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Original article

Sustainable bio-nano composite coatings for the protection of marble surfaces

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ABSTRACT

Water repellency on natural stone surfaces is the most important issue in the protection of stone monuments from effects of atmospheric pollutants. In this study, effectiveness of a bio-nano composite coating, composed of a biodegradable polymer (poly-L-lactide [PLA]) and montmorillonite clay (MMT) was investigated for the protection of marble surfaces from pollution. The clay dispersion in polymer matrices was analyzed by using Scanning Tunnel Electron Microscopy (STEM) and X-Ray Diffraction (XRD), while protection performance was investigated by the measurement of surface roughness, wettability, water vapor permeability, capillary water absorption, and color changes on the marble surfaces. As a result, no alteration on the color of coated marbles was observed, significant improvement was obtained for hydrophobicity of the surface and inhibition of sulfation reaction on the exposed marble surfaces under acidic atmosphere. It could be said that PLA based nanocomposites seem to be promising materials as protective coating agents in reducing the effects of water and atmospheric pollutants on marble surfaces.

1. Introduction

Since the early ages, natural stones have been the most commonly used material in construction of buildings, sculptures, temples, etc. in every culture, due to their durability, strength and low maintenance cost. Durability and strength of the stone depend on its mineral composition, pore structure, and pore size distribution which have significant effects on the transport of gas and water vapor from the surface to inside of the stone.

Atmosphere is the main pathway for the transport of gas and particulates to the Earth's surface. Atmospheric pollutants not only cause the detrimental effects on human, animals and vegetation, but also accelerate deterioration of the earth materials. Transport of gases and water vapor initiates the deterioration on the surface of stones due to dissolved pollutant gases emitted from stationary and mobile sources.

Deterioration mechanism on the stone starts with the deposition of pollutants on the surface of the material either by dry deposition that is the transfer of gas, particulates and aerosols by wind or gravity, or wet deposition [1]. The most important pollutant responsible for deterioration of stone is sulfur dioxide (SO_2) gas. SO_2 undergoes reaction with marble, composed of mainly calcite ($CaCO_3$) crystals, converts $CaCO_3$ into calcium sulphite hemi-hydrate ($CaSO_3$. $1/2H_2O$) in the presence of the water [2–5]. Then, calcium sulphite hemi-hydrate is rapidly oxidized to gypsum ($CaSO_4{\cdot}2H_2O$) by the oxygen in the presence of water.

Gypsum is a semi-soluble mineral and occupies more volume than calcite crystals. Consequently, the marble surface starts to erode [2–4]. Therefore, many studies have been conducted to protect the stone surfaces from the attack of pollutants and penetration of water and water vapor by using coating agents like acrylic polymers, waxes, fluorinated or partly fluorinated compounds, etc. [6–8].

International Conservation Community of Historic Monuments and Building suggests that the coating agents applied on the stone surfaces should not change their transparency, and should be reversible to allow renewability of the coating without needing extra removal technique of the old coating. Reversibility is defined as a vital condition for conservation products since the treatment applied to an object intended to last for a while should allow renovation without leaving any damage on the original surface.

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However, most of the applied products were neither reversible nor showed enough protection on the surface against the acid attack [4,9]. As a result, renewal of irreversible coating agents created more damages compared to uncoated ones due to mechanical removal requirement from the surfaces [4,10].

The use of biodegradable polymer (Poly-L-lactide [PLA]) as a coating agent on the marble surface showed a great potential to fulfill the principles of the International Conservation Community of Historic Monuments and Building. Its protection performance against the acidic atmosphere signified PLA as a new generation coating material for the stone protection [5].

It is reported that even though biodegradable polymers have great commercial potential for many applications, the properties such as brittleness, low-heat distortion temperature, high-gas permeability, low-melt viscosity, etc. limit their use for further processing. Therefore, nano reinforcement in polymers provided an effective way to improve the properties concurrently [11].

Nanoparticle addition into synthetic polymer coatings was used to increase protection efficiency of stone surfaces in a few investigations. Use of silicone containing polymer matrices formed by siloxane cage penetrated by fluoropolymer, polyolefin and acrylic resins [12]; nanosilica added flouro alkylsilane [13]; silica added polymethyl methacrylate (PMMA) and functionalized perfluorinated polyether (PFPE) [14]; organoclay addition into epoxy and silane [15], silica nanoparticles addition into siloxane [16] and polysiloxane [17] were the examples of these types of studies. All of these studies showed some level of increase in thermal, mechanical and morphological properties of different type of synthetic polymers [18–20], while optical, electronic, magnetic, catalytic, chemical, and tribological properties and hydrophobicity [14,16] of the surfaces changed significantly with the addition of nanoparticles into polymers [21,22]. Similarly, addition of nanoclays into biodegradable polymers improved mechanical, barrier, and thermal properties of the polymers in biomedical and food packaging applications [23–26].

2. Research aims

In this study, further improvements in nanofiller loaded biodegradable polymer coatings on marble protection was investigated. The protection efficiency of the bio-nano composite coatings was also explored for the inhibition or slowing down the effects of sulfation reaction on the Marmara marble surfaces.

3. Material and methods

3.1. Preparation of marble samples

Marmara marble has been widely used as natural stone at historic monuments and statues in the Marmara and Aegean regions. It is mainly composed of calcite minerals and has a moderate density (2.7 g cm^{-3}) and low porosity (0.2%) values [5]. Marble slabs were prepared by cutting them into rectangular shape (nearly 1.5 cm × 1 cm × 0.15 cm) and polished with 400-grit silicon carbide powder. Then, the samples were cleaned ultrasonically in deionized water to remove fine particulates, and dried at 105 °C. Marble slabs were kept in a desiccator to bring them into a constant weight prior the use.

3.2. Preparation of biopolymer nanocomposite coatings

PLA (PL-65, intrinsic viscosity: 6.5 dl/g, Purac Biomaterials) was dissolved in chloroform approximately 8 hours at room temperature by using magnetic stirrer. Similarly, montmorillonite (MMT) clay (Cloisite 10A, d = 1.92 nm basal spacing, Southern Clay Products Inc.), modified with quaternary ammonium salt (2MBHT, dimethyl, benzyl, hydrogenated tallow), was also dispersed in chloroform at different concentrations (0, 2, 5 and 7% by weight respectively) and sonicated for an hour. Later, these solutions were mixed and stirred approximately for 15 hours at the room temperature and sonicated approximately for an hour.

3.3. Coating of marble samples

Clean marble slabs were coated by neat PLA and PLA/MMT composites (called as PLA/MMT2, PLA/MMT5 and PLA/MMT7 based on prepared concentrations) using by dip-coating apparatus (Nima-dipper) at room temperature with a 100 mm min^{-1} retraction rate. Solvent was removed from coatings by keeping in oven at 40 °C for several hours. The average thickness of coating was measured between 15-25 μm by Scanning Electron Microscope (SEM), and the coated surface areas of marble were used to calculate amount of the coating agent on the each marble by taking into account of polymer percentage in the coated solution and the amount on surface ranged between 4 and 5 g m^{-2} for the all coated marbles.

3.4. Identification and characterization of the surface and physical properties

The film samples used for the determination of montmorillonite dispersion in polymer matrices were analyzed by using X-Ray Diffraction (XRD) and Scanning Tunnel Electron Microscopy (STEM), while protection performance was investigated by the measurement of surface roughness, wettability, water vapor permeability, capillary water absorption, and color changes on the uncoated and coated marble surfaces.

X-Ray Diffraction (XRD) analysis of the coatings were conducted by using Philips X'Pert Pro MRD with Cu Kα radiation (λ = 1.542 nm) under a voltage of 40 kV and a current of 40 mA between 2° and 8°. Basal spacings of layered silicates in the PLA matrix were calculated by using Bragg's Law Eq. (1), where λ corresponds to the wavelength of the X-ray source used, θ is the diffraction angle measured and d is the spacing between diffractional lattice planes.

$$\lambda = 2d\sin\theta \tag{1}$$

Surface wettability of the samples was determined by measuring the static contact angle with deionized water using goniometer (Kruss-G10). The samples' contact angle values were calculated from the average of ten measurements on the surface of each sample and the average value with standard deviation was reported.

The water vapor permeability of uncoated and coated marble experiments were conducted on circular samples. Each of the samples replaced in the partially water filled (1/2) cylindrical PVC containers. The samples were fixed in these containers in triplicates. Then, their lids were closed and put into the oven at a temperature of 40 °C, and relative humidity around 50%. The containers were weighed every 24 h, the differences in weight were used to calculate the water vapor fluxes for uncoated and coated plates. The details of the experiment and calculations were given in our previous work [5]. Capillary water absorption (WCA) of samples was measured by gravimetric sorption technique, while color variation was determined using a colorimeter (Avantes). According to Hunter system; L, a, and b values were averaged from ten readings across for each coated marble. In this system, color is represented as a position in a three-dimensional sphere where the vertical axis L indicates the lightness (ranging from black to white), and the horizontal axes, indicated by a and b, are the chromatic coordinates (ranging from a: greenness to redness and b: blueness to