Wear resistance of hydrophobic surfaces

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Abstract. Nature has been an inspiration source to develop artificial hydrophobic surfaces. During the latest years the development of hydrophobic surfaces has been widely researched due to their numerous ranges of industrial applications. Industrially the use of hydrophobic surfaces is being highly demanded. This is why many companies develop hydrophobic products to repel water, in order to be used as coatings. Moreover, these coating should have the appropriated mechanical properties and wear resistance. In this work wear study of a hydrophobic coating on glass is carried out. Hydrophobic product used was Sika Crystal Dry by Sika S.A.U. (Alcobendas, Spain). This product is currently used on car windshield. To calculate wear resistance, pin-on-disk tests were carried out in dry and water conditions. The test parameters were rate, load and sliding distance, which were fixed to 60 rpm, 5 N and 1000 m respectively. A chamois was used as pin. It allows to simulate a real use. The friction coefficient and loss weight were compared to determinate coating resistance

1. Introduction

For buildings with large glass areas, accumulation photovoltaic modules or windshields it is very interesting to get “Easy to Clean” effect on the surfaces. Self-cleaning surface are indeed important for the above applications, since the dust, pollution, and other particles accumulation reduce the transparency [1]. On the other hand, icing is the cause of numerous air accidents. If water is not deposited on the aircraft surface, these accidents can be avoided [2]. This property is related to hydrophobic character of the surfaces.

Substrates are permanently damaged by aggressive environmental conditions and dirt from both a visual and functional standpoint. Therefore costs and time needed for cleaning activities are increased. An additional problem is the possible photocatalysis, wherein organic contaminants adsorbed on film surface are decomposed under ultraviolet light [3].

Hydrophobic coatings counterbalance these negative influences by creating a repellent and non-stick effect from aqueous and organic liquids. It considerably reduces the adherence of dirt particles on the substrate surface. When the coated surfaces are in contact with water, non-stuck dirt particles are removed by the water. Consequently, it reduces cleaning activities and provides lasting protection from the aggressive environment influences to the surface.

There are some superhydrophobic coatings based on lotus leaf effect (water resistance by rough spots with air on the surface) on the market [4]. However, that technology does not work for organic or complex liquids. Besides, if the surface that is coated is damaged or is subjected to extreme conditions, liquid drops tends to stay on the surfaces or penetrate into them, instead of slipping.

One of the reasons that wetting and surface energy are often neglected in tribological studies and engineering design models is due to the lack of an understanding about the correlation between them [5]. However, another reason may be the lack of any direct evidence for their influence on tribological
Performance in engineering macro contacts. Namely, the effects of surface properties, such as wetting, surface energy, oleo/hydrophobicity, and oleo/ hydrophilicity, were investigated in only a small number of tribological studies using macro contacts with engineering materials and lubricants [6,7,8,9].

However, in literature, detailed analyses of the anti-soling film in term of structural properties, transparency, robustness and cost are still missing.

2. Experimental
Flat glass samples were ultrasonically cleaned with ethanol (EtOH) and air dried. As coating, Sika Crystal Dry (supplied by SIKA SAU, Alcobendas, Spain) has been used. On the surface the product was sprayed and the film thickness was evaluated by surface imaging.

Surface hydrophobicity is determined by static contact angle. For the contact angle measurements a goniometer Dataphysics Contact angle system OCA 30-2 from Data Physics Instruments (GmbH, Filderstadt, Germany) was used. The model is able to measure in a range of 1 to 180° with an accuracy of ± 0.5°. The instrument contains a 3x zoom and a software SCA 202 V.3.11.13 build 162. For these measurements, deionized water droplets volume was fixed at 3 μL, 2 drops per sample and 3 replicates were done.

Friction test was performed in a pin-on-disk tribometer (supplied by Microtest-Madrid Spain). The test was performed following ASTM G99. Abrasion test was carried out between a mobile probe fixed in a carriage with reciprocal movement and a fixed pin. The pin was manufactured by gluing a disk of 20 mm of diameter of polishing cloth Omega (supplied by ATM GMBH Gremaqny) to an aluminum plate of the same dimensions. In some cases during the test, the cloth was lubricated with water [10]. Test was fixed to 60 rpm, a turning radius of 8 mm and 500 m of total length, which corresponds to 9947 cycles of movement of the mobile surface with a load of 5 N. Tests were carried out at room conditions (25°C, 30% relative air humidity). After abrasion test the transparency of samples and weight loss were measured.

The aesthetic appearance of these coated surfaces was evaluated by transparency and color changes. The colorimetric data of the surface were calculated from the acquired spectra with the most common color space in the industry: the CIEL*a*b* color space. A ColorEye XTH colorimeter (Neurtek Instruments S.A, Eibar, Spain) was used for D65/10°-illuminant/observer condition and without specular gloss (SCE). CIELAB system measures color in a three-dimensional space, defined by the coordinates L*, a* and b* (figure 1). The first one corresponds to luminosity: 0 is black and 100 is white; coordinate a* measures variation between red (+a) and green (-a); and b* gives changes between yellow (+b) and blue (-b). Finally, ∆E is calculated (equation. 1) in order to measure the module of the vector from the reference to the measurement.

$$\Delta E = (\Delta L^*^2 + \Delta a^*^2 + \Delta b^*^2)^{1/2}$$  \hspace{1cm} (1)

![Figure 1. CIELAB system](image1.png)

![Figure 2. The pull-off test scheme](image2.png)

The pull-off test method is used to determine the force required to separate aluminium dolly (20 mm diameter) fixed to the coating glass with epoxy adhesive (figure 2). The test was performed
following the ASTM D 4541 standard. The standard procedure was developed for metal substrates, but it may also be suitable for other rigid substrates such as some type of polymers and glass. The system was tested with the tensile test (relative to the plane of the adhesive bond) was performed with an universal testing machine with a 1kN load cell and 0.1 mm/min speed (Microtest, Madrid, Spain).

Characterization of surface energy, aesthetical aspect, abrasion test and adherence measurements were performed before and after ultraviolet (UV) light irradiation (15 W mercury lamp–Techlux emitting 254 nm wavelength). The samples were exposed to light irradiation, 5 cm far from the light source. Aging consisted on 120 min cycles: 102 min of radiation and 18 min immersed in deionized water without radiation.

3. Results and discussion

The purpose of this coating is to make glass hydrophobic and to improve its facility of cleaning. To check it, variations of water and olive oil contact angles between uncoated and coated glass were measured (table 1). An increase of more than 100% was observed when the glass is coated. The uncoated hydrophilic surface becomes hydrophobic.

| Glass       | Cycles | Water      | Olive oil |
|-------------|--------|------------|-----------|
| Coated glass| 0      | 107±5      | 83±2      |
|             | 48     | 99±4       | 65±6      |
|             | 100    | 93±2       | 64±6      |
|             | 200    | 93±4       | 23±2      |

In table 1 it is observed that water contact angle is decreasing slightly after aging cycles. The decrease is more evident in the case of olive oil.

Variation of color defined by $\Delta E$ (equation. 1) is shown in table 2. In all cases, before and after aging, it is below the threshold of visibility to the human eye.

| Cycles | L*    | a*  | b*  | $\Delta E$ |
|--------|-------|-----|-----|------------|
| Glass  | 86.60 | 3.56| -12.07| 0.51       |
| Coated glass | 87.02 | 3.63| -12.35| 0.33       |
|         | 86.91 | 3.50| -11.97| 0.60       |
|         | 87.18 | 3.57| -11.90| 0.56       |
|         | 86.87 | 3.42| -11.60| 1.63       |
|         | 86.90 | 3.26| -11.10|           |

Pull-off test on glass and coated glass surfaces show epoxy-glass joint strength of 14.6 MPa, while epoxy-coated glass joint strength is 3.8 MPa, being the break through glass-coating interface.

Friction coefficient vs. time curves of the samples under friction test show two different behaviours depending on the conditions: dry or wet test (figure 3). Uncoated glass shows a friction coefficient of 2.2 when the test is carried out under dry conditions and 0.4 when it is done with water. In the case of coated glass, a reduction of the coefficient of friction of 2.4 in dry conditions (figure 5a, continuous line) and 0.3 in wet test (figure 5b, continuous line) is observed. Figure 4 shows abrasive wear marks obtained after water-submerged tests of glass and coated glass samples.

Differences on dry friction coefficient of aging plates at different number of cycles are not observed once the measured value has become stable (figure 5a). When the tests were carried out immersed in water, the curve is more similar to uncoated curve when the number of cycles is high (figure 5b).
Figure 3: Friction coefficient vs. time for uncoated glass: (a) Dry; (b) Immersion in water

Figure 4. Wear track immersed in water (a) uncoated glass test; (b) coated glass test
Figure 5. Tests on aging samples: Friction coefficient vs. time for coated glass. A) Dry; B) Immersion in water

Table 3 Values of the parameters obtained in friction tests

| Surface       | Cicles | Mass loss (g.10^-6) | Static friction coefficient | Initial dynamic friction coefficient |
|---------------|--------|---------------------|-----------------------------|--------------------------------------|
|               |        | Dry | Immersion in water | Dry | Immersion in water | Dry | Immersion in water |
| Glass         | --     | 4   | 2                   | 0.57 | 0.40               | 1.20 | 0.32               |
|               | 0      | 4   | 3                   | 0.54 | 0.28               | 1.69 | 0.44               |
| Coated glass  | 48     | 8   | 2                   | 0.44 | 0.35               | 1.51 | 0.54               |
|               | 100    | 6   | 2                   | 0.92 | 0.50               | 1.75 | 0.41               |
|               | 200    | 8   | 6                   | 0.84 | 0.43               | 1.46 | 0.33               |
On both dry and immersed in water tests, coated glass lost less mass than uncoated plates (table 3). It is also observed lower static friction coefficient (measured at the beginning of the test) for coated glass. Two seconds after the beginning of the test, initial dynamic friction coefficient was measured. This parameter is higher for coated glass due to the increase of surface roughness when glass is coated. The water acts as a lubricant which decreases the values of the friction coefficient and reduces the wear both in uncoated and coated glass. As the number of aging cycles increases it is possible to observe an increase in the static friction coefficient both in dry and wet tests. This same trend can be observed in the initial dynamic coefficient although it is not as clearly. Significant mass loss is observed in the test dry case.

4. Conclusions
The proposed wear test is similar to the effect of the wipers on the windshields. Wear produced by these tests is abrasive on both uncoated and coated glass.

All films presented abrasion resistant property in contact with polishing cloth in dry and immersed in water. It has been demonstrated that high transparency and self-cleaning have been obtained by a simple sprayed route presenting good potential to be applied on transparent super-hydrophobic surfaces.

Tests with hydrophobic surfaces revealed a reduction in friction, which may be attributed to lubricant slip against the hydrophobic surface.

5 References
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