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Polyacrylate/silica nanoparticles hybrid emulsion coating with high silica content for high hardness and dry-wear-resistant

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ABSTRACT

Polyacrylate/silica nanoparticles hybrid emulsion (PSHE) with high silica content was produced and used in the preparation of high hardness and dry-wear-resistant coating via a facile and environment-friendly method. Specifically, the surface of alkaline silica sol nanoparticles was modified by cationic polyacrylamide (CPAM), which was then added in an emulsifier-free polymerization system comprised of methyl methacrylate (MMA) and butyl acrylate (BA). Through electrostatic attractions, hydrogen bonds, and van der Waals force, the positive charged silica nanoparticles aggregate around polyacrylate emulsion particles to improve the hardness and dry-wear-resistant of PSHE coating. Our results confirmed an average size of the PSHE particles only 58.6 nm. A bimodal molecular weight distribution (MWD) and consequently two different glass transition temperatures (Tg) were found in such PSHE polyacrylate resin. Due to the presence of modified silica nanoparticles, a reduced polymerization degree of MMA monomer in the aqueous phase of core emulsion leads to a decreased first Tg and the high molecular weight fraction with highly compacted molecular structure, and the improved mechanical properties of the PSHE coating. The chains of relatively low molecular weight fraction of polyacrylate move more easily during film formation, which prevents the structural voids in the coatings. Better adhesion as well as higher hardness, impact resistance, dry-wear-resistance, and thermal stability are found when compared with its pure polyacrylate emulsion (PPE) coating counterparts. Although having high silica content, the PSHE coating still retains 90% transparency rate in visible light range.

1. Introduction

With growing attention on the environment protection, water-based inorganic/organic nanomaterial, particularly polyacrylate/silica nanoparticles hybrid emulsion [1] becomes more attractive due to their excellent mechanical, thermal, electrical, optical properties [2–7] and cheap price. However, due to their high specific surface area, surface energy and change of pH, silica nanoparticles tend to aggregate into large microparticles, even in gel if the content of silica nanoparticles was high [8]. Without appropriate chemical modification, the maximum allowance of silica nanoparticles is usually limited to 15 wt% or less [9]. Coatings made of such hybrid emulsion resins often exhibit low hardness, poor adhesion, and low transparency [10–12].

To improve the dispersion of silica nanoparticles, Hossein Riazi et al. [13] modified silica nanoparticles with a silane coupling agent bearing unsaturated carbon double bond to increase its hydrophobicity and enhance its ability to take part in free radical polymerization. After the polymerization, organic-inorganic hybrid particles of nanosilica encapsulated by Poly(methyl methacrylate-co-butyl acrylate) were synthesized. Christian Hübner et al. [14] synthesized nanosized silica spheres by the Stöber method. Then the silica spheres directly were modified with a silane coupling agent. The emulsion polymerization of styrene led to hemispherical single-core-structured silica–polystyrene composite particles. Zhang et al. [15] modified colloidal silica (R301) with water-soluble poly(ethylene glycol) monomethyl ether methacrylate (PEGMA) via hydrogen bonds, followed by dispersing modified silica (R301-PEGMA) into a waterborne UV-curable polyurethane (WUPU) via phase-inversion emulsification. However, the silica nanoparticles used in some reports were prepared with TEOS by sol-gel methods [16]. Organic solvents are needed to dissolve TEOS during the polymerization process, which is not environmentally friendly. Moreover, the involved complicated modification processes and expensive materials also hinder their future industrial practice.

In this paper, a polyacrylate/modified silica nanoparticles hybrid

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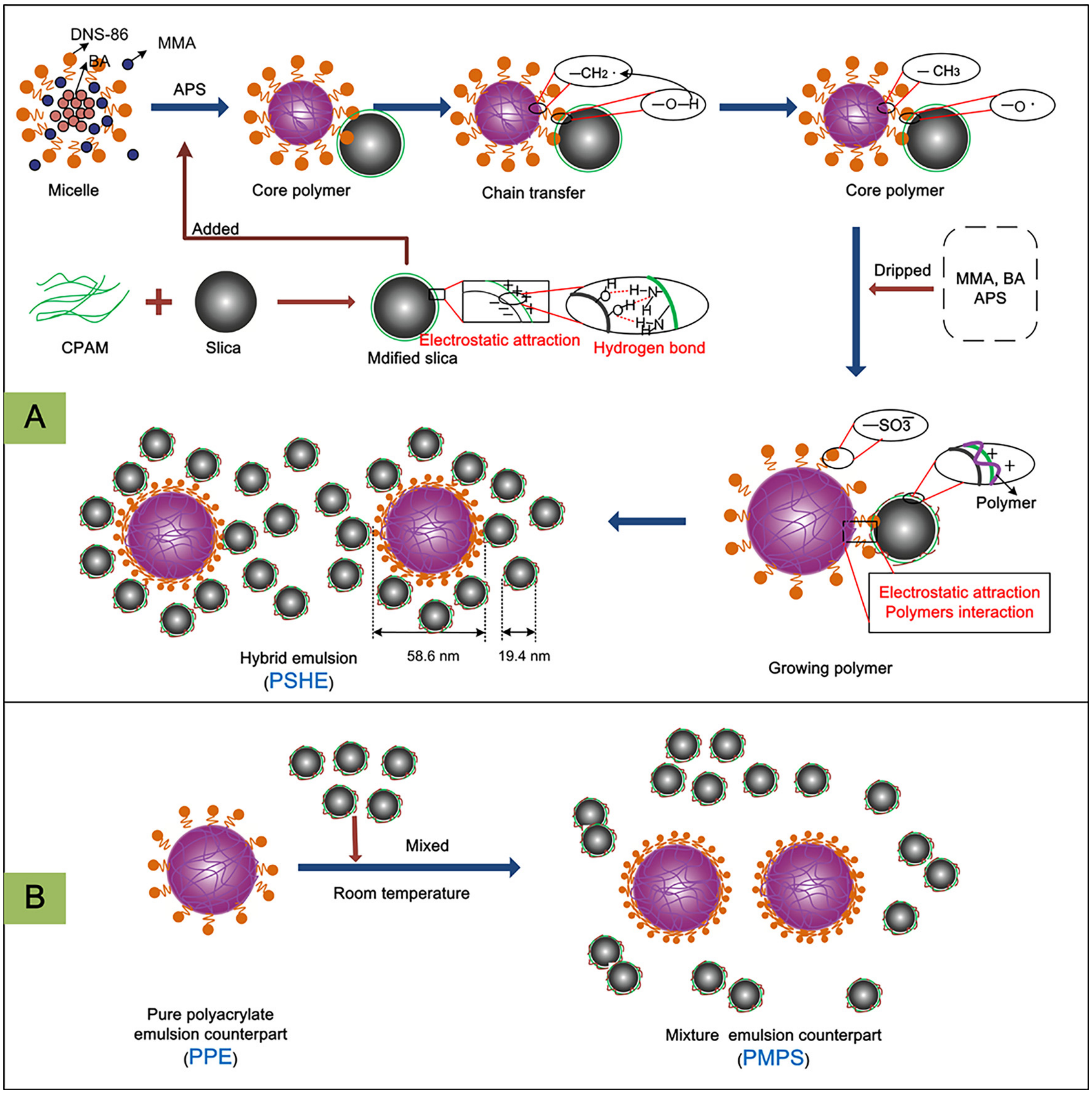

Scheme 1. Schematic illustration of the preparation of PSHE (A) and PMPS (B).

emulsion (PSHE) with high silica content (25 wt%) was prepared via an emulsifier-free polymerization. The specific procedure of PSHE is shown in Scheme 1(A). Firstly, because the alkaline silica sol is a cheap inorganic material and silica has high mechanical properties, alkaline silica sol nanoparticles are coated by cationic polyacrylamide (CPAM), whose positive charges and amino groups can promote their adsorption on the surface of alkaline silica sol nanoparticles by van der Waals force, electrostatic attraction, and hydrogen bonding [17]. It also somewhat scrambles the hydroxyl groups of silica. Modified silica nanoparticles are then added at the beginning of the emulsion polymerization. These modified silica nanoparticles are expected to uniformly adsorb on or stay close to the surface of the polyacrylate emulsion particles to form a hard shell so that the polyacrylate chains could be protected from breaking [18]. In this way, PSHE with high silica content, desired molecular weight distribution (MWD) and improved coating properties is expected.

2. Experimental

2.1. Materials

The cationic polyacrylamide (CPAM) was produced by Suzhou Shengyu Industry and Trade Co., Ltd. The alkaline silica sol (pH = 10–11, 30% silica content, the average diameter of alkaline silica sol nanoparticles is 18 nm) was bought from Guangzhou Suixin Chemical Co., Ltd. Methyl methacrylate (MMA), butyl acrylate (BA) and ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) (DNS-86) were obtained from Shanghai Outer Trade Co., Ltd. Ammonium persulfate (APS) was bought from Shanghai Lingfeng Chemical Reagent Co., Ltd. Sodium hydrogencarbonate ($NaHCO_3$) was bought from the Guangzhou Chemical Reagent Co., Ltd. Film forming additives 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol) was purchased from Eastman Chemical Company. Distilled water was prepared in our lab.

2.2. Modification of alkaline silica sol nanoparticles

An aqueous solution of CPAM (0.5 wt%) was made first, followed by mixing with 100 g alkaline silica sol in a 250 ml three-necked flask under agitation (150 rpm). The temperature of the mixture was kept at 75 °C in a water bath for 3 h to get the modified silica nanoparticles.

2.3. Synthesis of PSHE and physical mixture of pure polyacrylate emulsion and modified silica nanoparticles (PMPS)

The preparation route of PSHE is shown in Scheme 1(A). 44.3 g