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FUNCTIONAL COATINGS ON GLASS SURFACES BY THE SOL-GEL PROCESS

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ABSTRACT

The wetting behavior and thereby the surface free energy of coating materials for glass surfaces is tailored by incorporation of fluorinated side chains in inorganic organic nanocomposites, known as ORMOCERS (ORGANICALLY MODIFIED CERAMICS), synthesised by the sol gel process. We investigate the influence depending on concentration and chain length of the fluorinated precursor. The transparent coatings ($\approx 5 \mu\text{m}$) show good abrasion resistance and a good adhesion on glass surfaces. The incorporation of only small amounts of perfluorinated chains with a length of 6 or 8 leads to an hydrophobic and oleophobic behavior of the coatings similar to perfluorinated organic polymers because of an enrichment of fluorine at the surface. On the other hand the incorporation of hydrophilic groupings (C-OH, tensides) leads to hydrophilic behavior of the surface.

INTRODUCTION

Glass surfaces have to be modified in order to be adapted to very special application needs, e. g. to obtain reflection or antireflection, colors, wetting behavior or others. The intrinsic properties of glass surfaces are mainly based on the SiO_2 network, remaining after a leaching process (ion exchange of Na^+ against H^+). The surface consists of $\equiv\text{SiOH}$ groups with partially ionic properties ($\equiv\text{SiOH} = \text{SiO}^- + \text{H}^+$), responsible for a high polar part of the surface energy. This leads to a high wettability (contact angle of floatglass $\Theta_{\text{H}_2\text{O}} \approx 14^\circ$; see (1)) of "clean" glass surfaces. On the other hand, these surfaces show a strong absorption of contaminants from the environment leading to increased contact angles and to a non-wetting behavior of glass surfaces in practical use.

In order to overcome these problems, several attempts have been made. For example, solutions of tensides and glycerol are used to establish wetting behavior. To achieve hydrophobic behavior, surface modification based on polydimethylsiloxane silanization reactions with MeSiCl_2 are used. Disadvantage of these materials type of surface treatments is their short life time due to their long term instability against hydrolytic attack or lack of abrasion resistance. Low energy surfaces based on perfluorinated polymers show a hydrophobic and antiadhesion effect because of the very low surface free energy of 18 mJ/m^2 (2) but are non-transparent and have low adhesion on non-pretreated glass surfaces.

Our attempt is the use of coating materials based on inorganic-organic molecular or nanocomposites, known as ORMOCERs (ORGANICALLY MODIFIED CERAMICS) (3 - 8) as matrix for either surface energy decreasing components (fluorinated carbon chains) or hydrophilic groupings.

ORMOCERs, known for high abrasion resistance, transparency and, for example, good adhesion on glass surfaces already have been synthesized by the sol-gel process using organoalkoxysilanes, alkoxysilanes and metalalkoxides as starting materials for controlled hydrolysis and polycondensation, described in detail elsewhere (3 - 8). In a previous publication we described the incorporation of one side-chain fluorinated alkoxide in an ORMOCER-matrix (9). In this study we compare the influence of different side-chain lengths of fluorinated alkoxides on ORMOCER coating materials properties as well as of hydrophilic groupings.

EXPERIMENTAL

Fluorinated coating materials were prepared by reacting one mole 3-methacryloxypropyl trimethoxysilane (MPTS), purified by vacuumdistillation, with 1.5 mol H₂O dissolved in methanol at 50 °C for one hour. Subsequently the reaction mixture was cooled down to -10 °C, and a solution of 0.1 or 0.2 mole zirconium n-propoxide (ZR) in 1-propanol, complexed with varying amounts of methacrylic acid was added. The mixture was stirred for 90 minutes followed by the addition of water (0.5 mole per OR- group of ZR). After a reaction time of 12 hours at room temperature various well-defined (see table 1) amounts of 3,3,3-trifluoropropyl-methyl-dimethoxysilane (TPS), 1H,1H,2H,2H-perfluorooctyl-triethoxysilane (FTS1) or 1H,1H,2H,2H-perfluorodecyl-triethoxysilane (FTS2) are added, followed by a slow addition of water (0.5 mole per mole OR of the fluorinated precursor) 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 microscopic slides as substrates using a dip coating technique. The coatings were cured by UV light and then thermally treated at 130 °C for one hour.

The hydrophilic materials are prepared by hydrolizing 70 mmol of tetramethoxysilane in 6 ml methanol with 0,25 mole H₂O. After 2 h stirring the various well-defined amounts (2 - 50 mole%) of glycidylxypropyl trimethoxysilane (GPTS), 2 ml methylimidazol and 0.5 wt. % of a non-ionic tenside (Disponil 05, Henkel) is added, followed by additional stirring. The coatings, prepared by dip- coating, are thermally cured by 130 °C.

The advancing contact angles of the coatings were measured at 20 °C with a Wilhelmy balance apparatus (tensiometer, Krüss K12C).

RESULTS AND DISCUSSION

For incorporation of alkoxides with fluorinated side chains, we choose an ORMOCER material based on 3-methacryloxypropyl-trimethoxysilan (MPTS), zirconium-n-propoxide (ZR) and methacrylic acid (MAS). As starting point different compositions in this system with ratios between 10:1:0 and 10:2:2 (MPTS:ZR:MAS) according to table 1 without fluorine were prepared. In this base systems, three different side-chain fluorinated alkoxides (TPS, FTS1,

FTS2; see table 1) are incorporated. All precursors don't have fluorine groups in α and β position since such groups cause a low thermal and hydrolytic stability of the $-C-Si\equiv$ bond (10). For the preparation of the coating material the special procedure described in the experimental part and developed in (9) has to be used because a simple mixing of the precursors followed by the addition of water leads to phase separation and non-transparent coatings.

Table 1: Contact angles and crosscut test results for adhesion of different coating compositions in the system MPTS/ZR/MAS with varying TPS, FTS1 and FTS2 contents (glass and PTFE for comparison).

Compositition		Advancing Contact Angle				*Adhesion	
MPTS:Zr:MAS x:y:z mol	Fluoro-alkylsilane [mole %]	Water θ [°]	Glycerol θ [°]	1-Octanol θ [°]	Hexa-decane θ [°]		
10:1:0	-	66±1.8	76±5.5	25±4.3	22±3.5	0	
	4.5 TPS	76±1.9	89±4.2	38±7.1	-	2	
	8.6 TPS	78±2.3	89±7.6	35±6.1	-	3	
	15.8 TPS	82±1.2	88±3.0	23±6.5	-	3	
	22.1 TPS	80±2.6	88±4.5	30±8.6	-	4-5	
	0.6 FTS1	96±0.6	89±1.2	46±2.2	44±2.9	0	
	1.2 FTS1	102±0.3	97±1.4	59±0.3	55±0.9	0	
	1.7 FTS1	113±1.1	97±1.4	54±2.7	54±0.3	0	
	3.5 FTS1	117±2.4	93±4.7	51±4.2	49±3.5	0-1	
	6.5 FTS1	114±0.6	97±3.7	52±1.6	49±1.4	1-2	
	9.5 FTS1	114±5.7	97±0.6	49±2.5	50±1.4	4	
	10:1:1	-	74±1.2	65±1.9	spread	spread	0
		3.5 FTS2	102±1.7	99±3.1	67±2.4	-	4-5
	10:2:2	-	71±2.5	64±0.6	7±5.8	14±2.0	0
0.6 FTS1		116±1.7	90±4.7	52±5.1	64±2.3	0	
1.3 FTS1		117±0.3	96±1.4	57±1.2	67±0.7	0	
2.0 FTS1		117±1.4	100±5.0	55±1.6	65±0.5	0	
2.6 FTS1		117±1.2	90±0.5	50±1.5	63±1.4	0-1	
3.3 FTS1		117±2.0	96±2.4	50±1.5	62±0.9	4-5	
microscopic slides			14±4.4	63±1.8	37±2.0	13±3.5	
PTFE		110±7.9	89±2.8	45±10	48±5.9		

(* Crosscut test: DIN 51151, 0: best, 5: worst value)

PROPERTIES OF COATINGS

Crackfree transparent coatings on glass of about $5 \pm 2 \mu\text{m}$ were obtained after UV and thermal curing from all compositions. The transparency was determined to be $> 95\%$. Light scattering caused by phase separations were not observed. The adhesion remains unaffected by a 14 days storage at 100 % humidity and 40 °C or by the salt spray test (14 d, DIN 50021). The fluorine incorporation lowers slightly the abrasion resistance to 3 - 4 $\Delta\%$ haze in comparison to unfluorinated ORMOCERS (2 %) after taber abrader test (DIN 52347 E).

As it can be seen from table 1, the unfluorinated base systems show an increase of the contact angle for water and a decrease for unpolar liquids with increasing concentrations of

unpolar organic groupings (complexation of ZR by MAS). The increase of the ZR/MAS content shows no significant influence on the water contact angle, but increases slightly the contact angle for the unpolar substances due to the polar part of the zirconium oxide. The different compositions have only small influence on the wetting behavior of the surfaces.

With increasing TPS content in the 10:1:0 (MPTS/ZR/MAS) base system, only the contact angle for water and glycerol is increased by 15° and reaches a plateau at 10 mole %. The contact angle for the unpolar octanol is unaffected by the TPS content. The increase of the unpolar trifluoropropyl group increases the contact angle of polar liquids, but an increase of the oleophobic behavior by fluorine is not detected due to the low fluorine content of TPS. Because of relatively low adhesion of these coatings and missing oleophobic behavior, no further experiments were carried out.

The addition of the FTS1 component, containing C_6F_{13} fluorinated chains, in the 10:2:2 system has a remarkable influence on the wetting behavior. The addition of only 0.6 mole % FTS1 increases the water contact angle by 46° to 116° and the contact angle of hexadecane by 50° to 64° in comparison to the unfluorinated base system. These values are similar to perfluorinated polymers like polytetrafluorethylene (PTFE). The increase of the FTS1 content to 1.3 % leads to a further increase of the set of contact angles ($1 - 5^\circ$), but the further increase shows no significance on the set of contact angles. When FTS1 is incorporated in the 10:1:0 system, the wetting behavior is similar in comparison to the 10:2:2 system. The only difference is the need of a slightly higher concentration (1.7 mole %) to reach the plateau of the contact angles. The incorporation of the FTS2 compound causes problems during the synthesis because of the tendency to phase separations due to the longer fluorinated chain. The material with 3.5 % FTS2 shows a small decrease of the water contact angle ($\Theta_{H_2O} = 102^\circ$) and an increase of the oleophobic behavior ($\Theta_{octanol} = 67^\circ$) in comparison to the FTS1 materials. Because of the problems during the synthesis and the lower adhesion compared to the FTS1 material, no further experiments were carried out.

The reason for the large influence of only small amounts of the FTS compounds on the set of contact angles is the behavior of fluorine rich oligomers like tensides. This leads to an enrichment of fluorinated chains at the surface, responsible for the influence on the wetting behavior. It is known from Langmuir Blodgett model surfaces (11) that only the outermost few angstroms of the surface determine its wetting properties. We have shown in a previous paper (9) a fluorine enrichment of a material containing 1.7 % FTS1 of about factor 7 compared to the bulk by ESCA profiling.

Starting with the set of contact angles for the different surfaces, we calculated the free surface energy using the Young equation (12) and the well established model of Wu (13), assuming that each surface energy is the sum of the polar part and a dispersive one. The results are shown in figure 1.

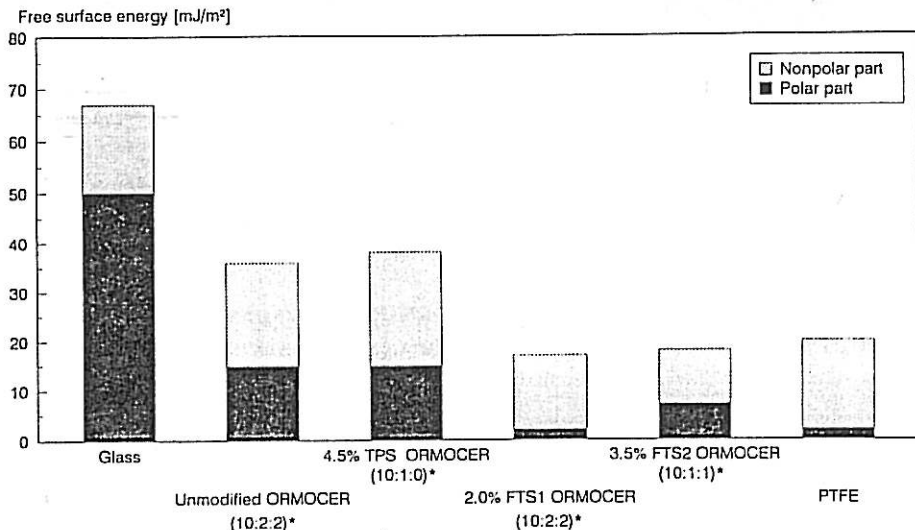


Fig. 1: Surface free energy of different synthesized ORMOCER coatings calculated from contact angle measurements (PTFE and glass for comparison; * molar ratios MPTS:ZR:MAS).

In comparison to glass, the free surface energy γ_s of the unmodified 10:2:2 system is decreased by 41 mJ/m² in comparison to the glass surface due to the organic polymeric network of the ORMOCER. The main effect is the decrease of the polar part of γ_s . The incorporation of TPS has no significant influence on the polar and dispersive part of the surface energy because of the low fluorine content of TPS. The incorporation of small amounts of FTS1 or 2 leads to a significant decrease of the polar and non-polar part of γ_s . The determined values for γ_s (FTS1: 17 mJ/m²; FTS2: 18 mJ/m²) are slightly lower than the determined value for PTFE (20 mJ/m²).

These results show that the variation of the composition of ORMOCER coatings is a powerful tool for tailoring the wetting properties and, as a result, the surface free energies of glass surfaces up to values similar to PTFE.

INCORPORATION OF HYDROPHILIC GROUPINGS

The hydrophilic coatings show water contact angles of 54 up to 32° depending on the GPTS content. Due to the reaction conditions, an epoxy ring opening reaction to a glycol grouping takes place, as proved by ¹³C-NMR. Thus, only 2 mole % of GPTS reduce the contact angle of the system after ring opening from 65 to 54°. The contact angle is reduced by

increase of GPTS and addition of 0,5 % tenside from 44° (25 mole % GPTS) to 32° (50 mole % GPTS). The coatings are highly transparent, can be applied with thicknesses up to 2 µm by spin or spray coating. The methyl imidazol acts as a base catalyst for sol-gel condensation, epoxy ring opening and polyethylene chain formation of residual unopened epoxy rings. About 60 % of the epoxy groups are hydrolyzed to diols, estimated from ¹³C-NMR analysis. The experiments show, that by combination of OH groups formed during reactions and tensides hydrophilycity of the coatings can be tailored. The systems are not optimized so far.

CONCLUSION

The incorporation of fluorinated chains in ORMOCER coating materials, synthesized by the sol gel process, is a powerfull tool to adjust the wetting behavior and thereby the surface energy of surfaces. The high hydrophobic and oleophobic properties leads to surface free energies similar to PTFE. Because of transparency, good adhesion and abrasion resistance these materials are of interest for use as mud repelling coatings for glass surfaces. On the other hand the incorporation of hydrophilic groupings (C-OH, tensides) produces hydrophilic behavior of the surface.

The modification of ORMOCER coating materials for example by oleo- and hydrophobic fluorinated chains or hydrophilic groupings is an easy way for tailoring the wetting behavior and thereby the surface energy of glass surfaces.

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