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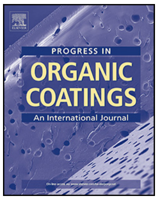

Double in-situ synthesis of polyacrylate/nano-TiO_2 composite latex

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ABSTRACT

Polyacrylate/nano-TiO_2 composite latex was prepared via double in-situ polymerization using acrylamide (AM), vinyl acetate (VAc), butyl acrylate (BA) and methyl methacrylate (MMA) as monomers, tetrabutyl titanate ($Ti(OBu)_4$) as precursor of TiO_2. The morphology, structure and distribution of composite latex were characterized by Transmission Electron Microscope (TEM), Fourier Transform Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS) and X-Ray Diffraction (XRD). The thermal stability, anti-yellowing and antibacterial properties of composite latex were also investigated. The results showed that nano-TiO_2 consisted in polyacrylate latex and it was located on the surface of latex particles. The average particle size of polyacrylate/nano-TiO_2 composite latex was 156.6 nm, which was bigger than that of pure polyacrylate (125.1 nm). The introduction of nano-TiO_2 improved the thermal stability, anti-yellowing and antibacterial properties of the latex film. At last, the polyacrylate/nano-TiO_2 composite latex was applied in leather finishing. Compared with polyacrylate latex, the properties of the leather finished by polyacrylate/nano-TiO_2 composite latex were enhanced: water vapor permeability increased by 58% and water uptake decreased by 3.52%.

1. Introduction

Finishing is an important process in leather manufacture. It can cover blemishes on leather and endow leather special effects to make the leather more beautiful and durable. Acrylate polymers, by far, are still the main film materials for leather finishing because of the advantages of good flexibility, toughness, and film-forming properties [1,2]. However, the poor mechanical and thermal resistance and low water vapor permeability restrict their applications. Moreover, if they are used for white leather and light leather finishing, the leather will suffer yellowing and plaque, which damage the appearance of leather greatly. Adding antioxidants, UV absorbers and anti-bacterial agents to the finishing formulation is a good way to delay the yellowing and plaque, but it is hard to keep a long-lasting effect.

Composites consisting of inorganic particles and polymers have attracted much attention due to the possibility to integrate the advantages of different materials, for instance, enhance the overall performance of polymer in mechanical, electrical and photonics properties [3–5]. In our previous researches, polyacrylate/nano-SiO_2 composite latex was synthesized via physical bending, in-situ polymerization, polymerization and sol–gel in one step [1,2,6]. The incorporation of nano-SiO_2 improved the mechanical and other applied properties of polyacrylate latex. Similarly, nano-TiO_2 not only has small size, high surface area and good mechanical properties, but also has some special functions such as ultraviolet radiation shield property and photocatalysis effect [7]. Jiang et al. [8] prepared polyacrylate/nano-TiO_2 composite and then applied it on the cotton fabric. The fabric after finishing exhibited excellent self-cleaning property. Xing et al. [9] studied the effect of nano-TiO_2 on the antibacterial and physical properties of polyethylene (PE)-based film. Results indicated that the antibacterial activity as well as the tensile strength and elongation at break of the TiO_2-incorporated PE film increased greatly.

In addition, there have been many researches on the bactericidal effect of nano-TiO_2, and the antibacterial mechanisms are various. Gogniat et al. [10] pointed out that the aggregation of bacterial onto TiO_2 particles was the key step in photo killing because hydroxyl radicals had an extremely short lifetime and must be generated near the cell membrane. Fu et al. [11] reported that the antibacterial effects of nano-TiO_2 were related to the particle size, surface area, band gap energy and active sites of nanoparticles prepared. Kuhn et al. [12] described that the microbial destruction was attributed to the direct damage of hydroxyl radical to cell walls. Mritunjai et al. [13] reported that antibacterial effect of TiO_2 was size and dose dependent. And Xing et al. [14] demonstrated TiO_2 nanoparticles

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Table 1
Main chemicals and their amounts.

	Stabilizer preparation					Composite emulsion polymerization				
	AM	BA	VAc	KPS	$NaHSO_3$	MMA	BA	KPS	$Ti(OBu)_4$	A-151
g	0.54	3.88	3.91	0.25	0.076	4.47	5.72	0.394	0.422	0.6
mmol	7.597	30.272	45.417	0.925	0.730	44.646	44.628	1.457	1.240	3.15

were effective for inhibiting both gram-positive and gram-negative bacteria.

The main preparation methods of polymer/nano-TiO_2 composite include physical blending [15–17] and in situ polymerization [18–20]. Chen et al. [17] synthesized poly(AA-co-MMA)/nano-TiO_2 composites latex via physical bends of poly (AA-co-MMA) and nano-TiO_2. Ahmad et al. [19] successfully prepared PMMA/TiO_2 nanocomposites by in-situ polymerization of methyl methacrylate using benzoyl peroxide as initiator in water medium. However, these methods are not easy to achieve the uniform dispersion of nano-TiO_2 in polymers since TiO_2 is synthesized in advance. At the same time, surfactant is indispensable during the preparation of polymer/nano-TiO_2 composite latex, which is easily to migrate towards the surface of latex film and result in the deterioration of latex film performance.

In this work, polyacrylate/nano-TiO_2 composite latex was prepared via double in-situ approach, where the polymerization of monomer and the production of nano-TiO_2 were carried out in one system simultaneously. Amphiphilic copolymer was utilized as stabilizer to avoid the use of emulsifier and to achieve emulsifier-free emulsion polymerization. On the other hand, amphiphilic copolymer has good compatibility with polyacrylate. Once nano-TiO_2 was produced, hydroxyl groups on it could immediately bond with the chain of polymer by coupling agent, leading to the uniform dispersion of nano-TiO_2 in polymers. Therefore, double in-situ method and the usage of amphiphilic copolymer as stabilizer are effective strategies to solve above problems. Nano-TiO_2 can be uniformly dispersed in polymers, and the stability of composite latex can be improved by chemical bonds. At the same time, the migration of emulsifier to the latex film surface can be avoided. But there are only a few reports about it because of the fast hydrolysis speed of the precursor into nano-TiO_2, which may cause the instability of polymerization process. Hence, the hydrolysis speed of the precursor was slowed down by controlling the process condition, such as, temperature and pH, to achieve the successful application of double in-situ approach in this work. The synthesis mechanism, structure and properties of polyacrylate/nano-TiO_2 composite latex via double in-situ approach were discussed in detail.

2. Experimental procedures

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), vinyl acetate (VAc), acrylamide (AM), potassium persulfate (KPS), sodium hydrogen sulfite ($NaHSO_3$) and tetrabutyl titanate ($Ti(OBu)_4$) were brought from Tianjin Haijin Fine Chemical Plant. Triethoxyvinylsilane (A-151) was made by Tianjin No.3 Chemical Reagent Factory. Deionized water was prepared in our laboratory. All the chemicals are of analytical pure and used without further purification.

2.2. Preparation of polyacrylate/nano-TiO_2 composite latex

A 250 mL three-necked round-bottom flask was equipped with a reflux condenser, a thermometer and a magnetic stirring bar. The reactor, charged with deionized water (60 g), AM (0.54 g), BA (3.88 g) and VAc (3.91 g), were immersed in a water bath at 60 °C. It was stirred at 350 rpm for 20 min. Then 5 g aqueous solution of $NaHSO_3$ (0.076 g) and KPS (0.25 g) was added to the flask. The temperature was heated to 85 °C and maintained for 1.5 h. After cooling the reactants down to 40 °C, A-151 (0.6 g) and $Ti(OBu)_4$ (0.422 g) were added to the flask. When the reaction temperature was risen to 75 °C, 10 g aqueous solution of KPS (0.394 g) and the mixture of BA (5.72 g) and MMA (4.47 g) were dividedly added into the flask dropwise. Then the reaction temperature was controlled to 80 °C, and the polymerization was carried out for another 2 h. The main chemicals and their amounts are gathered in Table 1.

2.3. Characterization

Fourier transform infrared spectrometer (FTIR) analysis was performed by FTIR-5DX FTIR (Nicolet Company, America). The samples were pressed into pellet with potassium bromide powder. X-ray diffraction was used to determine the crystal structure of samples. The X-ray diffraction pattern was recorded in the range of 2θ between 5° and 70°. The morphologies of polyacrylate latex and polyacrylate/nano-TiO_2 composite latex were observed by JEM-10OCXII TEM (JOEL Company in Japan). Before test, the polyacrylate latex was stained by phosphomolybdic acid, and the polyacrylate/nano-TiO_2 composite latex was not stained. The average particle size and zeta-potential of polyacrylate/nano-TiO_2 composite latex particles were obtained by a Zetasizer NanoZS (Malvern Instruments Ltd., UK). Thermogravimetric analysis (TGA) was carried out in a Perkin-Elmer thermogravimetric analyzer under air stream. The temperature gradient started from 25 °C to 600 °C at a heating rate of 10 °C/min. The latex samples before characterization was filtered by gauze of eight layers.

2.4. Determination of monomer conversion

The monomer conversion during the polymerization of amphiphilic copolymer P(BA/VAc/AM) and polyacrylate/nano-TiO_2 composite latex were determined by gravimetric method. First, 2000 g latex and three drops of hydroquinone (2%) were added into a weighing bottle pre-dried to a constant weight. Then the weighing bottle was placed into the oven at 105 °C, drying to constant weight again. The monomer conversion (Y%) was calculated according to the following equation:

$$Y\% = \frac{[(m_2 - m_0)/(m_1 - m_0) - A]}{B} \times 100\%$$

where m_0 is the weighing bottle mass, m_1 is the total mass of polymer and weighing bottle, m_2 is the total mass of polymer and weighing bottle after constant weightiness, A represents the mass fraction of the volatile components in polymerization formula, and B stands for the mass fraction of monomer composition in polymerization formula.

2.5. Determination of centrifugal stability

The stability of polyacrylate/nano-TiO_2 composite latex was determined by centrifugation. 10 mL of polyacrylate/nano-TiO_2 composite latex was put into a centrifuge tube and centrifuged under 3500r/min for 10 min. Then the precipitation was weighted to evaluate the centrifugal stability of composite latex.