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Original article

Assessment of plasma torches as innovative tool for cleaning of historical stone materials

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ABSTRACT

Cleaning of historical stone surfaces has always been a challenging task, moreover in the last decades arose new restorations issues such as the need to remove aged conservation polymeric materials to avoid further damage. Different cleaning methodologies flourished in the past, mostly based on chemical, mechanical methods and on laser technology too. Nevertheless, these methodologies could not be so efficient in the removal of epoxy resins, acrylic polymers and hydrophobic siloxanes, because of their low solubility in solvents when aged or their high adhesion with the substrate. More recently, atmospheric plasma has been tested for such application even if it is not yet widely applied due to the lack of knowledge about possible side-effects on the artefacts. In the present work, assessment of three commercial atmospheric plasma devices (plasma torches) illustrated the potentialities and drawbacks of polymers' removal from stone surface. Commercial epoxy resins, acrylic polymers and hydrophobic siloxanes were chosen for the removal test by plasma devices. Physical and chemical effects on the stone surface and the process efficiency were investigated by means of macro- and microscopic observations, preferring, when possible, non-invasive techniques and consolidated methodologies in the field of Stone Conservation Science. An introductory experimentation on coated Si specimen has allowed to find the proper working parameters, i.e. working distance, exposure time, to have an effective removal. The experimentation conducted on different lithic substrate, coated with the commercial protective, has showed that commercial devices are effective in the removal of epoxy and acrylic coatings via chemical and physical interactions. On the contrary, the removal of siloxane products is incomplete, because of the high stability of the bond Si–O in the back bone, which is not affected by the plasma. In general, the present trials highlighted that DBD apparatus used does not promote any macroscopic effects on the polymeric coating, while arc discharge ones guarantee satisfactory results. According to these preliminary trials, it was clearly evidenced that plasma is a potential cleaning tool, despite DBD systems need higher power or arc discharge needs treatment temperature mitigation and to avoid the deposition of metallic drops on the surface of the object due to electrode deterioration.

1. Research aims

The atmospheric pressure plasma instruments are already available on the market for several purposes in manufacturing processes, as packaging or automotive industry, for surface cleaning and activation or even in medical applications such as the wounds disinfection. In the field of cultural heritage, successful results were

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already obtained for organic layer removal with plasma in vacuum chambers, for example for soot removal or disinfection of paper. Few literature sources focus on the use of atmospheric low temperature plasma torches for the removal of organic coatings. This study was carried out with the aim of assessing the use of such type of plasma for the removal of polymers from stone surfaces demonstrating the potentials and the drawbacks of the new method.

2. Introduction

Outdoor stone monuments and buildings often undergo deterioration both due to natural and anthropogenic effects. Among all, water is responsible for most of the decay processes as, besides causing erosion by abrasion, it is the carrier of soluble salts (marine or pollutant-derivatives); it enables bio-colonisation, freeze-thaw phenomena or wet-dry expansion [1]. These physical-chemical effects induce erosion, fissuring and cracking, which are the major patterns of a deteriorated stone surface. To prevent the penetration of water and its effects or to reduce the fissures of deteriorated stones, several organic materials have been used. Natural products as linseed oil, bee wax and natural resins among others were mainly applied until the middle of the 20th century. Afterwards, a wide range of commercially available polymers both for consolidation and water proofing purposes were massively used for stone conservation purposes [2–4].

With time, ageing of polymers by exposure to oxygen, pollutants, light and heat causes the loss of their fundamental properties such as transparency, hydrophobicity and adhesion [5,6], requiring in many cases, their removal to ensure a better conservation [7].

Physical and/or chemical methods are usually employed to remove aged coatings. Chemical methods usually involve the use of solvents applied by compresses or poultices that cause swelling or dissolution of the polymers with their consequent dispersion on the surface or in depth migration. Moreover, the solubility of aged polymers could be lower than that of freshly applied ones [8,9]. If chemical cleaning is not effective, physical methods might be also considered. While the use of rotating abrasive discs or brushes is not advisable, because they might damage the original surface, microblasting or cryoblasting are frequently applied in the cleaning of historic architecture [10]. The latter methodologies guarantee quick results, good removal and the possible damage induced on the surface is considerable smaller than with the former ones. Among the physical methods, the laser technology has also been widely applied. The main advantages are the limited invasiveness, high precision and good selectivity on black or dark layers, while a careful selection of experimental conditions has to be made for heat sensitive materials [11–14].

A recent innovation in the field of conservation is the use of plasma, which enables the removal of otherwise intractable materials. Plasma is an ionised gas containing highly reactive species according to the gas used (air, oxygen, hydrogen, etc.) and its current industrial applications rely on chemical and physical etching, coatings deposition or ion implantation, etc. often at room temperature [15–17].

Plasma technique in the field of cultural heritage has been firstly applied to the conservation of metals, particularly archaeological iron artefacts and silver objects in vacuum conditions [18–21], allowing the removal of chlorides and the reduction of silver sulphide corrosion products. Disinfection and consolidation of bio-deteriorated paper [22], soot removal on paintings damaged by smoke [23] and the removal of superficial organic coatings from paintings [24] by means of plasma demonstrated the challenging potentials of this technique. Nevertheless, all these applications were carried out under vacuum conditions, suitable for cleaning small and firm objects, which fit into the vacuum chamber and withstand low pressure. Plasma can also be obtained at atmospheric pressure, but in this case a high density and low temperatures are difficult to combine. To obtain the best compromise between both features, different ignition mechanisms are used [25]. Few examples of atmospheric plasma as cleaning tool can be found in literature, i.e. the removal of soot from canvas and marble was tested with one of the first patented atmospheric plasma devices (working at atmospheric pressure instead of vacuum conditions) [26]. Later, atmospheric plasma was tested in the activation of polymeric surfaces in modern art to enhance the adhesion between a non-polar polymer substrate and a polar paint layer [27], and finally, the potentials of a corona discharge and a DBD jet plasma device for the removal of polymers and natural varnishes were explored [28] as well as for the treatment of oxidised metal surfaces or altered by the presence of sulphide [29].

In order to assess the applicability of atmospheric plasma as cleaning tool for historical stone surfaces, especially as an alternative or complementary technique to more invasive or low-effective traditional methodologies, different commercial plasma devices were tested for the removal of polymers used as protective coatings for stone. The selection of polymers to be removed relied on their widespread use in the field and their difficult removability with conventional techniques. Taking also into account the conservation restraints, the potentials and limitations of these plasma devices in such an application are reported in details.

3. Materials and methods

Different stone substrates and polymeric coatings were used to assess the cleaning performance of commercial plasma torches. The substrates chosen for the present study were Istria limestone, Serena sandstone and Carrara marble. The selection of the stone lithotypes relied on those which were widely used for monuments and sculptures [30–34]. The main petrological and physical features of the stone are reported in Table 1. Carrara marble used for the present tests was thermally aged according to the *marmo cotto* procedure [35], in order to reproduce as accurately as possible the natural weathering of outdoor marble surfaces. Artificial ageing was not used for Istria and Serena specimens because, as reported in the literature [36], it does not give any satisfactory results. The polymers used for the trials were an epoxy resin, a silicon-base polymer and an acrylic emulsion. These chemicals are used for stone protection (siloxane, acrylics), filling missing parts and adhesive purposes of detached pieces (acrylics and epoxy resins). The tested materials were reported in Table 1.

Firstly, trials were performed to test the effect of plasma on sound stone. Subsequently, the products were all applied by brush on one flat side of the stone specimens, sized $5 \times 5 \times 1$ cm and/or round slices 5×1 cm, and removal trials were carried out after complete drying of the polymer (constant mass of the samples). Three different commercial atmospheric plasma torches, as listed in Table 2, were tested. When possible, all the apparatuses were tested in similar conditions, i.e. working distance and exposure time. Moreover, in the removal of epoxy and acryl coating, PVATePla was tested by using two tips with different diameter, hereafter defined as standard (hereafter Plasmapen ST) and narrow (hereafter Plasmapen NT) tips.

Plasma effects on stone surface and polymer removal efficacy were assessed by complementary techniques:

- Optical Microscopy (VHX-500FD from Keyence, Axio Imager A2 m (Zeiss) equipped with a digital camera (ProgRes and Olympus BX51);
- FT-IR spectroscopy (Spectrum One from Perkin-Elmer);
- External Reflection IR spectroscopy (ER-FTIR, Alpha-R/BC Spectrophotometer from Bruker);
- Scanning Electron Microscopy (FEG-ESEM-EDS, FEI Quanta 200F).