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Surface patterning of micron-sized aluminum flakes by seeded dispersion polymerization: Towards waterborne colored pigments by gold nanoparticles adsorption

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ABSTRACT

The concomitant polymer embedding and surface patterning of micron-sized aluminum flakes by dispersion polymerization of styrene is reported. The aluminum pigments coated by a thin silica layer were modified by trimethoxysilylpropyl acrylate grafting (TMSPA-grafted Al@silica). Dispersion polymerization of styrene was further performed in alcoholic or hydro-alcoholic media in the presence of the organically modified TMSPA-grafted Al@silica pigments as a seed and poly(*N*-vinylpyrrolidone) (PVP) as a steric stabilizer to lead to hybrid aluminum flakes. The weight fraction of polymer onto the aluminum pigment surface was tuned from 14 to 29 wt.% by the hydro-alcoholic continuous phase composition and from 19 to 38 wt.% by the initiator content. The chemical nature of the initiator plays an important role in the surface patterning of the hybrid aluminum flakes as 2,2′-azobis(isobutyronitrile) initiator provided polymer nodules, *i.e.* due to a pattern of polymer protrusions with nodules shape at the surface of the inorganic substrate, while a flat and continuous polymer layer was obtained with 2,2′-azobis(2-amidinopropane) dihydrochloride initiator. Moreover, the introduction of ammonium groups at the surface of the polymer particles was possible by the delayed addition of a cationic acrylate co-monomer ([2-(acryloyloxy)ethyl]-trimethylammonium chloride) rendering the pigments dispersible in water. Finally, gold nanoparticles were successfully deposited onto the micro-patterned aluminum flakes to open the way towards new colored aluminum pigments. Both location of cationic ammonium function in the polymer nodule and nature of gold nanoparticles ligands were investigated with the aim to evaluate the amount of adsorbed gold nanoparticles. The final hierarchically patterned aluminum pigments dispersed in water exhibited an intense purple color.

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1. Introduction

Micron-sized aluminum flakes are an important class of pigments used in sectors of automobile, painting, and packaging to provide lustrous and shiny appearance to mimic metallic coatings. To enlarge their field of application, special efforts are still devoted to the design of new materials with more sophisticated and attractive visual appearance. Indeed, the elaboration of inorganic pigments with interference colors [1] or vivid and bright color remains challenging. In a first attempt on the synthesis of colored polymer mica or aluminum flakes, our group reported the adsorption [2–4] or covalent grafting by surface-initiated nitroxide-mediated controlled radical copolymerization [5] of colored hydrophobic polymer chains with a dye containing acrylate. Though this method enabled the synthesis of colored materials with organic dye covalently incorporated inside a polymer coating, only fade colors were achieved.

The first issue addressed by the present study concerns the improvement of visual aspects of the aluminum flakes and the

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second issue is devoted to the elaboration of waterborne aluminum flakes based formulation. We propose in the present work to design aluminum pigments patterned on their surface by polymer submicronic nodules decorated with adsorbed gold nanoparticles. Indeed, monodisperse gold nanoparticles are known for their unique optical properties providing intense color tuned by the particle size (plasmon absorption) [6]. Moreover, the surface patterning by anchored sub-micron latex particles could open the way towards physical colors depending on the quality of the pattern ordering as in colloidal crystals [7–9]. Seeded dispersion polymerization of styrene carried out in ethanol has previously proved to be a suitable method to control the morphology of polymer encapsulated inorganic particles by using silica particles as seeds after surface modification by methacryloxymethyltrimethoxysilane to promote the nucleation at the surface of the inorganic particles [10]. Dispersion polymerization of styrene in presence of platelet inorganic particles has been also described with nano-clays to prepare either polymer particles armored by modified clays acting as a stabilizer [11,12], or polystyrene clay nanocomposite colloidal particles [13]. Only one example reported the encapsulation of aluminum flakes by dispersion polymerization of styrene in ethanol using reactive surfactants with a polyoxyethylene chain [14]. Anionic and nonionic vinylic surfactants were adsorbed onto the surface of the metallic particles prior to perform dispersion polymerization of styrene which produced large polymer particles with size ranging between 10 and 30 μm [14]. For the present study, the flaky aluminum was coated by a thin silica layer prepared through the sol–gel process in order to first prevent corrosion of aluminum pigment in water [15–17] and secondly to allow the covalent attachment of trimethoxysilylpropyl acrylate (TMSPA) in order to copolymerize and then contribute to the nucleation step of polymer latex particles onto the aluminum surface. The hybridization of the TMSPA grafted aluminum flakes will be performed by seeded radical dispersion polymerization of styrene with the aim to pattern the pigment surface by polymeric nodules.

For sustainable development issues, the development of waterborne formulations is highly encouraged. As polystyrene embedded aluminum pigments are not readily dispersible in water, a cationic co-monomer will be introduced in the course of dispersion polymerization in order to facilitate the subsequent transfer of the polymer patterned aluminum flakes into an aqueous phase. Moreover, the cationic [2-(acryloyloxy)ethyl]-trimethylammonium chloride (AETMAC) co-monomer was envisaged to promote the amount of deposited carboxylic acid stabilized gold nanoparticles by electrostatic interactions. The adsorption of gold nanoparticles onto platelet inorganic particles has been previously studied with nanoclays [18,19], but to the best of our knowledge, no example of gold nanoparticle adsorption onto micrometric aluminum platelets has been reported yet. Herein, we describe for the first time the synthesis of stable waterborne polymer patterned aluminum pigments covered by gold nanoparticles for coloring purposes.

2. Experiment part

2.1. Materials

Absolute ethanol (EtOH, 99.9%, Aldrich), isopropanol (IpOH, 99.9%, Aldrich), ammonium hydroxide (28% in water, Aldrich), trimethoxysilylpropyl acrylate (TMSPA, 98%, Aldrich), poly(*N*-vinylpyrrolidone) (PVP, $\overline{M_w}$ = 360,000 g mol^{-1}), potassium tetrachloroaurate (III) ($KAuCl_4$, 99.995% Aldrich, trisodium citrate, ≤99% Fischer Scientific), 2,2′-azobis(2-amidinopropane) dihydrochloride (AAPH, 97%, Aldrich), 11-mercaptoundecanoic acid MUA (95%, Aldrich) and [2-(acryloyloxy)ethyl]-trimethylammonium chloride (AETMAC) (also called trimethyl(2-prop-2-enoyloxyethyl)azanium chloride, ADAMquat, Arkema®) were used as received. Styrene (99%, Aldrich) was distilled under vacuum prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN, 97%, Acros Organic) was recrystallized from ethanol. Silica-coated aluminum pigments, grade EMR 7640, with average sizes of 15 μm length, 0.4 μm thickness and specific surface area of 5 m^2 g^{-1} were supplied by Toyal Europe. The supplied aluminum pigments had been previously encapsulated in a thin silica layer of roughly 25 nm synthesized by a sol–gel process [17] and therefore named Al@silica in the present work. Prior to use, the aluminum pigments were washed with ethanol by centrifugation–redispersion cycles to remove residual products of sol–gel chemistry and dried under vacuum at room temperature.

2.2. Characterization techniques

Thermogravimetric analysis (TGA) experiments were carried out using a system TA 2950 apparatus to quantify the amount of encapsulating polymer in a temperature range of 50–600 °C at a scan rate of 10 °C min^{-1} under air atmosphere.

Size-exclusion chromatography (SEC) was running at 30 °C with THF as an eluent at a flow rate of 1 mL min^{-1}. The SEC system was equipped with three Waters Styragel columns HR 0.5, 2, 4 working in series (separation range 1×10^2–3×10^6 g mol^{-1}) and a Viscotek ERC 7515-A refractive index detector. Number-average molar mass ($\overline{M_n}$) and dispersity ($\overline{M_w}/\overline{M_n}$) were calculated with a calibration derived from PS standards using OmniSEC® software. All polymers samples were prepared at 1–5 g L^{-1} concentrations and filtered through PVDF 0.45 μm filters.

X-Ray photoelectron spectroscopy (XPS) analyses were performed with a Surface Science Instrument spectrometer at room temperature, using a monochromatic and focused (spot diameter of 600 μm, 100 W) AlK_α radiation (1486.6 eV) under a residual pressure of 5×10^{-8} Pa. The hemispherical analyzer worked at 50 eV for high resolution spectra and 150 eV for quantitative analysis. The binding energy scale was calibrated from the carbon contamination using the C(1s) line (284.6 eV) (a mean atomic percentage of 8% was determined).

UV–visible spectra of aqueous dispersion of particles were recorded on a Shimadzu UV 2101 from 800 nm to 400 nm.

Environmental scanning electron microscopy (ESEM) images were achieved using an Electroscan E3 scanning microscope, operated at an accelerating voltage of 25 keV. Electron micrographs of the sample were recorded at different magnifications, ranging from 500 to 3000.

Transmission electron microscopy (TEM) images were recorded using a Philips EM 120 electron microscope operating at 120 kV. PS-coated pigments covered by gold nanoparticles were observed by TEM. Drops of diluted suspensions were air-dried on carbon films deposited on 200-mesh copper grids. The excess liquid was blotted with a filter paper.

2.3. Synthesis

2.3.1. Modification of Al@silica pigment with TMSPA (TMSPA-grafted Al@silica)

TMSPA grafting was carried out according to a procedure previously described [20] and commonly used by ours groups to functionalize the silica nanoparticles surface [21,22]. Typically, to a mixture made of 45 g of absolute ethanol, 0.6 g of H_2O (1.7 mol L^{-1}) and 0.6 g of ammonium hydroxide solution (0.25 mol L^{-1}) were added 3 g of Al@silica pigments and 0.4 g of TMSPA. The resulting

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