

# Durable Modified Polyacrylic Coatings for Cultural Heritage Protection

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## INTRODUCTION

Deterioration phenomena of ancient and modern stone cultural heritage are natural and unrestrainable decay processes mainly arising from water adsorption and percolation into stone building materials<sup>1</sup>. Once water attacks and penetrates stone surfaces, several chemical, physical and biological degradation processes can occur altering significantly, and in some cases even irreversibly, the properties of stone materials.

The application of hydrophobic coatings to stone surfaces is mandatory to protect stone artefacts from the deleterious effects occurring in the case of water exposition. The protective agent must possess several features, *i.e.* high compatibility with the substrate, high durability, transparency, easiness of application and removal, water-repellency, capability to avoid the attack of organic and inorganic contaminants; moreover, it should be permeable to water vapor.

The aim of the present work was to synthesize new polymer coatings as stone protective with satisfactory water repellent properties and improved durability, thanks to the combined use of fluorinated and long alkyl chain monomers and without the use of any photo stabilizers agents.

## EXPERIMENTAL/THEORETICAL STUDY

New types of polymer protectives were prepared via free radical polymerization between either 1H,1H,2H,2H-Perfluoro-octyl-methacrylate (POMA) or commercial stearyl methacrylate (STEA, Sigma Aldrich) and methacrylic monomers (methyl, MMA, and n-butyl, nBuMA, methacrylates)<sup>2,3</sup>. Specifically, POMA was synthesized via esterification reaction using methacryloyl chloride and 1H,1H,2H,2H-Perfluoro-1-octanol.

## RESULTS AND DISCUSSION

The properties of the home-made hydrophobizing polymers in terms of macromolecular structure, molecular weights, thermal features and water repellency were determined. Furthermore, the long-term behavior of these polymeric protective agents was estimated by means of accelerated aging tests exploiting UV radiations (in according to UNI 10925:2001 standard method for 100h, 315-400 nm for UVA rays and 280-315 nm for UVB ones). Their behavior over time was checked via Size Exclusion Chromatography (SEC) by evaluating  $M_n$  and D data of aged polymeric samples (Table 1) and by Fourier Transform Infrared (FT-IR) spectroscopy.

Sample	$M_n$ (Da) unaged	$M_n$ (Da) aged	D unaged	D aged
MMA:POMA	27000	25000	2.1	2.2
MMA:nBuMA:POMA	27000	22000	2.1	2.2
EMA:nBuMA:POMA	27000	25500	2.3	2.1

Table 1. Number average molecular weights ( $M_n$ ) and molecular weights distribution (D) measured before and after the aging test.

By evaluating  $M_n$  and D data reported in Table 1, all the synthesized polymers seem to be unaffected by UV aging. Thus, the present stable resins were applied on both natural (Botticino marble) and artificial (mortar) stone substrates and their wetting properties together with their absorption by capillarity and water vapour permeability were successfully assessed and compared. All the covered substrates show an increase of water contact angle of around 50° and a decrease in water absorption and permeation of about 50% and 20%, respectively. Lastly, in order to evaluate the stability of the applied coatings towards degradation induced by solar radiation and interaction with the atmospheric pollution, exposure to a typical polluted urban environment for some months have been carried out. For this purpose, the following analyses have been performed: contact angle measurements, SEM-EDS (Scanning Electron Microscopy with X-ray microanalysis), IC (Ion Chromatography), and colorimetric tests by CIELab elaboration.

## CONCLUSION

The use of polymeric protectives is very advantageous in fields when the hydrophobic properties and high chemical stability are required. Within this context, the use of polymer resins bearing methacrylic and fluorinated monomers along the polymeric chain can be a way to create tailor-made water repellent materials with enhanced durability, without the addition of any stabilizing agent.

## REFERENCES

1. C.E. Corcione et al., Prog. Org. Coat. 103, 193 (2017).
2. V. Sabatini et al., Prog. Org. Coat. 144, 47 (2018).
3. V. Sabatini et al., Chem. Lett. 47, 3 (2018).