4.1.4 HYDROPHOBIC AND OLEOPHOBIC COATINGS

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1. INTRODUCTION

The formation of a solid-liquid interface between a liquid drop and a solid surface is called wetting. The extent of which wetting occurs is in most cases accurately described by the Young-equation (1).

$$\gamma_s = \gamma_{sl} + \gamma_l \cos \theta \tag{1}$$

where γ_s is the solid-atmosphere interfacial tension, γ_l is the liquid-atmosphere interfacial tension, γ_{sl} is the solid-liquid interfacial tension, and θ is the contact angle. Three aspects of this equation should be held in mind:

1. Wetting can be expressed and quantified by the contact angle θ. A surface is completely wetted, if $\theta = 0°$ (film formation), and there is no wetting at all, if $\theta = 180°$. If θ is high, the shape of a droplet is spherical, leading to a reduced contact area between the liquid and the surface.
2. Wetting depends on 3 phases: the solid surface, the liquid and the atmosphere.
3. The central parameter of the Young equation is the surface tension γ, an interface property related to the energy dU necessary to increase the surface of the substance ($\gamma = dU/d\sigma$). In principle, the free energy of the surface is readily calculated by determination of the surface tension γ_s. Whereas contact angles are meaningful only in a given context of surface, liquid and atmosphere, the free surface energy allows a more general characterization of a surface.

The Young equation (1) ("sessile drop situation") does not apply if liquid drops move on (tilted) solid surfaces. Here, dynamic contact angles should be used. In this case, the contact angles at the front ($\theta_{adv(ancing)}$) and at the rear ($\theta_{rec(eding)}$) of the drop are usually unequal. A small difference between the θ's (hysteresis) results in an easy sliding of liquid droplets. The sliding angle (tilt angle of the substrate at which a liquid drop starts to move down the plane) may be used to quantify the dynamic wetting behavior [2]. Smooth hydrophobic surfaces have typically a hysteresis and sliding angle of 20 to 30°.

Materials with low free surface energy are antiadhesive because (1) the contact area of a liquid on the surface is reduced (high contact angle) and (2) the

chemical interaction is low. Therefore, the force per contact area necessary to remove a contamination is low. A helpful estimation is given by the critical surface tension γ_c, an empirical quantity defined by the intercept of the plot of $\cos \theta$ vs. γ_l for $\cos \theta = 1$ measured for a homologous series of nonpolar liquids (Zisman-plot) [2]. In general, liquids with $\gamma_l < \gamma_c$ wet the surface, in contrast to liquids with $\gamma_l > \gamma_c$.

The surface free energy of polyolefins is in the order of 32 mJ·m^{-2} and the contact angle for water is 60° to 80°. Such surfaces repel water ($\gamma_l = 72$ mN·m^{-1}), but not oily liquids ($\gamma_l \approx 30$ mN·m^{-1}). The surface free energy of PTFE or other polyfluorinated polymers is considerably lower (ca. 20 mJ·m^{-2}) with a contact angle up to 110° against water. The surface free energy of silicate glass is high, about 70 mJ·m^{-2} and the contact angle vs. water is in the order of 40°. It is wetted by almost any liquid and is therefore easily soiled and laborious to clean. Therefore, antiadhesive, low-free surface energy coatings are very attractive, especially for the automotive, architectural and display industry.

2. HYDROPHOBIC COATINGS ON GLASS

Academic research on the preparation and characterization of hydrophobic coatings on glass is rare and most methods are described in the patent literature, stressing their importance for industry. Three different approaches exist: a) simple molecular systems, b) sol-gel matrices doped with organic fluoropolymers, and c) organic-inorganic sol-gel nanocomposites.

a) Molecular systems consist of a solution of an organically substituted silane with reactive Si-X bonds (X: e.g. Cl, OAlkyl). These are cleaved by the surface Si-OH groups, generating stable Si-O-Si bonds and volatile HX. This approach has been reviewed however without focus for glass substrates [3]. Aprotic solvents such as (chlorinated) alkanes, or mixtures of them are employed [4-6]. Coating compositions that contain a hydrolyzed fluoroalkyl silane in alcohol solution are rarely employed [7] as their shelf-life is limited. The obtained surface energy depends greatly on the organic substituent: alkyl usually leads to surface free energies comparable to those of polyolefins (ca. 32 mJ·m^{-2}) [8]. Accordingly modified substrates are hydrophobic but not oleophobic. Hydrophobic and oleophobic surfaces with energies of ca. 20 mJ·m^{-2} can be obtained by using silanes with polyfluoroalkyl substituents [9, 10]. Such films are industrially manufactured and employed in automotive applications [11]. Surfaces with a sliding angle of only 10 to 15° against water can be realized. The contact angle *vs.* water remains above 100° even after 1000 h weathering or 5000 cycles abrasion with a flannel cloth (0.3 kg/cm²). The effective film thickness is in the order of one molecule, so a specific advantage of such formulations is the possibility to produce ultrathin coatings [12] but coating homogeneity is difficult to achieve and the presence of coating defects may lead to a higher surface free energy.

b) The second approach comprises organic polyfluoropolymers imbedded in a sol-gel matrix [13] deposited by wet chemical processes and then thermally cured. A high amount of organic polymer increases the time-stability against boiling water and attack by high pH values solutions but soften the coatings so that mechanical stability is not a specific advantage of these hybrid materials [14, 15]. The organic polymers are introduced for instance as PTFE particles, polyfluoro-co-polymers or perfluoroethers with hydroxyl end groups [16]. To ensure transparency, the mixed phases should be finely dispersed at the nanometer or even molecular scale. Also, attention is needed to abide this dispersive state. For that purpose a specially silyl-modified organic co-polymer has been developed to enhance the binding of the polymer to the sol-gel matrix [17].

c) The third approach uses sol-gel formulations of fluoroalkylsilanes in combination with other silanes to obtain co-condensates [18]. These materials are called ORMOCER® ("organically modified ceramics") or CERAMER ("ceramic polymer") [19, 20]. The solvents are mostly alcohols, but some water-based systems have been described [21, 22]. In these nanocomposites, the organic and the inorganic network are covalently bound and homogeneously intermingled at the nanometer-scale, so that the coatings present enhanced mechanical stability. Patents claim a sol prepared from tetraethoxysilane (TEOS), (perfluorooctyl)ethyltrialkoxysilane (FOS) and water for improved abrasion resistance of the obtained hydrophobic coatings [23, 24]. This composition has been investigated in detail in [25, 26]. Contact angles as high as 118° against water and surface free energies below 10 mJ·m^{-2} are reported for 80 μm thick coatings [26] containing only 2 mol% fluorosilane (FOS). This was explained by an accumulation of fluoroalkyl groups at the surface. The surface free energy of the coating is not affected by a subsequent thermal treatment at 250 °C for 1 h. Firing at T > 300 °C leads to a loss of the fluoroalkyl groups, the surface free energy is drastically increased and the contact angle decreases considerably down to 70°. An enhanced linkage of the FOS improving the thermal stability was however achieved by an additional ammonia-treatment after a thermal curing at 300 °C for 30 min. The initial contact angle of 110° against water is kept after tempering for 250 h at 300 °C.

The major advantage of this approach lies in its high versatility. Various silanols or their precursors can be used in the sol-gel synthesis to tailor the material properties such as surface free energy, color, hardness, abrasion resistance, mechanical or chemical stability [19, 20, 27-29]. The shelf-life or weatherability is for instance increased by using aminogroup- or methacrylgroup-substituted silanes apart from fluoroalkylsilanes and TEOS as starting materials [21, 30]. The use of nanoparticles together with suitable silane precursors, solvents and additives allows to obtain NANOMERs® ("nano-polymers") materials with many different additional properties [31]. The homogeneous incorporation of nanoparticles enhances the densification and improves the mechanical scratch resistance and chemical durability of the nanocomposites and may confer additional features such as anti-microbial or UV protection functions [19, 32]. Due to the nanometer size of the particles, the coatings maintain a high transparency

between 400 and 1000 nm. Hydrophobic and oleophobic properties comparable to that of PTFE (20 mJ·m⁻²) can be obtained by using fluoroalkyl-substituted alkoxysilanes such as FOS or (perfluorohexyl)ethyltriethoxysilane (FHS) [33-36] (contact angles > 100° for water and > 45° for hexadecane). The materials have a pronounced gradient structure, with a high concentration of fluoroalkyl groups at the coating - air interface so that only a small amount (1.7 mol%) of fluoroalkyl silane is necessary to obtain an effective repellency [34, 35, 37]. Also, this accounts for an excellent adhesion of the coatings on various substrates such as glass, metals and polymers [40]. The gradient is due to the accumulation of surface-active fluorosilanol molecules and -condensates at the interface [38]. Therefore, the atmosphere needs to be controlled carefully during application and curing. If the fluorosilane concentration is above the critical micelle concentration (CMC), the fluoroalkylsilanol micelles are homogeneously distributed within the coating [39]. The inner structure of the coating is fixed during the curing process, usually performed by thermal treatment. The thermal stability of Nanomers can be increased by about 100 °C compared to conventional Ormocers, but the temperature should be kept below 400 °C to prevent thermal degradation of the organic components. Nanomers can also be tailored by curing at a lower temperature or even by UV light [19]. These possibilities are especially interesting for tempered glass.

A benefit of antiadhesive sol-gel coatings lies in the "easy-to-clean" effect [41]. Antiadhesive coatings soiled by different mixtures such as flue ash and graphite (1wt.-%), or water, oil and pyrogenic silica are easily cleaned even by using low-impact cleaning procedures like showering (rain model). Good abrasion resistance and weatherability are also important properties to be satisfied for outdoor applications [21, 30, 41]. Nanomer coatings with a low content of organic substituents show no yellowing after 30 d of UV irradiation and the adhesion as well as the contact angle are maintained in wet climate and under weatherometer conditions. Very low haze values (2-4%) are obtained after 100 abrasion Taber test cycles [20, 33, 35].

3. SUPERHYDROPHOBIC COATINGS ON GLASS

Apart from the chemical constitution, wetting is also influenced by the chemical homogeneity and the morphology of surfaces. Rough hydrophobic surfaces called "superhydrophobic", "ultrahydrophobic", or "Lotus effect" surfaces [42] have found increasing academic and industrial interest, because of their drastic increase of the contact angles and the disappearance of the hysteresis effect. As the Young equation (1) is only valid for ideal smooth, homogeneous surfaces, a more sophisticated approach is necessary to describe rough substrates.

The equation of Cassie and Baxter describes the behavior of a liquid drop which rests on two different mediums at the same time (e.g. a textile) by defining a macroscopically observable contact angle θ_{obs}. If one of them is a gas, the equation reduces to:

$$\cos \theta_{obs} = Q_1 \cos \theta_0 - Q_2 \qquad (2)$$

where Q_1 is the fraction area of the liquid drop in contact with the solid, Q_2 is the remaining fraction area of the drop in contact with the atmosphere ($\theta = 180°$), and θ_0 is given by the Young equation (1).

The same idea can be applied to extremely porous or rough hydrophobic substrates, where air is enclosed between liquid and substrate.

Typical superhydrophobic surfaces have a roughness > 5 μm [43]. They scatter the light, are generally opaque, and are unsuitable for glass, where transparency is demanded. The roughness of such coatings can be however controlled down to values lower than 100 nm, too small to scatter the visible light [44]. Unfortunately, information about scattering effects (haze value) of superhydrophobic films is scarcely available.

Transparent superhydrophobic surfaces can be realized by depositing a thin hydrophobic coating (see above) on a suitably patterned substrate [45] obtained for instance by dip coating a sol prepared from aluminum-*sec*-butoxide, ethylacetoacetate and water in *iso*-propanol. After firing at 400 °C and immersion into boiling water the alumina coating turns transparent, but highly porous [46]. The 20 to 50 nm roughness can be controlled by varying the immersion time, leading to a transparency of up to 92%. After hydrophobizing the structure with a fluoroalkyl silane solution, the static contact angle against water is as high as 165°. In another approach the patterning was accomplished by spin-coating a suspension of boehmite particles and aluminum acetylacetonate onto a glass substrate with subsequent firing at 500 °C [47]. The structure is believed to evolve because of the sublimation of the aluminum acetylacetonate. The transparency of the film is $> 90\%$, but pronounced Rayleigh scattering is observed at small wavelengths. Doping with 2% TiO_2 (using titanium acetylacetonate) leads to improved UV resistance of the coating. A contact angle $> 140°$ *vs*. water remained even after 800 h UV illumination and after 1800 h of outdoor exposure [48, 49].

A suitable structure was also obtained by a phase-separation technique [49]. The addition of 1wt.-% of an acrylic polymer to a TEOS sol leads to a turbid, phase-separated emulsion. Spin-coating onto Pyrex glass and firing at 500 °C for 30 min results in rough transparent films with a high hardness (1-2 GPa). Presumingly, the acrylic polymer is thermally decomposed in the firing step, leaving 100 to 1000 nm crevices in the silica film. The structure was hydrophobized by a fluoroalkylsilane solution and shows a contact angle against water of 151° and a transmittance of $> 90\%$ at 500 nm.

A one-step approach for superhydrophobic coatings has been developed by adding suitable pyrogenic silica nanoparticles (Aerosil) to a TEOS/FHS sol system [50, 51]. A rough structure evolves without additional patterning during the spin-coating process. A static contact angle *vs*. water of 150° and a hysteresis of $< 1°$ was obtained. A transparency of $> 95\%$ transmission (400-800 nm) and a haze value of only 2% was achieved [52]. The mechanical stability of the coating is however poor.

4. CONCLUSION

The sol-gel technology is a versatile tool for the preparation of hydrophobic and oleophobic coatings on glass. Smooth organic-inorganic nanocomposites coatings have been developed to an elaborate state with tailor-made properties. Apart from excellent repellency due to the low surface free energy, the materials are robust and applicable by conventional wet-coating techniques. Moreover, the sol-gel technology offers interesting possibilities in the development of superhydrophobic coatings, but considerable development is still necessary to reach technical application.

5. REFERENCES

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