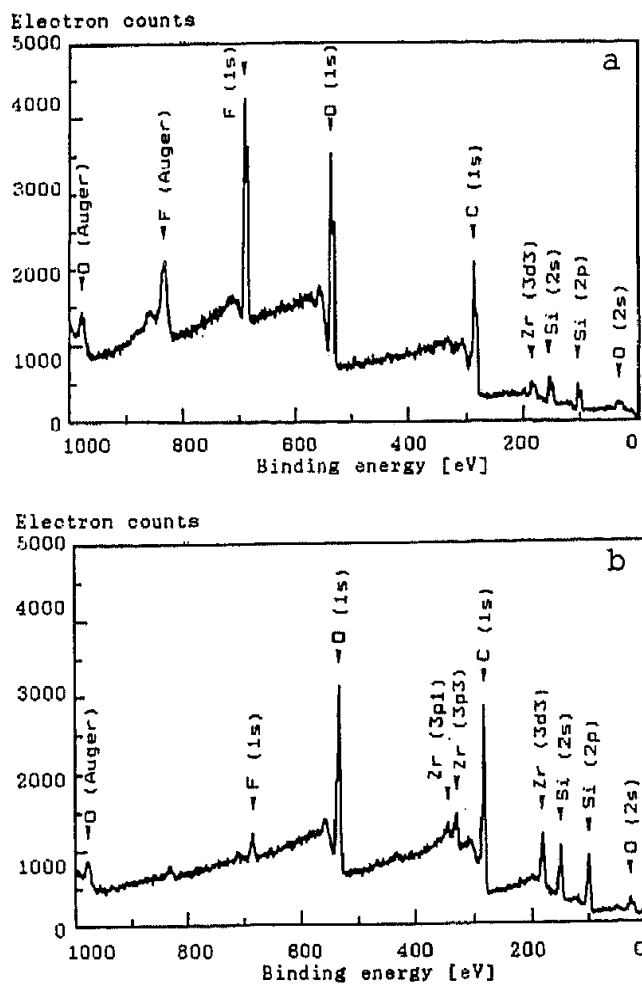


Fig. 2. XPS spectra of a 1,7 mole-% FTS containing ORMOCER coating; a: surface, b: after removing about $0,1 \mu\text{m}$ by Ar^+ sputtering.

The results of the surface free energy calculations are shown in fig. 3.

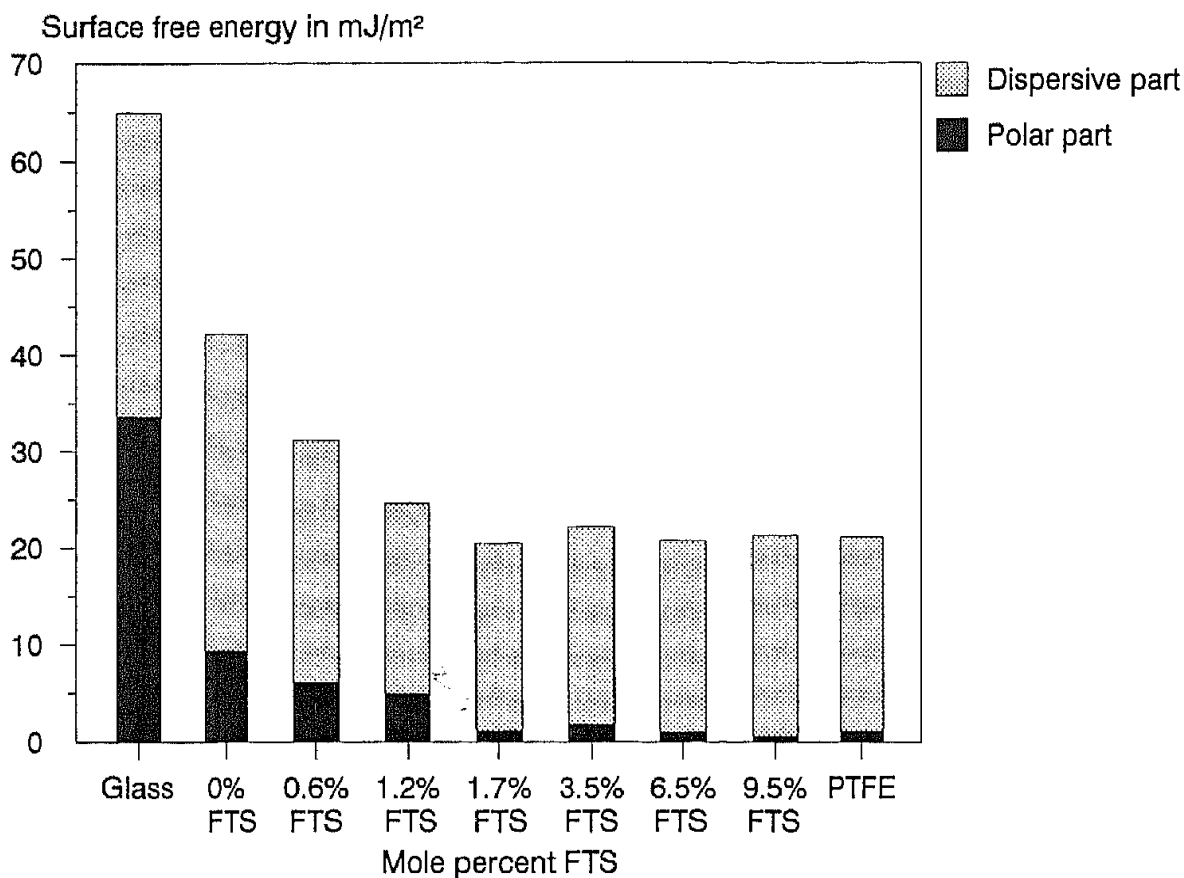


Fig. 3: Surface free energy of ORMOCER coatings with various FTS-contents calculated from contact angle measurements (PTFE and float glass for comparison).

For the unmodified ORMOCER, γ_s is determined to 42,2 mJ/m². The lowered surface free energy in relation to the float glass surface ($\gamma_s = 65.0$ mJ/m²) is due to the polymeric organic network of the ORMOCER which decreases the polar part of γ_s .

Through the fluoroalkoxysilane incorporation, the dispersive part as well as the polar part of γ_s are decreased. The decrease of γ_s with increasing FTS content was determined to reach its final value ($\gamma_s = 20,4$ mJ/m²) at 1,7 mol% FTS. That means, the addition of such small amounts of FTS (1,7 mol%) leads to a coating with a surface free energy similar to PTFE by fluorine surface enrichment. Therefore, a sufficient mobility of the monomers during the condensation step has to be assumed. A similar decrease of γ_s was observed in [26] after addition of small amounts of fluorotensides ($\approx 0,5$ %) to organic polymers (PVC, PMMA) before polymerization.

5. Conclusions

Only very small amounts of a side chain fluorinated alkoxy-silane are needed to produce ORMOCER coatings with very low surface energies which are comparable to those of perfluoropolymers. Such low values are explained by fluorine enrichment at the solid/air interface. Despite the fact that the employed synthesis technique could avoid random phase separation completely, the system shows an ordered phase separation in an "intelligent" sense, enriching the fluorine content of the surface and thus saving costly precursors.

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