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Unique structure and properties of inorganic–organic hybrid films prepared from acryl/silica nano-composite emulsions

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ABSTRACT

Transparent films were prepared from nano-composite emulsions, which contained nano-size core–shell-type particles (ca. 60 nm in diameter) consisting of colloidal silica (inorganic core, ca. 30 nm in diameter) and poly(methyl methacrylate-co-*n*-butyl acrylate) (organic shell). The silica content in the film could be increased up to 150 wt/wt% by keeping its homogeneity. It was revealed that the formation of such a core–shell structure is guided by the surface sedimentation of a nonionic surfactant above its clouding point to form an organic thin layer that can provide the sites for monomer adsorption and polymerization. The thermal and mechanical properties of the resultant nano-composite films were evaluated by various methods and compared with those of simple blend films of the corresponding acrylic emulsion and colloidal silica. It was clarified that the high-temperature resistance of the nano-composite films can be improved by the reinforcement effect of silica particles.

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1. Introduction

In the past decades, many research papers have been published on a variety of nano-composite systems consisting of polymeric materials and inorganic nano-particles. These composite systems are characterized by the unique properties originating from the nano-dispersion state of the inorganic components in the polymer matrix in which the polymer matrix provides excellent processability and flexibility while the inorganic nano-particles provide high mechanical properties and thermal stability [1–19]. These nanocomposite materials usually exhibit much better properties than the conventional organic/inorganic composites having micro- and macro-size structures and can be used for various purposes including plastics, rubbers, fibers, adhesives, and coatings [20–26].

The ordinary nano-particle composites can be obtained by simply mixing inorganic particles in polymeric matrices. However, the nano-particles dispersed likely agglomerate to form an inhomogeneous mixing state with which the nano-size effect of the particles is minimized. In order to achieve the well dispersed state of nano-particles, core/shell-type structure where the inorganic particles are embedded into polymer particles ought to be effective. With

this structure, the inorganic particles are separated from each other even when the core/shell-type particles are allowed to aggregate, and the interfacial adhesion between the polymer matrix and the inorganic particles can be retained in maximum. It has been uneasy, however, to encapsulate such nano-particles with polymeric materials. Various physicochemical and chemical processes have ever been tried for such purposes thus far. For instance, polymers are physicochemically precipitated or adsorbed onto the surface of inorganic particles by solvent evaporation or by means of electrostatic force or chemical or biochemical techniques [3–8]. More often, polymerization is performed in the presence of inorganic particles for their coating or inclusion [8–17]. In this case the surface of the inorganic nano-sized particles ought to be modified in order to make it compatibilize with the organic interface and to prevent the particles from agglomerating during the polymerization. In many cases, the modifiers are covalently bonded onto the surface of inorganic particles prior to the polymerization. For example, the silica particles are pre-treated with an acrylic siloxane coupling agent for producing nano-composite emulsion consisting of nano-scale silica (up to 33 wt%) and poly(ethyl acrylate) (PEA) [8–10]. Alternatively, some surfactants and amphiphilic block copolymers such as urethane-acrylate nonionomers were used for surface modification of the particles [13–16]. They are usually adsorbed on the surface of the particles to afford a monomer-absorbing layer on surface.

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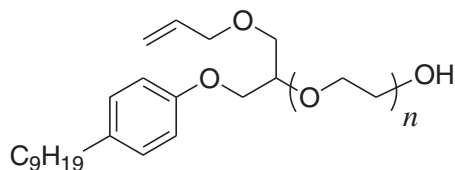
In our previous study, we succeeded in preparing a core/shell-type nano-composite emulsion (NC emulsions) by using a simple emulsion polymerization technique. In the resultant NC emulsion, each of the nano-scaled particles consisted of a silica nano-particle core of 20–30 nm in diameter and a polyacrylate coating layer having a thickness of ca. 15–20 nm [27]. This nano-scaled encapsulation of silica nano-particles was possible in the presence of nonionic surfactants of low cloud point as the modifiers. Mixing of such a nonionic surfactant in an aqueous dispersion of silica particles allowed the surfactant to precipitate on the surface of the particles above its cloud point to form an organic thin layer that can provide the sites for monomer absorption and polymerization by which the stable NC emulsions having a silica-to-polyacrylate ratio up to 150/100 in wt/wt% could readily be prepared. The NC emulsion thus obtained could form stable coating films on various substrates to show various interesting properties.

It has been well known that when inorganic particles are uniformly dispersed in a polymer matrix various improved properties involving mechanical and thermal properties can be attained [7]. With our NC emulsion silica particles may be dispersed more uniformly in the polymer matrix than with the ordinary blends of colloidal silica and polymer emulsion, and various interesting properties specific to the nano-dispersed structure are expected to be realized. The primary distinction of the NC emulsion was in the appearance of the hybrid film because its transparency can be retained at high silica contents. This feature is very important not only for their application to optical materials [25], but also to paint and ink for which color matching is necessary. In this study, therefore, we evaluate various properties of the inorganic–organic hybrid films prepared from acryl/silica NC emulsions in relation to the nano-dispersed structure.

2. Experimental

2.1. Materials

The colloidal silica used in the present study was ADEKA Corporation ADELITE AT-50 (abbreviated as AT-50) for which the average diameter of the silica particles was reportedly 20–30 nm and the silica content was 50 wt%. A nonionic surfactant, ADEKA REASOAP NE-10 (abbreviated as NE-10), was used as the reactive nonionic surfactant, which was also the product of ADEKA Co., Japan. Sodium dodecylbenzenesulfonate (SDS), butyl acrylate (*n*-BA), methyl methacrylate (MMA), methacrylic acid (MAA), and other chemicals were industrial grade reagents and were used as received.



NE-10: $n=10$

2.2. Polymerization procedure

The procedure used for preparing NC1-4 (vide infra) is shown as an example. Prior to the polymerization, a monomer mixture consisting of 69 g of MMA, 130 g of *n*-BA, and 1.0 g of MAA (or 99.5 g of MMA, 99.5 g of BA, and 1.0 g of MAA for NC2) was prepared. Into a 1 L flask equipped with a condenser, a dropping funnel, and a mechanical stirrer was charged 340 g of AT-50 under nitrogen. A solution of 0.5 g of ammonium peroxydisulfate and 5.0 g of

NE-10 in 140 g of water was added dropwise to AT-50 with vigorous stirring at 60 °C. After the addition, the temperature of the mixture was raised to 70 °C. To this mixture was added dropwise 5 g of the monomer mixture, and the contents were kept at 70 °C for 1 h. Then, a mixture of 0.6 g of APS and 24 g of SDS in 50 g of water and the rest of the monomer mixture were added dropwise sequentially. The reaction mixture was kept at 70 °C for an additional hour to complete the polymerization. After the mixture was cooled to room temperature, 3.6 g of an aqueous ammonia solution (25 wt%) was added to control the emulsion's pH to pH = 9–10.

Silica-free emulsions having monomer compositions corresponding to those of NC1-4 were also prepared by the conventional emulsion polymerization. Each of the resultant emulsions was blended with a predetermined amount of colloidal silica AT-50 to prepare the silica-polymer emulsion blends.

2.3. Temperature dependence of a colloidal silica containing NE-10

In an ordinary test tube (A), At-10 was diluted with distilled water to obtain a colloidal silica of 33.4 wt% in solid content. In another test tube (B), an aqueous solution of NE-10 was prepared in a concentration of 5.0 wt%. In the other test tube (C), a mixed solution of colloidal silica (33.4 wt%) and NE-10 (12 wt%) was prepared. The three tubes were kept at 60 °C for 16 h, cooled down to room temperature overnight, and warmed up again to 60 °C. The precipitation and gelation feature of each solutions were observed time to time.

2.4. Preparation of nano-composite films

A certain amount of each of the emulsions was cast on a polyethylene sheet or a glass plate (100 mm × 150 mm) with an applicator to prepare a coating film of ca. 100 μm in thickness. The coating film was dried at 50 °C for 16 h to obtain a solid film having a thickness of ca. 40 μm.

2.5. Measurements

Tensile properties of the films were measured on an Orientec (Tokyo) STA1150 tensiometer. The sample films were cut into a size of 15 mm × 50 mm, and each specimen was stretched at a crosshead speed of 30 mm/min at 25 °C. The tensile properties were automatically calculated by the computer connected to the machine, and the average of at least six measurements was taken for each measurement. Dynamic mechanical analysis (DMA) was performed on a Rheogel-E4000 in tension mode at 32 Hz in a temperature range of –30 to 250 °C at a heating rate of 3 °C/min under nitrogen. DSC analysis was conducted at a heating rate of 10 °C/min on a Shimadzu DSC-50 thermal analyzer under nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Instruments Hi-Res Modulated TGA 2950 analyzer under nitrogen or in air at a heating rate of 15 °C/min.

3. Results and discussion

3.1. Preparation of nano-composite (NC) emulsions

Several series of NC emulsions consisting of acrylic resin and silica particles were prepared according to the previously reported method [27], which is briefly described in Section 2. We chose three monomer compositions for the acrylic resins for preparing the NC emulsions; MMA: *n*-BA = 35:65, 50:50, and 65:35 (wt/wt%). The resultant emulsions consisted of hybrid particles of 50–60 nm in diameter, and in each of which a silica particle of 20–30 nm in diameter was surrounded by an acrylic layer cage.

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