



Synthesis of functionalized polyolefins with novel applications as protective coatings for stone Cultural Heritage

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ABSTRACT

Ethylene copolymers were synthesized for application as protective coatings for stone surface monuments. An increased compatibility of the apolar polyethylene with inorganic materials was obtained by introducing some oxydril and ester groups in the polymers. Two different copolymerizations of ethylene were followed: with 10-undecen-1-ol (UDO) and 7-methyl-1,6-octadiene (MOD) catalyzed by Ziegler–Natta metallocene/methylaluminumoxane (MAO) catalyst. In the first case the polar comonomer UDO was reacted with MAO prior to copolymerization to improve its compatibility with the catalyst. Residual double bonds in the copolymerization with MOD were hydroesterificated/hydrogenated. Some synthesis were performed in the presence of hydrogen as chain transfer agent to reduce molecular weights and increase solubility of the products. The polyolefins were characterized by analytical and spectroscopic techniques and their photochemical stability in environmental conditions was tested through an accelerated ageing chamber. Polyolefins were applied on stone specimens showing a slight chromatic change of the surfaces, not perceptible by naked eye. The protection performances were also evaluated in terms of water repellency, photo-oxidative stability and colour change of the treated stone surfaces in comparison with *Paraloid B-72*, an acrylic resin widely applied in the field of conservation. Ethylene/10-undecen-1-ol copolymer kept its protective efficiency after the ageing cycles thanks to its good stability to photo-oxidative degradation.

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1. Introduction

The protection of stone materials outdoor exposed from the action of atmospheric agents is one of the most critical and important aspects for the conservation of civil and historical building surfaces. Water is the main cause of stone degradation as it plays several important roles in chemical, physical, and mechanical mechanisms of degradation [1]. Water is involved in transport of air pollutants (e.g. CO₂, SO₂, NO_x) inside stones, moreover it improves biodeteriogen growth and causes mechanical stress as a consequence of the crystallization of soluble salts and freezing/thaw cycles [2,3].

Several materials, either natural or synthetic, can be employed to protect stone from water and especially synthetic polymers were

largely employed, but their application in the Conservation and Restoration has always been a controversial topic. When applied on a stone surface the synthetic protective forms a film that should minimize the alteration of the surface leaving unchanged as far as possible the permeability to water vapor. Furthermore it should provide good mechanical properties, stability over time and solubility in the common solvents for end of life polymer removal. It is well known that commercially available products generally do not meet these requirements, because they are mainly developed for other purposes. Different classes of synthetic polymers have often been applied without any consideration of the characteristic and state of conservation of the substrate and without proper knowledge of the interaction between polymers and stone surfaces. In the last few years scientists began the development of molecules with optimized molecular properties, specifically designed for the protection of stone surfaces with a special attention of those of monumental heritage.

During the last 50 years synthetic polymers have been widely employed on stone materials as adhesives, consolidants and surface protectives of Cultural Heritage. Acrylic resins have been the synthetic materials more widely used as protective coating for

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stone, due to their adequate hydrophobicity and adhesion to the surface [3]. However acrylics, both as acrylates and methacrylates homo- and co-polymers, showed a rapid ageing and decrease of the water repellence especially when applied in outdoor environments [4–7]. Natural and synthetic waxes are another class of materials employed as stone protective. Among these, microcrystalline waxes are the most promising for the protection of stone as well as metal artefacts. They show water repellence and weathering resistance comparable with acrylic materials. However microcrystalline waxes application requires rough conditions and shows very poor efficiency on porous substrates [3].

A remarkably effort in the synthesis of new products for stone protection comes from the development of fluorinated polymers. They represent a good example of a *tailor-made* product, that is a product designed for a specific application. The early fluoropolymer coatings, derived directly from the photo-oxidative polymerization of hexafluoropropene, showed promising hydrophobic and stability performances but low solubility in the common solvents and a rather poor interaction with the stone surface [8]. In order to improve their solubility, partially fluorinated polymers were synthesized through copolymerization with non-fluorinated monomers. On the other hand functional groups were introduced to improve compatibility with inorganic surfaces, thereby providing more persistent protection [9,10]. The best results were achieved during the last decades by perfluoropolyethers [8], fluorinated acrylics [11,12] and polyether-amides [13] and, more recently, by insertion of perfluoro groups into polymers obtained from renewable feedstock [14–16].

In this work we report the possible advantages of a polyolefinic product as protective for stone surface monuments avoiding the use of fluorinated compounds. Synthetic products with a hydrocarbon structure are already employed in the field of conservation, such as microcrystalline waxes (e.g. *Cosmolloid 80*), polyethylene glycols (*Carbowax*) and aliphatic varnishes (e.g. *Regalrez 1094*). On the other hand Ziegler–Natta polymerization of simple functionalized olefins has greatly advanced in the last decades and a large amount of polyolefins is commercially available to meet different requirements. At the same time the development of homogeneous *single site* metallocene catalysts greatly increased the synthetic possibilities. Metallocene catalysts are able to catalyze the synthesis of polymers with narrow molecular weight distributions and well defined microstructures, characteristics that are in agreement with the idea of *tailor-made* products even if Ziegler–Natta catalysis have never been applied to the synthesis of materials for conservation.

Two classes of copolymers, ethylene/10-undecen-1-ol (UDO) and ethylene/7-methyl-1,6-octadiene (MOD), were synthesized through Ziegler–Natta polymerization and their characteristics were optimized for stone protection purpose. The compatibility of polar inorganic substrate with apolar polyethylene was improved by insertion of polar groups along the polymer chains in the form of oxydril and ester moieties. Performances of these polymers were tested on selected marble and Lecce stone specimens with very different porosity and pore size distribution. The protection performances were evaluated in terms of water repellency, photo-oxidative stability and colour change of the treated stone surfaces in comparison with *Paraloid B-72*, an acrylic resin widely applied in the field of conservation.

2. Experimental

2.1. Materials

MeOH, EtOH, HCl 37%, toluene-*d*₈, *o*-trichlorobenzene, decalin and 1,4-bis(diphenylphosphino)butane (dppb) were purchased from Sigma–Aldrich and used without any further purification.

10-undecen-1-ol and 7-methyl-1,6-octadiene (MOD) were purchased from Sigma–Aldrich and purified through a short alumina column and dried with 4 Å molecular sieves. Toluene from Aldrich was distilled under N₂ and dried with 4 Å molecular sieves. The cocatalyst methylaluminumoxane (MAO) for polymerization was prepared by removing toluene and AlMe₃ from a commercially available MAO toluene solution (10%wt aluminium, Crompton). The MAO solution was filtered on a D4 funnel and evaporated to dryness at 50 °C under vacuum. The resulting white residue was further heated to 50 °C under vacuum overnight. The white powder was stored in a dry-box. A stock solution of MAO (100 mg/mL) was prepared by dissolving solid MAO in toluene. The solution was used within three weeks to avoid self-condensation effects of MAO. [Me₂Si(Cp*)(*t*-BuN)]TiCl₂, *rac*-[Et(Ind)₂]ZrCl₂ were purchased from MCAT GmbH, stored in a dry-box and toluene solutions were prepared immediately before use. Pd(OAc)₂, Co₂(CO)₈ and Ru₃(CO)₁₂ were purchased from Sigma Aldrich. Ethylene (Air Liquide, 99.99% pure) was deoxygenated and dried through two columns containing the BASF catalyst R3-11 and activated 10 Å molecular sieves. Argon (99.998% pure), CO (99.3% pure) and H₂ (99.9995% pure) were supplied by Siad.

The marble used for protective performance evaluation was a calcitic white marble collected from a modern quarry in the Carrara basin. Lecce stone specimens were made of a bioclastic calcarenite stone with 39% porosity and particle size distribution of 100–200 μm. All samples used had the dimension of 5 cm × 5 cm × 2 cm.

2.2. Apparatus for polymerization

Polymerization reactions were carried out in a 150 mL *Brignole AU 0,15 Ex* autoclave, at temperatures between 30 and 90 °C and ethylene pressures between 1.5 and 5 bar. Some reactions were carried out in the presence of hydrogen (3–7 bar). A mass flow controller connected to a computer with an acquisition frequency of 1 Hz was employed.

2.3. General polymerization procedure

The reactor was dried at 100 °C under vacuum for at least 2 h and purged several times with Ar prior to polymerization. It was allowed to cool to room temperature, then toluene (40 mL) was added, followed by the desired amount of comonomer and 5 mL of a 100 mg/mL MAO solution in toluene. When the polymerization temperature was reached, hydrogen was supplied, ethylene feed was started and mechanical stirring activated. Consumption of ethylene was followed with the mass flow controller. After equilibrium was reached, polymerization was initiated by injecting 1 mL of a toluene solution of the pre-catalyst (3.5 mmol/L) into the reactor using a *gas tight* syringe. The partial pressure of ethylene was kept constant with a pressure controller, and the reactor temperature was kept constant using a thermostat. The pressure control was accurate within 0.03 bar and the reactor temperature within 1 °C. The conversion of the comonomer was kept low in order to keep constant its concentration in the solution. After 90 min the polymerization was quenched with 1 mL of EtOH and the reactor degassed. The resulting polymer was washed with an acid solution (15% HCl in H₂O/EtOH) and stirred overnight. The solution was then filtered and the polymer dried under vacuum.

2.4. 10-Undecen-1-ol (UDO) copolymerization

Toluene was introduced into the dried reactor followed by 0.1–0.5 mL of (UDO). A toluene solution of MAO (1 eq) was then added and the solution stirred at 25 °C in Ar atmosphere. After 5 h another aliquot of MAO solution was introduced, ethylene supplied

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