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PROPERTIES OF STEEL SURFACES COATED WITH ORGANIC MOLECULES.

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Abstract

Superhydrophobic state is one of the most interesting and attractive topic in these years due to the wide application possibilities. Roughness and surface tension are the main parameters to be controlled to obtain a surface with hydrophobic properties. The topic of this thesis is to investigate how substrate roughness and coating deposition parameters influence wettability properties. Different chemo-physical surface properties were performed by creating different substrate roughness and by applying different coatings. As substrate has been chosen mild carbon steel, use both as received and after sandblasting treatment. Over these substrates a thin organic film coating has been applied. The employed coatings were purchased or were synthesized and characterized in laboratory. Their deposition procedure was made of three main steps: cleaning, etching and post thermal treatment. Etching time and post thermal treatment has been widely surveyed to respectively improve active sites concentration on the metallic substrate and to improve the strength of anchoring bonding. For each kind of coating, three different alkyl chain lengths have been studied to understand their role in the wettability. Optical contact angle analysis was used to establish wetting properties, atomic force microscopy (AFM) was used to characterize samples mechanical properties (roughness and coatings adhesion force). Glow discharge optical emission spectroscopy (GDOES) characterization was used to quantify coatings thickness and to determine their chemical composition. Electrical samples properties were studied by electrochemical impedance (EI), while surface morphologies were detected by using scanning electron microscopy (SEM).

Keywords: Self assembly monolayer, wettability, roughness, anchoring groups, pre and post treatments

Nomenclature

CAx_y = carboxylic acid: x = the chain carbon atoms, y = test number
CxP_y = phosphonic acid: x = chain carbon atoms, y = test number
PAx_y = polyacrylic acid partially esterified (see test); x is the number of carbon atom of the branches, y = test number.

1. Introduction

Surface science is a topic of particular interest in recent years due to the possibility to address material uses only by changing surface properties without altering bulk properties as reviewed by Darmanin et al. (2015) and Woidyla et al. (2014).

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The study of physical-chemical phenomena that occur at interface includes two fields: surface chemistry and surface physics.

Surface chemistry, even called surface engineering, Qu (2007), Gugliuzza (2013), Van Alsten (1999), aims to modify surface chemical composition by incorporation of selected elements or functional head groups to improve surface properties.

Surface physics studies physical changes that occur at interface concerning on surface states, surface diffusion, surface self-healing and self-assembly of nanostructures on the surface, Zoua (2011).

To produce a surface modification, the surface coating cycle is an easy and economical way to achieve an object tailored for a specific applications. Several material properties can be controlled; for instance wettability, roughness, hardness, reactivity, biocompatibility, thermal and/or electric conductivity, wear and corrosion resistance.

A superhydrophobic surface is a non-wetting surface with high water contact angles (WCAs>150°) obtained acting on two parameters: surface roughness or surface tension. This topic has received a strong attention in recent year because of its wide range of application, from self-cleaning to anti-bacterial and anti-icing surfaces.

The aim of this work is to achieve superhydrophobic state on common mild carbon steel, with easy and cheap techniques for industrial applications. It surveys how the roughness and the surface tension could influence the wettability: the first is modified by sandblasting the sample surface, while surface tension is lowered by coating the samples with self-assembled monolayer technique or polymer deposition. The investigation of the application parameters is the key for the of process optimization. Among these the parameters of the etching step that allows the creation of active sites. It comes first than the dipping step in a solution containing molecules that coat the surface. A thermal treatment usually is accomplished, to enhance the adhesion of the coating to the substrate. The obtained samples are then analyzed at OCA (Optical Contact Angle), and characterized at AFM (Atomic Force Microscopy), SEM (Scanning Electron Microscopy), GDOES (Glow Discharge Optical Emission Spectroscopy). OCA tells us if the samples are hydrophobic, and it is possible to estimate also surface tension of the coatings. AFM gives information about the roughness and adhesion force, while GDOES shows the composition of the coatings layer-by-layer. Images of the coated surfaces are obtained at SEM.

2. Materials and methods

2.1. Substrate

Common mild carbon steel substrate was used both as received and after sandblasting treatment. Its chemical composition is reported in tab. 1:

Tab. 1. Chemical composition of mild carbon steel substrate (Spectrolab metal analyzer/OES/fixed)

Elements	%	Elements	%
C	0.05	Mo	<0.01
Si	0.01	Ni	0.01
Mn	0.23	Cu	0.02
Cr	0.03	V	0.001

Sandblasting was performed with a Lampugnani S-SAB using corindone (chemical composition: Al_2O_3 95.8% - SiO_2 0.7% - FeO_3 0.3% - TiO_2 3%; particle size 150-210 μm; gun pressure 4-5 bar).

After sandblasting treatment, substrates were stocked in a Inert and dry nitrogen atmosphere to avoid surface oxidation and corrosion, including silica gel, in order to avoid oxidation of the surface and prevent from humidity corrosion, respectively.

2.2. Organic coatings

Commercial coatings applied on the sample as purchased are butyric acid (99+% Alfa Aesar), tridecanoic acid (Fluka), nonadecanoic acid (99.5% Fluka) and 1-butylphosphonic acid (98% Alfa Aesar). 1-dodecylphosphonic acid and 1-octadecylphosphonic acid were synthesized using the following commercial reagents: triethyl phosphite (98% Aldrich), 1-Br-dodecane (97% Sigma Aldrich), 1-Br-octadecane (97% Sigma Aldrich), hydrobromidric acid (HBr, 48% Fluka), n-pentane (98% Alfa Aesar), n-hexane (95+% Alfa Aesar). Partially esterified polyacrylates with alkyl chain of several lengths C4 (PA4), C12 (PA12) and C18 (PA18) were obtained employing polyacrylic acid(PAA, m.w.=1515), 1-butanol (99.5% Fluka), 1-dodecanol (98% Alfa Aesar), 1-octadecanol (97% Alfa Aesar), sulfuric acid (96% Sigma Aldrich) and diethyl ether (99% Sigma

Aldrich). Further solvents were used in the deposition process: dichloromethane (DCM, 99.9% Sigma Aldrich), tetrahydrofuran (THF, 99.9% Sigma Aldrich) and an oxidizing powder called NoChromix® (GODAX Laboratories Inc.).

2.3. Syntheses

2.3.1 Phosphonic acids

Phosphonic acids have been synthesized from their brominated precursors via the Michaelis-Arbuzov reaction.[24] The acids were characterized by FTIR (the three peaks at 2954-2916-2848 cm^{-1} attributed to CH_3^{as}-CH_2^{as}-CH_2^s stretching vibrations respectively, at 2266 cm^{-1} ; P-OH vibration is found, while P=O stretching is present at 1213 cm^{-1}. Peaks at low frequencies are due to P-O-C and P-C vibrations), DSC, DTG/TG (weight loss starts at 377.0 °C, in accordance with the predicted ACD/Labs boiling point b.p. = 380 °C, confirming the product occurrence). ^{1}H-NMR
ChemNMR H-1 Estimation software, the peak at 0.88 ppm is related to CH_3 chain terminal group, while the high intensity peak at 1.26 ppm is related to CH_2 of alkyl chain.[24]

2.3.2 Octadecyl Phosphonic Acid

A mixture of 1-Br-octadecane (6.674 g) and triethyl phosphite (3.323 g) put inside a flask was stirred and heated up at 170 °C for 4 h. Then HBr 48% (35.638 g) was added to the flask, keeping on stirring and heating at reflux T (70-90 °C) for 3 h. After cooling down at room temperature, distillation of water and BrEt was performed at 125°C. Product was washed with n-pentane, recrystallized with n-hexane, washed again with n-hexane and finally dried for 3h at 70C. The product was characterized by FTIR (the three peaks at 2955-2914-2849 cm^{-1} characteristic of CH_3^{as}-CH_2^{as}-CH_2^s stretching vibrations respectively, at 2359 cm^{-1} P-OH vibration, while P=O stretching is present at 1213 cm^{-1}. Peaks at low frequencies are due to P-O-C and P-C vibrations), DSC and TG (endothermic peak at 95.3 °C, corresponding to the literature melting point at 98.4 °C, and thermal degradation over 350 °C with the most significant weight loss sets at 474.6 °C).

2.3.3.Butyl Polyacrylic Acid

Butyl Polyacrylic acid was synthetized by using a Fischer esterification between PAA and 1-butanol using sulfuric acid as catalyst. The product was characterized by FTIR, DSC, DTG/TG, ^{1}H-NMR, (peak at 0.93 ppm is referred to CH_3 terminal group of alkyl chain, while the ones at 1.37 ppm and 1.60 ppm are due to the central CH_2 of alkyl chain. CH_2 on alkyl chain near the oxygen of the ester produces the peak at 4.05 ppm. Peak at 1.90 ppm is linked to CH_2 of PA4 backbone, while the one at 2.28 ppm contains CH of the backbone bound to carboxyl groups), Titration in order to know the obtained esterification degree.

2.3.4   Dodecyl Polyacrylic Acid

To synthesized dodecyl polyacrylic acid, a classical Fischer esterification between PAA and 1-dodecanol using sulfuric acid as catalyst was used. Characterization was performed using FTIR (the carbonyl peak moves at 1731 cm^{-1}, meaning a partial esterification of PAA occurred; the peak shows a right-shoulder, so the presence in the PAA of both esterified and not esterified carboxyl group can be easily supposed), DSC (a softening is set at 0.3°C and 6.2°C; the melting point is at 12.6 °C, but after one thermal cycle it shifts at lower T (2.3 °C). There are no reference in literature about this molecule), , DTG/TG (the molecule begins to deteriorate at 100 °C and its weight loss begins at T higher than 250 °C), ^{1}H-NMR (peak at 0.88 ppm is referred to CH_3 terminal group of alkyl chain, while the ones at 1.27 ppm and 1.59 ppm are due to the central CH_2 of alkyl chain. CH_2 on alkyl chain near the oxygen of the ester causes the peak at 4.02 ppm. Peak around 1.9 ppm is linked to CH_2 of the backbone of PA12, while the one at 2.4 ppm contains CH of the backbone bound to carboxyl groups), Titration.(The standard ISO 2114:2000(E) was followed; esterification degree of 75%

2.3.5 Octadecyl Polyacrylic Acid

A classical Fischer esterification between PAA and 1-octadecanol using sulfuric acid as catalyst was used.
Characterization performed by FTIR (The reference carbonyl peak moves to 1734 cm^{-1}; it has to be noted that this peak has lower intensity with respect the others spectra due to the longer alkyl chain, and it showed a very important right-shoulder, meaning a non-negligible presence in the product of unesterified carboxyl group), DSC

(melting point in the range 61.9-62.2 °C; the peak was asymmetric probably meaning that a mixture of esterified/unesterified polymer was obtained), Titration (the standard ISO 2114:2000(E) was followed: an esterification degree of 44%).

2.4. Methods

2.4.1 Instrumental analysis

Characterization methods used for this project can be classified as methods for molecule characterization and methods for samples characterization.
   a) Fourier Transform Infrared Spectroscopy (FTIR), with a Thermo scientific mod. Nicolet iS10;
   b) Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR), With a Bruker AV 400 (400MHz) equipped with a 5 mm multinuclear probe with reverse detection was employed. The sample was dissolved in CDCl$_3$;
   c) . Differential Scanning Calorimetry (DSC) with a Seiko instruments SII Exstar 6000 DSC 6200 was employed
   d) d) Thermal Gravimetric Analysis (DTG/TG/DTA) with a Seiko instruments SII Exstar 6000 TG/DTA 6300 was employed;
   e) Atomic Force Microscopy (AFM), with a NT-MDT Solver Pro was employed. Measurements were performed in contact mode, area 50x50μm, tip CSG10 (constant force 0.01-0.5N/m), scanning frequency 0.8Hz;
   f) Optical Contact Angle (OCA),with a Dataphysics mod. OCA 15 plus device was employed;
   g) Scanning Electron Microscopy (SEM) In this work a Tescan Mira3 LM was employed;
   h) Electrochemical Impedance Spectroscopy (EIS) with a Potentiostatic galvanic Solartron analytical modulab model 2100A was employed;
   i) Glow Discharge Optical Emission Microscopy (GDOES) In this work a Spectruma Analytik GmbH, GDA750 HR was employed;
   j) Optical Emission Spectroscopy (OES) with a SPECTROLAB metal analyzer/OES/fixed was employed.

2.4.2 Titration

Titration was performed following the specification of ISO 2114:2000(E).

2.5. Deposition Procedure

Thin coating formation on the metallic surface is highly influenced by oxidizing agent, its concentration and treatment time. Optimization of these three parameters was necessary, depending on the selected substrate. Hereafter a typical deposition procedure is reported.

2.5.1 Substrate pretreatment

Substrate pretreatments were the same for both untreated and sandblasted substrate and it was formed by three steps in a row:
   ➢ Cleaning: substrate is soaked in DCM(dichoromethane) for 2 min under a gently agitation DCM removes all organic residues, like grease, present on the substrate.
   ➢ Etching: substrate is dipped in a solution of sulfuric acid and NoChromix® for 1/3/6 min as indicated by Van Alsten (1999). This step allows the formation of active sites for the anchorage of polar head groups. The amount of NoChromix® was added to sulphuric acid to enhance etching strength on the metallic substrate.[32] NoChromix® is the trade name of a metal free oxidizer agent. Changing etching time it was evaluated if this parameter influences the deposition, *e.g.* on the number of available active sites or on their strength.
   ➢ Rinsing: substrate is dipped in de-ionized water for 15 s. Rinsing step with de-ionized water removes NoChromix® residues from the substrate that can hinder a correct deposition of the coating molecules.

2.5.2 Coating deposition

This step was differently performed depending on the anchoring group:

1. for SAMs molecules with phosphonic head group the substrate was dipped in a 1 mM solution of alkyl phosphonic acid dissolved in THF for 22 h at room temperature (23 °C), then it underwent a post thermal treatment (1 h at 110 °C) or directly rinsed in fresh THF for 15 s.
2. for carboxylic acids and partially esterified polyacrylates with free carboxyl head the substrate was dipped in a warm(50 °C) 1 mM THF solution of the respective acid for 2 h, then stored in an oven (120 °C for 18 h) and eventually rinsed in fresh THF for 15 s.

3. Results and discussion

In the following we discuss the influence of the process parameters on coating properties. The pre-treatments of the substrate and the post thermal treatment of the coating have been investigated. However the properties deeply depend on the organic molecule structure and correlations have been drawn with the macroscopic surface behaviour. Finally the energy related properties have been analysed.

3.1. Sandblasting

AFM characterization shows that sandblasting treatment increase substrate roughness respect the untreated substrate (Ra changes from 0.201 μm to 0.290 μm).
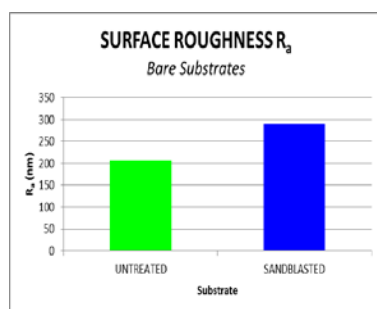

Fig.1. Surface roughness of bare untreated (green) and sandblasted (blue) substrate.

Tab. 2 Contact angle data of bare substrates

CONTACT ANGLE	BARE UNTREATED SUBSTRATE	BARE SANDBLASTED SUBSTRATE
ϑavg (°)	60	57
ϑmax (°)	78	71
ϑmin (°)	39	49
Std. Dev. (°)	10	5

From a different point of view (water contact angle), looking at Tab. 2, it can be seen that sandblasting treatment of the bare substrate slightly lowers contact angles, both ϑ_{avg} and ϑ_{max}. At the same time it greatly reduces standard deviation with respect to the untreated substrate (one half) and significantly decreases the range among the maximum and minimum contact angle ($\Delta_{untreated}$=39° , $\Delta_{sandblasted}$=22°). The two observations could be reasonably explained supposing that the sand treatment causes a more homogeneous morphology of the substrate surface than that existing on the not-treated surface and, at the same time, the increased roughness has a kind of topography suitable to support the Wenzel behaviour.

It appears straightforward that the morphology changes due to the sandblasting has some implications in coating homogeneity (Tab. 3): sandblasting significantly increases the contact angles and greatly reduces their standard deviation leading to the conclusion that a more homogeneous coating was obtained on sandblasted substrate with respect to the untreated one.

The contact angles are reported in Tab. 3 for 3 types of phosphonic acid coating: we can observe clearly an improvement of hydrophobicity on sandblasted substrate.

Tab. 3-Sandblasting role on wettability for alkyl phosphonic acids (alkyl-P).

	Static sessile drop analysis by OCA	
	SANDBLASTING	
COATING	UNTREATED SUBSTRATE	SANDBLASTED SUBSTRATE
	ϑ_{avg} (°) [Std. Dev.]	ϑ_{avg} (°) [Std. Dev.]
C4P	88 [20]	139 [2]
C12P	103 [17]	157 [5]
C18P	147 [5]	164 [6]

About the alkyl chain influence, we observe that the contact angles increase with the alkyl chain length and they have closer values when applied on sandblasted surfaces. The roughness appears one important physical factor.

The observations agree with a scenario where a uniform roughness is compulsory for the hydrophobic behaviour, is created. Going deeper in the analysis, the contact angles of C4 and C12 alkyl chain phosphonic acid increased with a larger increment than the C18 one when the substrate is sandblasted. The last has the same standard deviation obtained without sandblasting treatment of the substrate. The angle however remains the highest among those reported.

Due to the fact that a long chain might assume a cloud conformation, not ordered, very different from a SAM assembly, and then create many very small hills and valleys over the blasted surface, we can suppose that a micro- nano-roughness has been formed due to the organic layer over a macro-roughness of the sandblasted steel. SEM microphotographs (e.g. Fig. 2 and Fig. 3) sustain our hypothesis.
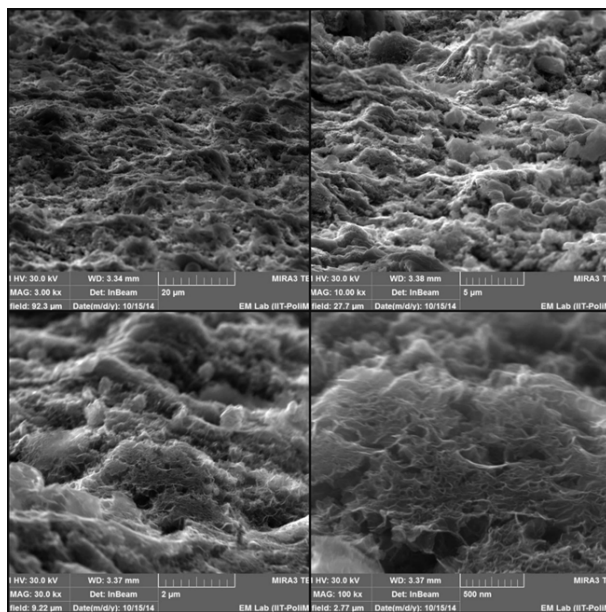

Fig. 3. SEM microphotographs of bare sandblasted 6 min etched at different magnification
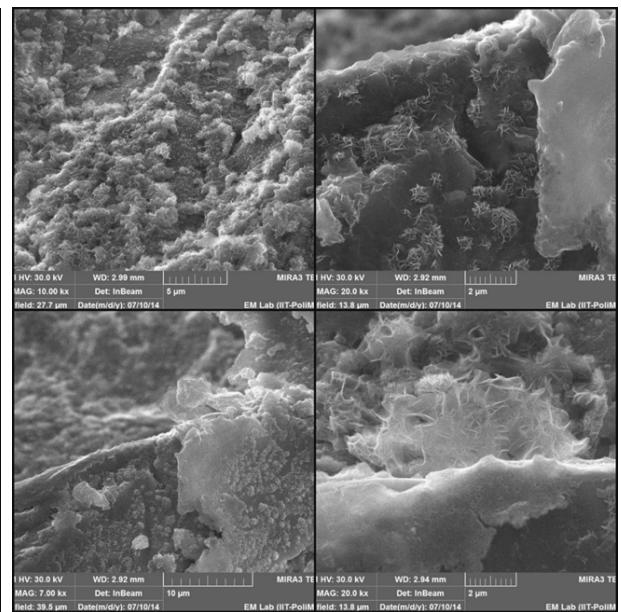
Fig. 2. SEM microphotographs of C12P at different magnification

Further confirmation derive by the analysis in details of the roughness data (Fig. 4 and Fig. 5), bare sandblasted substrate has higher roughness than bare untreated substrate.
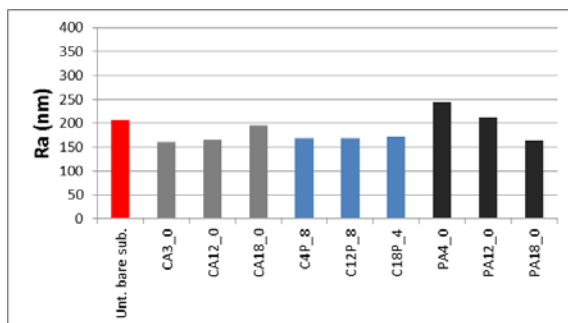

Fig. 4 Comparison of surface roughness (Ra) of coatings on untreated substrate.
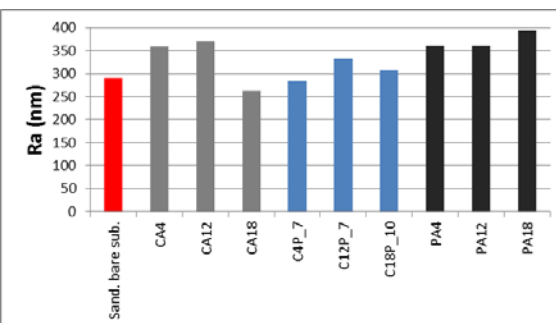
Fig. 5 Comparison of surface roughness (Ra) of coatings on sandblasted substrate

It is however significant to highlight that in the case of untreated substrate, the amplitude roughness parameters decrease with almost all the coatings (Fig. 4). It occurs probably due to the coating material in the valleys. On the other side, starting from sandblasted substrate the application of the coating increased more and more the roughness (Fig. 5).

3.2. Etching time

The amount of active sites onto the substrate and the kind of those is relevant for the surface tension and adhesion of coatings. The amount is directly linked to the etching time, the kind being a substance characteristic. We suppose that the higher the number of available active sites, created by a prolonged etching reaction, the higher is the number of anchored SAMs. The relation between wettability and etching time is graphically reported in Fig. 5 for phosphonic acids before(dotted lines) and after the thermal treatment at 110°C for 1 h (continuous lines)

Before the thermal treatment any increase of the etching time has little or unimportant effect on the contact angle for the short 4 carbon as well as for the C12 chain. The C18 chain contact angle shows a 60 degree reduction with a constant slope from 1 to 6 min of etching time. The decreasing of the C18 derivative could be explained by the bending of the alkyl chain due to its excessive length (cloud conformation) that causes a steric hindrance and a consequent low coating. The thermal treatment seems to slightly increase the contact angle of C4 and C8 and more evidently stabilises the angle of C18 chain acid. The result agrees with the observation of Lim (2010), as a more stability and hydrophobicity of the monolayer was observed probably due to the formation of a chemical bond with the surface and to a well-ordered chain assembly achieved by heating respectively.
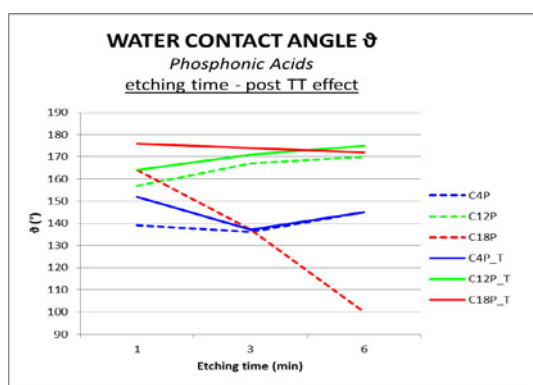.

Fig. 6. Graphical relation of the etching time and of the post thermal treatment (T) effects on the contact angle..

Tab. 4. Contact angle before and after TT.

Organic	ETCHING TIME		
substance	1 min	3 min	6 min
	ϑ_{avg} (°) [Std. Dev.]	ϑ_{avg} (°) [Std. Dev.]	ϑ_{avg} (°) [Std. Dev.]
C4P	139 [2]	136 [5]	145 [4]
C12P	157 [5]	167 [2]	170 [4]
C18P	164 [6]	137 [18]	100 [11]
	POST THERMAL TREATMENT		
C4P	152 [3]	137 [7]	145 [1]
C12P	164 [9]	171 [7]	175 [4]
C18P	176 [5]	174 [8]	172 [7]

3.3. Thermal treatment

Thermal treatment effect after the organic layer deposition can be evaluated analysing the data reported in Tab. 4: it positively influence hydrophobic properties of the coating, probably enhancing the strength of the chemical bond with the substrate and allowing an optimization in the re-organization of alkyl chain as stated by Danahy (2004) and Gawalt (2001). At the same the etching time all contact angles were improved, independently of the coating type. The effect is strongly evident for C18P layer after 6 min. of etching: the contact angle increase is 72 degrees, sufficient to change the behaviour from hydrophobic to superhydrophobic.

3.4. Chain length, Structure and Functional groups of organic molecules.

Since the deposition parameters have been set for all the coating types, it is possible discuss the chain effect on the wettability grade. Longer alkyl chains produced higher contact angle values, with no significant difference between C12 and C18, in presence of the post thermal treatment. Without thermal treatment this trend can be confirmed at high etching time excluding the anomalous data of C18P. The rate of increasing the contact angles seems to depend mainly on the chain length: C18 (treated)>C12 (both treated and untreated) > C4 (both treated and untreated). We examined two functional groups: straight chain phosphonic acids and carboxylic acids. The– COOH groups were examined linked both to linear C≤ 18 alkyl moieties or to a polymer chain (polyacrylic acid). In the last case some of them were similarly esterified with linear C≤ 18 alkyl moieties. The results obtained examining linear alkyl carboxylic acids and comb polymer functionalized with the carboxylic groups, are reported in Tab. 5. Very low contact angles characterize linear chain, while, on the contrary some

controversial data are obtained for the polymeric coatings, that require to be more deep discussed. For the first series, our opinion is that the deposition procedure has to be optimized in order to enhance the chemical bond strength between carboxyl head group and the activated surface. Carboxyl group have been reported to have a lower bond strength in comparison with phosphonic acid (this one has 3 functional group that can link the substrate, one polar carbonyl and two hydroxyl groups, while carboxyl acid is the only one polar function) so most likely, we have to just increase the deposition procedure, time, concentration and temperature. Also the qualitative kind of active adsorption sites would be examined.

Tab. 5. Contact angles for linear and branched acids.

SAMPLE	ϑ_{avg} (°) [Std. Dev.]	Esterification degree (%)
CA3	<10 [-]	-
CA12	37 [6]	-
CA18	67 [54]	-
PA4	93 [9]	91
PA12	158 [17]	75
PA18	64 [8]	44

Our interest on carboxylic acid is great because they represent a cheaper substance, sometimes green. We have to consider that with a weak bond of adsorption, all the parameter that are important for a SAM homogeneous adsorption have more relevance.

Our tentative was to block the carboxyl groups with a backbone (the acrylate backbone) in order to build a more rigid structure suitable for a stronger adsorption in comparison to the linear acid.

With partially esterified polyacrylates, synthesized in our laboratory, the great challenge was a better control of the esterification grade. Certainly the study of the reaction to obtain a right esterification grade is a key point for further analysis, since it influences the molecule adhesion on the substrate: the higher the number of anchoring groups (lower esterification grade) the easier the anchorage to the substrate The 2nd order structure (macro) is also influenced by the esterification degree as, at high degree, the backbone is more and more outstretched out the surface, covering a larger volume.

Another important parameter to be taking into account during the synthesis is the regioselectivity of the esterification, but it requires a complete control of the reaction. Here very different wettability properties were obtained between the coatings: PA12 (esterification degree = 75%) showed superhydrophobic behaviour, while PA4 (esterification degree = 91%) was slightly hydrophobic and PA18 has a very low contact angle with respect the bare substrate (esterification degree = 44%). The results let us to foresee some positive trends but the relation with a structure is not clear.

3.5. Adhesion with AFM

The adhesion force of the coatings are reported in Tab. 6 and Fig. 7 and 8. They refer to the AFM tip-surface interaction, which is sensitive to the chemical nature of both the tip and the coating surface.

Tab. 6. Adhesion forces on surfaces(*UT= untreated; SB= Sandblasted)

SAMPLE	Substrate*	Adhesion force (mN) [Std. Dev.]	SAMPLE	Substrate*	Adhesion force (mN) [Std. Dev.]
C4P_8	UT	24.5 [3.4]	C4P_7	SB	20.3 [5.7]
C12P_8	UT	28.6 [7.9]	C12P_7	SB	16.5 [6.5]
C18P_4	UT	31.7 [11.8]	C18P_10	SB	20.0 [10.6]
CA3_0	UT	14.1 [3.8]	CA4	SB	20.7 [4.1]
CA12_0	UT	12.2 [2.0]	CA12	SB	28.1 [8.5]
CA18_0	UT	15.2 [2.1]	CA18	SB	11.3 [6.9]

The higher the adhesion force the higher the physicochemical/mechanical interactions of the tip on the surface. The interfacial force between film coating and substrate could not be probed directly due to the nano dimension of the coatings. Actually no valuable experimental characterization exists for the adhesion forces of the molecules to the metallic surface. One would need to devise a new method of sticking the AFM probe to the coating and measure the force required to lifting the film from the substrate surface.

The values of Tab. 6 seem to indicate a difference between the no-sandblasted and sandblasted uncoated steel surface: the adhesion appears poorer for phosphonic acids on sandblasted substrates than on untreated substrates.

Regarding carboxylic acids the trend seems to be the opposite. The opposite behaviours clearly appear examining the data series of the interactions with the bare substrate.

a   Among the phosphonic coating, the interactions are greater and grow with chain length for the untreated surfaces respect to the bare surface

b   Among the carboxylic coating the interactions of CA4 and CA12 samples are greater and grow with chain length, for the treated surfaces respect to the bare surface (the 18 carbon chain length has a not linear behaviour one time more).
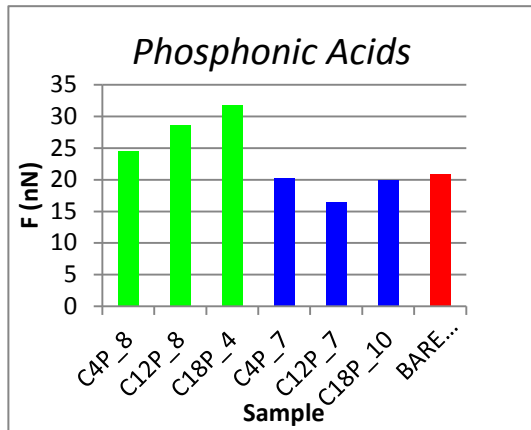

Fig. 7 Adhesion force on phosphonic acids coating untreated (green) and sandblasted (blue) substrate; adhesion force on bare sandblasted substrate (red).
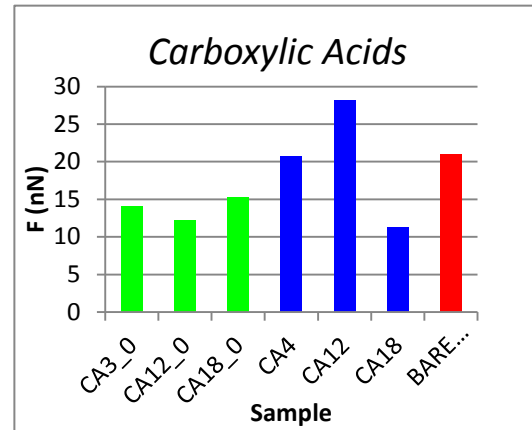

Fig. 8 - Adhesion force on carboxylic acids coating untreated (green) and sandblasted (blue) substrate; adhesion force on bare sandblasted substrate (red).

3.6. Surface tension

Considering the Young model, the wettability properties of coated surfaces, strongly depends on the physical properties of coating and mainly by the surface tension of the coating: the lower the surface tension, the lower the wettability (or greater is the hydrophobic behaviour) of the coated surface. The samples that reached superhydrophobicity had surface tension lower than 2 mN/m or about.

In Fig 9 we report the surface tension medium values of the samples treated with two different chain length phosphonic acid (C12P and C18P). The data show the effects of thermal treatment on the 12 carbon chain and of sandblasting and thermal treatment on the 18 carbon chain. The thermal treatment generally positively affects the contact angles (Fig. 6 and Tab. 4) for phosphonic acids. Indeed for C12P molecules a slight increase of surface tension is observed but however the medium value remains around the 0.5 mN/m. Supposing a similar effect on the C18P acid, the effect of sand blasting can be evaluated alone and coupled with thermal treatment. The first treatment increase the surface tension, but this it is reduced by the thermal treatment to a value similar to that obtained with C12P.

The low values both of the 12 and 18 carbon chains, probably indicate an easier rearrangement into different conformations, probably more homogeneous than 4 shorter chains that lower the surface tension. C4P acid
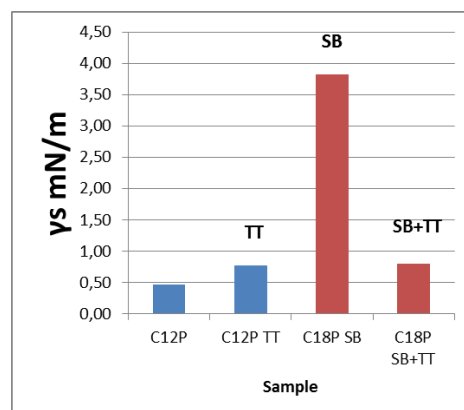

Fig. 9. Medium surface tension values. (TT= thermal treatment; SB= Sand blasting)

indeed shows higher values in a very large range of surface tension values from 1 to 40 mN/m.

This observation let us to suppose that the optimum chain length probably is > 4 and < 18.

In Fig. 10 we compare the surface tensions of carboxylic and polycarboxylic coatings. All the values are very high respect to the phosphonic acids. Carboxylic acids surface tensions indicate that the higher the chain length the higher the contact angle the lower the surface tension. Dissimilar data have been obtained with PA samples, probably meaning variability in the adsorption conformation for polymer molecules.
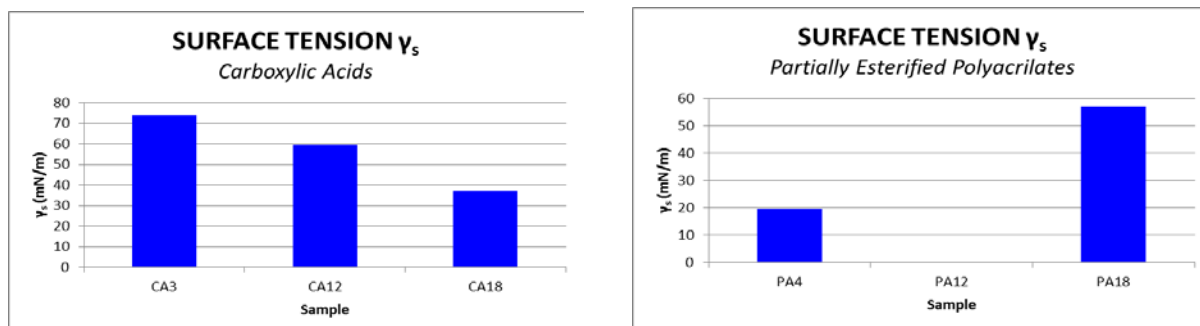

Fig. 10. Surface tension of carboxylic and polycarboxylic coatings. The bar of PA12 cannot be seen due to the graph scale since it has a value of only 0.097 mN/m.

3.7. Thickness and composition

GDOES analysis has been done to survey film coating thickness and chemical composition. Both C12P_7 and CA12 samples were coated by self-assembled monolayer dodecyl phosphonic acid and dodecyl carboxylic acid, respectively. A nanometric thickness coating should be expected in accordance to SAM thickness evaluated in literature. On the other hand, coatings show thickness higher than microns or in the order of microns (1.5 μm thickness for C12P_7 and 0.3 μm thickness for CA12). It can be explained by the anchoring mode: theoretically it has been assumed a bidentate mode, but actually in the case of phosphonic acid other anchoring mechanisms were proposed and observed in previous studies: the linkage of organophosphorus coupling molecules to oxide surfaces involves the formation of M-O-P bonds by hetero condensation of surface hydroxyl groups (-OH) with P-OH groups and by complexation of the phosphoryl oxygen to the surface metal atoms.

Hydrogen bonds between surface hydroxyl groups and residual P-OH and P=O groups may also be involved as reported by Lim et al. (2010).
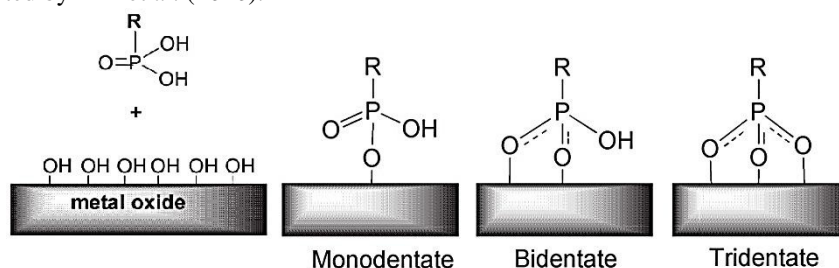

Fig. 11. Different bonding modes of a phosphonate unit to a metal oxide surface.

The bonding mode of organo-phosphorous coupling molecules likely depends on the nature of both the coupling molecule and the inorganic surface, and on the conditions of the surface modification.

Moreover looking at, it is clear that more than one layer have been deposited on the surface. Indeed the GDOES curve for carbon and phosphorous are characterized by two peaks. These appear at the same depth for the two elements.

For PA12 the film was made by a polymer that did not self-assembly on the substrate, and the bonds and polymer configuration were rather unpredictable.

SEM images confirmed that coating application successfully occurred. They show the different morphology of bare substrate, etched substrate, and C12P and PA12 coatings with comparable magnification. As it can be seen they were very different: etching role can now be understood more in detail, showing that it increased significantly the porosity of the surface (it has been not possible to measure the roughness at AFM) allowing a better anchorage of the molecules. The coated substrates were very different with respect to the bare substrate,

with C12P_7 sample showing a homogeneous crystalline film completely coating the substrate. Also for PA12 sample the surface is homogeneously coated, but it look more like a wax than a crystalline structure.

4. Conclusions

The physical and chemical parameters of the surface have to be optimized to obtain advanced surface properties on inexpensive raw materials as mild carbon steel by using easy and low-cost technologies like the self-assembly methods. Among them, when the organic coating is applied with the aim to gain hydrophobicity, roughness and etching physical factors appear to influence the surface tension (contact angle) and adhesion forces. Roughness can be modified by sandblasting operation: on stainless steel surface the roughness increases and the contact angles seems increase too. Others correlated aspects like of the surface morphology, e.g. peak intensity and peak height, have to be analyzed to explain the trends. Etching mainly changes the physical parameters of surface and it can be evaluated only by the properties of the coated surface. The polar functions that are created by the etching application may be well dispersed or densely grouped, also depending on roughness, as it is possible to argue from the data of contact angle at long time etching. Thermal treatment redistributes the adsorbed molecules homogenizing the contact angles.

Among the chemical parameters, we analyzed the effect of carboxylic groups linked to a polymer chain with the aim of open the knowledge towards additives suitable for a more stable hydrophobicity attainment. The maintenance of surface properties is nowadays the problem to solve. The results are encouraging and a significant contact angle increase is obtained respect to the free chain acids. The observation is also encouraging in order to increase the adhesion force of carboxylic functions.

5. References

Danahy, M.P., Avaltroni, M.J., Midwood. K.S., Schwarzbauer, J.E., Schwartz, J., 2004, Self-assembled Monolayers of α,ω-Diphosphonic Acids on Ti Enable Complete or Spatially Controlled Surface Derivatization. Langmuir, 20, 5333-5337.

Darmanin, T, Guittard, F, 2015, Superhydrophobic and superoleophobic properties in nature, Materials Today Volume 18, Number 5 _ June 2015.

Gawalt ES, Avaltroni MJ, Koch N, Schwartz J., 2001Self-Assembly and Bonding of Alkanephosphonic Acids on the Native Oxide Surface of Titanium, Langmuir,17, 5736-5738.

Gugliuzza A., Drioli E., 2013, A review on membrane engineering for innovation in wearable fabrics and protective textiles, J. Membrane Science, 446, 350–375.

Qu Mengnam, Zhang Bingwu, Shiyong Song, Li chen, Junyam Zhang and Xiaoping Cao, 2007, Fabrication of Superhydrophobic Surfaces on Engineering Materials, Adv. Funct. Mat., 17, 593-596,DOI 10.1002/adfm.200600472.

Van Alsten J.G., Self-Assembled Monolayers on Engineering Metals: Structure, Derivatization, and Utility,1999, Langmuir, 15, 7605-7614.

Wojdyla, A. M., Durand, G. G., Taylor, A., and Boyd, I.W., 2014, Advanced low-energy durable coatings, Int. J. Energy Res. DOI: 10.1002/er.3214. Published online in Wiley Online Library (wileyonlinelibrary.com).

Zoua, M., Beckforda S., Weib R., Ellis C., G. Hattonc, Miller,M.A., 2011, Effects of surface roughness and energy on ice adhesion strength, Applied Surface Science 257, 3786–3792.