Preparation and characterization of polymeric nanocomposite films for application as protective coatings

Cite as: AIP Conference Proceedings **1873**, 020007 (2017); https://doi.org/10.1063/1.4997136 Published Online: 02 August 2017

S. Gagliardi, F. Rondino, C. D'Erme, F. Persia, F. Menchini, M. L. Santarelli, B.-R. Paulke, L. Enayati A., and M. Falconieri



ARTICLES YOU MAY BE INTERESTED IN

Light absorption spectra in oligothiophene molecules AIP Conference Proceedings **1873**, 020001 (2017); https://doi.org/10.1063/1.4997130

Plasma enhanced hot filament CVD growth of thick carbon nanowall layers AIP Conference Proceedings **1873**, 020006 (2017); https://doi.org/10.1063/1.4997135

Preface: Nanoinnovation 2016 AIP Conference Proceedings **1873**, 010001 (2017); https://doi.org/10.1063/1.4997129

AP Conference Proceedings



Get 30% off all print proceedings!

Enter Promotion Code PDF30 at checkout

AIP Conference Proceedings **1873**, 020007 (2017); https://doi.org/10.1063/1.4997136 © 2017 Author(s).

1873, 020007

Preparation and Characterization of Polymeric Nanocomposite Films for Application as Protective Coatings

S. Gagliardi^{1,a)}, F. Rondino²⁾, C. D'Erme^{1,3)}, F. Persia⁴⁾, F. Menchini⁵⁾, M. L. Santarelli³⁾, B.-R. Paulke⁶⁾, L. Enayati A.^{1,7)}, and M. Falconieri¹⁾

¹⁾Fusion and Nuclear Security Department, Physical Technologies for Safety and Health Division ENEA, C.R. Casaccia, via Anguillarese 301, 00123 Roma Italy

²⁾Fusion and Nuclear Security Department Physical Technologies for Safety and Health Division ENEA C.R. Frascati Via E. Fermi, 45 00044 Frascati (RM), Italy

³⁾Department Chemical, Materials and Environmental Engineering and CISTeC - Research Centre in Science and Technology for the Conservation of the Historical-Architectural Heritage, "Sapienza" University of Rome, Via Eudossiana, 18, 00184 Roma, Italy

⁴⁾Territorial and Production Systems Sustainability DepartmentENEA, C.R. Casaccia, via Anguillarese 301, 00123 Roma Italy

⁵⁾Energy Technologies Department, Photovoltaic and smart Network Division, ENEA, C.R. Casaccia, via Anguillarese 301, 00123 Roma Italy

⁶⁾Fraunhofer-Institutfür Angewandte Polymerforschung Geiselbergstrasse 69 Potsdam-Golm 14476 Germany ⁷⁾Faculty of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran.

^{a)}Corresponding author: serena.gagliardi@enea.it

Abstract. Addiction of ceramic nanoparticles to acrylic polymers provides a simple and effective means to produce paints with important properties, such as mechanical resistance and tailored wettability, even though for optimal performances, an engineered nanoparticle distribution would be desirable. In this paper we report on the realization and on the morphological and functional characterization of nanocomposites where the nanophase is distributed on the surface of acrylic polymer films, in order to enhance the expression of surface-related properties. To this aim, commercial titanium oxide and silicon oxide nanopowders were dispersed in water and the suspensions were air-sprayed on polymeric films prepared by paint brushing, thus producing a nanostructured ceramic surface coating. Control of the pH of suspensions and acrylic acid functionalization of the surface of titania were used together with high power ultrasonic treatments in order to control dimension of the aggregates in the sprayed suspensions. Optical microscopy, mechanical profilometry, and atomic force microscopy were used to characterize the nanocomposite surface morphology and correlate it to the coating functional properties, evaluated through mechanical abrasion tests and contact angle measurements; also, colorimetry on coated stones was performed in order to test the impact of the coatings on the aesthetical appearance and their photostability under UV irradiation. Results show that the nanostructured ceramic layer slightly improves the resistance of coatings to mechanical abrasion in case of polymer films prepared from latexes. The nanocomposite surface layer does not affect the wettability of the polymer, which remained slightly hydrophilic; this behavior is likely due to inadequate distribution of the nanophase. On the other hand UV-induced superhydrophilicity was observed when the concentration of surface titania nanoparticles is about 0.6 mg/cm². Colorimetric analysis on historical and Carrara marbles before and after coating evidenced the good transparency of the nanocomposites.

> NANOINNOVATION 2016 AIP Conf. Proc. 1873, 020007-1–020007-9; doi: 10.1063/1.4997136 Published by AIP Publishing. 978-0-7354-1553-9/\$30.00

> > 020007-1

Accelerated aging tests permitted to demonstrate that, on the historical marbles, the presence of the nanoparticles has a protective action against UV-induced damage of the underlying polymer film, preventing photodegradation.

INTRODUCTION

In the field of restoration and preservation of cultural heritage stone artefacts have great relevance, and large efforts are devoted to the development of new protective materials with improved properties and longer lifetime. In particular, in the last 40 years polymeric resins have been widely used in order to consolidate the material and slow down the deterioration process [1-2], often accelerated by anthropic causes. Recently, the introduction of nanomaterials in the polymeric coatings has been demonstrated to be an effective tool to tailor specific important protective characteristics. Dispersion of ceramic nanopowders in polymers provides a simple and effective mean to produce protective coatings in which morphology and distribution of the nanophase are key factors to confer the desired properties to the composite [3-7]. For example, several characteristics such as optical properties, wettability or mechanical resistance to abrasion, are strictly related to the coating surface, so that the distribution of the nanophase on the surface coating allows an optimized expression of such a kind of functional properties. Hence, an engineered nanoparticles distribution would be desirable. Moreover, the interface properties of the nanoparticles with the surrounding matrix, which are determined by their surface termination, also concur in the attainment of optimized performances.

Among the more extensively polymers used, acrylic and methacrylic compounds are employed in different industrial applications, such as media in the formulation of paints and surface coatings, and bases for adhesives [8, 9]. Their widespread use has evidenced several limits such as the shortened lifetime especially when used in outdoor conditions [10, 11]. The introduction of a nanophase can help overcoming limits and extends lifetime.

In this context, we fabricated nanocomposite coatings using acrylic polymers films and ceramic nanopowders deposited as a surface layer. We used two innovative latexes, both of them composed by a balanced mixture of butyl acrylate and butyl methacrylate and differing for the particles cross-linkers (ethylene glycol dimethacrylate and 2,3-epoxypropyl methacrylate). Besides, we also used a well-known commercial protective and consolidating product, Paraloid B72, to compare the results obtained with the new latexes.

To prepare the nanocomposite, commercial anatase titania and fumed silica nanopowders were dispersed in water with the help of high power ultrasonic probe treatment. Variations of pH in the suspensions and functionalization of the titania surface allowed to control the dimensions of the suspended aggregates.

The surface morphology of the coatings was studied on different scales by means of optical microscopy, mechanical profilometry and atomic force microscopy. The characterization of the surface topology at different scales was used to study the nanoparticles distribution on the polymeric film; the results were used to optimize the aqueous dispersion and the deposition process, in order to attain a homogeneous distribution of nanoparticles on the polymeric films surface.

Two important functional properties of coatings, such as resistance to mechanical abrasion and wettability, were tested on samples prepared on glass substrates; while the resistance to photodegradation of nanocomposites was assessed through colorimetric characterizations performed on different coated lithotypes, before and after artificial aging procedures.

MATERIALS

Two new acrylic latexes were studied in this work, both of them being balanced butyl-acrylate and metacrylate copolymers with methacrylic acid; the two formulations differ in the binder used: ethylene-glycol-dimethacrylate (EGDMA) for sample named P1 and glycidyl-methacrilate (EPMA) for sample P2. The solid content, the diameter of the two latexes and their composition are shown in Table1.

 TABLE 1. Specifications of the different polyanionic latexes studied in this work: HEMA – hydroxyethylmethacrylate,

 EGDMA – ethyleneglycoldimethacrylate, BuA – butylacrylate, BuMA – butylmethacrylate, MAA – methacrylic acid, EPMA – 2,3-epoxypropyl methacrylate (glycidylmethacrylate).

Sample name	Solid Content	Diameter	Components
P1	34.1%	145.7 nm	EPMA, BuA, BuMA, MAA
P2	32.2%	172 nm	HEMA, EGDMA, BuA, BuMA, MAA

Paraloid B-72, an ethyl-methacrylate copolymer purchased by Rohm and Haas, was dissolved in acetone at 5% weight/volume for the preparation of polymer films.

Commercial anatase TiO_2 (20 nm diameter) and fumed SiO_2 nanopowders, purchased by Sigma Aldrich were used as nanophase ceramic materials in the preparation of water based suspensions.

EXPERIMENTAL METHODS

Suspensions were prepared at a desired concentration (1%) by weighting the powders and dispersing them, after mortar grinding, in 18 M Ω ·cm de-ionized water (MilliQ water OM140) with the help of a high power ultrasonic probe (Branson Sonifier 450) equipped with a 3 mm micro-tip. Control of the surface charge of the nanoparticles, which is a key factor to prevent aggregation of the nanoparticles, was achieved by changing the pH of the suspensions by addition of NaOH or HCl (1M in water). pH measurements were performed by a Carlo Erba-Forlab 707 pHmeter. The procedure to prepare nanoparticles suspensions aimed to the attainment of finely dispersed nanoparticles, avoiding the aggregation due to electrostatic forces and breaking down soft links between particles. The control of the quality of the suspension preparation procedure was made by measuring the particles size in the dispersions by dynamic light scattering (DLS), using a Malvern PCS 4700 apparatus; data analysis provided the scattered-light weighted particle diameter $Z_{average}$ and the polydispersity index of the suspended nanoparticles.

Surface functionalization of ceramic nanopowders can improve the chemical bonding to the acrylic polymers and also create a proper surface charge to obtain well dispersed and stable dispersions. Acrylic acid (AA) functionalization of titanium oxide was selected for the compatibility with our acrylate polymers. In order to overcome the poor reactivity of this acid, a ligand exchange process was performed, using oleic acid (OA) as intermediate [12]. Briefly, the procedure consisted in adding an excess of oleic acid to titania dispersed in ethanol and then stirring the suspension at room temperature for 8 h. The titania nanopowder was then collected after 3 cycles of centrifugation and washing, in order to remove all the unreacted acid, and finally it was dried for 4 h at 80 °C. The OA-functionalized nanopowder was then dispersed in cyclohexane and the resultant dispersion was added to AA diluted with 10% of water. The two liquids, due to their different polarity, separated and the nanoparticles precipitated at the interface where the oleic acid functionalization is slowly replaced by the acrylic acid diffusing in the apolar phase. Following this functionalization exchange the nanoparticles slowly transfer into the aqueous polar phase where they could be collected [13] and after washing and drying re-dispersed for further use. The presence of surface groups linked to the nanopowders surface was revealed by Attenuated Total Reflectance Fourier Transform InfraRed absorption (ATR-FTIR) measurements with a KRS5 crystal in a Spectrum One Perkin-Elmer instrument.

The nanocomposites were prepared using a two-step deposition procedure consisting firstly in the application of the latexes on selected substrates by paintbrush; subsequently, before the films were completely dry, the suspensions were airbrushed on the film surface keeping the tool at a distance of 7 cm; finally the samples were left to cure in oven at 60°C for 20 minutes. For ease of characterization the nanocomposites were first deposited on microscope glasses.

Optical microscopy, mechanical profilometry with a Kla-Tencor P10 instrument and Atomic Force Microscopy (AFM) with a Quesant– Nomad instrument were used to characterize at different length scales the morphology of the coatings and the distribution of the nanophase. Mechanical profilometry was performed using a triangular tip (radius 2 μ m) scanning the sample at a rate of 100 μ m/s. For data analysis a suitable quantitative descriptor of the surface topography is represented by the root mean square roughness R_q defined by

$$R_q = \frac{1}{n} \sqrt{\sum_{i=1}^n z_i^2} \tag{1}$$

where z_i is the i-th value of the quote measured by the profilometer tip. Values were obtained from averages on several tens scans.

AFM topological information were recorded in contact mode with an Al coated silicon tip, nominal radius 5 nm, spring constant 0.15 N/m.

AFM was used not only for the surface morphological characterization, but also to verify the good adhesion of the nanoparticles to the polymeric film. In fact, it was demonstrated that poorly anchored nanoparticles are swept

from the surface by the AFM tip and accumulate on the edges of the scanned area [14]. So a $3x3 \ \mu m^2$ area was repeatedly scanned with an increasing pressure of the probe on the surface, trying to pull off the nanoparticles. After that, a larger area ($6x6\mu m^2$) was scanned in order to verify the possible detachment of the particles or the formation of ridges on the edges. It was possible to increase the pressure of the probe on the surface by forcing the cantilever to work at a deflection higher than the normal operating conditions, but it was not possible to know the absolute force, in absence of a calibration curve.

The resistance to mechanical abrasion was studied by tailoring a standard certification test for hard coatings. The certified test kit was purchased by Pieplow & Brandt GmbH, and the standard procedure [15] consisted in 20 abrasion cycles on the sample with a cheesecloth tip ($\sim 20 \text{ mm}^2$) exerting a force of $\sim 5.5 \text{ N}$, after which the surface was examined to assess the removal of the coating; to characterize our relatively soft coatings we reduced the abrasion cycles to 5 to avoid the total removal of the nanocomposite, and then examined the scratched surface by optical microscopy and mechanical profilometer.

Contact angle measurements were performed in order to evaluate the wettability of the surface using a camera and calibrated water droplets (4 μ L).

The properties of bare polymeric and polymeric nanocomposite layers fabricated with the same above-detailed two-step deposition procedure were also tested on historical and Carrara marbles samples. In order to evaluate the changes of colour induced by the coatings, colorimetry (Minolta CM-525i colorimeter) was performed before and after their application on the different lithotypes. The colour of the samples was expressed as a point in the CIE lab space (a*, b*, L*) and the variation of colour ΔE was calculated as the Euclidean distance between points according to:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$
(2)

To study the photosensitivity of the coatings to UV irradiation we referred to the standard practice ASTM D904-94, performing colorimetry measurements of the coated stones before and after exposure to Xe lamps (Ultra Vitalux 300 W) irradiation for 168 and 336 hours, and calculating the variation of colour between as-prepared and irradiated samples.

RESULTS AND DISCUSSION



FIGURE 1. Normalized absorption spectra of bare titania (black), OA functionalized (blue) and AA functionalized (red); for a better comparison the spectra were normalized on the common peak at 1636 cm⁻¹ attributed to the OH bonds on the titania surface.

In the spectrum of the pristine TiO₂, the broad peak from 1000 cm⁻¹ to 1100 cm⁻¹ and the narrow band at 1636 cm^{-1} were attributed to the surface adsorbed water and hydroxyl groups. The successful functionalization of TiO₂ nanopowder with OA was proved by the presence in the spectrum of the symmetric and asymmetric stretching modes of the COO- group at 1429 cm⁻¹ and at 1529 cm⁻¹. The absence of absorption peak at 1700 cm⁻¹, attributed to carboxyl group vibrations, demonstrates that the OA layer on TiO₂ was chemically bound rather than physically adsorbed and thus, after the washing process there was not unbound OA [12, 16, 17]. The functionalization of the titania surface with AA by the ligand exchange process was mainly proved by the comparison of the IR spectra of OA-functionalized TiO₂. In particular, the peaks corresponding to the stretching modes of COO- group at 1437 cm⁻ ¹and 1546 cm⁻¹ were blue shifted with respect to those of OA-functionalized titania. A less intense peak at 1721 cm⁻¹ evidences the presence of a small amount of unbound AA. Moreover, the distance between the peaks attributed to the symmetric and antisymmetric carboxyl stretching modes could be used to distinguish the type of interaction between the carboxyl group and the TiO₂. In the case of the AA- and OA- functionalizations, the difference between the two peaks obtained from the spectra is equal to 109 cm⁻¹ which indicated the formation of a bidentate chelate bond [18]. Differently from the pristine titania dispersions, the pH of the AA-functionalized titania was not adjusted for optimum dispersion and stability. In fact, at the end of the process, the aqueous dispersion possessing pH equal to 5.8 was quite stable and DLS measurements revealed a value of Z_{average} equal to 550 nm, not too far from the above reported optimized value obtained with pristine titania. Attempts to improve this figure by further changing the pH were not successful, demonstrating that some kind of hard aggregation was actually produced during the functionalization process.

Regarding the fumed silica suspensions, a reasonable value of $Z_{average}$ equal to 141 nm was attained using only the ultrasonic probe-assisted dispersion. The pH of the as-prepared dispersion was equal to 8, which is close to the reported optimum value for this material [19].

Characterization of films on glass slides

After the first attempts to deposit the nanocomposites on glass substrates with the two-step paintbrush and airbrush process, optical microscopy revealed the formation of the well-known coffee-ring structures [20], shown for example in Fig. 2 (a).



FIGURE 2. Optical microscopy (10X) of isolated coffee-ring titania structures on P1 (a); dense and overlapped titania coffee-rings produced by repeated air brushing coatings (b).

The formation of coffee ring nanostructures was also detected with AFM topography, as reported for two different samples in Fig. 3. These structures demonstrated a non-uniform particles distribution on the polymer surface that can affect the full exploitation of the nanophase properties in the coating. A denser, more homogeneous distribution, as that shown in Fig. 2(b), was then obtained by optimizing the airbrush nanoparticles deposition, and particularly using repeated coating cycles with smaller spray nozzle.



FIGURE 3. Topography of P2 coated by TiO₂ (a) and SiO₂ (b) nanoparticles.

The root mean square roughness R_q from mechanical profilometry of the samples surface before and after the nanoparticles depositions is reported in Table 2. The polymeric films P1 and P2 have low roughness values, and therefore, when the nanoparticles are deposited on the surfaces, R_q increases drastically. Differently, the Paraloid film has a much rougher surface, which is not affected by particles coating. After the abrasion test the bare polymeric films P1 and P2 have a rougher surface while the Paraloid seems to be polished by the mechanical abrasion. The introduction of nanoparticles coating does not influence the Paraloid resistance to mechanical abrasion. On the contrary, after mechanical abrasion, the roughness increases in the case of titania-coated P1 and P2 nanocomposites, and particularly for the ones coated with larger particles. A quite different mechanical resistance to abrasion is observed instead on the silica-coated films: their values of R_q are quite similar (around 200 nm) for the two polymers and do not change after the test abrasion. In all the cases, the severe abrasion process, developed for hard films testing, deeply alters the surface of our coatings, even if the presence of small silica nanoparticles is a promising way to improve the polymeric mechanical properties.

Sample	R _q (nm) before abrasion	R _q (nm) after abrasion	
P1	2.9	142.3	
P1 / titania nanocomposite	51.4	171.5	
P1 / AA-functionalized titania	47.2	137.9	
P2	4.7	141.3	
P2 / titania nanocomposite	64.6	144.4	
P2 / AA-functionalized titania	54.5	184.3	
P3	101.5	55.2	
P3 / titania nanocomposite	110.9	48.9	
	test		

TABLE 2. Roughness values measured on polymers and titania nanocomposites before and after the mechanical abrasion.

Regarding the adhesion test using the AFM we show in Fig. 4 an example test performed on a P2 based titania nanocomposite. The test performed on P1 and P2 polymers coated with titania prepared in different conditions (basic or acid suspensions, AA-functionalized), and with silica show that the large nanoparticles (hundreds of nm) cannot be removed by the AFM tip, being firmly anchored on the polymeric surfaces. Further tests are necessary on smaller particles which, having a smaller contact area, could be easier to remove, and/or substituting the probe with one with a higher spring force constant.



FIGURE 4. AFM scans on a P2 based AA-functionalized titania nanocomposite, performed on a $3x3 \ \mu\text{m}^2$ surface area at the minimum tip pressure (a) and at the maximum one (b), in (c) the control scan at the minimum pressure on a larger $6x6 \ \mu\text{m}^2$ surface area.

The two bare polymeric samples P1 and P2 are slightly hydrophilic since the contact angles measured are $(87\pm3)^{\circ}$ and $(89\pm4)^{\circ}$ respectively. A proper micro and nanostructuring of the surface can give a superhydrophobic behavior, as exploited in the "lotus effect" [21]. Nevertheless, we verified that our nanoparticles coated films maintain the slightly hydrophilic behavior observed on the bare polymers, demonstrating that the present preparation procedure does not produce the optimal the surface structure necessary to induce the "lotus effect". On the other hand, when a very large amount of titania nanoparticles (0.6 mg/cm²) is deposited on the polymeric surface an UV-induced superhydrophillic behavior is observed after few minutes of Hg lamp irradiation, resulting in a contact angle below 10°, as shown in Fig. 5.



FIGURE 5. Water droplet on a sample coated with large amount of TiO_2 nanoparticles, at the beginning of the UV irradiation (a) and after 5 minutes: contact angle lowers below 10° (b).

Characterization of films on marbles

The influence of the application of nanocomposites on the appearance of different lithotypes, namely historical marbles and Carrara marbles, was evaluated by colorimetry. The ΔE values calculated for each kind of lithotype before and after nanocomposite application were lower than 5, that is the maximum value admitted by UNI EN ISO 3668:2002 regulation for protective coatings, demonstrating a reduced impact on the optical appearance of substrates.

In order to test the stability of the coatings in regard to photodegradation, both kind of marbles were then exposed to UV-irradiation. While Carrara marbles samples showed very small changes in colors (ΔE <2) under168 h of UV exposure, strong changes were observed on the historical marbles, as reported in Table 3. These results may be due to the different surface finishing of the two lithotypes, since Carrara marbles are smoother, clearer and somewhat more reflecting than historical samples, thus reducing light absorption phenomena.

Among the bare polymers P2 suffered the strongest variation of colour after 336 h of irradiation. The titania nanoparticles prepared in basic suspension seemed to protect the polymer underneath better than silica and functionalized titania: for these samples ΔE values were just slightly below that calculated for the bare polymer coated sample. For P1 all the values of ΔE were lower than 2, this being the minimum value that the human eye can appreciate, and in all the samples the nanoparticles presence improved the resistance of the coating on long term irradiation. On the other hand, the samples treated with Paraloid (P3) were more sensitive to the UV exposure and the presence of nanoparticles did not preserve the original color of the protective film, which underwent a variation higher than the value tolerated by the UNI-EN regulation.

Sample name	Polymer	Nanoparticles	ΔE after coating	ΔE after 168 h UV	ΔE after 336 h UV
				exposure	exposure
MSP1	P1	-	1.92	1.23	1.53
MSP1T	P1	titania in basic suspension	0.31	1.43	0.39
MSP1TAC	P1	AA functionalized titania	0.19	1.25	0.50
MSP1S	P1	Fumed silica			
			0.62	1.12	0.21
MSP2	P2	-			
MSP2T	P2	titania in basic suspension	1.54	4.11	5.06
MSP2TAC	P2	AA functionalized titania	1.49	2.05	0.60
MSP2S	P2	Fumed silica			
			0.67	3.79	4.76
MSP3	P3	-	2.18	1.80	4.18
MSP3T	P3	titania in basic suspension			
MSP3TAC	P3	AA functionalized titania	2.19	2.88	2.67
MSP3S	P3	Fumed silica	1.83	2.16	3.64

TABLE 3. Description of the historical marbles samples with different protective coatings and the colours difference before and after protective coating deposition, and after 2 periods of UV aging.

CONCLUSIONS

In this work, polymeric nanocomposites formed by a polymer film and by a ceramic nanostructured surface layer were prepared starting from proprietary latexes or from Paraloid B72 polymer solutions, and nanopowders suspensions. Stable water dispersions of bare or acrylic acid surface-functionalized nanopowders were obtained and characterized and subsequently spray-brushed on the polymer films. Particles resulted always well bonded to the underlying polymer.

Abrasion tests permitted to highlight an evident difference of mechanical performances between the latexes and Paraloid B72. In fact, the formers have similar low values of roughness, which increase following the nanostructured layer deposition; after abrasion the bare polymers are more strongly affected than the coated ones. Paraloid B72 presents a rougher surface and seems to be polished by the abrasion test irrespective of the presence of the nanoparticles.

Colorimetric analysis on historical and Carrara marbles before and after coating evidenced the good transparency of our nanocomposites. Accelerated aging tests permitted to demonstrate that, in the historical marbles, the presence of the nanoparticles has a protective action against UV-induced damage, preventing the degradation.

The nanocomposite surface layer did not affect the wettability of the polymer, which remained slightly hydrophilic; this behavior is likely due to inadequate distribution of the nanophase. On the other hand UV-induced superhydrophilicity was observed when the concentration of surface titania nanoparticles on 0.6 mg/cm². Work is in progress to find optimized deposition conditions providing both homogeneous surface coverage and the proper micro- and nanostructuring for hydrophobic behavior.

ACKNOWLEDGEMENTS

This work was partially funded by Regione Lazio, in the framework of CoBRA Project. Authors are thankful to Dr. Piero Morales (ENEA-SSPT Department) for the use of AFM and for the fruitful discussions.

REFERENCES

- 1. A. Tsakalof, P. Manoudis, I. Karapanagiotis, I. Chryssoulakis, C. Panayiotou, J. Cult. Herit 8, 69-72 (2007).
- 2. M. Robson, in Polymers in Conservation, edited by E.S. Allen, M. Edge, C.V. Horie (The Royal Society of Chemistry, London, 1992).
- 3. L. Pinho, F. Elhaddad, D. S. Facio, M. J. Mosquera, App. Surf. Sci. 275, 389-396 (2013).
- M. F. La Russa, S. A. Ruffolo, N. Rovella, C. M. Belfiore, A. Palermo, M. T. Guzzi, G. M. Crisci, Prog. Org. Coat. 74, 186–191 (2012).
- 5. X. Zhang, F. Shi, J. Niu, Y. Jianga, Z. Wanga, J. Mat. Chem. 18, 621-633 (2008).
- 6. G. Momen, M. Farzaneh, App. Surf. Sci. 258, 5723–5728 (2012).
- 7. R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Nature **388**, 431–432 (1997).
- 8. J. P. Brusien, N. G. Gaylord, N. M. Bikales, H. F. Mark in Acrylic Esther Polymers Encyclopaedia of Polymer Science and Technology (Wiley & Sons, New York, 1964) Vol. 1, p. 246-336.
- 9. M. Favaro, R. Mendichi, F. Ossola, U. Russo, S. Simon, P. Tomasin, P.A. Vigato Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering. Polymer degradation and stability. Elsevier, 2006, 91, p. 3083-3096.
- M. Lazzari, O. Chiantore Thermal-ageing of paraloid acrylic protective polymers Polymer 41 (2000) 6447– 6455
- 11. O. Chiantore, M. Lazzari, Polymer 42, 17–27 (2001).
- 12. M. Jafarpour, M. Ghahramaninezhad and A. Rezaeifard, New J. Chem. 38, 2917-2926 (2014).
- 13. D.Q. Vo, E.J. Kim, S. Kim, J. Colloid Interface Sci. 337, 75-80 (2009).
- 14. B. Kokuoz, K.G. Kornev and I. Luzinov, Applied Materials and Interfaces, 1, 3,575-583 (2009)
- 15. MIL-C-00675, MIL-M-13508 and MIL-F-48616 norms
- 16. K. H. Park, J.Kim, O. S. Kwon, D. Lee, J. Kim, H. Yoon, C. Ahn, S. H. Song, Polymer composites, doi:10.1002/pc.23930 (2016).
- 17. D. Chen and J. Li, J. Phys. Chem. C 114, 10478–10483 (2010).
- 18. L. J. Kirwan, P. D. Fawell, W. van Bronswijk, Langmuir 19, 5802-5807 (2003).
- 19. C. Carneiro, R. Vieira, A. M. Mendes, F. D. Magalhaes, J. Appl. Polym. Sci. DOI: 10.1002/APP.37582 (2013).
- 20. R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten. Phys. Rev. E. 62, 756-765 (2000).
- 21. H. C. von Baeyer, The Sciences, 40, 12–15 (2000).