

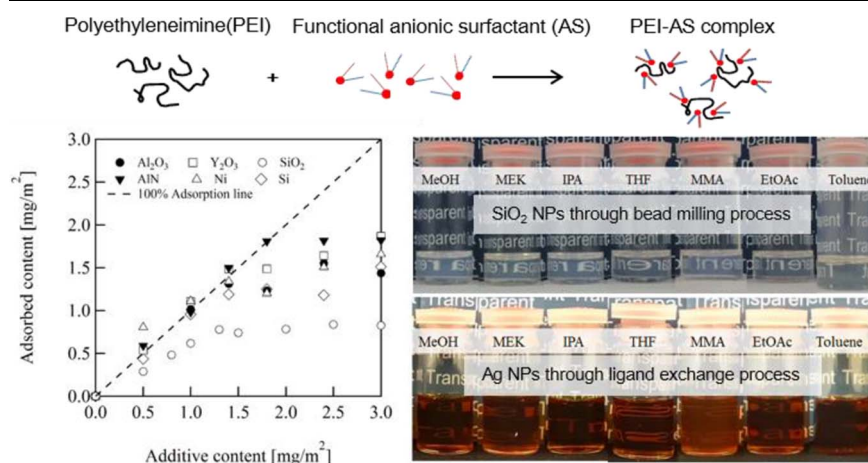
Complex of polyethyleneimine and anionic surfactant with functional chain: a versatile surface modifier applicable to various particles, solvents, and surface modification processes



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GRAPHICAL ABSTRACT



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ABSTRACT

An anionic surfactant (AS) comprising a phosphate ester head group and a functional organic chain branched into a hydrophilic polyethylene glycol-based chain and a hydrophobic alkyl-based chain was complexed with polyethyleneimine (PEI) and applied as universal surface modifier for the fabrication of nanoparticles dispersible in various solvents. The complex formation could be achieved by simply mixing PEI with the AS in solvents such as toluene. While PEI was insoluble in toluene due to its hydrophilic nature, addition of the AS assisted its dissolution due to complex formation between the amine group of PEI and the phosphate group of the AS. The designed PEI-AS complex effectively adsorbed on numerous particles including metal oxides (Al₂O₃, Y₂O₃, and SiO₂), metal nitrides (AlN), and metal species (Si and Ni), and was applicable to various surface modification processes. For simultaneous bead milling pulverization and surface modification of gas-phase synthesized SiO₂ nanoparticles with 2.6 mg/m² of PEI-AS, the number-based size distribution of the SiO₂ nanoparticles reduced to several tens of nanometers after milling, and the resultant pulverized/surface-modified nanoparticles were dispersible in a wide range of organic solvents such as methanol, MEK, IPA, THF,

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MMA, EtOAc, and toluene. The ligand-exchange process of oleylamine-capped Ag nanoparticles in toluene with 2.0 mg/m² of PEI-AS was also effective in dispersing Ag nanoparticles in various organic solvents without forming severe aggregation.

1. Introduction

Ever since nanoparticles have reported to possess unique size dependent electro-magnetic, optical, and physical properties different from their bulk substances [1–5], they now have become indispensable reagents for manufacturing composites in the form of polymer composites [6–8], ceramic composites [9], and/or nanostructured films [10,11] applied in various fields such as electronic devices [6,7,11], optical components [8], battery systems [9], sensing devices [10] etc. One of typical process to fabricate these composite devices involves dispersing the nanoparticles in a solvent/polymer; shaping them into desired structures through molding and/or casting; and fixing the structures by drying, polymerization, and sintering. The common keys to design and improve the properties of these composite devices are to be able to precisely control the dispersed/assembled structure of nanoparticles in the devices. Therefore, developing protocols to prevent formation of uncontrolled nanoparticle agglomerates and improving their dispersion stabilities throughout the entire manufacturing process is quite essential.

Up to date, many surface-modification techniques such as direct adsorption/reaction on colloidal particles [12,13], ligand-exchange [14–16], and simultaneous surface modification during pulverization [17,18] of nanoparticle dry powders have been reported. Full coverage of surface modifiers, for instance, polymer dispersants [14,16,18], anionic surfactants [12], and silane coupling agents [13,15,17] with solvent-compatible organic chains, afforded functional nanoparticles highly dispersible in solvents. One of the challenges in the fabrication of composite materials is the agglomeration prevention of the highly dispersed nanoparticles upon slight changes in the solvent polarity, induced during the process of mixing different solvents and/or polymers into the nanoparticle suspensions, drying nanoparticle suspensions with mixed solvents, and polymerization of nanoparticle/monomer suspensions. To overcome this issue, we have designed a functional anionic surfactant (AS) having an organic chain branched into a hydrophilic polyethyleneglycol-based chain and hydrophobic alkyl chain near the head group (Fig. 1) [12]. Saturated adsorption of AS on TiO₂ nanoparticles yielded TiO₂ nanoparticles that were highly dispersible in a wide range of organic solvents with different polarities. As a result, uniform dispersion of TiO₂ nanoparticles was achieved during the processing of transparent TiO₂ nanoparticle/epoxy and TiO₂ nanoparticle/poly-methylmethacrylate nanocomposites, without strong aggregation. Although this AS showed high affinity toward various solvents, the types of nanoparticles (for instance, SiO₂ and Ag) on which it can be effectively adsorbed were limited. Therefore, a complicated layer-by-layer process, which involves saturated adsorption of polyethyleneimine (PEI) and treatment with a suitable amount of AS, was required to fix the AS so that it shows unique dispersion properties in various organic solvents [19].

On the view point of improving the adsorption properties of the surface modifier on various species of particles, we also have developed the concept of designing a complex of PEI with fatty acids [20]. The PEI–fatty acid complex, which could be prepared by simply mixing PEI and fatty acids in toluene, adsorbed on particles with different characteristics, such as Si₃N₄, Y₂O₃, and MgO, and their dispersion stability in toluene improved drastically. Inspired by this newly designed PEI

complex system, herein we report the fabrication of PEI-AS as a universal “all- purpose” surface modifier, which effectively adsorbs on a wide range of particles, improves the dispersion stability of nanoparticles in various solvents, and has applications in different types of surface-modification processes. As a model study, the application of PEI-AS to simultaneous bead milling and surface modification of aggregated SiO₂ nanoparticles, and the ligand exchange of oleylamine-capped Ag nanoparticles will be demonstrated.

2. Experimental

2.1. Materials

Polyethyleneimine (PEI, average MW 1800), toluene (99.5%), L-ascorbic acid (99.6%), and oleylamine were purchased from Wako Pure Chemical Industry Ltd., Japan. Silver nitrate (99.8%) was purchased from Kanto Chemical Co., Inc, Japan. All materials were used without further purification. The anionic surfactant with hydrophilic and hydrophobic chain (AS, Fig. 1) was prepared similar to that mentioned in our previous report [12]. Al₂O₃, Y₂O₃, SiO₂, AlN, Ni, and Si were purchased from Sumitomo Chemical Co., Ltd., Japan (AKP30, 6.4 m²/g), Shin-Etsu Chemical Co., Ltd., Japan (RU-P, 9.3 m²/g), Nippon Aerosil Co., Ltd., Japan (AEROSIL 200, 200 m²/g), Tokuyama Corporation, Japan (F-grade, 6.4 m²/g), Sumitomo Metal Mining Co., Ltd., Japan (YH-643, 2.2 m²/g), and Yamaishi Metal Co., Ltd., Japan (No.600, 3.5 m²/g), respectively.

2.2. Fabrication of the PEI-AS complex

0.50 g of PEI (MW = 1800) and 2.97 g of AS (30 mol% of AS based on the number of PEI monomer units, calculated assuming all amines were secondary amines) were mixed with 6.53 g of toluene in a 50-mL glass vial and treated in an ultrasonic bath for 1 min. The toluene solution was then magnetically stirred for 24 h. The structure of the resulting PEI-AS complex in toluene was characterized by FT-IR analysis performed on a JASCO FT/IR-6000.

2.3. Adsorption of PEI-AS on various particles

19.00 g of a toluene solution of PEI-AS was prepared, where the concentration of PEI-AS was controlled in the range 0–3.00 mg/m² based on the total surface area of particles added in the following process. Then, 1.00 g of particles (Al₂O₃, Y₂O₃, SiO₂, AlN, Ni, or Si) was added to the prepared PEI-AS solution and stirred for 24 h. The adsorbed amount of PEI-AS on each particle was analyzed by determining the amount of unadsorbed, free PEI-AS in the slurries and subtracting it from the amount of PEI-AS originally added. After 24 h of adsorption, the slurries were centrifuged for 10 min at 20,000 G to characterize the free PEI-AS content, and the particle-free supernatant solution was collected. 10.0 g of the supernatant solution was then mixed with 20.0 g of absolute ethanol, and its conductivity was analyzed by Horiba LAQUA F-74. The concentration of PEI-AS in the supernatant solution was calculated from the standard curve obtained by analyzing the

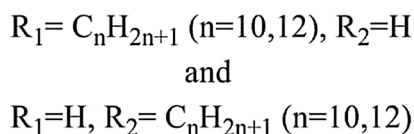
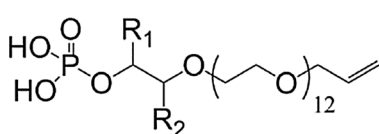


Fig. 1. Anionic surfactant with hydrophilic polyethyleneglycol-based group and hydrophobic alkyl group branched near the head group. Reprinted with permission from Ref. [12]. Copyright 2009 American Chemical Society.

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