Progress in Organic Coatings 77 (2014) 892–903

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Novel coatings from renewable resources for the protection of bronzes

Giulia Giuntoli [a,b], Luca Rosi [a], Marco Frediani [a], Barbara Sacchi [b], Barbara Salvadori [b], Simone Porcinai [c], Piero Frediani [a,*]

[a] Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia, 13, 50019 Sesto Fiorentino, Italy
[b] Institute for Conservation and Valorization of Cultural Heritage, National Research Council, Via Madonna del Piano, 10, 50019 Sesto Fiorentino, Italy
[c] Opificio delle Pietre Dure, Via degli Alfani, 78, 50121 Florence, Italy

ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form
11 December 2013
Accepted 22 January 2014
Available online 20 February 2014

Keywords:
Coating
Corrosion
Metals
Polymer
Benzotriazole
Renewable resource

ABSTRACT

End-capped poly(lactic acid)s with a benzotriazole moiety were synthesized by Ring Opening Polymerization of lactide, characterized by spectroscopic methods and tested as protective coatings on selected bronze surfaces. Performances of functionalized polymers were evaluated in terms of colour changes of the treated metal and stability of the coating. A comparison between end-capped polymers and a mixture of poly(lactic acid) and benzotriazole was also run. End-capped poly(lactic acid)s showed excellent stability to photochemical and thermo-hygrometric ageing and better performances than a blend of poly(lactic acid) and benzotriazole. These polymers show promising performances for metal's coating.

1. Introduction

Conservation and restoration of metallic objects, especially those having a historical and artistic importance have improved their relevance in the last years. Degradation phenomena due to corrosion processes and leading to alteration and disfiguring effects of the surfaces must be avoided. Preventive conservation measures, i.e. a proper control of environmental conditions (in terms of relative humidity, pollutants, etc.) are generally accepted as the best way to reduce the deterioration of metallic surfaces. However, in many situations, primarily in the case of outdoor artworks, it is difficult or not possible to assure adequate environmental conditions [1–6]. Therefore a common practice for the protection of metals is the application of a polymer-based coating on the surface.

Coating materials for conservation treatments of cultural heritage should meet different requirements if compared with coatings for industrial applications [7]. They should be transparent and leading to none or negligible changes in the appearance of the original substrate, reversible that is removable after many years without any damage for the object. Furthermore they should not modify the original artefact, including in most cases, changes suffered by the object due to its history (e.g., patinas, crusts and corrosion layers), as far as they do not threaten conservation and legibility of the object. The coating should also have a long shelf-life, that is a long stability and efficiency over time and they should be easily applied and removed with eco-friendly operations [3,7].

The most common coating materials for the protection of historic metals are acrylic resins, such as *Incralac®*, *Paraloid B44®*, microcrystalline waxes, and in some cases their combinations [8–10]. For outdoor bronzes, the most common protective coating used by conservators and restorers is the commercial *Incralac®*, a toluene solution of an acrylic resin containing benzotriazole (**BTA**) [11]. **BTA** is a heterocyclic compound which has been extensively used as anti-oxidant in many formulations for the protection of metallic surfaces. It is a very efficient corrosion inhibitor for copper and its alloys (e.g., bronze, brass) by preventing surface reactions through the formation of copper–**BTA** interactions [12–14]. However this compound is toxic for many plants, aquatic organisms and bacteria and suspicious carcinogenic agent for human [15]. Moreover its stability to UV radiation and its high water solubility, makes it very persistent and mobile in the environment.

Commercial coatings may not satisfy all the necessary requirements for application in cultural heritage, due to undesirable aesthetic features [16] and lack of stability [11,17]. Failure has been reported in many cases, often with severe damage to the underlying metallic surface [2]. Therefore, considering the special requirements necessary for metal conservation and the unique value of most of metallic cultural heritage, the scientific community takes

* Corresponding author. Tel.: +39 0554573522; fax: +39 0554574913.
E-mail addresses: piero.frediani@unifi.it, piero.frediani@gmail.com (P. Frediani).

0300-9440/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.porgcoat.2014.01.021

interest in the development of new materials that can provide a better protection, while fulfilling conservation criteria.

Nowadays, following a green chemical approach, polymers from renewable resources were tested as potential substitutes for petrochemical-based materials in many fields.

Among these compounds, particular attention has been devoted to poly(lactic acid) (**PLA**). The starting material, lactic acid, is produced using 100% annually renewable resources and the polymer may be biodegraded only if exposed to specific conditions. Furthermore both structure and molecular weight of the polymer can be easily controlled and modified through appropriate synthesis obtaining tailor made products [18].

Besides other uses (e.g., packaging, biomedical, textile), **PLA** may represent an appealing alternative to synthetic polymers commonly employed in conservation of artistic objects. On this basis, recent studies have been focused on the synthesis and characterization of modified **PLA** with particular properties for a potential application in cultural heritage. In this respect, fluorine-containing **PLA**s showed interesting performances as protective coatings for stone, such as water-repellence, chemical and photochemical stability and negligible short- and long-term modification of the appearance of the original substrate [19,20].

In this paper results concerning synthesis, characterization and performance of innovative **PLA**-based polymers useful for the protection of metallic surfaces, are reported. A benzotriazole moiety (**BT**) was chemically bonded at the end of the **PLA** chain in order to avoid the leakage of the anticorrosive agent leading to an enhanced efficiency of the coating and to a lower toxicity for operators and environment.

A series of end-capped polymers was synthesized using ^{1}H-benzotriazole-1-methanol (**HO-BT**) as initiator in the well-known Ring Opening Polymerization (ROP) [21,22]. L-lactide (the dimeric ester of lactic acid) and *rac*-lactide (the racemic mixture of L-lactide and D-lactide) were employed as monomer in the ROP catalyzed by tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) and products were characterized by NMR, FTIR, UV–vis, GPC and DSC methods. A selected polymer was applied on bare or patinated bronze substrates simulating different metal's conservation states and evaluating colour changes of the bronze surface. Morphology of the polymer coating was also investigated by SEM-EDS observations. Finally stability of the coating was tested in the course of accelerated photochemical and thermo-hygrometric ageing.

2. Experimental

2.1. Materials

L-lactide, *rac*-lactide, ^{1}H-benzotriazole-1-methanol (**HO-BT**), $Sn(Oct)_2$, *n*-hexane, chloroform ($CHCl_3$), tetrahydrofuran (THF) and deuterated solvent ($CDCl_3$, DMSO-d_6) were commercial products purchased by Aldrich, Normapur and Riedel-De Haën.

HO-BT ($CDCl_3$ as solvent) showed resonances in ^{1}H NMR spectrum at δ: 8.10 (d, 1H, H4, $^{3}J_{HH}$ = 6.0 Hz), 7.70 (d, 1H, H7, $^{3}J_{HH}$ = 6.0 Hz), 7.57 (dd, 1H, H6, $^{3}J_{HH}$ = 6.0 Hz, $^{3}J_{HH}$ = 6.0 Hz), 7.43 (dd, 1H, H5, $^{3}J_{HH}$ = 6.0 Hz, $^{3}J_{HH}$ = 6.0 Hz), 7.26 (s, 1 2H, N-CH_2-OH) ppm and in ^{13}C NMR spectrum at δ 1 1 1 1 C, C7), 70.22 (s, 1 C, N-CH_2-OH) ppm.

Efficacy of polymers as protective coating was tested on samples of a quaternary bronze alloy. Elemental analysis (%) of alloy was Fe 0.12–0.14; Ni 0.36–0.43; Cu 88.2–88.3; Zn 3.87–3.93; Sn 5.62–5.69; Pb 1.5–1.7.

An artificial patina was realized by the foundry, on several samples, using K_2S and NH_4Cl, to simulate the natural alteration of bronze. FTIR characterization of the patina revealed that it was composed by atacamite (copper hydroxychloride) and antlerite (copper hydroxysulphate) (Fig. 1).

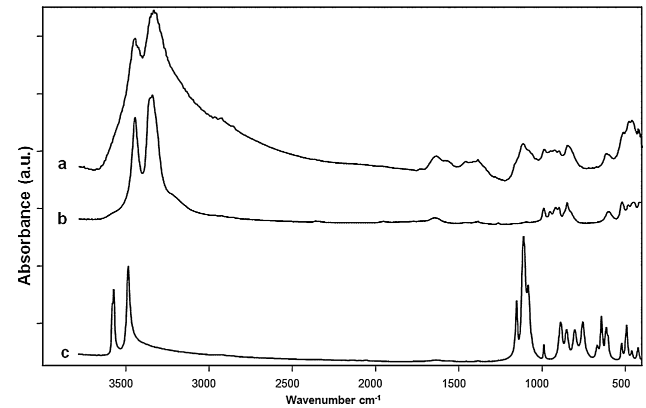

Fig. 1. FTIR spectra of micro-samples collected from (a) patina present on test specimens; (b) standard atacamite; (c) standard antlerite.

Size of bronze coupons was 5.0 cm × 2.5 cm × 0.5 cm for ageing tests in Solar Box and 5.0 cm × 5.0 cm × 0.5 cm for ageing tests in climatic chamber. Both bare and patinated coupons were used.

2.2. Synthesis of polymers

Monomer (L-lactide or *rac*-lactide) was introduced in a dried Schlenk tube under a nitrogen atmosphere. 0.5:100 $Sn(Oct)_2$/lactide molar ratio and the desired amount of **HO-BT** as initiator was then added. The polymerization was run by heating the Schlenk tube in an oil bath thermostated at 130 °C under magnetic stirring. After 3 h the reactor was cooled to room temperature. The crude polymer was purified by dissolution-precipitation method using chloroform and *n*-hexane and dried under reduced pressure overnight to remove any residual solvent.

2.3. Instruments

2.3.1. NMR spectroscopy

^{1}H and ^{13}C NMR spectra were collected using a *Varian VXR* 200 MHz spectrometer, working at 199.958 MHz for ^{1}H and 50.294 MHz for ^{13}C, using $CDCl_3$ as solvent. Residual hydrogens of the solvent were employed as reference and chemical shifts were referred to tetramethylsilane (TMS).

2.3.2. FTIR spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed with a *Shimadzu* FTIR spectrometer model *IRAffinity-1*, using either NaCl disks or a *Specac Golden Gate* single reflection diamond ATR (attenuated total reflectance) accessory. Polymer films were cast on NaCl disks using $CHCl_3$ as solvent. ATR accessory was used to collect the infrared spectra directly on neat polymers. Reflection FTIR spectra were recorded also on coated bronze coupons using a portable Bruker Alpha spectrophotometer (*OPUS* Software) with spectral range 400–7000 cm^{-1}, resolution 4 cm^{-1}, background on gold plate, 100 scans, spot size 3.4 cm × 1.4 cm. Preliminary characterization of the patina was performed collecting some spectra on micro-samples taken from the surface of the specimens with a continuum infrared microscope linked to a *Nicolet Nexus* FTIR spectrometer, with a spectral resolution of 4 cm^{-1} (128 scans) in transmission mode. The samples were flattened on a KBr support.