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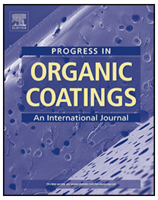

A water dispersed Titanium dioxide/poly(carbonate urethane) nanocomposite for protecting cultural heritage: Preparation and properties

L. D'Orazio*, A. Grippo

Istituto per i Polimeri, Compositi e Biomateriali del CNR, Via Campi Flegrei, 34, Fabbricato 70, 80078 Pozzuoli, Napoli, Italy

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ABSTRACT

A water dispersed Titanium dioxide/poly(carbonate urethane) nanocomposite was prepared by means of cold mixing of single components via sonication. The work was aimed at achieving a new material with properties suitable for eco-sustainable applications in cultural heritage as protective coating. The nanocomposite water dispersion prepared was subsequently deposited on Petri dish and, after water casting at room temperature, homogeneous, transparent, colourless film samples were obtained. TGA, DSC, DMTA, ATR-FTIR, FESEM and WAXS techniques were then applied in order to investigate the thermal and visco-elastic behaviours along with morphology and structure of the nanocomposite. Moreover, through methylorange decomposition, an azoic dye representative of environmental pollution, a photocatalytic test was set up on nanocomposite film samples assessing that the 1% (wt/wt) content of Titanium dioxide nanoparticles was able to confer self-cleaning ability. Interrelationships among structure, properties and uses in conservation of this kind of nanomaterial were appraised.

1. Introduction

Increasing air pollution, together with climatic change and abundant biological activity, are responsible for the growing deterioration in the last decades of the movable and immovable cultural heritage [1–4]. This cultural heritage deterioration is an inexorable process caused by several factors related both to the intrinsic characteristics of the constituent materials and to environmental conditions. Anthropogenic and climatic factors, pollution, humidity, light and heat simultaneously contribute to the material decay with different action mechanisms and extent.

A wide variety of coating and adhesive is used in the field of restoration and conservation of cultural heritage, ranging from natural products to different classes of synthetic polymers. Since the beginning of modern conservation, i.e. the second decades of the last century [5], acrylic and vinyl polymers were the most widely used. Afterwards, silicon-based products have been introduced as consolidants and water-repellents together with fluorinated compounds. In conservation and restoration such materials are mainly known with their trade names (Paraloid, Mowilith, Primal, Fluormet, etc.) and in general employed without taking into due account their structure-properties relationships and long term durability [6], despite the importance of the application and stringent requirements in terms of chemical and physico-mechanical stability. The unsuccessful experiences of the last decades on stone consolidation/protection showed that main problems are yellowing, loss of performance, trapping of deposits, formation of aggressive substances, soluble salts sub-florescences, low durability, non-reversibility. Recently, important results have been achieved for cultural heritage preservation through the application of nanotechnologies and nanomaterials both in the consolidation of wall paintings and in the paper deacidification [7–12], as biocides [13], as additive to improve the carbonation of mortars [14], and as consolidant for stone (EU project STONECORE) [15]. Although nanotechnologies are now considered the most important theoretical and applicative framework and of enhanced benefits for the development of many research areas, in literature few data are reported on polymer nanocomposites for conservation and restoration. In particular the matching of polymers with proper end properties, including eco-sustainable usage and harmless to health, and inorganic photocatalytic nanocompounds is almost uninvestigated. The development of photocatalytic products active in de-soiling as Titanium dioxide [16], is a possible way to avoid or limit soiling damage

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* Corresponding author. Tel.: +39 0818675064; fax: +39 0818675064.
E-mail address: loredana.dorazio@ictp.cnr.it (L. D'Orazio).

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Table 1
Physical properties of the nanoparticles TiO_2 water dispersion.

Aspect	White liquid
pH	5.04
TiO_2 content, wt/wt	6.24
Na content, wt/wt	1.72
Density (25 °C), g/cm^3	1.099
Viscosity (25 °C), mPa/s	2.14
Dynamic light scattering (DLS) average particle size, nm	31.08
DLS polydispersity index	0.241

slowing down such a process and reducing the frequency of onerous and costly cleaning operations.

In this work, we report on the preparation of a new water dispersed Titanium dioxide/polyurethane nanocomposite and on effects of the addition of Titanium dioxide nanoparticles on PU optical, thermal and viscoelastic behaviour. The work was aimed at achieving new coatings with self-cleaning properties imparted by the presence of Titanium dioxide nanoparticles for the safeguard of outdoor stony heritage. By means of the polymeric nanocomposites technology highly innovative and outstanding performances are expected also in terms of stability and durability as compared with other treatments. A polycarbonate urethane matrix was selected considering that PUs exhibit performances better than those shown by acrylic and vinylic polymers widely used in conservation and restoration [6,17]. Structure and morphology of nanocomposite film samples obtained by water casting at room temperature were investigated by means of ATR-FTIR, WAXS and FESEM, whereas thermal and viscoelastic properties were assessed through TGA, DSC and DMTA. A methylorange dye solution simulating pollutant agent was used to soil nanocomposite film samples and the UV–vis methylorange absorption peak monitored as a function of time. Moreover correlations among Titanium dioxide/PU nanocomposite structure, properties and uses as eco-sustainable coating in conservation were also appraised.

2. Experimental

2.1. Materials

The raw materials used in this work are reported as follows: a linear aliphatic poly(carbonate urethane) (trade name Idrocap 994) was prepared, following the prepolymer mixing process, in water dispersion by ICAP-SIRA (Parabiaco, Milano, Italy). Prepolymer is formed by reacting polycarbonate diol, $M_w = 2000$, with a molar excess of isophorondiisocyanate (IPDI), $M_w = 222.29$; in this reaction mixture an internal emulsifier 2,2-bis(hydroxymethyl)propionic acid (DMPA) is added to allow the dispersion of the polymer in water. After polymerization, the resin is dispersed in hot water in the presence of triethylamine. The M_w values of the poly(carbonate urethane) so achieved are in the range between 30,000 and 50,000 in GPS with standard PS. Titanium dioxide (TiO_2) nanoparticles synthesized and kindly supplied in water dispersion by the research center CE.RI.Col of Colorobbia Italia (Sovigliana, Vinci, Florence, Italy). The physical properties of such a dispersion are reported in Table 1.

Methylorange dye supplied by BDH Chemical, England. All the reactants and solvents were used as received.

2.2. Preparation of the nanocomposite

The preparation of TiO_2/poly(carbonate urethane) nanocomposite was performed by cold mixing the single components via sonication. The subsequent deposition of the water dispersion so achieved on Petri dish allowed the formation of nanocomposite film from water casting at room temperature, in line with our final research goal of obtaining nanocoatings with low environmental impact suitable to be safely applied on substrates with cultural value. TiO_2/poly(carbonate urethane) nanocomposite containing 1% (wt/wt) of TiO_2 nanoparticles were prepared in a sonicator MSE PG.1254 MK2. To promote TiO_2 nanoparticles dispersion the sonication process was carried out at 10 μS for the first 5.00 min and then at 12 μS for further 5.00 min.

Film samples with an average thickness of 1.00 mm of TiO_2/poly(carbonate urethane) nanocomposite and of plain poly(carbonate urethane) were achieved pouring 10 g of sonicated dispersion in Petri dishes with 7.00 cm diameter at room temperature for a water casting time of 36 h. By visual inspection both plain poly(carbonate urethane) and TiO_2/poly(carbonate urethane) films look homogeneous, colourless and transparent, Such a film aspect falls within the main properties required to protective and/or consolidant agents. Typical FTIR spectra of the poly(carbonate urethane) without and with TiO_2 nanoparticles are compared in Fig. 1. As shown, a part of the absorption peak at 680 cm^{-1} to be assigned to TiO_2, the characteristic absorptions peaks of the plain PU remain unchanged in the nanocomposite. Frequencies and assignments of the main absorption bands of the poly(carbonate urethane) phase are reported in Table 2.

Table 2
Frequencies and assignments of the main absorption bands of the poly(carbonate urethane) phase.[a]

Assignment	Frequency
N—H(ν)	3342 cm^{-1} (m)
C—H(ν)	2920 cm^{-1}
	2940 cm^{-1} (s)
C=O(ν) (carbonate)	1740 cm^{-1} (s)
C=O(ν) (urethanic)	1732 cm^{-1} (s)
N—H(β)	1541 cm^{-1} (m)
C—O(ν) (urethanic)	1242 cm^{-1} (s)
C—O(ν) (etheric)	1135 cm^{-1}
	1145 cm^{-1} (w)

s = strong, w = weak, m = medium: peak relative intensity.

[a] Main assignments: ν=stretching, β=bending.

2.3. Experimental techniques

The thermal stability of the TiO_2/poly(carbonate urethane) nanocomposite and of the plain poly(carbonate urethane) was evaluated by ThermoGravimetric Analysis (TGA) with a thermogravimetric analyzer Perkin Elmer TG – DTA Pyris Diamond instrument. Film samples were initially kept at 50 °C for 15 min to stabilize their initial weight and then heated from 50 to 650 °C with a rate of 10 °C/min under nitrogen flow of 25 ml/min.

The TiO_2/poly(carbonate urethane) nanocomposite thermal properties were analyzed by Differential Scanning Calorimetry (DSC) with a Mettler DSC 822 instrument and compared to that shown by the plain polymer. 5.00 mg film samples were subjected to the following cycle: heating from 25 to 100 °C with a rate of 10 °C/min, isothermal heating at 100 °C for 3 min, cooling from 100 to −100 °C with a rate of −10 °C/min and finally heating from −100 to 150 °C with a rate of 10 °C/min.

The viscoelastic behaviour of both nanocomposite and plain poly(carbonate urethane) was investigated through dynamic mechanical thermal analysis (DMTA) using a Perkin Elmer Pyris Diamond DMA apparatus. Tests were performed in bending mode, applying a strain of 1%. Single-frequency measurements at 1 Hz were performed at constant heating rate of 0.5 °C/min, in the temperature range from −100 °C up to 150 °C. Multi-frequency tests were performed at constant heating rate of 0.5 °C/min in the temperature range from −100 °C up to 150 °C in tensile mode at frequencies: 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10 and 20 Hz.