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XPS study of five fluorinated compounds deposited on calcarenite stone Part I. Unaged samples

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Abstract

In this work the application of XPS technique to the study of five fluorinated compounds deposited on actual calcarenite samples is presented. It has been found that the composition derived from the high-resolution XPS spectra together with the results of the C 1s fitting, allow us to derive a surface chemical formula for each of the studied compounds. These formula are in good agreement with those reported in the manufacturer data sheets if one hypothesise an arrangement of these molecules on the surface of the calcarenite stone that take into account the content of the different hydrophobic groups. In addition, the thickness of the deposited film has been calculated on the basis of the Ca and C content as well as an estimation of the coverage degree has been done. The results of this XPS study has been compared with that obtained by means of the static contact angle test.

Keywords: XPS; Protective; Calcarenite

1. Introduction

Most of the macroscopic properties of a surface, like wettability, hydrorepellence, adhesion, are strongly related to microscopic properties, like micro-porosity, roughness, elemental and molecular compositions.

One of the most powerful technique that allows to acquire deep chemical information both on elemental and molecular composition of a surface is the X-ray Photoelectrons Spectroscopy (XPS) [1]; moreover this technique allows to distinguish different chemical states of the same element and to obtain their depth distribution along thickness of about 5–10 nm [2].

XPS has been used since long time in the wide field of the cultural heritage: one has to mention the pioneering work of Lambert and McLaughlin that starting 30 years ago have published several papers on application of XPS to archaeological artifacts [3,4]. Among the large number of published articles, I would mention only few that report study of ceramics and pigments [5–11] and metals [12,13]. Two reviews should be cited [14,15] reporting different applications and interesting discussions.

Nevertheless, at least of my current knowledge, few papers have been published reporting XPS studies of products used for the protection of stones in spite of the enormous analytical potential of this technique. Among them I would signal those reported in the references list as [16,17].

Recently it has been hypothesised [18] that, in addition to the chemical modification due to the oxidative processes, UV radiations and heat release do modify the arrangement of the surface of the polymeric coating. In this respect the use of a very surface-sensitive technique should allow a deeper insight on these phenomena.

In this paper this technique have been applied to study five compounds of the Zonyl family (Zonyl is a trademark of Du Pont) in order to compare the chemical information with the results obtained from measurement related to macroscopic properties like hydrorepellence. All these compounds contain fluorinated alkyl chains, that are well known to reduce the surface energy so improving the water repelling efficiency. Because most alteration processes of a stone are water-driven, delaying the water adsorption should preserve for a longer time the stone appearance. The five compounds studied here were chosen because of their interesting chemical structure: three of them (FSP, 9361 and 9027) are phosphoric esters [19] and should differ each other mainly for the nature of the counter-ion bonded to the oxygen atoms of the phosphate group and/or for

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the number and the length of fluorinated chains. The phosphate group should have a quite strong interaction with the Ca ions of the carbonate structure of stones like calcarenite, thus assuring, in principle, a good adhesion of these products. The calcarenite stones were widely used in the Southern part of Italy for construction and decoration of the most important monuments and building of the Baroque period. Some of these represent the pinnacle of the works of art, thus the preservation and the conservation of these artifacts are among the most demanding problems for the time to come. As to the other two compounds chosen for this study: one of these (FSA) should contain a fluorinated alkyl chain bonded to an alkyl-thio-ether terminated at the other side by a carboxylate group [19]. This group should behave similarly as the phosphate group with respect to the interaction with the calcarenite stone. The second one (8740) should be a fluorinated-acrylic copolymer [19]. The family of acrylic polymers have been used since a long time in the restoration and conservation of monuments [20]. Last but not least, all these compounds are soluble in water–isopropanol mixture, at variance with other widely used products soluble in aromatic and/or in chlorine containing solvents [21,22]. Their solubility properties and the very thin thickness used in this study should allow an easier removability in comparison to other thicker and less soluble products. The reversibility of a treatment indeed will be one of the most important requirements of a product intended to be use as protective. Aim of this work is to explore the potentialities of this nearly old analytical technique in the study of some products that could be used in the preservation of calcarenite stone artifacts.

2. Experimental

Calcarenite samples were taken from materials left over from previous restoration actions in the Benedictine monastery of Catania (Italy) and cut through using an electrical saw of the same kind used for cutting the marble. The samples used for the XPS spectra were about 0.5 cm × 1 cm × 0.5 cm, while those used for the contact angle test was roughly 1 cm × 2 cm × 0.5 cm. After the cutting, the samples were gently polished by a fine carborundum paper, then repeatedly washed with deionised water and finally dried in an oven at 60 °C. The Du Pont products were kindly provided by Garzanti Chimica S.p.A (Italy). For each product a solution 4% (v/v) was prepared by using a 2:4.5 isopropyl alcohol/water solvent mixture. The calcarenite samples were immersed for 1 min in the solutions previously prepared. For comparison few calcarenite pieces was treated by brushing the surfaces with a small amount of the solution containing the various products. No relevant differences were found in contact angle test and XPS spectra. After treatment the samples were dried under a light Ar flux.

Contact angle measurements were performed on a Kernco apparatus. The drop (5 μL) of double deionised water was applied by a micro-syringe. For each sample six different measurements were done and the average, with the calculated standard deviation, was reported.

The XP spectra were obtained on a Perkin-Elmer 5500 spectrometer, equipped with a Mg and Al double anode. In addition an Al monochromatic source was available. The spectra were acquired in FAT (fixed analyser transmission) mode by using the Mg source at 300 W. The survey spectra were acquired in the following conditions: pass energy = 93.9 eV, V/step = 0.4 V, time/step = 50 ms. The high-resolution spectra were acquired in the following conditions: pass energy = 11.75, V/step = 0.05, time/step = 70 ms. The pressure in the analysis chamber was better than 6×10^{-9} atm. The take off angle was maintained at 45° in order to minimise the effect of the roughness of the calcarenite substrate on the determination of the thickness of the overlayer of the deposited compounds [23]. In order to check the effect of the radiation on the samples, the C 1s and the F 1s high-resolution spectra were acquired two times, at the beginning and at the end of the analysis cycle. The Ca $2p_{3/2}$ (347.2 eV) and the C 1s (289.6 eV due to carbonate and 285.0 eV due to adventitious carbon) peaks of bare calcarenite were used as reference to set the binding energy (B.E.) scale. In the deposited samples the C 1s of fluorinated components (293.9 eV for $–CF_3$ and ≈291.9.0 eV for $–CF_2–$), as well as that of F 1s peak (688.8 eV), were used as reference peaks. The convolution on the C 1s high-resolution spectra was done by means of the XPS-peak freeware routine by using a peak shape sum of a gaussian function (90%) and lorentzian function (10%). The presence of calcium in all wide scan spectra, likely due to calcarenite substrate, prompt us to include in the C 1s fitting a component at 289.6 ± 0.1 eV, attributed to calcium carbonate. The area of this component should have been set on the basis of the high-resolution Ca 2p peak area, taking into account the C 1s(CO_3^{2-})/Ca 2p peaks area ratio found on the bare calcarenite. However, during the C 1s fitting procedure, while the binding energy was fixed at the above value, the area of the carbonate component was not subjected to this constraint. Nevertheless, the amount of calcium, found in the quantitative analysis derived from the XP high-resolution spectrum, was in good agreement with that calculated from the (CO_3^{2-}) component of the C 1s fitting. The assignment of all peaks of the spectra and of the components of the fitting was accomplished referring to previously reported data [16,24–27, and references therein].

Information on the chemical composition of the product here analysed were taken from Du Pont data sheets [19] and are reported below:

FSP → $(R_fCH_2CH_2O)_xPO(O^-NH_4^+)_y$,
where $R_f = CF_3CF_2(CF_2CF_2)_n$, $n = 2–4$ and $x + y = 3$;

9361 → $(R_fCH_2CH_2O)_xPO(O^-NH_2^+[CH_2CH_2OH]_2)_y$,
where $R_f = CF_3CF_2(CF_2CF_2)_n$, $n = 2–4$ and $x + y = 3$;

9027 → $R_fCH_2CH_2OPO(O^-NH_2^+[CH_2CH_2OH]_2)_2$
$+ (R_fCH_2CH_2O)_2POO^-NH_2^+(CH_2CH_2OH)_2$;

FSA → $R_fCH_2CH_2SCH_2CH_2COO^-Li^+$;

8740 → Perfluoroalkyl-methaacrylic copolymer.