Preparation of Polypropylene-Composite Particles and Its Characterization

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博士論文

Preparation of Polypropylene-Composite Particles and Its Characterization

（ポリプロピレン複合粒子の調製とその特性評価）

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General Introduction

Nearly 70 years have passed since Giulio Natta and Karl Rehn discovered in 1954 that a mixture of titanium trichloride ($TiCl_3$) and dialkyl aluminum chloride gave highly active isotactic polypropylene. Since this discovery, PP has become one of the most widely used polymer materials today and remains an exciting industrial material with a very bright future. PP is obtained by coordination polymerization of propylene (Figure 1), which is refined from naphtha cracking or other processes, in the presence of a catalyst. Its polymer includes light weight, high strength, high heat resistance, high resistance to various chemicals and solvents, and easy molding and processing, so PP is widely used around the world as materials for daily necessities, various packaging materials, and industrial parts such as automobile bumpers.
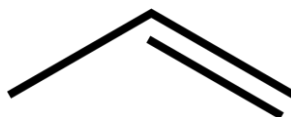
Figure 1. Chemical structure of propylene

PP can be classified into three types in terms of stereo-regularity: isotactic, syndiotactic, and atactic (Figure 2). The tacticity of PP varies depending on the polymerization method, with isotactic and syndiotactic PP chains showing relatively high crystallinity in the range of 40-70%. High crystallinity requires high tacticity, i.e., the presence of long, uninterrupted stereo-regular sequences along the molecular chain. Therefore, atactic PP cannot form crystalline structures. Most industrially available PPs are composed mainly of crystalline isotactic

polymers and contain trace amounts of atactic polymers.
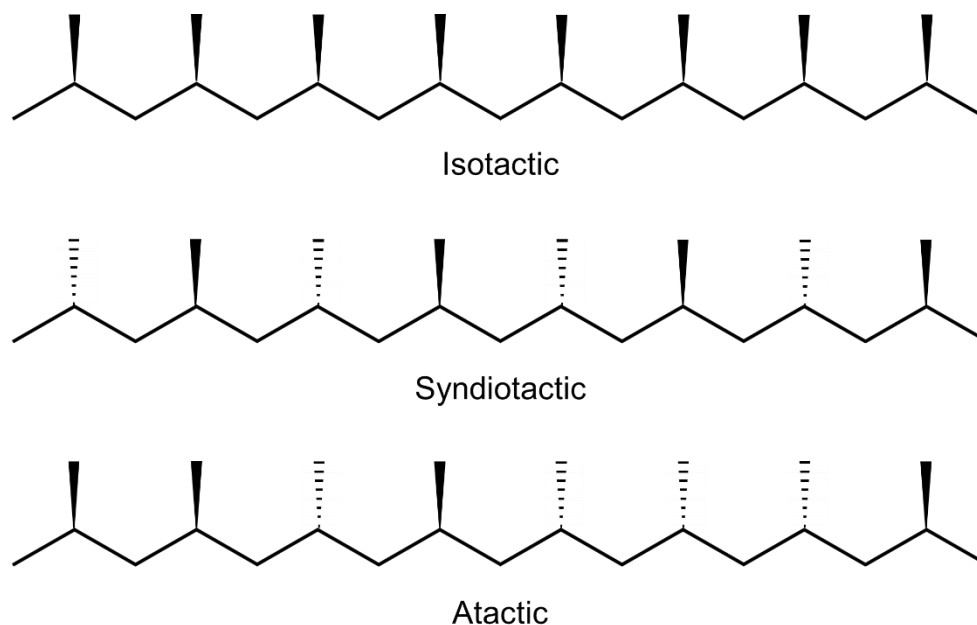
Figure 2. Tacticity in polypropylene

The global market of PP is estimated to grow from US\$ 76.0 billion in 2021 to US\$ 108.6 billion in 2028 at a compound annual growth rate (CAGR) of 5.2% in period, 2021-2028.[1] This explosive and tireless growth can be attributed to the advantages of the material's outstanding cost performance and superior physical properties. It is no exaggeration to say that the most significant influence on this development has been the steady improvement of the catalysts used in polymerization and the manufacturing process.

Catalyst for polypropylene polymerization

Currently, the catalysts industrially used for the polymerization of propylene are mainly solid magnesium-titanium type catalysts, so-called Ziegler-Natta (ZN) catalysts. Since

their discovery in 1953-1954[2–4], ZN catalysts have been continuously improved in terms of performance, and the improvement of their polymerization activity and stereo-regularity has greatly simplified the polymerization process and improved the performance of PP. Catalysts for PP production have been classified into six generations, including metallocene catalysts.

First and second-generation ZN catalysts containing $TiCl_3$ as active ingredient were used suspended in inert hydrocarbon to achieve industrial productivity. The "hydrocarbon slurry" containing the catalyst is continuously fed to multiple stirred tank reactors, where the propylene monomer is polymerized at temperatures between 50°C and 80°C. After polymerization, unreacted propylene is recovered, hydrocarbons are distilled, and the polymer fraction is dried to obtain the final PP particles. In the process using first-generation ZN catalysts, large amounts of alcohol and water were used to deactivate and neutralize the catalyst components, respectively. Therefore, the facilities for polymerization at that time had to be large. In addition, since the processes using the first- and second-generation ZN catalysts yielded polymers with a low isotactic index, a technique to remove the atactic fraction was also essential. Homo PP produced with those $TiCl_3$ is limited to products with relatively large molecular weights, and their melt flow rate (MFR) 230°C/2.16 kg is smaller than 15 g/10 min.

The next generation catalyst used titanium tetrachloride as the active ingredient and a magnesium chloride ($MgCl_2$) type support. Although this third-generation catalyst showed excellent polymerization activity, it had low stereospecificity and produced more than 60% atactic PP as a byproduct. Therefore, the conventional slurry-based polymerization process had to be applied. Subsequently, joint research by Montedison and Mitsui Petrochemical showed

that the introduction of an internal donor such as benzoate ester into the catalyst dramatically improved the isotactic index.[5]

In 1981, the fourth-generation catalysts were developed, in which phthalate esters were added instead of benzoate esters. Furthermore, catalysts with alkoxysilanes or silyl ethers added as external donors showed a better balance between catalytic activity and stereo-regularity than the third-generation catalysts. These catalysts can be used in both gas-phase and liquid-phase polymerization processes.[6,7]

In the late 1980s, a new catalyst was developed with the addition of a diether compound as an internal donor. This catalyst contains 1,3-diether compounds in addition to the conventional $TiCl_4$ and $MgCl_2$ supports and does not require external donors such as alkoxysilane.[8] This fifth-generation ZN catalyst exhibits extremely high propylene polymerization activity and can yield more than 100 kg of PP per 1 g of catalyst. With the advent of catalysts containing its diether compound, PP with high stereo-regularity and excellent molding processability is now readily available. Compared to the fourth-generation catalysts, the molecular weight distribution of the resulting polymers tends to be narrower.

Catalysts consisting of methylaluminoxane (MAO) and metallocene coordinated to transition metals such as zirconium and hafnium can produce isotactic or syndiotactic PP with very high stereo-regularity.[9–11] This catalyst is called "metallocene catalyst" and is attracting attention as the sixth-generation of catalysts for the polymerization of propylene. By using metallocene catalyst, PP with sharp molecular weight distribution and composition distribution can be obtained. In addition, the ability to copolymerize various comonomers with propylene

is one of the factors increasing the industrial value of metallocene catalysts.

Properties of Polypropylene

The properties of PP are similar to those of polyethylene, the same polyolefin, with some specific differences. PP has the following advantages:

● ***Heat-resistant*** － PP exhibits very good heat resistance among commodity plastics. Commonly used isotactic homo-PP has a melting point of 160-166°C.[12] The melting point can be lowered by random copolymerization with ethylene or 1-butene.

● ***Lightweight*** － The density of PP is around 0.9 g/cm3 and varies depending on crystallinity. The small density of the polymer means that the amount of plastic parts that can be loaded per product can be increased.

● ***Chemical-resistant*** － PP has excellent resistance to many chemicals, including acids, alkalis, and hot water. In addition, PP is impervious to most organic solvents such as aliphatic and aromatic hydrocarbons, aldehydes, ketones, esters, and amides at room temperature.

● ***Mechanical properties*** － Typical injection-molding grade PP has a tensile modulus of 1.5 GPa and a charpy impact strength of 140 kJ/cm3 at 23°C.[13] PP randomly copolymerized with ethylene or 1-butene is sometimes used for applications requiring impact strength and flexibility.

● ***Electric properties*** － PP exhibits excellent electrical insulation properties, which is derived from the fact that it is composed only of sigma electrons. In addition, PP has a low dielectric constant and dielectric loss tangent, making it suitable as a coating material for

electric wires.

On the other hand, PP has the following disadvantages:

● Difficult to paint and poor adhesion.

● Easily burned.

● Weak to ultraviolet rays and prone to deterioration outdoors.

● Difficult to dye.

● Large thermal expansion coefficient.

In order to maximize the value of products made of PP, it is necessary to carefully consider how to overcome the above disadvantages; compositing PP with other materials has long been studied as an effective technique to compensate for these disadvantages.

Application of polypropylene

1. Fiber

PP fibers are used for the production of ropes, container bags and rugs, among others. PP chips are melted by heat and extruded through tiny holes to produce PP fibers. To pass through this 0.3-0.8 mm diameter tiny hole (i.e., spinning nozzle) at high speed, PP with low melt viscosity must be extruded at high temperature.

One of the most important applications of PP fibers is nonwoven fabrics. Nonwoven

fabrics composed of PP fibers offer excellent tensile strength and filtration properties on account of their ability to resist chemical attack and provide a moisture barrier. These applications include geotextiles, hygiene, medical, packaging, filtration material, and oil absorbents *etc*. In today's COVID-19 epidemic, PP non-woven masks play a very important role and are expected to remain in steady demand.

2. Injection moulding

Injection molding is an industrial method that offers significant cost advantages in the mass production of PP products with three-dimensional shapes. In this process, PP is melted at high temperature and injected into a mold with low temperature to solidify. This method is used in the manufacture of a variety of PP products, including plastic furniture, food trays, home appliances, sporting goods, and bottles. Furthermore, PP parts manufactured by injection molding are widely used in automobiles. Injection molded PP is used for bumpers, instrument panels, trims, etc., and its light weight contributes to reducing CO_2 emissions from automobiles.

Fiber reinforced materials are often produced as injection molding grades of PP for the purpose of increasing the elastic modulus. Most of them are PP reinforced by glass fibers, and even the addition of less than 10 vol% can significantly improve the strength of PP.[14]

In recent years, PP blended with cellulose nanofibers, which is obtained by micronizing plant fibers through chemical or mechanical treatment, has been actively researched,[15,16] and some companies have commercialized their products.[17]

3. Film

PP film has excellent transparency, gloss, heat resistance, and moisture resistance, and is used in a variety of applications from food to industrial use. In particular, PP films are used in large quantities for food packaging, and play an important role in maintaining quality in a safe and hygienic manner and enabling efficient transportation and storage.

Films made from PP are classified into cast polypropylene (CPP) films and oriented polypropylene (OPP) films based on differences in manufacturing methods. CPP films have low crystallinity, which is derived from the rapid cooling of molten, high-temperature resin. This low crystallinity gives CPP films excellent transparency and flexibility. Because of its heat sealability, CPP film is used as a sealant for sealed packaging. Since PP-based sealants have a higher melting point than polyethylene-based sealants, CPP is laminated with nylon, PET, or aluminum foil and used as a sealant layer for retort pouches that require heat resistance.

OPP film is a material produced by stretching PP at temperatures above its glass transition. OPP has higher rigidity, transparency, impact resistance, and heat resistance than CPP, and it is also characterized by its high printability. Because of these advantages, OPP is widely used in packaging for food products, personal care products, pharmaceuticals, and the electrical and electronics industries. Growing consumer interest in more convenient packaging is one of the factors that continue to drive demand for OPP film. Additionally, the low surface free energy of PP also allows OPP film to be used as a release film.

4. Foam

Foam-like materials made by molding PP with finely dispersed air bubbles are manufactured and sold by several companies. Compared to PP blocks that do not contain air bubbles, PP foam is flexible, lightweight, and has excellent cushioning properties. Foaming agents can be used to generate bubbles in PP, which can be broadly classified into physical blowing agents and chemical blowing agents. PP foam is used in large quantities in automotive components and is an essential material in the manufacture of seats, trunk components, and door pads.

The properties and preparation methods of polymer particles are very different from the plastic blocks of visible size, and these differences have long fascinated many researchers. Polymer particles are materials that play a pivotal role in products such as paints, adhesives, cosmetics, spacers, and chromatographic carriers. In recent years, there has been a great deal of research into polymer particles with new and improved functions and properties for application in a wider range of fields. Polymer particles can be produced by heterogeneous polymerization as described below, depending on the raw materials and applications.

Preparation Methods of Polymer Particles

1. Emulsion Polymerization

Emulsion polymerization is a type of heterogeneous radical polymerization in which a medium such as water, a monomer only slightly soluble in the medium, and an emulsifier are

mixed, and then initiator soluble in the medium is added. Emulsion polymerization is one of the most important polymerization methods in industry because it has advantages such as high polymerization speed, ability to obtain polymers with large molecular weight, and use of water as a medium. The resulting particles are generally submicron in size, and the dispersion stability is maintained by electrostatic or steric repulsive force of the emulsifier.

In 1948, Smith and Ewart were the first to develop a quantitative theory based on the qualitative emulsion polymerization reaction mechanism proposed by Harkins.[18] At that time, they showed that in ideal emulsion polymerization, the average number of radicals (n) in a polymer particle is n ≈ 0.5, but many researchers later explained that the majority of emulsion polymerizations deviate from their theory.[19,20]

In emulsion polymerization, water-soluble polymers such as polyvinyl alcohol (##) as well as low molecular weight surfactants can be used as emulsifiers. Emulsifiers should not be included because they are a factor that reduces the physical properties of the dried film made from the emulsion. In emulsifier-free emulsion polymerization, polymer particles can be synthesized without the use of emulsifiers. Its polymerization system consists only of initiator, monomer, and water as medium. In emulsifier-free emulsion polymerization, there are no micelles as particle nuclei, so it takes time to generate particle nuclei, and the number of particles generated in the system is not large. Therefore, the polymerization rate is slower than in normal emulsion polymerization. However, because of this, particles with a larger diameter can be obtained in emulsifier-free emulsion polymerization. In emulsifier-free emulsion polymerization, the dispersion stability of polymer particles must rely on the electrostatic

repulsive force of the ionic group of the initiator and the steric repulsive force of the hydrophilic comonomer.

2. *Dispersion Polymerization*

Dispersion polymerization is a polymerization process which is initiated from a homogeneous solution of all raw materials including monomers, initiators, and dispersion stabilizers. The medium used in this system must be a poor solvent for the target polymer. As the polymerization proceeds in a homogeneous solution, the polymer that has reached critical molecular weight precipitates and generates particle nuclei. Since these particle nuclei are unstable, they aggregate with other particles until they reach a stable state. Subsequently, particle growth also proceeds by polymerization of the monomer absorbed by the stabilized particles, eventually resulting in monodisperse polymer particles of 0.1 to 10 μm in size. The dispersion stability of polymer particles depends on the steric repulsive force of the dispersion stabilizer, which is grafted to the polymer particles by covalent bonds during the polymerization process. Dispersion stabilizers are selected according to the polarity of the medium, and hydrophilic polymers such as polyvinylpyrrolidone (PVP) and Poly(acrylic acid) are particularly frequently used. In dispersion polymerization, the size of polymer particles can be controlled by changing the polarity of the reaction medium or the amount and molecular weight of the dispersion stabilizer.

3. *Suspension Polymerization*

Suspension polymerization is a heterogeneous polymerization process that starts with monomer droplets containing an initiator suspended in a medium. The preparation of the monomer droplets requires mechanical shear forces, and dispersion stabilizer that is soluble in the medium must be added to the system to maintain dispersion stability of the droplets. Suspension polymerization produces polymer particles that are similar in size to the initially prepared monomer droplets, i.e., 10 to 1000 μm. The diameter of the monomer droplets can be controlled by the strength of the mechanical shear and the concentration of the dispersion stabilizer, but in general, polymer suspensions obtained by suspension polymerization are very polydisperse. On the other hand, monodisperse polymer suspensions can be prepared by suspension polymerization using Shirasu Porous Glass (SPG) membranes, which are porous membranes with uniform pore size.[21,22] Suspension polymerization systems can be regarded as bulk polymerization proceeding within each monomer droplet, so the system exhibit a polymerization rate similar to that of bulk polymerization of the same composition. On the other hand, in cases where radicals in the monomer droplets escape into the medium, the polymerization rate must be discussed from a different perspective than in bulk polymerization.

4. *Mini-emulsion Polymerization*

Miniemulsion Polymerization is a process in which submicron-scale monomer droplets are created in an aqueous medium by very strong shear forces in the presence of a surfactant, and polymerization proceeds within those monomer droplets. To prevent particle

size increase due to Ostwald ripening, the monomer phase must contains a ultrahydrophobic compound called hydrophobe, which is not soluble in the medium. Miniemulsion Polymerization is characterized by the fact that the particle-size distribution of the emulsion does not change before and after polymerization.

Polymer particles are attractive materials with a variety of functions, but the majority of polymer particles produced by the above mentioned production methods are materials composed of acrylate or styrene. If we want to apply PP particles to create novel smart materials, it is unwise to start with heterogeneous polymerization of propylene monomer. This is because it requires a very large plant and advanced technology to synthesize PP from propylene gas and catalyst. To develop a material with excellent supply stability, commercially available PP emulsions can be used as a raw material. Most materials that combine the advantages of PP with those of other materials have been fabricated by melt-kneading. There have been no successful attempts to create composite particles composed of PP and other polymers. In this study, we aimed to create unprecedented PP composite particles by using commercially available PP emulsions as seed particles.

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Chapter 1

Preparation of Polypropylene-Composite Particles

by Dispersion Polymerization
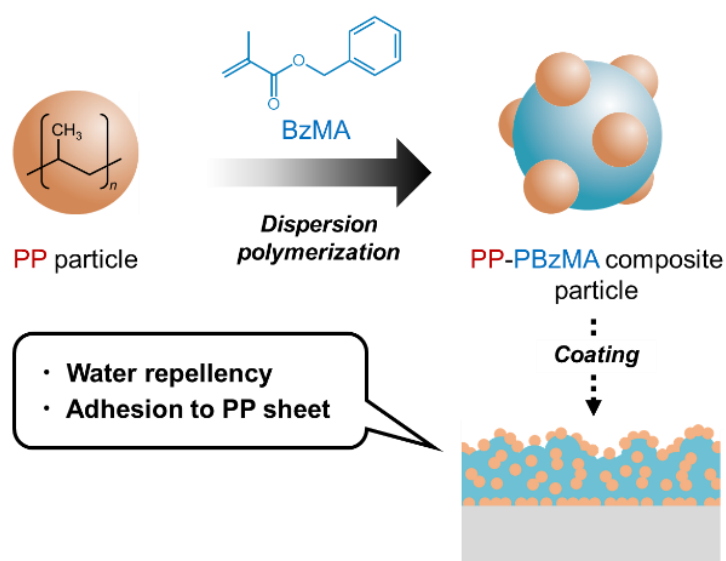
Abstract: Polypropylene (PP)/poly(benzyl methacrylate) (PBzMA) composite particles were prepared by dispersion polymerization of benzyl methacrylate (BzMA) in the presence of PP particles without a conventional dispersant. The polymerization process yielded a stable emulsion of composite particles with a "currant bun"-like morphology consisting of a PBzMA core and PP bumps, indicating that the PP particles operate as colloidal stabilizers. Conversely, when BzMA was replaced with styrene as the monomer, dispersion polymerization yielded a large amount of aggregates. Finally, a stable emulsion was formed by copolymerizing a small amount of methyl methacrylate (MMA) with styrene. This result suggested that PP must interact with a second polymer to prepare stable composite particles. The surfaces of the PP particles, which are highly hydrophilic due to their carboxyl groups, were involved in the attachment and stabilization of the polymer precipitated in the medium. A film prepared from the obtained PP/PBzMA composite particles was highly hydrophobic and strongly adhesive to a PP sheet.

Introduction

Composite particles comprising two or more components are variously applied as coatings,[1,2] biomedicines,[3–5] resin modifiers,[6] and other materials. Thus far, composite particles made of various polymers such as acrylic polymer,[7–9] polyurethane,[10,11] epoxy,[12,13] fluoropolymer,[14,15] and silicone[16,17] have been reported. Such composite particles are commonly prepared by polymerizing a second monomer in the presence of polymer seed particles.[18–20]

One of the effective techniques for preparing composite particles would be dispersion polymerization in the presence of polymer seed particles, which is called "seeded dispersion polymerization". As opposed to the emulsion polymerization system, many types of monomers are available with dispersion polymerization regardless of their solubility in water.[21] The preparations of composite polymer particles with various morphologies, such as core−shell[22-24] and sea-island[7] structures, by seeded dispersion polymerization have been reported. In seeded dispersion polymerization, the colloidal stability of composite particles is afforded by not only additional colloidal stabilizers at the second polymerization but also the steric or electrostatic stabilization of original seed particles without an additional stabilizer, which depresses the production of by-produced particles.[23,25-27]

Polyolefin is obtained by polymerizing an α-olefin with a double bond between its #1 and #2 carbons. Polyolefins are the largest group of plastics with an expected market growth of US$70.60 billion from 2020 to 2024.[28] The market has expanded because polyolefins are produced from readily available raw materials by an economically acceptable method.

Polyolefins can be said to be necessary for the manufacture of automobiles, daily necessities, electronic devices, and building materials. Among the most important common polyolefins produced on industrial scales is polypropylene (PP). The intrinsic properties of PP, such as excellent heat resistance, solvent resistance, mechanical strength, water repellency, and electrical characteristics, are exploitable in numerous applications. The drawbacks of PP are poor adhesion and high flammability. Combining PP with other polymers, including composite particles, is the most promising way of overcoming these disadvantages. Polyolefins such as natural rubber,[29,30] polybutadiene,[31,32] and polyethylene-based elastomers[33] have been used as seed particles in the fabrication of composite particles with other polymers such as polystyrene (PS) or poly(methyl methacrylate) (PMMA). Although these rubber-like polyolefins have excellent flexibility, they lack heat or solvent resistance, which limits their practicability. These properties, which are derived from an amorphous or lowly crystalline structure, also increase the ease of swelling the monomer, which is important for successful seeding of polymerization. The preparation of composite particles from PP, which is a typical crystalline polyolefin, has been scarcely reported. Zu and co-workers prepared PP–silica composite particles via a modified sol gel approach.[34] However, to our knowledge, no successful cases of composite particles of PP and other organic polymers exist in the literature, although the morphology and physical properties of composite PP particles are of great interest.

In this article, we report the preparation of composite particles from PP and polymethacrylate or polystyrene using a commercially available PP emulsion.

Experimental Section

Materials

A PP aqueous emulsion (Arrowbase YA-6010, aqueous dispersion, 25% solid content) was kindly provided by Unitika Co., Ltd. (Osaka, Japan). The number-averaged particle diameter and coefficient of variation were 0.28 µm and 6.9%, respectively. The zeta potential in water was -40.6 mV. Benzyl methacrylate (BzMA), methyl methacrylate (MMA), and styrene were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Reagent-grade 2,2′-azobisisobutyronitrile (AIBN) (Nacalai Tesque Inc., Kyoto, Japan) was purified by recrystallization. Reagent-grade ethanol (Nacalai Tesque Inc., Kyoto, Japan) was used as received. In all experiments, deionized water with a resistivity of 18.2 MΩ·cm was obtained from an Elix UV (Millipore Co., Ltd., Japan) purification system.

Preparation of PP-Composite Particles

PP-composite particles were produced by dispersion polymerization as follows: Monomer (0.3 g), AIBN (0.012 g), ethanol (8.6 g) and water (0.05 g) were mixed with the PP aqueous emulsion (2.8 g, giving 25% solid in water). Polymerization was performed in a sealed glass tube under a nitrogen atmosphere at 60 °C for 24 h with shaking at 80 cycles/min (3-cm strokes). Styrene, BzMA (0.3 g), or styrene/MMA (0.21 g/0.09 g) was used as the monomer. The conversion of each monomer was determined by gravimetry. After polymerization, the obtained emulsions were diluted with ethanol/water (50/50, w/w) and centrifuged at -5 °C in six times to remove free PP particles, in which free PP particles floated but the obtained particles

sedimented.

Characterization

Prior to centrifugal washing, aggregation of the obtained emulsions was checked under an optical microscope (ECLIPSE 80i, Nikon). The PP-composite particles were coated with platinum and observed with a scanning electron microscope (SEM, JSM-6510, JEOL, Tokyo, Japan) operated at an acceleration voltage of 20 kV. Their number-averaged diameter (Dn) was measured by dynamic light scattering (DLS) (DLS-700, Otsuka Electronics, Kyoto, Japan). The DLS data were taken at a light-scattering angle of 90° at room temperature. The polymer compositions of the composite particles were determined from their 1H nuclear magnetic resonance (NMR) spectra collected with a JEOL ECA 500 (500 MHz) spectrometer at 140°C in 1,1,2,2-tetrachloroethane-d2. The glass transition temperature (Tg) and melting temperature (Tm) were measured on approximately 10 mg of the composite particles after drying at room temperature by differential scanning calorimetry (DSC7000X, HITACHI, Tokyo). These thermal properties were identified by a DSC second heating　process. The water contact angles were measured on a Contact Angle System (DropMaster 500, Kyowa Interface Science Co., Ltd., Saitama, Japan) and were recorded as the average contact angles of six droplets of deionized water (2.3 mg per droplet). Films for the measurement of water contact angle were prepared by casting each emulsion or solution on a clean glass slide at room temperature.

Results and Discussion

The PP particles used in this work were composed of modified PP, in which a small amount of carboxylic acid derivative was grafted to PP. Owing to their hydrophilic carboxyl groups, the PP particles were well dispersed in aqueous medium. To prepare the composite particles, the dispersion polymerization of styrene was carried out in the presence of PP particles without a conventional colloidal stabilizer with the expectation that PP particles worked as seeds. Styrene has an excellent affinity for PP because PP is swelled with styrene at high temperatures.[35] However, the polymerization yielded a large number of aggregates (see Figure 1a, a′), indicating that the precipitated polystyrene (PS) was not compounded with the PP particles and aggregated with one another due to the absence of a colloidal stabilizer. In contrast, the emulsion derived from the BzMA monomer was well dispersed in the medium without coagulation (Figure 1b,b′). The BzMA conversion (measured by gravimetry) was 97.9%.

The aromatic ring in BzMA is similar to that in styrene, so the Hansen solubility parameter (HSP) distance from PP to the monomers is relatively small.[36] In fact, PP dissolved in BzMA or styrene under reflux conditions (data not shown). However, the hydrogen-bonding HSPs (δh) slightly differed between BzMA and styrene. The δh values of PBzMA and PS (estimated in HSPiP software) were 3.4 and 1.9, respectively, indicating that PBzMA is more hydrophilic than PS. This hydrophilicity is attributable to the ester group ($-$COO) on PBzMA. As the PP particles used in this paper contain a carboxyl group, they should also be hydrophilic and PBzMA should exhibit a higher affinity to PP particles than to PS. Therefore, a colloidally

stable emulsion of composite particles is expected.

To verify the above hypothesis, dispersion copolymerization of styrene with the hydrophilic monomer MMA (styrene/MMA, 7/3, w/w) was performed under the same conditions in the presence of PP particles. This reaction generated no aggregates (Figure 1c), and fine particles were observed under the optical microscope (Figure 1c′). The conversion of monomers (measured by gravimetry) was 79.7%. Dispersion copolymerization with different weight ratio of styrene/MMA (7.5/2.5, 8/2, 8.5/1.5, and 9/1; w/w) revealed that a colloidally stable dispersion could be obtained when the amount of MMA in the total amount of monomers was more than 10 wt% (Figure 2). From these results, it was inferred that an appropriate hydrophilicity of the second polymer is important for the preparation of PP-composite particles.
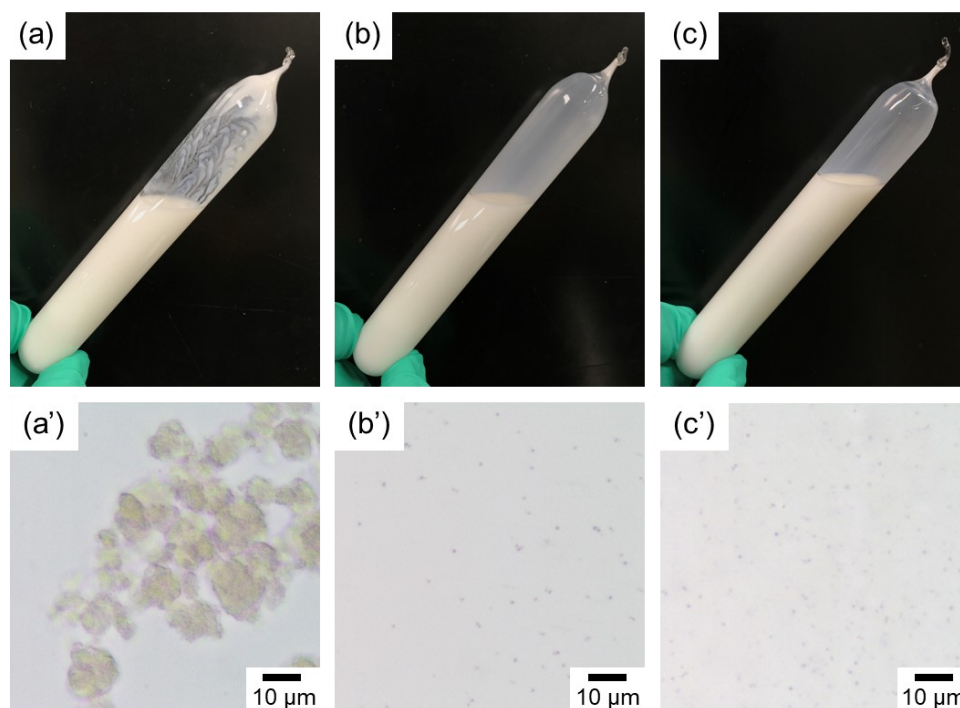
Figure 1. Photographs (a−c) and optical micrographs (a′−c′) of the samples obtained by dispersion polymerization of styrene (a, a′), BzMA (b, b′), and styrene and MMA (c, c′) in the presence of PP particles.
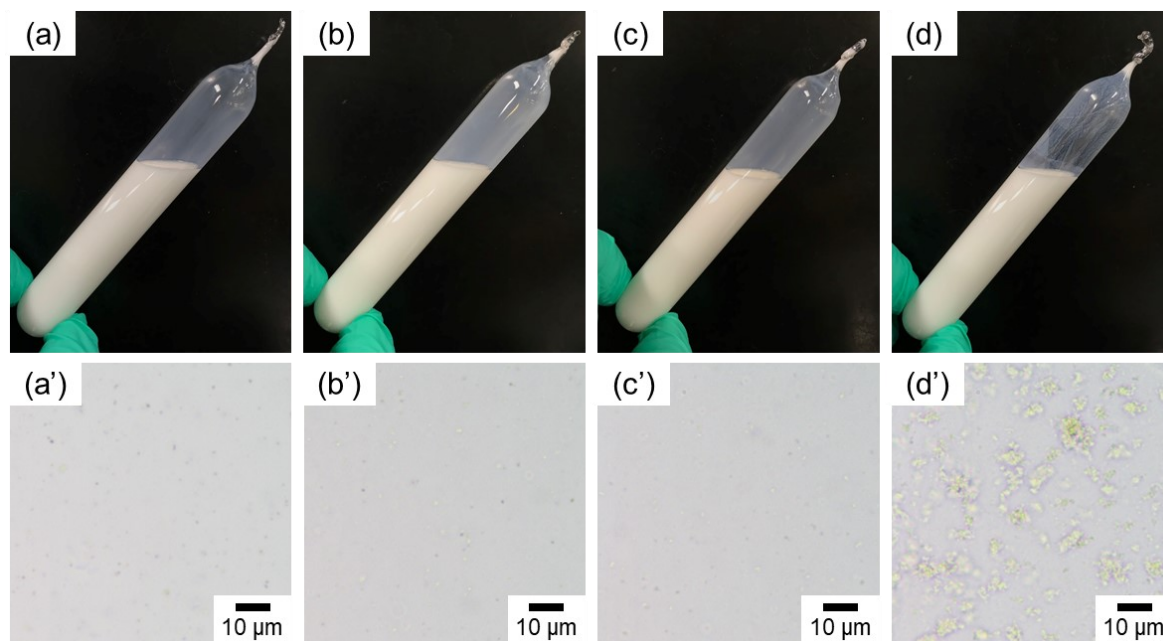
Figure 2. Photographs (a-d) and optical micrographs (a′-d′) of the samples obtained by dispersion polymerization of styrene and MMA (styrene/MMA, 75/25 (a,a′), 80/20 (b,b′), 85/15 (c,c′), 90/10 (d,d′), w/w) in the presence of PP particles.

Figure 3 shows the sizes and size distributions of the PP particles and the two types of PP-composite particles prepared by dispersion polymerization after centrifugal washing. If the obtained PP-composite particles were composed of the PP-core and second polymer-shell, the particle size should have slightly increased by the amount of the second polymer. Considering the conversion of BzMA and the densities of PP[37] and PBzMA,[38] the theoretical D_n of the composite particles should be 294 nm. However, the sizes of the obtained composite particles were much larger than the theoretical particle size and presented a unimodal distribution. According to these results, the seeded dispersion polymerization did not proceed well because the polymerized second polymer did not accumulate on the PP seed particles.
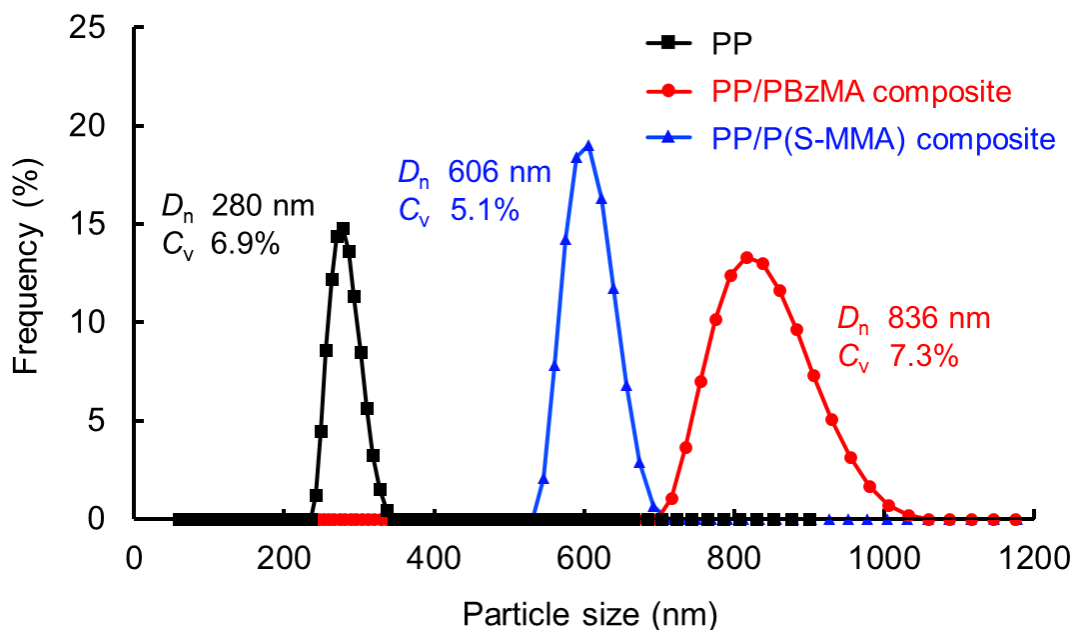
Figure 3. Sizes and size distributions of PP particles (black curve), PP/PBzMA (red curve), and composite PP/poly(styrene-methyl methacrylate) (P(S-MMA)) particles (blue curve).

Figure 4a, b shows the SEM photographs of the obtained composite particles prepared by dispersion polymerization with PP particles. In both cases, the obtained particles exhibited a "currant bun"-like morphology, in which one large particle was surrounded by several small particles. The PP particle-free second polymer particles mostly were not observed in either case. As the small particles almost matched the PP particles in size (Figure 5), they were inferred as the PP particles. Indeed, when the second polymers were extracted from the composite particles in DMF, which readily dissolved PBzMA and P(S-MMA) but not PP, only the small particles remained (Figure 4a′,b′). In the same polymerization system without PP particles, the stable dispersion was not obtained. These results indicate that the PP particles worked as dispersants rather than seeds during dispersion polymerization.

Figure 4. SEM images of PP-composite particles prepared by dispersion polymerizations of (a) BzMA and (b) styrene and MMA. Images a′ and b′ present the samples after extraction of PBzMA and P(S-MMA) with DMF, respectively.

Figure 5. SEM image of the PP particles used in this work.

Composite particles with a currant bun- or raspberry-like morphology are typically prepared by mini-emulsion or suspension polymerization of monomer droplets stabilized with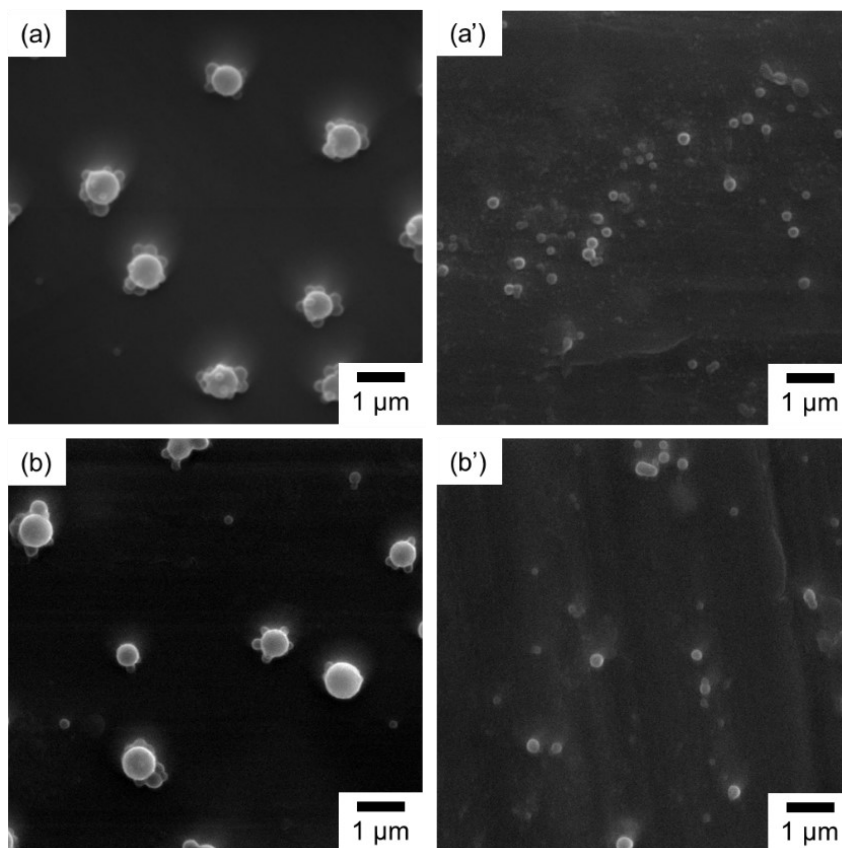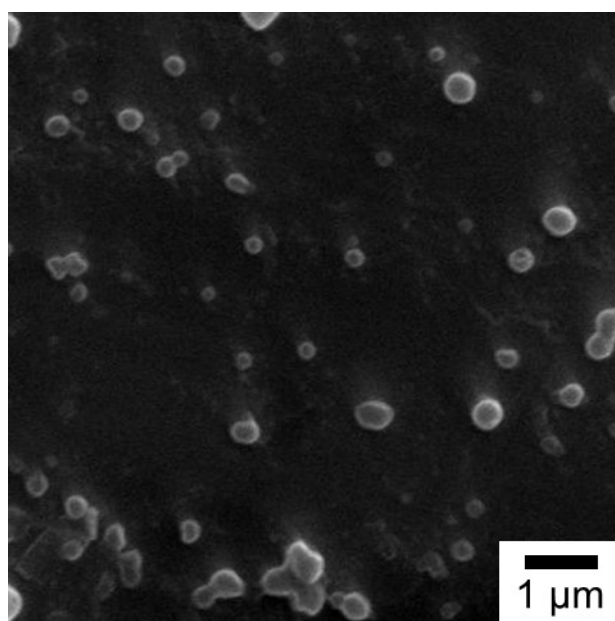 solid particles (so-called Pickering emulsions). In various dispersion polymerization systems, polymer particles have been prepared using silica particles as the "solid dispersant".[39-42] In previous works, aqueous dispersion polymerization of water-soluble monomers with colloidal silica as a stabilizer had been studied.[43-46] Barthel and co-workers revealed that the interaction between 4-vinylpyridine and the surface of silica particles gave the successful synthesis of composite particles.[47] Additionally, based on the mechanism of Pickering dispersion polymerization proposed by Kawano and co-workers,[48] early-stage adsorption of oligomeric PBzMA or P(S-MMA) on the surface of the PP particles might trigger the formation of stable composite particles. In our dispersion polymerization system, the hydrophilic interaction between the vinyl polymer and the surface of PP particles should be important in the formation of PP-composite particles. In these experiments, the hydrophilic component of the PP particles repelled the highly hydrophobic oligomeric PS. As the PS oligomers had low affinity to the PP particles, they were not adsorbed on the PP particles and instead precipitated in the medium. Conversely, when styrene was copolymerized with the hydrophilic monomer MMA, the affinity to PP particles increased and the PP particles tended to attach to the secondary polymer particles. In this case, the PP particles operated as a particulate dispersant. After polymerization, all the PP particles not adsorbed on the second polymer remained in the medium. The percentage of free (unabsorbed) PP particles was large (87.6%). The composition ratio of the obtained composite particles, determined by 1H NMR after centrifugal washing, was 10.2/89.8

(PP/PBzMA, w/w). This ratio significantly differed from the weight ratio (70/30) of PP particles and BzMA in the polymerization system, but the two ratios were consistent after subtracting the free PP particles from the PP particles added at the start of the reaction. In the P(S-MMA) system, the composition ratio was 22.5/77.5 (PP/P(S-MMA), w/w), and the ratio of styrene and MMA in the second polymer particles was calculated as 65.7/34.3 (styrene/MMA, mol/mol).

Figure 6 shows the DSC thermograms of the PP-composite particles prepared by dispersion polymerization. Both the PP/PBzMA and PP/P(S-MMA) particles (Figure 6d,e) presented the glass transition temperature of the second polymer and the melting point of PP, indicating that composite particles were formed. The melting point of PP was slightly reduced in the composite particles, which can be explained by its lower molecular weight after β-scission reactions or grafting of the secondary polymer.
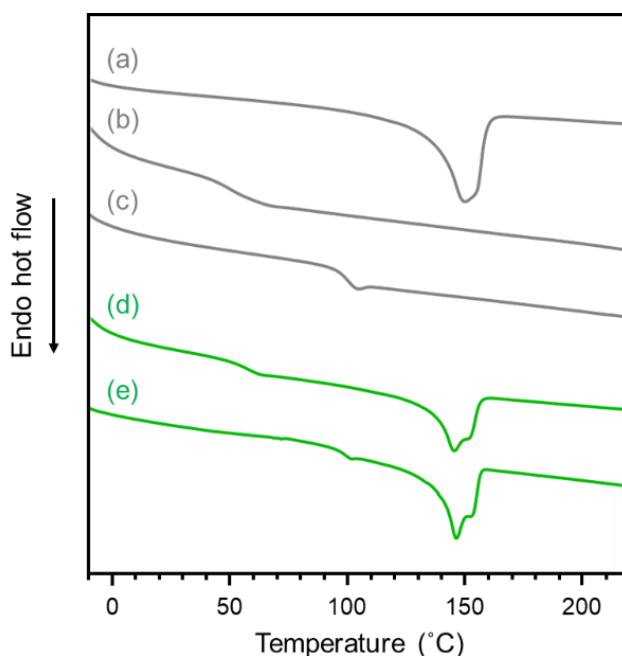

Figure 6. Second DSC heating curves of the (a) PP particles, (b) PBzMA prepared by bulk polymerization, (c) P(S-MMA) prepared by bulk polymerization, and PP-composite particles prepared by dispersion polymerizations of (d) BzMA and (e) styrene and MMA. The scanning rate of all measurements was 10 °C/min.

To confirm the superiority of the PP composite particles, we prepared films from the PP/PBzMA composite particles after centrifugal washing and subjected them to water contact angle measurements. The contact angle on the film from the composite particles increased to $131° \pm 1.8$ as compared with that of films prepared from PP aqueous emulsion ($111° \pm 3.3$) and PBzMA solution ($84° \pm 0.7$), respectively (Figure 7). These results indicate that an increase in water repellency of the film was based on the rough surface structure of the film prepared from the currant bun-like PP/PBzMA composite particles, in which the a Cassie–Baxter[49] or a Wenzel states[50] would be achieved. In addition, the PP bumps were bound to PBzMA core particles instead of water-soluble dispersants such as polyvinylpyrrolidone (PVP) and polyacrylic acid, so the film prepared from PP/PBzMA composite particles was water-repellent. Indeed, when a film with the composition of the composite particles was prepared from a mixture of PVP-stabilized PBzMA particles ($D_n = 912$ nm, $C_v = 8.2\%$) and PP particles for comparison, its water contact angle was $86.2° \pm 4.4$ (Figure 7). Therefore, adding PP particles as the colloidal stabilizer is expected to realize a water-repellent coating material.
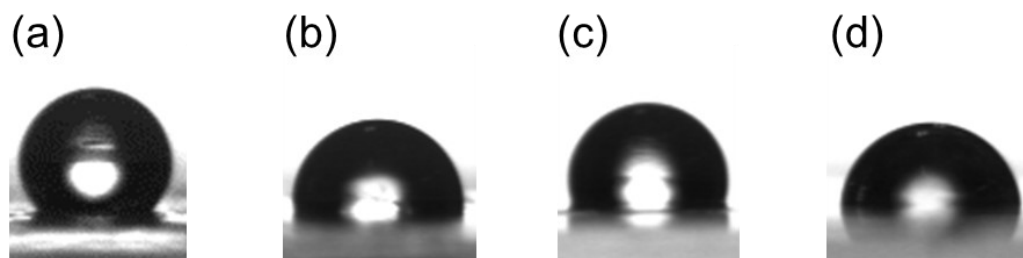
Figure 7. Visual images of the water contact angle on the film prepared from (a) PP/PBzMA composite particles, (b) mixture of PVP-stabilized PBzMA particles and PP particles, (c) PP aqueous emulsion and (d) PBzMA solution.

Finally, to investigate the adhesion property of the PP/PBzMA composite particles, the emulsion of composite particles was dried on a PP sheet at 135 °C and subjected to a peeling test with scotch tape. The PP/PBzMA composite film adhered more strongly to the PP sheet than the mixture of PVP-stabilized PBzMA particles and PP particles (Figure 8) and remained on the PP sheet after the peeling test (unlike the film prepared from the mixture, which was mostly peeled off). This result indicates that the PP particles occupied the surfaces of the composite particles.
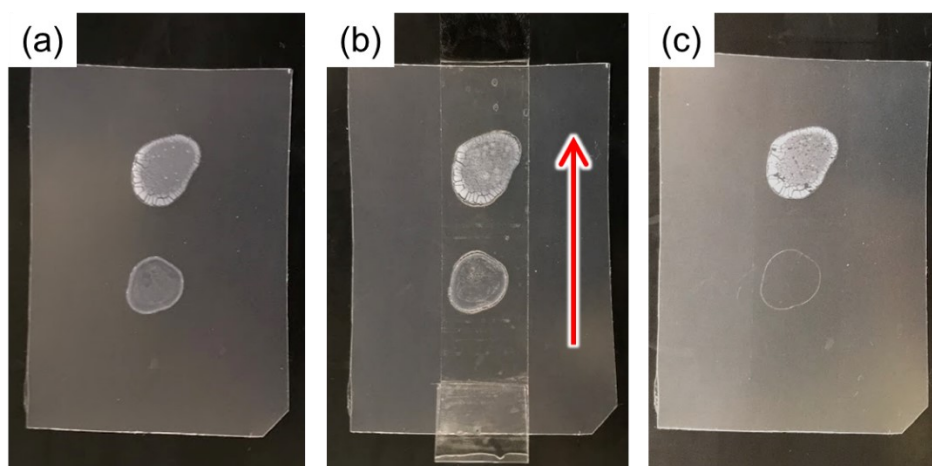
Figure 8. Visual appearance of the peeling test with scotch tape. (a) Films of PP/PBzMA composite particles (top) and the mixture of PVP-stabilized PBzMA particles and PP particles (bottom) prepared by drying of emulsions on the PP film at 135 ˚C for 3 h. (b) 15 mm wide scotch tape applied on the films and arrow showing the peeling direction. (c) Films after peeling off the scotch tape.

Conclusions

The PP-composite particles were successfully prepared by dispersion polymerization without a dispersant. Judging from the morphology of the composite particles, the PP particles themselves dispersed the particulates. Appropriate hydrophilicity was essential for the preparation of composites with PP particles. In the presence of styrene, composite particles were not obtained, but when styrene was copolymerized with MMA, a stable emulsion was formed. The surface of the film prepared from PP/PBzMA composite particles was highly hydrophobic. This preparation method for polymer particles without water-soluble dispersants is expected to provide coating materials with new functions.

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Chapter 2

Preparation of Polypropylene/Polystyrene Composite Particles with Multilayered Inner Morphology by Seeded Emulsion Polymerization
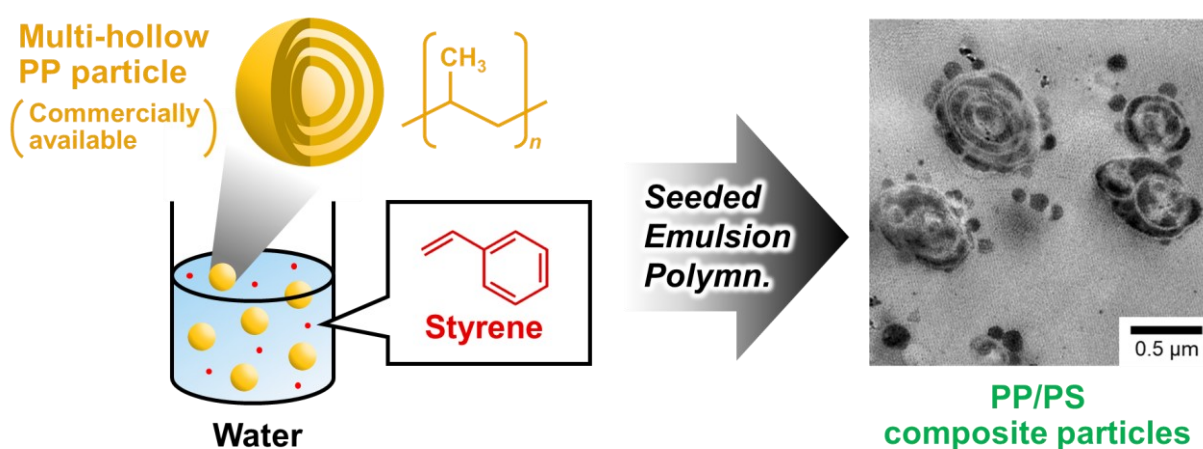
Abstract: Submicron-sized polypropylene (PP)/polystyrene (PS) composite particles were successfully prepared by seeded emulsion polymerization of styrene with a water-soluble cationic initiator. From the observation of the resulting composite particles through scanning and transmission electron microscopies, it was revealed that the particles were surrounded by many patches composed of PS. Surprisingly, the PP/PS composite particles showed an interesting internal morphology in which the PP and PS phases form multilayered structures. It is proposed that this interesting internal morphology was derived from the multi-hollow structure of seed PP particles. The results of the microscopy analysis revealed that the morphology of the composite particles was obtained by infiltration of PS into the voids in seed PP particles. Moreover, the PS phase that could not be extracted using hot tetrahydrofuran was detected by proton nuclear magnetic resonance; therefore, some parts of the PS chain should have been covalently bonded to PP. We also clarified that adhesive performance was superior to the PP/PS emulsion blend system, which indicated that the obtained composite particles would be useful for an application as an adhesive.

Introduction

Polypropylene (PP) is one of the most important industrial polymers; it is an indispensable material for the manufacture of automobiles, daily necessities, electronic devices, and building materials and is one of the largest markets of forming plastics, with 69 Mt of production in 2018.[1] PP is produced by coordination polymerization of propylene (and a small amount of comonomer such as ethylene) with a Ziegler−Natta[2,3] or metallocene catalyst.[4] The productivity of PP fabrication has increased with significant advances in catalytic chemistry and chemical engineering, leading to lower prices. In addition to its economic advantage, PP has attractive characteristics, such as high mechanical strength, good heat and chemical resistance, molding processability, and favorable electrical characteristics. However, PP lacks adhesiveness and dyeability due to its low surface free energy, and it burns easily when exposed to flames. To overcome these disadvantages, modifying the properties of PP and alloying it with other polymers have been shown to be the most effective methods.

In a previous study, we reported the preparation of PP composite particles by dispersion polymerization of benzyl methacrylate in ethanol.[5] The obtained PP/poly(benzyl methacrylate) (PBzMA) composite particles showed a "currant-bun"-like morphology consisting of a PBzMA core and PP bumps, suggesting that the polymerization proceeded via the Pickering-dispersant mechanism[6−9] (i.e., the PP particles acted as colloidal stabilizers). The PP/PBzMA cast film prepared from the composite particles adhered more strongly to the PP sheet than that prepared from a mixture of PBzMA and PP particles. However, the composite particles prepared by Pickering dispersion polymerization did not contain a sufficiently large amount of Pickering dispersants (PP particles), where the PP content was only approximately 10 wt%.

The other useful technique for preparing polymer composite particles is emulsion polymerization in the presence of polymer seed particles, called seeded emulsion

polymerization.[10−15] The seeded emulsion polymerization technique is a valuable method from a practical point of view because the polymerization of the second monomer can be completed in a short time and it is easy to control the morphology of composite particles. Moreover, water can be used as an eco-friendly solvent in seeded emulsion polymerization.[16] Health hazards and environmental pollution caused by volatile organic compounds in paints and adhesives have triggered an increase in water-based products on the market. Therefore, the demand for aqueous emulsions with better performance than solvent-based products is increasing yearly. However, emulsion polymerization of olefin monomers that are gas at ordinary temperatures and pressures is technically complicated. Although catalytic emulsion polymerization has been successful for some polyolefins,[17,18] the large-scale production using a pressure vessel is not a practical method. Thus, assuming manufacturing in a factory, the polyolefin seed particles that are commercially available or easily fabricated should be used. Although polymer composite particles were previously prepared in an aqueous medium with seed particles composed of polyolefins, for example, polybutadiene[19] and polyethylene-based elastomers,[20] the polyolefin properties derived from the amorphous or poorly crystalline structure severely limit their application as paints for harsh application conditions. Moreover, there has been no previous report on the preparation of polymer composite particles with seed PP particles by seeded emulsion polymerization. In this study, the preparation of PP/polystyrene (PS) composite particles was investigated by seeded emulsion polymerization of styrene in the presence of commercially available PP particles.

Experimental Section

Materials

A PP aqueous emulsion with 25 wt% (Arrowbase YA6010, Unitika Co., Ltd, Osaka, Japan) was offered. Styrene (Nacalai Tesque, Kyoto, Japan) was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Ammonia persulfate (APS), 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan), and tetrahydrofuran (THF; stabilizer free, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) were used as received. Water used in all experiments was purified by an Elix UV purification system (Millipore, Tokyo, Japan).

Swelling degree of PP with styrene

PP aqueous emulsion was heated to 65 °C to completely remove the medium. The dried emulsion was melt-pressed at 165 °C to produce PP films with a thickness of approximately 0.8 mm. The obtained PP film (0.07 g) was soaked in styrene (3.5 g) and heated to 40 °C for decided time intervals. Thereafter, the PP film taken out of styrene was wiped with paper towel and weighed. Based on the weight of PP film before (W_1) and after (W_2) soaking in styrene, swelling amounts of styrene in PP were calculated as follows:

$$\text{Swelling amounts of styrene in PP (wt\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Preparation of PP/PS Composite Particles

PP/PS composite particles were prepared by seeded emulsion polymerization as follows. Styrene (0.5 g) and VA-044 (2.9 mg) were added to an aqueous PP seeded emulsion, which was Arrowbase YA-6010 mixed with water (10.5 g). Polymerization was performed in a closed glass tube purged with nitrogen gas at 40 °C for 24 h by shaking at 100 cycles per minute (3 cm strokes). To measure the time conversion of styrene, the polymerization time was increased to 48 h under the same conditions. The conversion of styrene was determined using gravimetric data. After polymerization, the obtained emulsions were diluted with water and centrifuged twice at 3 °C to remove byproduct PS particles (or small particles), in which the obtained composite particles floated, whereas the PS particles sedimented.

Emulsifier-Free Emulsion Polymerization of Styrene

PS particles were prepared by emulsion polymerization under emulsifier-free conditions as follows: styrene (20 g), APS (81 mg), and water (116 g) were added into a 300 mL round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen. Polymerization was carried out at 70 °C for 20 h by stirring at 300 rpm. After the polymerization, PS particles were centrifugally washed two times with water and resuspended in water.

Characterization

The weight-average diameter (D_w) and coefficient of variation (C_v) were measured using dynamic light scattering (DLS; FPAR-1000RK, Otsuka Electronics Co., Ltd., Osaka, Japan). The DLS measurements were carried out at a light-scattering angle of 90° using a glass cell at room temperature. The ζ-potentials of PP seeded particles and obtained composite particles were measured using a ζ-potential analyzer (ELSZ, Otsuka Electronics Co., Ltd., Osaka, Japan). The obtained composite particles were sputtered with platinum and observed using scanning electron microscopy (SEM; JSM-6510, JEOL, Tokyo, Japan) operated at an accelerating potential of 20 kV. To observe the inner morphology of the composite particles, freeze-dried particles were stained with ruthenium tetroxide (RuO_4) vapor at room temperature for 30 min in the presence of the RuO_4 crystal, which were embedded in an epoxy resin matrix, cured at 40 °C overnight and subsequently sliced using a microtome. Ultrathin (100-nm-thick) cross sections were observed using transmission electron microscopy (TEM; JEM-1230, JEOL, Tokyo, Japan) at 100 kV. Furthermore, field emission-SEM (FE-SEM) observations were performed to study the interior structure of the composite particles and PP seeded particles. The freeze-dried composite particles and PP seeded particles were ion beam milled (Gatan Ilion model 693) at 4 kV, coated with platinum, and subsequently observed using FE-SEM (SU8020, Hitachi High-Tech, Tokyo, Japan) operated at an accelerating potential of 2 kV. The chemical components of the composite particles were analyzed by Fourier transform infrared spectrometry (FT-IR; FT/IR-6200, Jasco Co., Ltd., Tokyo, Japan) using the pressed KBr pellet technique. The polymer composition ratios of the obtained composite particles were quantified

from their proton nuclear magnetic resonance (^{1}H NMR, ECA 500, JEOL, Tokyo, Japan)

spectra collected at 140 °C in 1,1,2,2- tetrachloroethane-d_2.

Preparation of Adhesive Samples and Measurement of Peeling Strength

Emulsion of PP/PS composite particles without centrifugally washing was dried at

40 °C for 44 h. The dried solid and aluminum plate (0.2 mm thick) for controlling the thickness

of the adhesive layer were sandwiched between the PP sheet and the aluminum foil, and heat-

pressed at 165 °C for 1 min. The prepared laminate sheet was cut to 10 mm width. The T-peel

test of the specimen prepared with the PP/PS composite emulsion was carried out six times at

room temperature using a tensile tester machine (Autograph AGS-5kNX; Shimadzu Seisakusho

Corp., Kyoto, Japan) at a tensile speed of 200 mm/min and the average value was taken. An

emulsion blend with the same PP/PS weight ratio was prepared by mixing of Arrowbase YA-

6010 (PP emulsion) and emulsifier-free PS emulsion, and the laminate sheet was prepared by

the same methods noted above. The T-peel test of the specimen prepared with the blend

emulsion was carried out under the same conditions as mentioned above.

Transparency of adhesive layer prepared by PP/PS composite emulsion and blend
emulsion

The PP/PS composite emulsion prepared by seeded emulsion polymerization and

PP/PS blend emulsion were dried at 40 °C for 44 hr. The blend emulsion with the same PP/PS

ratio as the PP/PS composite emulsion was obtained by blending seed PP emulsion and PS

emulsion, which was prepared by emulsifier-free emulsion polymerization. The dried solid

prepared from each emulsion was sandwiched between the same two glass slides and heat-

pressed at 165 °C for 1 min. After cooling at room temperature, the transparency of each

adhesive layer between two glass slides was visually checked.

Results and Discussion

The aim of this study was to prepare PP composite particles by aqueous seeded emulsion polymerization of styrene in the presence of PP particles. The commercially available PP emulsion (Arrowbase, D_w 262 nm) was used as the seed emulsion in this study, which has an anionic surface charge (−49.0 mV) and water medium. Styrene was selected as the second monomer in our experiments because of its affinity to PP.[21] Actually, when the films prepared from the PP emulsion were heated in styrene at 40 °C, the PP films absorbed around 15 wt% of styrene based on the film (Figure 1). Furthermore, the cationic azo-initiator VA-044 was used in seeded emulsion polymerization in anticipation of ionic interaction between anionic PP particles and the end groups of the second polymer. Styrene (0.5 g), PP seeded aqueous emulsion (2 g, giving 25% solid in water), and VA-044 (2.9 mg) were added to water (10.5 g), followed by polymerization at 40 °C for 24 h under a nitrogen atmosphere in a sealed glass tube by shaking at 100 cycles per minute (3 cm strokes). The conversion of styrene determined by gravimetry was 83.5%. DLS analysis revealed that the particle size distribution of the obtained emulsion slightly shifted to a larger average size (from 262 to 274 nm), and small (approximately 70 nm) particles were generated after polymerization (Figure 2a). The results of SEM observations after seeded emulsion polymerization (Figure 2c) showed that patch-like particles with multiple spherical protrusions as well as small particles (approximately 70 nm) (Figure 2b), which did not exist before polymerization, were observed. The small particles were expected to be PS particles generated in the water medium by emulsifier-free emulsion polymerization with VA-044.[22] To obtain the pure PP/PS composite particles, centrifugation

after dilution with water was performed, in which the composite particles with a lower density than that of water floated, whereas PS particles with a higher density sedimented. After centrifugation, the low-density particles in the top layer were collected. As shown in Figure 2a,d, only large irregular particles without small particles were obtained. On the other hand, SEM analysis of sedimentation after centrifugation showed small particles similar to ones observed in the emulsion before centrifugal washing (Figure 3a). Contrary to expectations, FT-IR analysis showed that the precipitate contained not only PS but also PP; however, sedimented PP/PS composite particles should have higher density than 1 (Figure 3b). Based on the density of PP[23] and PS,[24] the PS content of the sedimented PP/PS composite particles was considered to be more than 72 wt% (density higher than 1). The amount of sedimentation was only 0.73 wt% relative to the total solid content, which means that most PS phase generated in the seeded emulsion polymerization combined with PP particles. Actually, the ζ-potential of the large patch-like particles collected by centrifugation was more positive than that of PP seeded particles (−29.2 mV); thus it was implied that the particles consisted of the PP and PS phases originating from the cationic initiator VA-044. In subsequent experiments, characterization was performed using the large patch-like particles.
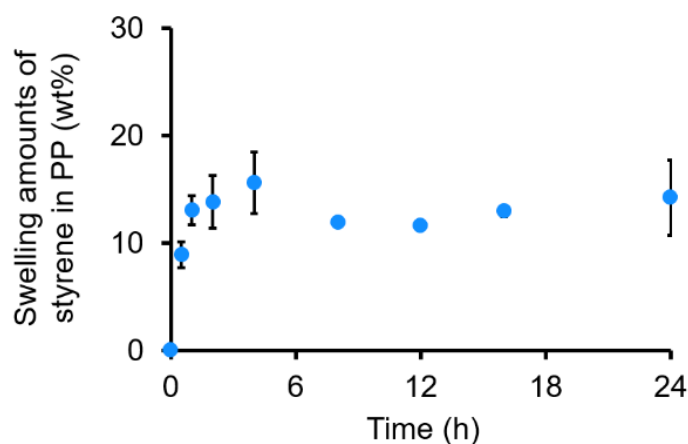

Figure 1. Swelling degree of PP with styrene at 40 °C over time. Results represent mean ± standard deviation of two replicates.

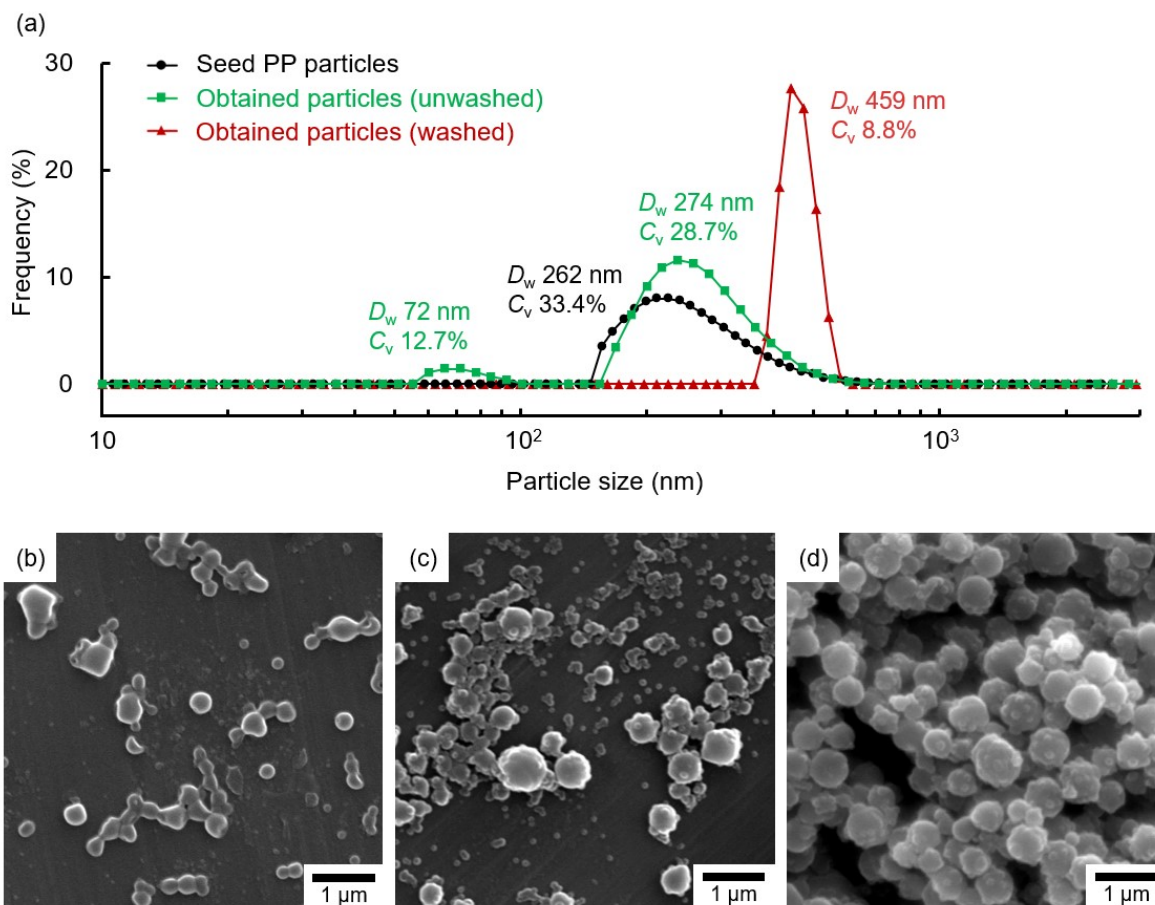**Figure 2.** (a) Weight average diameter of PP seeded particles and particles obtained by seeded emulsion polymerization before and after centrifugal washing. SEM images of (b) PP seeded particles and particles obtained by seeded emulsion polymerization (c) before and (d) after centrifugal washing.
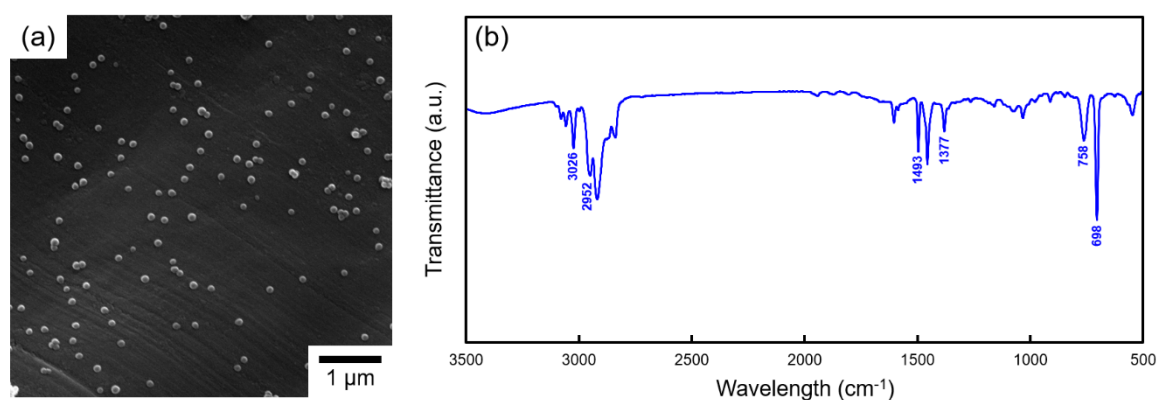

Figure 3. SEM image (a) and the FT-IR spectrum (b) of the particles in the precipitate collected by centrifugation.

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SEM observations showed that the PP seeded particles were fused together because of the low glass-transition temperature (T_g) of PP[23] (Figure 2b). In contrast, no fusion of the obtained PP/PS composite particles was observed (Figure 2d), which indicates that the surface of the obtained particles had different properties to those of the PP seeded particles. To confirm the formation of the PP/PS composite particles, FT-IR was used (Figure 4, red line). The absorption peaks at 698 and 757 cm^{-1} are due to C−H out-of-plane bending vibration of benzene rings in PS.[25] The absorption band at 974 cm^{-1} is due to CH$_3$ asymmetric rocking and C−C asymmetric stretching vibrations in PP.[26] The peak at 1378 cm^{-1} can be attributed to CH$_3$ symmetric deformation vibrations in PP.[26] The peak at 1493 cm^{-1} results from the aromatic C=C stretching in PS.[27] A small amount of the carboxylic acid derivative was grafted on the PP particles used as seeds in our experiment; therefore, a broad peak due to C=O bonds was observed at approximately 1713 cm^{-1}. Furthermore, the peak at 2954 cm^{-1} is characteristic of the CH$_3$ asymmetric stretching vibrations in PP.[26] The absorption band at 3027 cm^{-1} is due to aromatic C−H stretching vibrations in PS.[28] In addition, the composition ratio of the resulting irregular particles, determined by ^{1}H NMR after centrifugal washing, was 61.1/38.9 (PP/PS, w/w). The results of FT-IR and ^{1}H NMR analyses indicate the successful preparation of PP/PS composite particles by seeded emulsion polymerization.
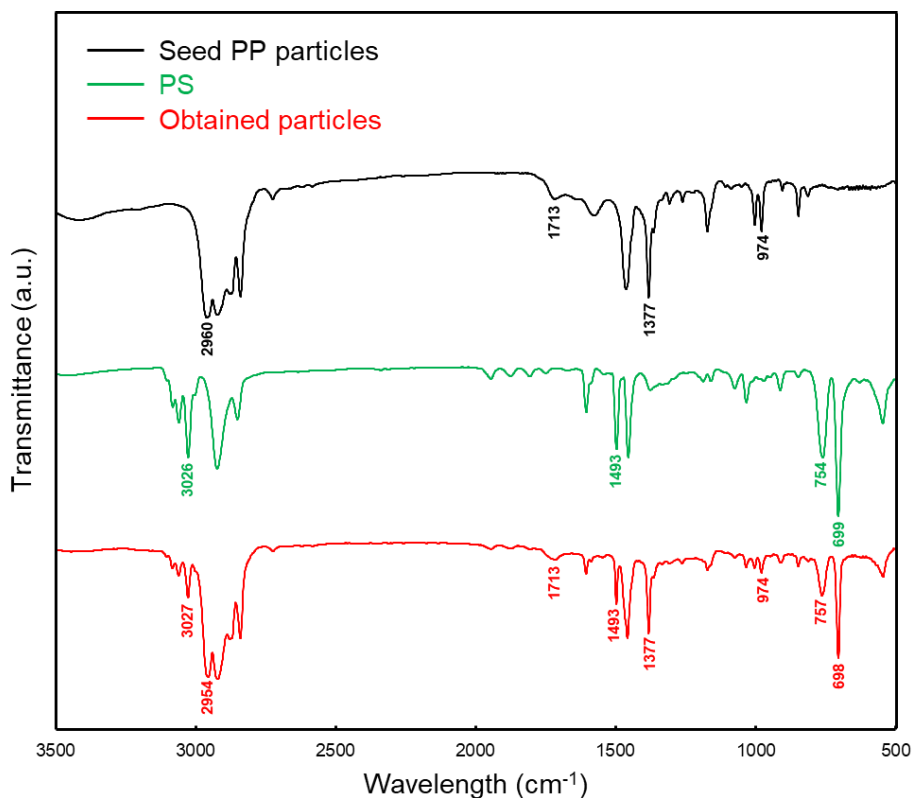
Figure 4. FT-IR spectra of PP seeded particles, PS pellets, and particles obtained by seeded emulsion polymerization.

Ultrathin cross sections of the PP/PS composite particles were stained with RuO$_4$ vapor for 30 min, which selectively stained the PS phase, and then, the cross sections were observed using TEM to reveal the surface and internal morphology of the composite particles (Figure 5). As shown in the TEM photograph, PS patches on the surface of the composite particles were found, which had a much higher T_g than room temperature and should have acted as the physical barrier,[29] thereby preventing the fusion of the composite particles (Figure 2b). Surprisingly, it was clearly observed that the inner morphology of the PP/PS composite particles was composed of multilayered structures consisting of PP (low-contrast phase) and PS (high-contrast phase). Okubo et al. reported the preparation of multilayered onion-like PS/ poly(methyl methacrylate)

composite particles using the solvent-adsorbing/releasing method (SARM) as a means to control the morphology of composite polymer particles,[30,31] in which dissolving polymers phase-separate to form a thermodynamically stable morphology during evaporation of the solvent in the composite particles. However, PP seeds should not dissolve in a monomer at low temperature; thus, formation mechanisms of the PP/PS composite particles should be different from the SARM. The multilayered structure is expected to be based on the structure of the PP seeded particles. Figure 6 shows FE-SEM images of the cross sections of PP seeded particles processed by milling using an argon ion beam. The FE-SEM observations indicated that the PP particles used in this study originally had a multi-hollow structure consisting of inner vesicles. The PP particles might be prepared by emulsification using the PP-grafted carboxylic acid derivative, which promotes the absorption of water and the formation of a water pool in the PP particles during emulsification, resulting in the formation of multi-hollow structures. Additionally, the multilayered structure was clearly observed under a transmission electron microscope with ultrathin cross sections of PP particles (Figure 7).
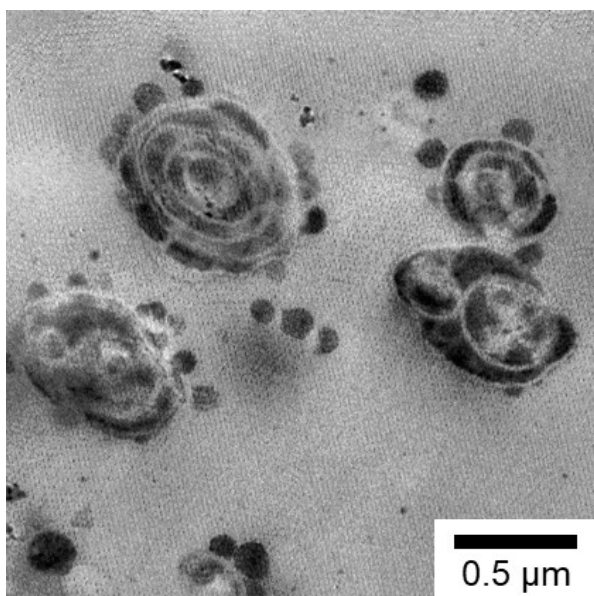
Figure 5. TEM image of an ultrathin cross section of PP/PS composite particles stained for 30 min with RuO_4 vapor.

Figure 6. FE-SEM image of the ion beam-milled PP seeded particles.

Figure 7. TEM image of an ultrathin cross section of PP seeded particles

According to the FE-SEM analysis of the cross sections of PP/PS composite particles processed by milling using an argon ion beam (Figure 8a), the inside of the particles was solid, indicating that the hollow structures were filled with the PS phase. To confirm this, the PS

phase of PP/PS composite particles was extracted by reflux with THF, which can dissolve PS but not PP. The reflux was carried out for seven days, in which no PS homopolymer should be left in the sample except for the PS grafted to PP backbones. Figure 8b shows the FESEM image of the cross section of PP/PS composite particles after refluxing, where a multi-hollow structure was observed, similar to that of the original PP seeded particles. Moreover, the composition ratio of the sample after reflux in THF, determined by ^{1}H NMR, was 86.9/13.1 (PP/PS, w/w). This suggests that a small amount of styrene was covalently bonded to PP (PP-*g*-PS). From the TEM observation (Figure 9) of the ultrathin cross sections of the obtained samples after reflux, the high-contrast phase stained with RuO_4 was observed on the PP phase, which strongly indicates the existence of grafted PS chains on the PP multilayered structures. Therefore, graft copolymerization of styrene onto the surface of the PP particles occurred. Based on the composition ratio of PP/PS composite particles before and after reflux in THF, it was calculated that 23.7 wt% of PS in PP/PS composite particles covalently bonded to PP. After extraction of PS from the composite particles by THF refluxing, many protrusions, which were not found in the original PP seeded particles, were observed on the multilayered structures (Figure 8b). These features may have been formed by the assembly of grafted PS chains, which were fixed on the PP multilayered structures.
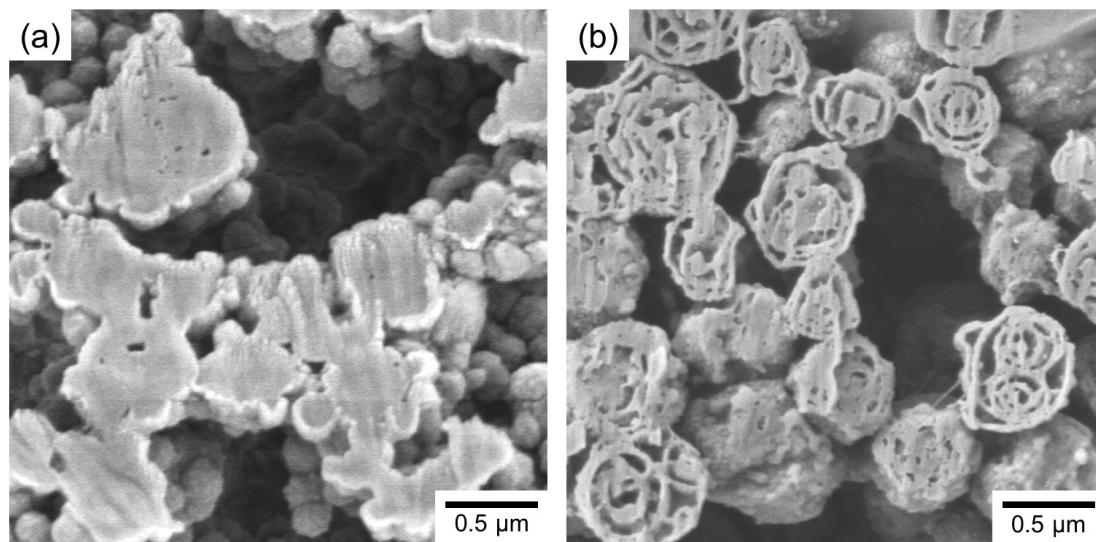
Figure 8. FE-SEM images of the ion beam-milled PP/PS composite particles (a) before and (b) after reflux with THF.
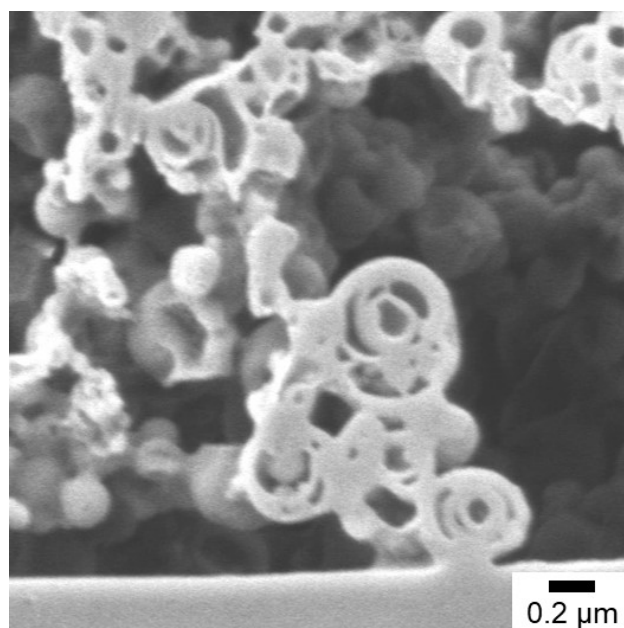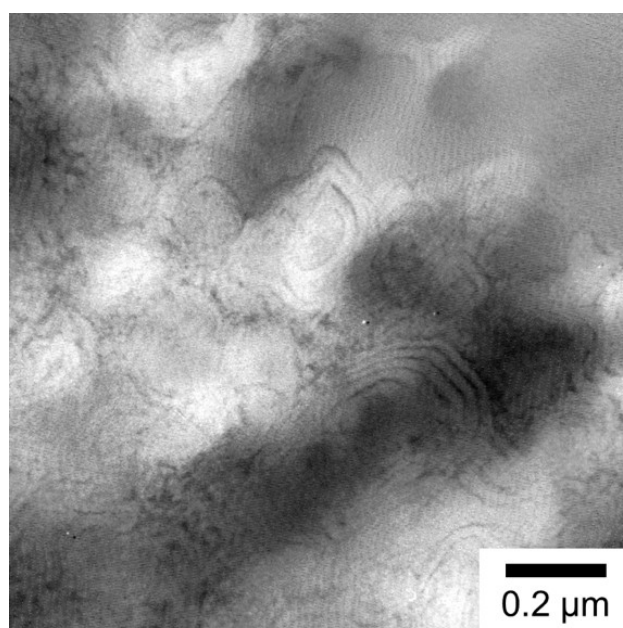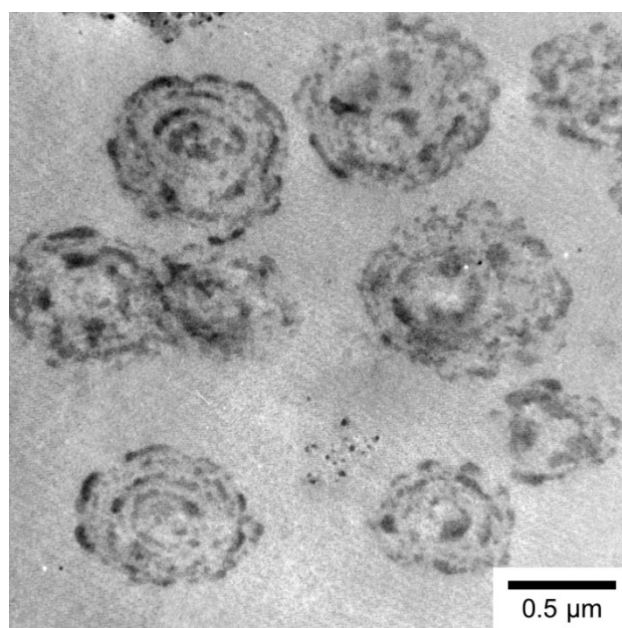

Figure 9. TEM image of an ultrathin cross section of PP/PS composite particles after reflux with THF stained for 30 min with RuO$_4$ vapor.

Figure 10a shows the conversion of styrene as a function of time during seeded emulsion polymerization. The long induction period (~20 h) shown in the curve was probably related to the low solubility of styrene in water at 40 °C.[32] Moreover, Figure 10b shows FE-

SEM images of ion beam-milled cross sections of the PP/PS composite particles at various conversions of styrene. In the early stages of polymerization, PS domains should have grown both inside and outside of PP seeded particles as shown in Figure 10b. As polymerization proceeded, it was clearly observed that the hollow structure (space inside the PP seeded particles) was gradually filled with the PS phase to decrease the PS/waste interface. This structure would be a thermodynamically preferable structure in comparison with the generation of individual PS particles due to the absence of the surfactant. The internal morphology formation of the PP/PS composite particles appeared to be almost complete when 59.7% of styrene had been polymerized. The PP particles were swollen with the styrene monomer (Figure 1) before polymerization, and the polymerization locus should be mainly the PP phase, and then PS was phase-separated from the PP phase as polymerization proceeded.
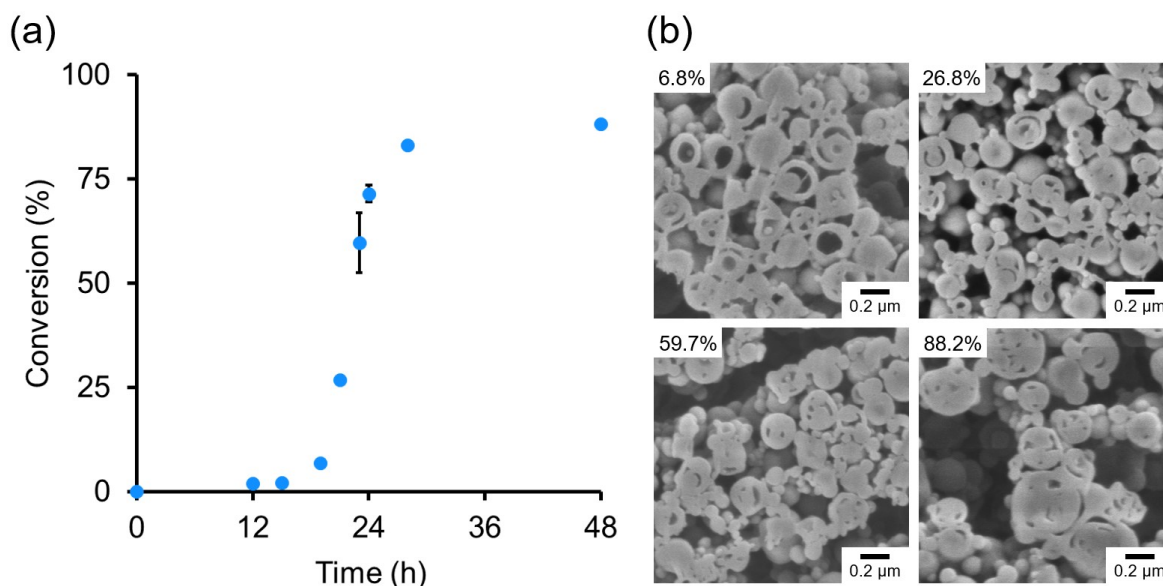

Figure 10. (a) Styrene conversion over time during seeded emulsion polymerization with PP seeded particles in a PP/styrene system of 50/50 (w/w). (b) FE-SEM images of ion beam-milled cross sections of PP/PS composite particles at various conversions of styrene.

Finally, to investigate the practical advantages of the PP/PS composite particles, the adhesion strength test of the PP/PS composite emulsion was carried out in comparison with an emulsion blend system at the same PP/PS weight ratio. The blend emulsion was prepared by mixing of emulsions of the PP seeded particles and PS particles (D_n 1.32 μm, C_v 13.8%) prepared by emulsifier-free emulsion polymerization. The peeling strength of the PP/PS composite particle bonded PP sheet with aluminum was stronger (1.09 N/cm ± 0.07) than that of the emulsion blend system (0.61 N/cm ± 0.05). The mechanical strength of the adhesive layer is one of the significant factors for adhesive performance. Multilayer morphology consisting of the PP and PS phases inside the composite particles, which is a nanocomposite structure, should contribute to the reinforcement of an adhesive layer. Actually, when comparing the transparency of the adhesive layer, the adhesive layer prepared using the PP/PS composite emulsion was more transparent than that of the PP/PS emulsion blend system (Figure 11). Moreover, the surface of the obtained multilayered PP/PS composite particles was patchily covered with the PS phase, indicating that the surface of the composite particles had properties of both PS and PP, where morphology should also contribute to adhesion to the PP sheet.
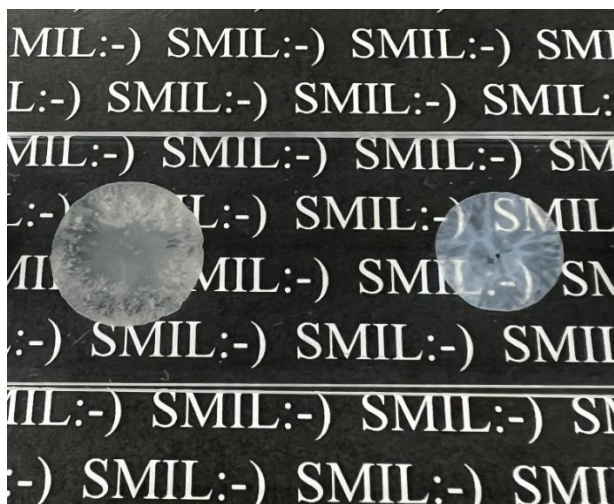
Figure 11. Visual appearance of the adhesive layer prepared by the PP/PS blend emulsion (left) and the composite emulsion (right).

Conclusions

Preparation of the PP/PS composite particles was achieved for the first time by seeded emulsion polymerization at 40 °C using a cationic initiator. The PP/PS composite particles contained ~60 wt% PP. The composite particles had a unique multilayered structure, in which the PS phase filled the multi-hollow structure of PP seeded particles, and it appeared that the PS chain in the obtained composite particles was partially grafted to the PP backbone. It was revealed that the complicated internal morphology of the PP/PS composite particles was obtained via infiltration of PS into voids in PP seeded particles. The adhesion test showed that the PP/PS composite particle system had advantages over the emulsion blend system with the same PP/PS weight ratio, indicating that the composite particle would be useful for the development of novel adhesives that bond PP substrates to other materials. Further experiments to clarify the effects of the ionicity of the initiator, monomer types, and other polymerization conditions are in progress and will be discussed in detail in future reports.

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Chapter 3

Morphology of Polypropylene/Polystyrene Composite Particles Prepared by Seeded Emulsion Polymerization: Influence of Azo Initiator Intrinsic Charge
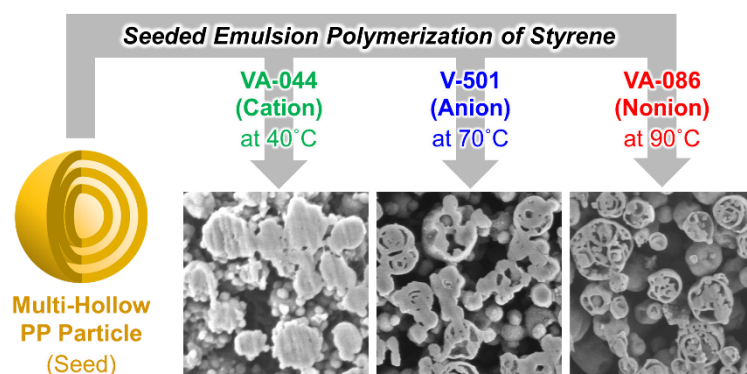
Abstract: We previously reported an interesting multilayer structure in polypropylene (PP)/polystyrene (PS) composite particles prepared by seeded emulsion polymerization. Herein, we investigate the influence of initiator type on PP/PS composite particle morphology. Three kinds of water-soluble azo initiators, each of a different charge, were used in seeded emulsion polymerization. In the case of the cationic initiator VA-044, the obtained PP/PS composite particles showed multilayer structures consisting of PP and PS phases. When the nonionic initiator VA-086 was used, the composite particles had a void structure, with the PS phase encapsulated by a PP shell, but the total amount of PS incorporated was lower than in the VA-044 system. On the other hand, most of the small amount of PS was not inside the PP shells but rather attached to the outer surfaces of PP particles in the case of the anionic initiator V-501. These differences were due to electrostatic interaction between the initiator and PP particles of negative zeta potential. Prior to polymerization, the cationic initiator VA-044 adsorbed to the negatively charged PP particles, thereby inducing the polymerization of styrene at the surface and within the PP particles. This behavior resulted in the formation of composite particles containing large amounts of PS. Moreover, the formation mechanism of the voids in PP/PS composite particles in the case of VA-086 was found to depend on the osmotic pressure and polymerization temperature rather than on the intrinsic charge of the initiator.

Introduction

Composite particles composed of multiple components have attracted a great deal of attention because they can be used in many products such as coatings,[1,2] resin modifiers,[3] catalysts,[4] and adhesives.[5] Preparations of composite particles consisting of various kinds of polymers,[6–8] ceramics,[9,10] and metals[11,12] have been reported, and the functions or structures of polymer composite particles are particularly easy to tune to a particular purpose. Since polymer composite particles have unique properties that cannot be achieved by simply mixing particles of individual polymers,[13,14] great attention has been paid to the various phenomena that occur during the process of composite particle formation. In order to obtain polymer composite particles with the desired morphology or function, it is crucial to understand how the types of polymers, monomers, initiators, media, and reaction conditions in the system affect composite particle formation.

Seeded emulsion polymerization and miniemulsion polymerization[15] are useful methods for preparing polymer composite particles. Water can be used as an eco-friendly solvent in these methods for preparing polymer composite particles. The environmental importance of aqueous media for material production is due to the easy availability of water as well as its low stress on the natural environment and the human body. In recent years, rules policing the content of volatile organic compounds in products have become stricter in many countries around the world, precipitating growing interest in water-based adhesives and paints.

Polypropylene (PP) is a commodity plastic produced by coordination polymerization of propylene and a small amount of comonomer such as ethylene over a Ziegler–Natta[16,17] or

metallocene[18] catalyst. One of the benefits of using PP is that it is more economically accessible than other plastics. Its economic advantages have led to the use of PP in a wide range of applications from household to industry. As with other plastics, the demand for PP has been affected by COVID-19 and oil prices; however, the global market for PP is predicted to grow steadily in the future.[19] While PP has very good heat resistance, mechanical strength, and chemical resistance, it also has shortcomings such as high flammability and poor adhesion. To overcome these disadvantages, methods of compositing PP with other polymers and inorganic fillers have historically been studied.[20–22] However, there had been no report about preparation of composite particles of PP and other organic polymers. In a previous study, we successfully prepared polypropylene/polystyrene (PP/PS) composite particles by seeded emulsion polymerization of styrene with a cationic azo initiator for the first time.[14] Transmission electron microscopy (TEM) analysis of ultrathin cross-sections of the obtained PP/PS composite particles revealed that the particles had a multilayer structure consisting of PP and PS. However, the factors affecting the morphology of PP-composite particles have not yet been fully investigated. In order to develop a universal method for preparing PP-composite particles with the desired properties, it is important to understand the relationship between polymerization conditions and composite particle morphology. In this study of seeded emulsion polymerization, the influence of initiating system factors on the morphology of the obtained PP/PS composite particles was investigated. Herein the influence of azo initiator intrinsic charge on the morphology of composite particles was mainly investigated. In seeded emulsion polymerization with cationic initiator VA-044, it has been found that the space inside the seed

PP particles was mostly filled with the PS phase (Figure 1a).[14] In the case of anionic (V-501) and nonionic (VA-086) initiators, it was expected that the amount of PS composited to the seed particles would decrease due to negative charge of PP seed particles (Figure 1b and c).
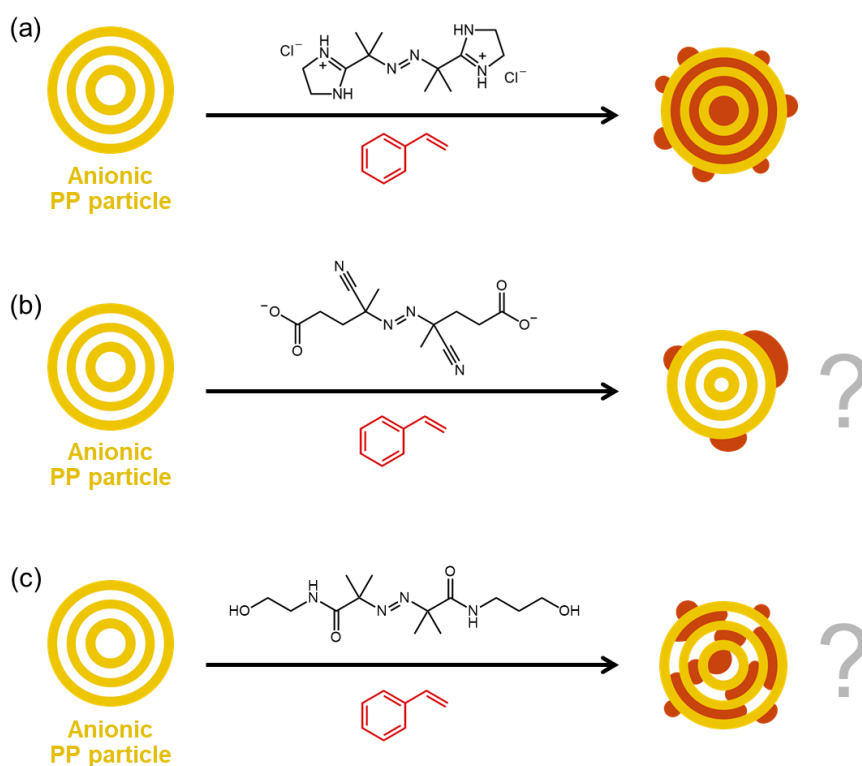

Figure 1. Schematic diagram of the (predicted) morphologies of PP/PS composite particles obtained using different type of the initiator in the seeded emulsion polymerization of styrene with PP seed particles: (a) VA-044, (b) V-501 and (c) VA-086 (c) systems.

Experimental section

Materials

A 25 wt% PP aqueous emulsion (Arrowbase® YA-6010, Unitika Co., Ltd, Osaka, Japan) was offered. Styrene (Nacalai Tesque, Inc., Kyoto, Japan) was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. 2,2′-Azobis[2-(2- imidazolin-2-yl)propane]dihydrochloride (VA-044, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan), 4,4′-azobis(4-cyanovaleric acid) (V-501, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan), 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and sodium chloride (NaCl) (Nacalai Tesque, Inc., Kyoto, Japan) were used as received. Water used in all experiments was purified by an Elix ultraviolet purification system (Millipore, Tokyo, Japan).

Swelling degree of polypropylene with styrene

A polypropylene (PP) aqueous emulsion was heated to 65°C to completely remove the medium. The dried emulsion was melt-pressed at 165°C to produce PP films with a thickness of approximately 0.8 mm. The obtained PP film (0.07 g) was soaked in styrene (3.5 g) and heated to 40°C, 70°C, or 90°C for a set duration. Thereafter, the PP film was removed from the styrene, wiped with paper towel, and weighed. Based on the weight of the PP film before (W_1) and after (W_2) soaking in styrene, the swelling degree of styrene in PP was calculated as

$$\text{Swelling degree of styrene in PP (wt\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Preparation of PP/PS composite particles

PP/PS composite particles were prepared by seeded emulsion polymerization as follows. Styrene (0.5 g), seed PP aqueous emulsion (2 g, giving 25% solid in water), and azo initiator (9 μmol of azo group equivalent) were added to water (10.5 g). VA-044, V-501, or VA-086 was used as the azo initiator. Polymerization was performed in a closed glass tube purged with nitrogen gas for 24 h by shaking at 100 cycles per minute (3 cm strokes). The polymerization temperature was 40 °C or 90 °C in the VA-044 system, 70 °C in the V-501 system, and 90 °C in the VA-086 system. The conversion of styrene was determined by gravimetry or gas chromatography (GC; GC-2014, Shimadzu Corp.). After polymerization, the obtained emulsions were diluted with water and centrifuged twice at 3 °C to remove by-product PS particles and small particles. During this centrifuging, the obtained composite particles floated, whereas the PS particles sedimented.

Preparation of PP/PS composite particles under conditions using high concentration of styrene

Styrene (1 g or 2 g), seed PP aqueous emulsion (2 g, giving 25% solid in water), and VA-086 were added to water (10.5 g). The ratio of [styrene]/[VA-086] was 533 in all experiments. Polymerization was performed in a closed glass tube purged with nitrogen gas for 24 h by shaking at 100 cycles per minute (3-cm strokes). After polymerization, the obtained emulsions contain a large amount of byproduct particles. The composite particles and byproduct particles could not be separated by centrifugation due to increase in the density of composite

particle.

Characterization

The weight-averaged diameter (D_w) and coefficient of variation (C_v) were measured using dynamic light scattering (DLS; FPAR-1000RK, Otsuka Electronics Co., Ltd, Osaka, Japan). The DLS measurements were carried out at a light scattering angle of 90° using a glass cell at room temperature. The ζ-potentials of PP seed particles were measured using a ζ-potential analyzer (ELSZ, Otsuka Electronics Co., Ltd). The obtained composite particles were sputtered with platinum and observed using scanning electron microscopy (SEM; JSM-6510, JEOL, Tokyo, Japan) operated at an accelerating potential of 20 kV. To observe the interior morphology of the composite particles, freeze-dried particles were stained with ruthenium tetroxide (RuO_4) vapor at room temperature for 30 min in the presence of RuO_4 crystals, which were embedded in an epoxy resin matrix, cured at 40 °C overnight, and subsequently sliced using a microtome. Ultrathin (100 nm-thick) cross-sections were observed using TEM (JEM-1230, JEOL, Tokyo, Japan) at an accelerating potential of 100 kV. Furthermore, field-emission SEM (FE-SEM) observations were performed to study the interior structure of the composite particles and PP seeded particles. The freeze-dried composite particles and PP seeded particles were ion-beam-milled (Gatan Ilion model 693) at 4 kV, coated with platinum, and subsequently observed using FE-SEM (SU8020, Hitachi High-Tech, Tokyo, Japan) operated at an accelerating potential of 2 kV. The chemical components of the composite particles were analyzed by Fourier-transform infrared spectrometry (FT-IR; FT/IR-6200, Jasco Co., Ltd,

Tokyo, Japan) using the pressed KBr pellet technique. The polymer composition ratios of the obtained composite particles were quantified from their proton nuclear magnetic resonance (^{1}H NMR, ECA 500, JEOL, Tokyo, Japan) spectra collected at 140 °C in 1,1,2,2-tetrachloroethane-d2.

Analysis of the interaction between PP particles and azo initiators

Seed PP aqueous emulsion (2 g, giving 25% solid in water) and azo initiator (9 μmol) were added to water (10.5 g) and vigorously mixed with a touch mixer for 20 s. VA-044, V-501, or VA-086 was used as the azo initiator. The mixture was allowed to stand at 3 °C for 24 h and was then centrifuged twice at 3 °C to remove PP particles. The concentration of azo initiator in the medium collected by centrifugation was analyzed with liquid chromatography–mass spectrometry (LC–MS). LC–MS analysis was performed on an Agilent 6100 LC/MS system of single-quadrupole MS (Agilent Technologies, Waldbronn, Germany) with an electrospray ionization source. A Cadenza CD-C18 (2.0 mm inner diameter × 150 mm, 3 μm) column was used for separation. Each sample for analysis was dissolved in methanol, and 1 μL of the resulting sample solution was injected into the instrument. The instrument operated at a flow rate of 0.2 mL/min using methanol and 10 mM ammonium acetate in water as the mobile phase. The ratio of the amount of initiator in the medium after removal of PP particles to the total amount of initiator initially added to the water was calculated as

$$\text{Initiator ratio in medium (\%)} = \frac{[I_2]}{[I_1]} \times 100,$$

where $[I_1]$ is the molar concentration of the initiator calculated based on weight values for water (including water in the seed PP aqueous emulsion) and for the initiator added in preparing the mixture, and $[I_2]$ is the molar concentration of the initiator in the medium after removal of PP particles as determined by LC–MS. Initiator adsorption on the PP particles would be expected to produce a small initiator ratio in the medium because the initiator would be removed by centrifugation along with the PP particles.

Gel permeable chromatography analysis

Molecular weights and polydispersity index (PDI) of PS extracted from the composite particles were analyzed by gel permeable chromatography (GPC) using PS standard and eluted in THF flow rate of 1 mL/min on a Shimadzu LC-20AD GPC instrument fitted with RID-20A refractive index detector and Shodex columns (KF-803 and two KF-804). PS was extracted from the composite particles prepared with VA-044, V-501, or VA-086 by reflux with THF, which can dissolve PS but not PP. The resulting PS solution was heated to 70°C for 1 hour to evaporate the THF, followed by standing under reduced pressure for 12 hours to dry completely. 10 mg of the dried solid was dissolved in 5 mL of THF, and 10 µL of the resulting sample solution was injected into the instrument.

Results and Discussion

Three kinds of water-soluble azo initiators, each with a different intrinsic charge, were used to investigate the effects of electrostatic interaction on formation of PP-composite particles in seeded emulsion polymerization. In these experiments, VA-044, V-501, and VA-086 were used as the cationic, anionic, and nonionic initiators, respectively. Styrene, which has a high affinity for PP across a range of temperatures (Figure 2), is generally used as a second monomer in seeded emulsion polymerization. The seed PP emulsion used in these experiments (Arrowbase®, D_w = 221 nm) consists of negatively charged PP particles and water medium. The obtained emulsions in each system had good dispersibility after seeded emulsion polymerization, and no large aggregates were observed. The conversion of styrene as determined by gravimetry was 82.4% in the VA-044 system, 94.6% in the V-501 system, and 96.3% in the VA-086 systems. Figure 3 shows the size distributions of the seed PP emulsion and the emulsions obtained by seeded emulsion polymerization for each initiator after centrifugal washing. Our previous reports showed that the mean size of PP/PS composite particles obtained in the VA-044 system was larger than that of the original seed PP particles.[14] In the present study, the similar results were found for V-501 and VA-086, which were newly used in this study. These results suggest that PP/PS composite particles were successfully prepared using each initiator regardless of intrinsic charge.
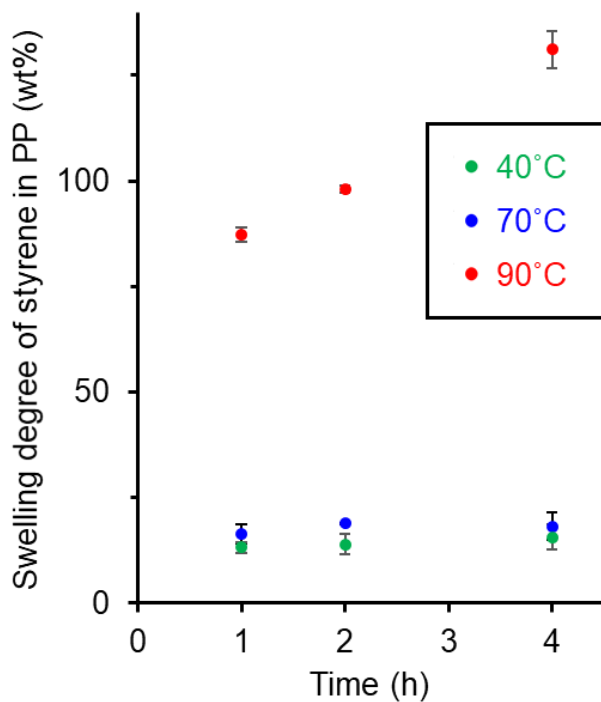
Figure 2. Swelling degree of polypropylene (PP) with styrene at 40°C, 70°C, or 90°C over time. Results represent mean ± standard deviation of two replicates for each treatment.
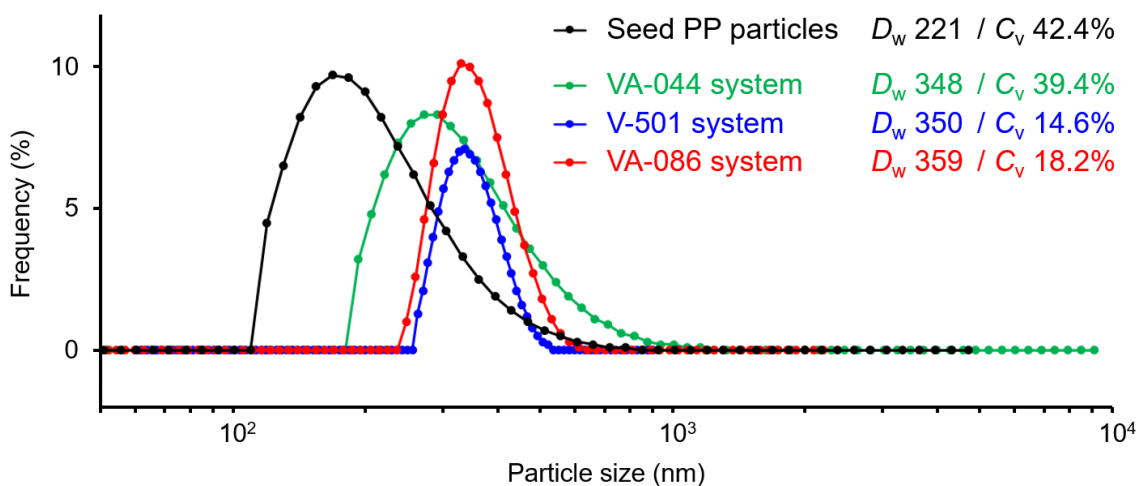

Figure 3. Weight-averaged diameter of seed polypropylene (PP) particles and particles obtained by seeded emulsion polymerization with each azo initiator.

The chemical compositions of the particles prepared with each initiator were analyzed by using FT-IR (Figure 4 and Table 1). The peaks attributed to methyl groups in PP[23] and benzene rings in PS[24–26] were observed in the FT-IR spectra of the particles prepared with each initiator. Moreover, the seed PP particles used in this study consisted of modified PP, in which trace amounts of carboxylic acid derivatives were grafted to PP; therefore a broad peak derived from carbonyl groups was detected at approximately 1713 cm−1. These results clarified that the seeded emulsion polymerization using VA-044, V-501, or VA-086 had produced PP/PS composite particles.
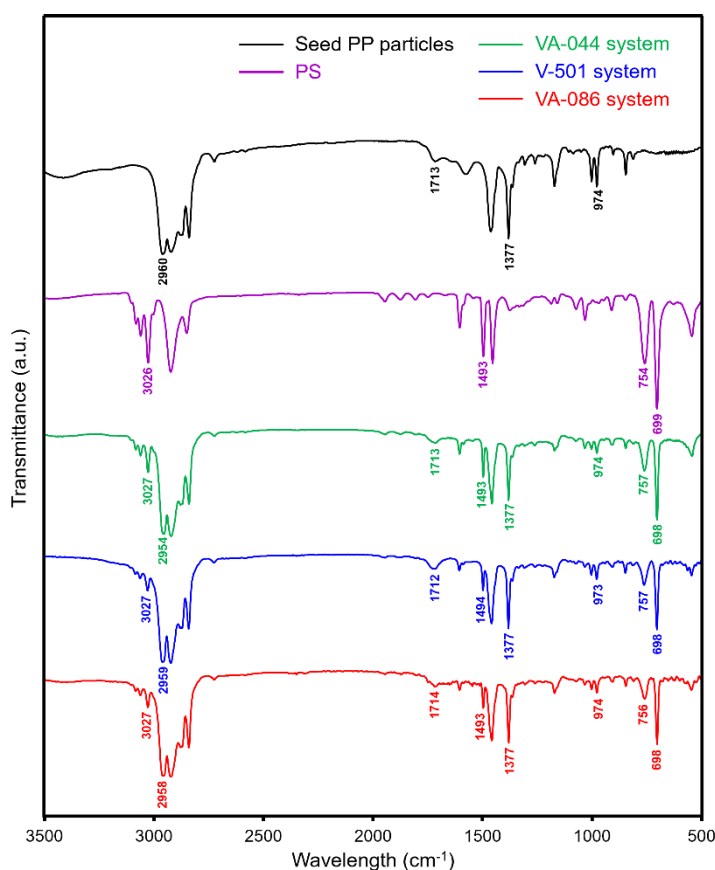

Figure 4. Fourier-transform infrared spectra of seed polypropylene (PP) particles, polystyrene (PS), and the composite particles obtained by seeded emulsion polymerization using different type of azo initiators (green, VA-044; blue, V-501; red, VA-086).

Table 1. Characteristic bands and polymer assignments based on Fourier-transform infrared spectra of seed polypropylene (PP) particles, polystyrene (PS), and PP/PS composite particles.

Wavelength (cm^{-1})	Characteristic band	Polymer assignments
698, 699	C–H out-of-plane bending vibration of benzene rings	PS
754, 756, 757	C–H out-of-plane bending vibration of benzene rings	PS
973, 974	CH$_3$ asymmetric rocking vibrations C–C asymmetric stretching vibrations	PP
1377	CH$_3$ symmetric deformation vibrations	PP
1493, 1494	C=C stretching vibrations of benzene rings	PS
1712, 1713, 1714	C=O stretching vibrations of carbonyl groups	PP
2954, 2958, 2959, 2960	CH$_3$ asymmetric stretching vibrations	PP
3026, 3027	C–H stretching vibration of benzene rings	PS

SEM analysis revealed that the morphologies of the PP/PS composite particles prepared with the three types of initiators were clearly different from that of the seed PP particles (Figure 5a). In the VA-044 system, spherical particles with multiple surface protrusions were obtained (Figure 5b). On the other hand, the PP/PS particles prepared with V-501 or VA-086 were found to be irregularly shaped (Figure 5c and d). The particles prepared with V-501 appeared to be irregular shape with a few protrusions. Particles with wrinkled surfaces were also often observed in the VA-086 system (Figure 5d), which would be due to void structure inside the particles. It was assumed that the particles were buckled during the drying process, resulting formation of wrinkles on the particle surface. Indeed, the wrinkles on the surface of particles were no longer observed (Figure 6) by increasing the styrene

concentration per PP seed particle. The results suggest that the degree of wrinkling of VA-086 composite particles depends on the amount of PS encapsulated in the particles. Based on SEM observations, the seed PP particles were fused together due to their low glass transition temperature T_g. On the other hand, three types of PP/PS composite particles commonly showed no fusion of the particles. This lack of fusion indicates the partial or total coverage of PP/PS composite particle surfaces by the polymer of higher T_g, namely PS.
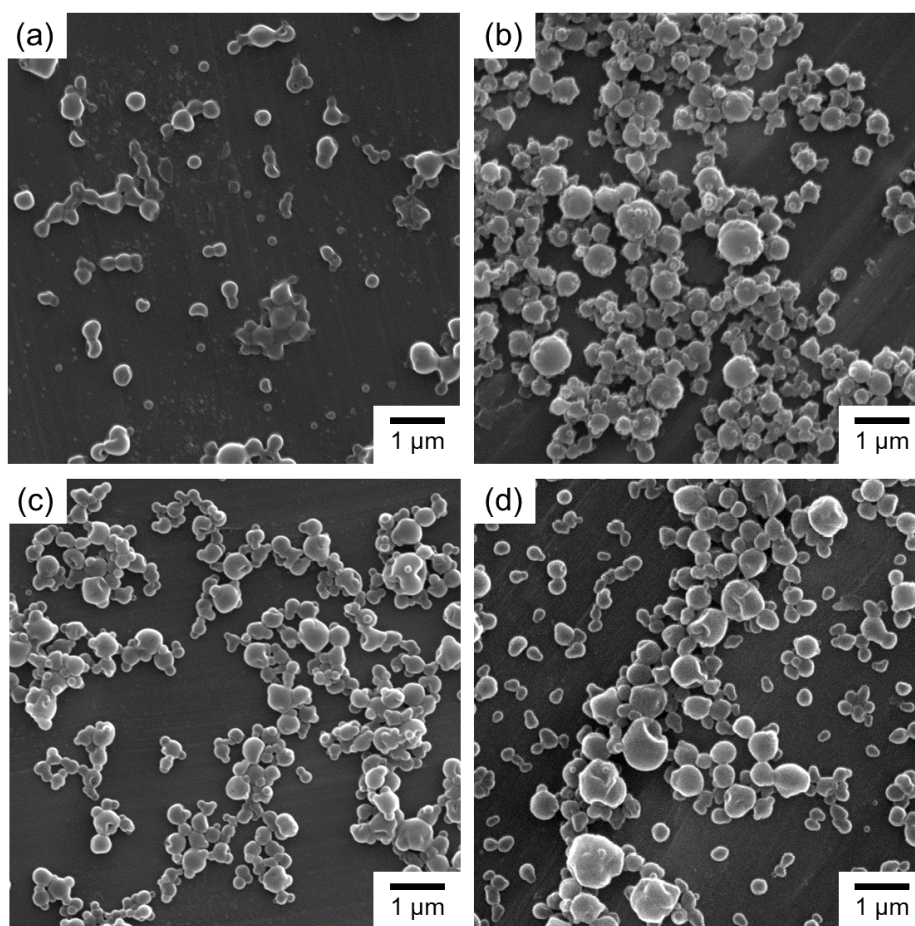

Figure 5. Scanning electron microscopy images of (a) seed polypropylene particles and (b–d) polypropylene/polystyrene composite particles obtained by seeded emulsion polymerization using (b) VA-044, (c) V-501, and (d) VA-086.
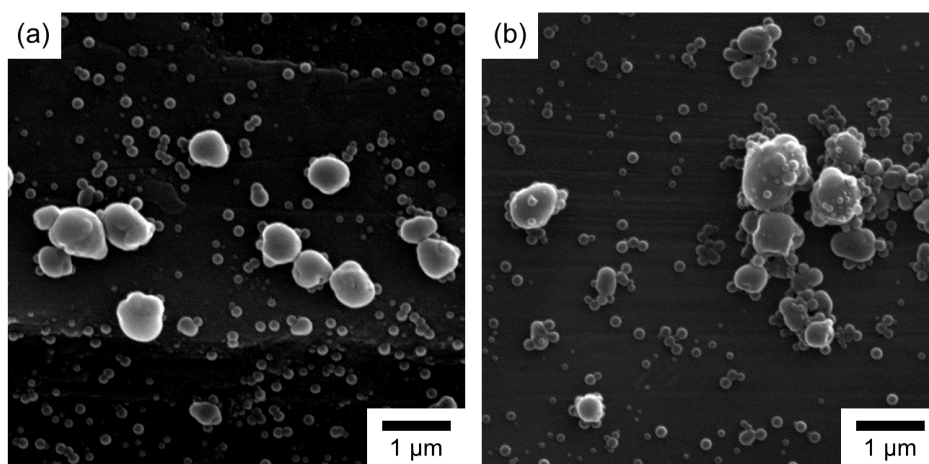
Figure 6. Scanning electron microscopy images of the composite particles obtained by seeded emulsion polymerization with (a) 2 and (b) 4 times the amount of styrene per seed PP particle.

To investigate the internal morphology of PP/PS composite particles, cross-sections of composite particles formed using each azo initiator were observed using TEM and FE-SEM (Figure 7). Prior to microtome slicing for TEM analysis, the composite particles were stained with RuO$_4$ vapor, which selectively stained PS domains. This staining showed that the PP/PS composite particles derived from VA-044 had a multilayered inner structure consisting of PP (low-contrast phase) and PS (high-contrast phase) (Figure 7a). This internal morphology was formed as the PS phase filled voids originally present in the seed PP particles as polymerization proceeded (Figure 8).[14] The existence of multi-hollow structure of PP particles has been revealed in previous paper,[14] which would be formed by adsorption of water due to the slight grafted carboxylic acid derivatives in the PP during the preparation of PP particles. On the other hand, TEM analysis of cross-sections of PP/PS composite particles obtained using V-501 revealed that the PS phase was attached on the outer surfaces of seed PP particles and was

hardly present in particle interiors (Figure 7b). Moreover, in the case of VA-086, multiple small PS particles were encapsulated by PP shells (Figure 7c and c′). In addition, the ion-beam-milled cross-sections (Figure 7a′) of PP/PS composite particles formed using VA-044 showed almost no voids. On the other hand, PP/PS composite particles formed using V-501 or VA-086 exhibited a multi-hollow structure (Figure 7a′–c′). The morphological differences are interpreted as resulting from differences in the initiator intrinsic charge or polymerization temperature. VA-044 is a catanionic initiator, so it would be expected to interact with negatively charged PP seed particles. This interaction would induce the polymerization of styrene both at the surface of and within PP particles, resulting in the formation of composite particles containing plentiful PS. On the other hand, when V-501 or VA-086 was used as the initiator, no such interaction would be expected. The precipitated PS particles generated by homogeneous nucleation have less negative charge, and such PS particles acquired colloidal stability by coagulation with each other or by precipitating onto negatively charged seed PP particles.[27,28] Moreover, the PS domains attached onto the outer surfaces of seed PP particles swollen with styrene and grew to large size as polymerization progressed. The fine domains of PS in the composite particles prepared with each initiator are expected to form nanocomposite coating films having high transparency. It seems to be difficult to prepare such films by emulsion blend systems using each emulsion, in which macro phase separation will easily occur.
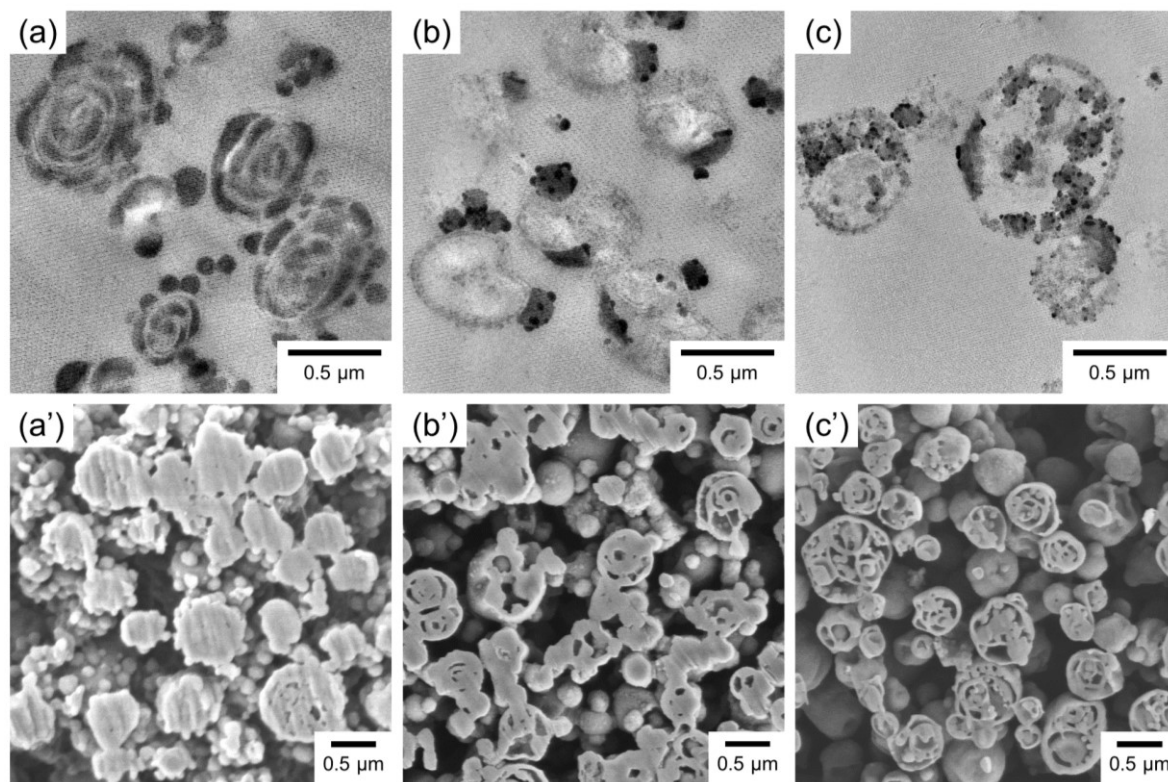
Figure 7. (a–c) Transmission electron microscopy (TEM) images and (a′–c′) field-emission scanning electron microscopy (FE-SEM) images of cross-sections of polypropylene/polystyrene composite particles obtained by seeded emulsion polymerization with (a and a′) VA-044, (b and b′) V-501, and (c and c′) VA-086. The composite particles were stained for 30 min with RuO$_4$ vapor for TEM analysis and cut by an ion beam for FE-SEM.

Figure 8. Field-emission scanning electron microscopy image of ion-beam-milled polypropylene seed particles.

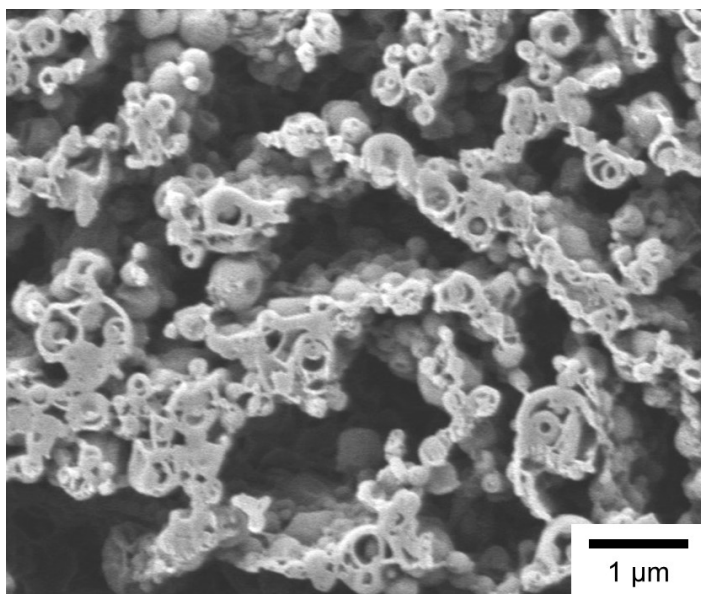To clarify the nature of the interaction between the seed PP particles and each azo initiator, the concentration of the initiator in the aqueous medium, which was collected from the seed PP emulsion by centrifugation, was measured prior to polymerization. As shown in Figure 9, the VA-044 content remaining in the aqueous solution after removal of PP particles constituted 16% of the total amount of added initiator. This result means that most of the VA-044 was adsorbed on seed PP particles. Because the ζ-potential of seed PP particles is negative (-51.9 mV), the cationic initiator VA-044 would be expected to interact electrostatically with the surfaces of PP seed particles. On the other hand, in the case of nonionic initiator, VA-086, all of the added initiator remained in the medium, indicating no interaction between the initiator and the seed PP particles. Although V-501 has an anionic charge, the amount of V-501 remaining in the medium was somewhat less than the total amount of added initiator, indicating that V-501 interacted slightly with the PP seed particles. This behavior was expected based on the dipolar interaction between the nitrile group in V-501 and the carbonyl group of the carboxylic acid derivative grafted to PP.[29] The PP/PS compositional ratios of the composite particles obtained using VA-044, V-501, and VA-086 were 61.1/38.9, 71.7/28.3, and 69.8/30.2 (w/w), respectively. PS content was highest in composite particles obtained using VA-044. Additionally, GPC analysis of the PS extracted from the composite particles prepared with each initiator revealed that the PS in the composite particles of the VA-044 system had the lowest molecular weight (Table 2). This result also supported the interaction between the cationic initiator and the anionic PP seed particles, in which a high concentration of the initiator existed around the seed PP particles.
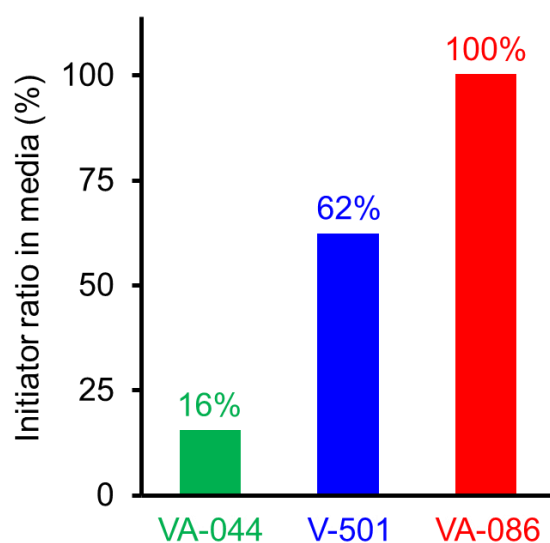
Figure 9. Ratio of the amount of each initiator in medium after removal of polypropylene particles to the total amount of initiator initially added to water.

Table 2. Molecular weight and polydispersity index of PS extracted from the composite particles prepared with each initiator

System[*]	M_n	M_w	PDI
VA-044	136,000	588,000	4.3
V-501	640,000	1,440,000	2.3
VA-086	486,000	1,021,000	2.1

* The PP/PS composite particles prepared under the conditions described in *Experimental Section* were analyzed. In the VA-044 system, the polymerization temperature was 40°C.

In cross-section observations, void structures within particles were clearly observed in the VA-086 system (Figure 7c′). In order to clarify the formation of void structures, ion-beam-milled cross-sections of PP/PS composite particles formed using VA-086 were observed at various styrene conversion degrees using FE-SEM (Figure 10). Figure 10a shows the conversiontime profile of the seeded emulsion polymerization of styrene using VA-086. The polymerization was almost complete at 150 min. On the other hand, in the case of the VA-044 system, the polymerization of styrene reached to 80% polymerization after about 28 h.[14] This result was based on the larger the propagation rate constant of styrene at the higher polymerization temperature.[30] FE-SEM observation revealed that the PP shell was greatly expanded compared to its pre-polymerization state even though the polymerization of styrene had not progressed fully at the time of observation (Figure 8 and 10b). This result implies that the formation of the PS phase in PP/PS composite particles did not affect void development in composite particles. During seeded emulsion polymerization, the commercially available PP emulsion was diluted 6.25 times with water. The dilution of the emulsion created an osmotic pressure difference inside and outside the PP shell, causing penetration of the medium into the PP shell and expansion of PP/PS composite particles.
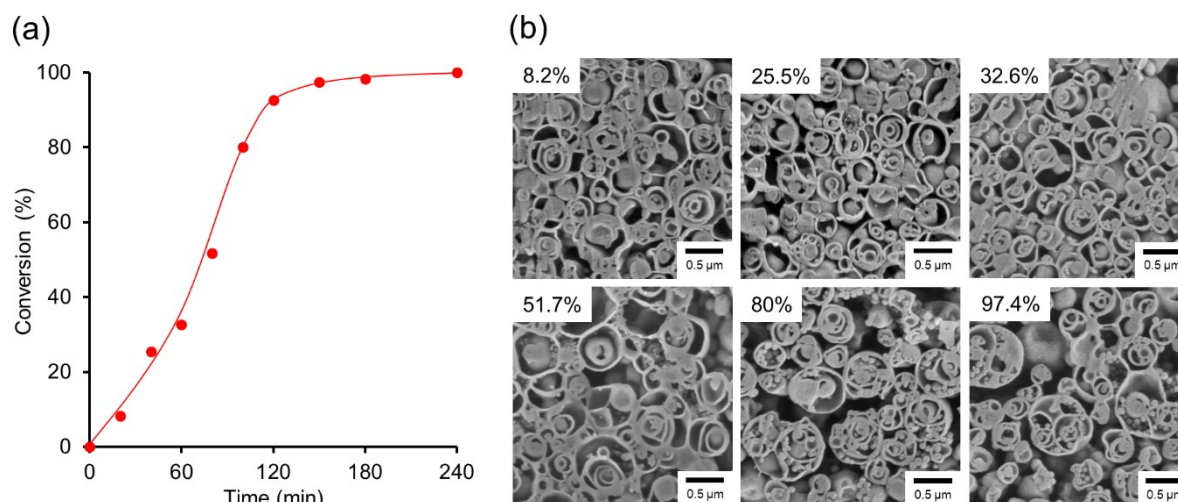
Figure 10. (a) Styrene conversion over time during seeded emulsion polymerization with VA-086 as initiator at 90 °C. (b) Field-emission scanning electron microscopy images of ion-beam-milled cross sections of polypropylene/polystyrene composite particles at various styrene conversion degrees.

To verify the above hypothesis, seeded emulsion polymerization using VA-086 was performed in a medium containing a high concentration (0.24 mol L−1) of NaCl as an electrolyte. According to SEM observations of the resulting PP/PS composite particles (Figure 11a), wrinkles on particle surfaces were not observed, and particle shapes were close to spherical. FE-SEM analysis of ion-beam-milled cross-sections of these PP/PS composite particles (Figure 11b) showed that voids within these PP/PS composite particles were smaller than those within particles produced in the absence of NaCl (Figure 7c′). Indeed, the mean size of PP/PS composite particles as measured by DLS (D_w = 306 nm, C_v = 37.4%) was smaller than that of particles obtained without NaCl (D_w = 359 nm, C_v = 18.2%). These results strongly indicate that the void structure within PP/PS composite particles produced in the absence of NaCl was generated by osmotic pressure. In this scenario, the medium penetrated within PP

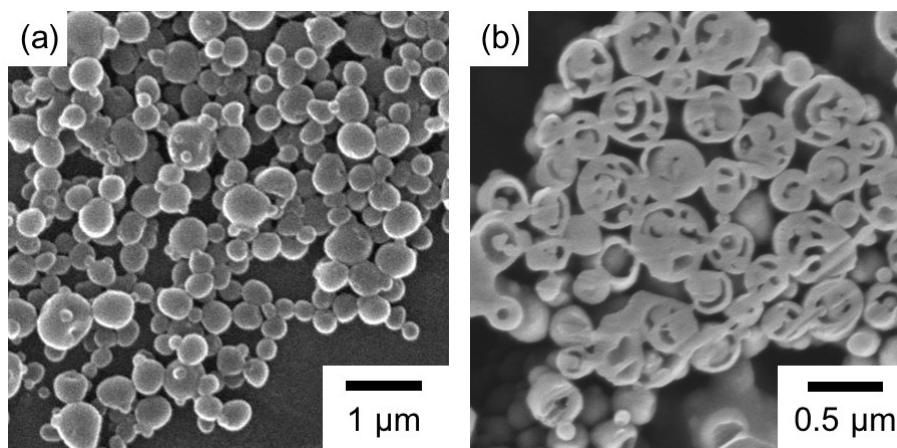particle by the osmotic pressure difference between the aqueous medium and the interior of the PP shell.

Figure 11. (a) Scanning electron microscopy image and (b) field-emission scanning electron microscopy image of ion-beam-milled cross-sections of polypropylene/polystyrene composite particles obtained by seeded emulsion polymerization using VA-086 in an NaCl aqueous solution.

If such an osmotic pressure difference between the interior and exterior of the PP shell caused infiltration of the medium into the PP shell for PP/PS particles formed using VA-086, then PP/PS composite particles formed using VA-044 should also have shown such a hollow structure. However, the actual composite particles using VA-044 were solid and lacked voids (Figure 7a′). This difference is interpreted as a result of the difference in the polymerization temperature: 40 °C for VA-044, 90 °C for VA-086. When seeded emulsion polymerization using VA-044 was instead performed at this higher temperature of 90 °C, the obtained PP/PS composite particles showed rugged shapes, and many voids were observed within the particles

(Figure 12). Additionally, DLS analysis revealed that in the VA-044 system, PP/PS composite

particles polymerized at 90 °C were larger (D_w = 360 nm, C_v = 25.4%) than those polymerized

at 40 °C. Based on these results, the higher temperature induced the plasticization of the PP

shell, resulting in penetration by the medium. Given the ~150 °C melting point of the seed PP

particles, the PP shell might not have had the flexibility at 40 °C that it had at 90 °C to expand

with penetration of the medium. In the VA-044 system at 90 °C, the PP shell would have

become flexible due to absorption of more styrene and could have expanded with penetration

of the medium. Indeed, PP was found to absorb more styrene at higher temperatures (Figure 2).
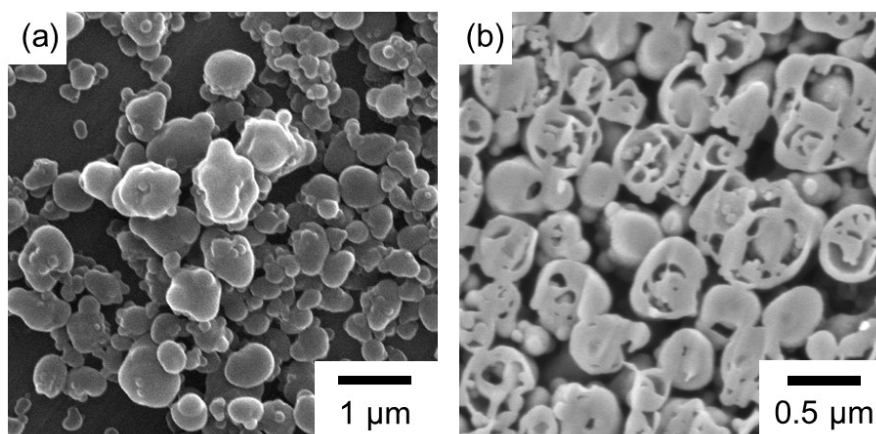

Figure 12.   (a) Scanning electron microscopy image and (b) field-emission scanning electron microscopy image of ion beam-milled cross sections (b) of the polypropylene/polystyrene composite particles obtained by seeded emulsion polymerization with VA-044 at 90 °C.

Conclusions

The influence of the intrinsic charge of the azo initiator on the morphology of PP/PS composite particles prepared by seeded emulsion polymerization was investigated. When a cationic or nonionic initiator was used, PP/PS composite particles were obtained in which the PS phase was encapsulated by the PP shell. On the other hand, in PP/PS composite particles derived using an anionic initiator, most of the PS phase was attached to the outer surfaces of seed PP particles. The amount of initiator adsorbed on the seed PP particles depended on the initiator's intrinsic charge. PP/PS composite particles obtained using VA-044, which showed the greatest degree of adsorption on seed PP particles, exhibited a higher PS content than composite particles obtained using either of the other types of initiator. Further analysis suggested that void formation in PP/PS composite particles is due to the infiltration of medium facilitated by the osmotic pressure difference between the interior and exterior of the PP shell. This study provides fundamental mechanistic insights for the development of novel PP-composite materials without volatile organic compounds or surfactants.

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Chapter 4

Preparation of Polypropylene-Composite Particles by Seeded

Emulsion Polymerization of (Meth)acrylates with Different Structures
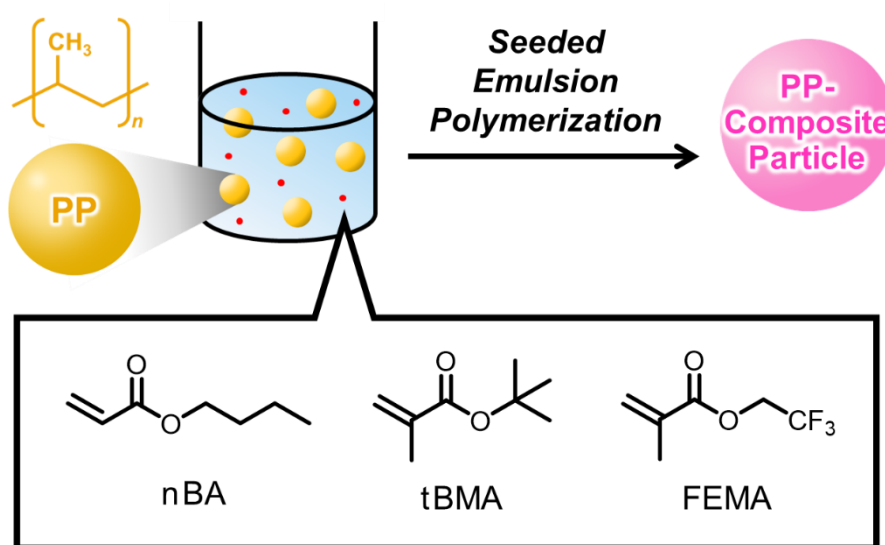
Abstract: Three (meth)acrylates were used as second monomers to prepare PP-composite particles by seed emulsion polymerization. When each monomer was homo-polymerized, the progress of seed emulsion polymerization depended on the polymerization temperature. In addition, when 2,2,2-trifluoroethyl methacrylate (FEMA) is copolymerized with styrene, the conversion in the seed emulsion polymerization at 40°C changes significantly. Furthermore, the film prepared from PP/poly (butyl acrylate) (PnBA) composite emulsions showed better tensile properties than emulsion blend systems. This result specifically illustrates the advantage of preparation of the composite particles from PP and second polymer. In this chapter, we provide a universal technique for obtaining of PP composite particles from monomers of various structures.

Introduction

Polymer/polymer composite particles are of interest not only for their morphology and manufacturing techniques, but also for what polymers they contain. The functionality of polymer/polymer composite particles strongly depends on properties of polymers in the composite particles (thermal, mechanical, interfacial properties). The technique for preparing composite particles should not be limited by the type of polymer, but should be a method that can be applied to a wide variety of polymers.

As described in **Chapters 2** and **3**, we have successfully prepared the composite particles composed of PP and PS in seeded emulsion polymerization system. PS has long been actively used as a model material in the study of polymer colloids, but the polymer is a common material with no noteworthy properties. The more second polymers that can be selected to obtain more highly functional PP-composite particles, the better.

Unsaturated compounds such as styrene, acrylate, acrylamide, acrylonitrile, and conjugated diene can be used as monomers for radical polymerization. Among them, acrylate monomers offer a high degree of freedom in molecular structure design, allowing polymers to have various functions. To date, polymer particles have been prepared from acrylates such as ionic liquid monomers[1,2], fluorine monomers[3], and liquid crystal monomers[4] as well as simple acrylate monomers with alkyl groups as side chains.

In **Chapter 4**, the PP-composite particles were prepared by seeded emulsion polymerization with three different (meth)acrylate monomers. Based on the results of seed emulsion polymerization, the influence of polymerization temperature and comonomers on the

formation of composite particles is discussed.

Experimental Section

Materials

25 wt% of PP aqueous emulsion (Arrowbase YA-6010, Unitika Co., Ltd, Osaka, Japan) was offered. n-Butyl acrylate (nBA) (Nacalai Tesque, Inc., Kyoto, Japan), tert-butyl methacrylate (tBMA) (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), 2,2,2-trifluoroethyl methacrylate (FEMA) (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan), and styrene (Nacalai Tesque, Inc., Kyoto, Japan) were purified by distillation under reduced pressure in a nitrogen atmosphere and stored in a refrigerator. Ammonia persulfate (APS), 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) and 2,2′-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) were used as received. Water used in all experiments was purified by an Elix ultraviolet purification system (Millipore, Tokyo, Japan).

Swelling degree of PP with each monomer

PP aqueous emulsion was heated to 65°C to completely remove the medium. The dried emulsion was melt-pressed at 165°C to produce PP films with a thickness of approximately 0.8 mm. The obtained PP film (0.07 g) was soaked in nBA, tBMA, FEMA or styrene (3.5 g) and heated to 40°C or 90°C for 4 hours. Thereafter, the PP film taken out of monomer was wiped with paper towel and weighed. Based on the weight of PP film before (W_1) and after (W_2) soaking in monomer, swelling amounts of each monomer in PP were calculated as follows:

$$\text{Swelling amounts of each monomer in PP (wt\%)} = \frac{W_2 - W_1}{W_1} \times 100$$

Seeded emulsion polymerization

Seeded emulsion polymerization with seed PP particles was performed as follows: Monomer (0.5 g) , seed PP aqueous emulsion (2 g, giving 25% solid in water), and azo initiator (9 μmol of azo group equivalent) were added to water (10.5 g). nBA, tBMA, FEMA (0.5 g), or FEMA/styrene (0.25 g/0.25 g) was used as the monomer. VA-044 or VA-086 was used as the azo initiator. Polymerization was performed in a closed glass tube purged with nitrogen gas for 24 h by shaking at 100 cycles per minute (3-cm strokes). The polymerization temperature was 40°C in the VA-044 system, and 90°C in the VA-086 system. The conversion of monomer was determined by gravimetry. After polymerization, the obtained emulsions were diluted with water and centrifuged twice at 3°C.

Emulsifier-free emulsion polymerization of nBA

PnBA particles were prepared emulsion polymerization under emulsifier-free condition as follows: nBA (20 g), APS (81 mg), and water (116 g) were added into a 300 ml round-bottom Schlenk flask, sealed off with a silicon rubber septum, and purged with nitrogen. Polymerization was carried out at 80°C for 15 h with stirring at 300 rpm. After the polymerization, PnBA particles were centrifugally washed with water 1 time and resuspended in water.

Characterization

To observe the interior morphology of the composite particles, freeze-dried particles were stained with ruthenium tetroxide (RuO_4) vapor at room temperature for 30 min in the presence of RuO_4 crystals, which were embedded in an epoxy resin matrix, cured at 40°C overnight, and subsequently sliced using a microtome. Ultrathin (100 nm-thick) cross-sections were observed using TEM (JEM-1230, JEOL, Tokyo, Japan) at an accelerating potential of 100 kV. To observe the interior morphology of the films prepared PP/PnBA composite emulsion or blend emulsion, these films were embedded in an UV-curable resin matrix, cured by irradiation of UV. The UV-cured resins were shaved until the embedded films appear on the surface, which were stained with ruthenium tetroxide (RuO_4) vapor at room temperature overnight in the presence of RuO_4 crystals, and subsequently sliced using a microtome. Ultrathin (90 nm-thick) cross-sections were observed using TEM (JEM-1230, JEOL, Tokyo, Japan) at an accelerating potential of 100 kV. The chemical components of the composite particles were analyzed by Fourier-transform infrared spectrometry (FT-IR; FT/IR-6200, Jasco Co., Ltd., Tokyo, Japan) using the pressed KBr pellet technique.

Preparation of tensile specimens and measurement of tensile strength

Emulsion of PP/PnBA composite particles without centrifugally washing was dried at room temperature under reduced pressure. The dried solid was melt-pressed at 160°C for 1 min

to produce a film with a thickness of approximately 0.15 mm. The prepared film was cut to 10 mm width. The tensile test of specimen prepared with PP/PnBA composite emulsion was carried out at room temperature and 60°C with a tensile tester machine (Autograph AGS-5kNX; Shimadzu Seisakusho Corp., Kyoto, Japan) at a tensile speed of 10 mm/min. An emulsion blend with the same PP/PnBA wight ratio was prepared by mixing of Arrowbase YA-6010 (PP emulsion) and emulsifier-free PnBA emulsion, and tensile specimen was prepared by the same methods noted above. Tensile test of specimen prepared with the blend emulsion was carried out under the same conditions as above.

Results and Discussion

The nBA, tBMA, and FEMA used in this study are monomers used to prepare adhesives, gas generating particle[5], and water repellent materials[6], respectively. In seeded emulsion polymerization, the seed particles are the polymerization field for the second monomer, so the second monomer must be absorbed by the seed polymer. Initially, to investigate the affinity of the seed PP particles for the three monomers, the films prepared from seed PP emulsion were heated in each monomer at 40°C or 90°C. Figure 1 shows the rate of weight change of PP film after 4 hours. At both 40°C and 90°C, styrene as a monomer for comparison was found to be absorbed most by PP, and FEMA was found to be least absorbed by PP. The affinity between three acrylates and PP increased with higher temperature, but the rate of increase was lower than that of styrene and PP.
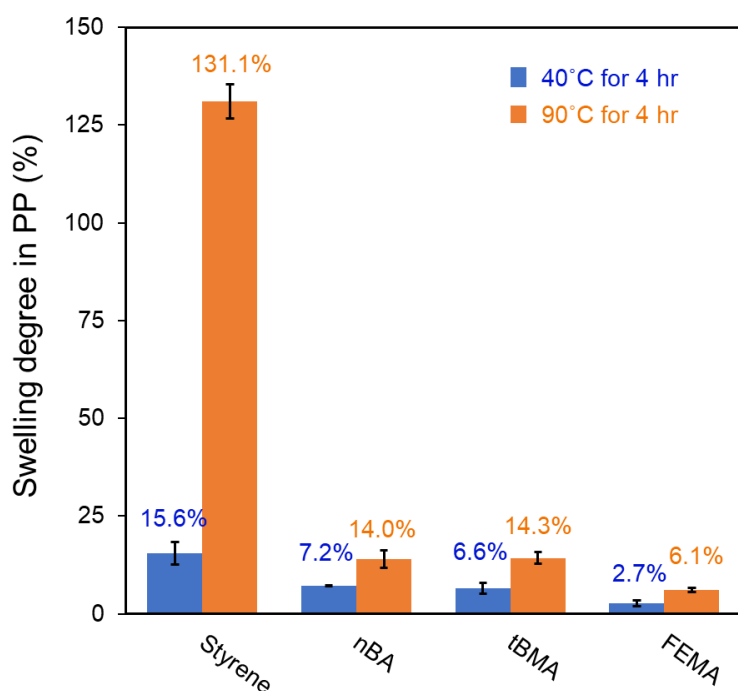

Figure 1. Swelling degree of PP with styrene, nBA, tBMA, or FEMA at 40°C and 90°C. Results represent mean ± standard deviation of two replicates.

Seeded emulsion polymerization of nBA, tBMA, and FEMA was performed at 40°C using the cationic initiator VA-044, resulting in conversion of 0%, 13.9%, and 0%, respectively. The low conversion of these monomers may be due to the low amount of each monomer absorbed by the seed PP particles at 40°C. When seeded emulsion copolymerization was carried out at 40°C by replacing 50 wt% of FEMA with styrene, the conversion was found to increase to 92.8%. On the other hand, in the same experiment using nBA or tBMA, the conversion was less than 10%. These results indicate that the addition of styrene promoted seeded emulsion polymerization of only FEMA among the three acrylates. Octanol-water partition coefficients for styrene, nBA, tBMA, and FEMA are 2.95, 2.36, 2.54, and 1.56, respectively, indicating that FEMA is the most hydrophilic[7]. In seeded emulsion polymerization, the second monomer dissolves and diffuses in water to reach seed particle which is the polymerization site. It is assumed that the seeded emulsion copolymerization was promoted because of the efficient absorption of FEMA dissolved in water by the styrene-swollen seed PP particles.

To prove the formation of the PP/P(FEMA-S) composite particles, FT-IR analysis was carried out (Figure 2 and Table 1). In the FT-IR spectra of the particles obtained by seeded emulsion copolymerization with VA-044, the peak derived from CF_2 groups[8] of FEMA was detected, as well as peaks attributed to CH_3 groups of PP[9] and the benzene rings of PS[10–12]. The result of FT-IR analysis revealed that PP/P(FEMA-S) composite particles were successfully prepared.
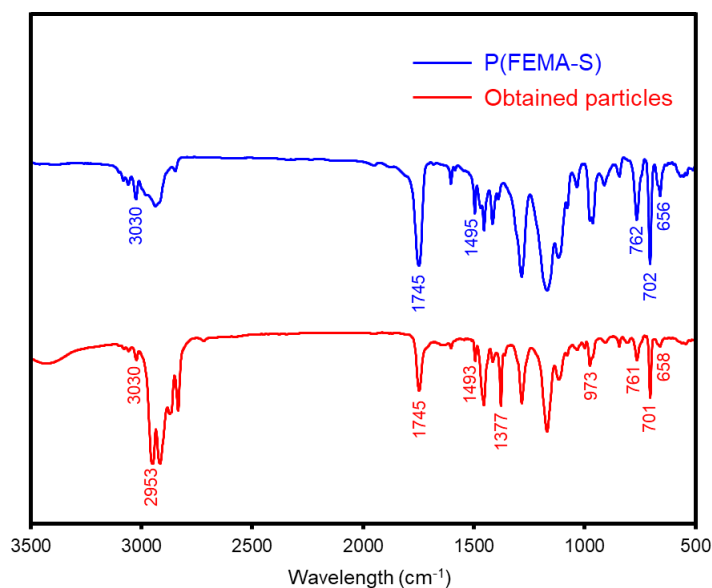
Figure 2. Fourier-transform infrared spectra of P(FEMA-S) and the particles obtained by seeded emulsion copolymerization of FEMA and styrene at 40°C.

Table 1. Characteristic bands and polymer assignments based on Fourier-transform infrared spectra of P(FEMA-S) and the particles obtained by seeded emulsion copolymerization of FEMA and styrene at 40°C

Wavelength (cm^{-1})	Characteristic band	Polymer assignments
656, 658	CF$_2$ wagging and rocking vibration	P(FEMA-S)
701, 702	C–H out-of-plane bending vibration of benzene rings	P(FEMA-S)
761, 762	C–H out-of-plane bending vibration of benzene rings	P(FEMA-S)
973	CH$_3$ asymmetric rocking vibrations C–C asymmetric stretching vibrations	PP
1377	CH$_3$ symmetric deformation vibrations	PP
1493, 1495	C=C stretching vibrations of benzene rings	P(FEMA-S)
1745	C=O stretching vibrations of carbonyl groups	P(FEMA-S)
2953	CH$_3$ asymmetric stretching vibrations	PP
3030	C–H stretching vibration of benzene rings	P(FEMA-S)

Ultrathin cross sections of the PP/P(FEMA-S) composite particles were stained with

RuO_4 vapor for 30 min, and then, the cross sections were observed using TEM to reveal the surface and internal morphology of the composite particles (Figure 3). Just like the PP-composite particles prepared using only styrene[13], patches composed of second polymer were seen on the surface of the particles, and the internal morphology of the particles showed a multilayer structure consisting of PP and second polymer. As the polymerization of the second monomer swollen in the PP phase progressed, the P(FEMA-S) phase must have separated from the PP shell to form a complicated multilayer structure. In other words, the electron microscopic analysis suggests that even at the low temperature of 40°C, the addition of styrene caused FEMA, which has low affinity for PP, to be absorbed by the seed PP particles.
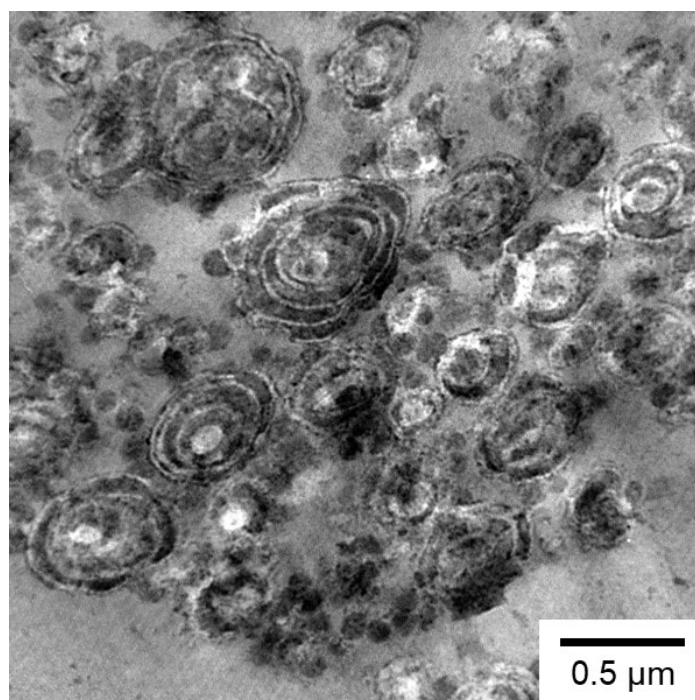

Figure 3. TEM image of an ultrathin cross sections of PP/P(FEMA-S) composite particles stained for 30 min with RuO_4 vapor.

In order to investigate the effect of polymerization temperature, seeded emulsion

polymerization of nBA, tBMA, and FEMA was carried out at 90°C using VA-086 as an initiator, resulting in conversion of 95.9%, 92.1%, and 82.6%, respectively. It is assumed that raising the polymerization temperature to 90°C increased the amount of each acrylate absorbed by the seed PP particles, thus promoting seeded emulsion polymerization. Seeded emulsion polymerization of nBA and tBMA produced particles with good dispersion stability. The chemical composition of the resulting particles was analyzed by FT-IR after centrifugal washing (Figure 4 and Table 2). In addition to peaks derived from the CH_3 groups of PP, sharp peaks derived from the carbonyl groups in PnBA or poly(tert-butyl methacrylate) (PtBMA) were detected. These FT-IR spectra indicate that PP/PnBA and PP/PtBMA composite particles were successfully prepared. On the other hand, aggregation was observed in the emulsion obtained in the system in which FEMA was used as second monomer. The increased water solubility of FEMA at high temperatures must have promoted homogeneous nucleation in aqueous phase, resulting in the formation of large amounts of unstable P(FEMA-S) particles.
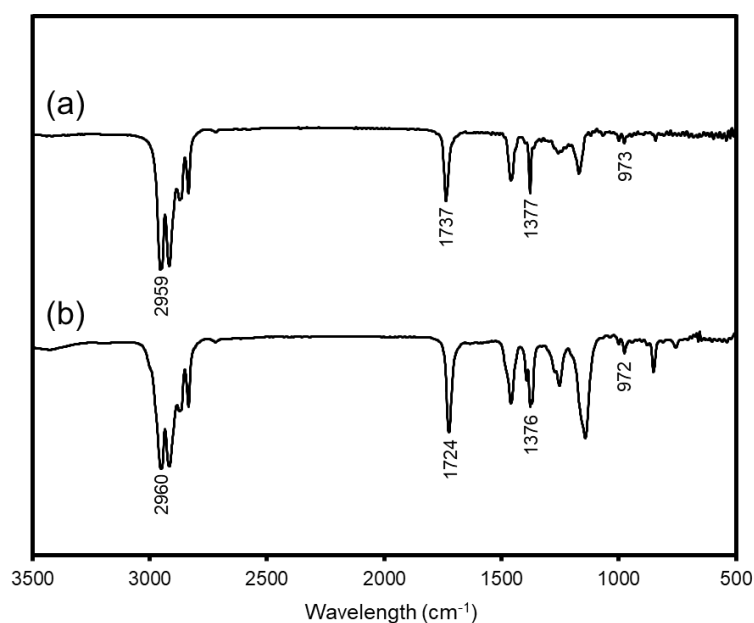

Figure 4. Fourier-transform infrared spectra of the particles obtained by seeded emulsion polymerization of (a) nBA and (b) tBMA at 90°C.

Table 2. Characteristic bands and polymer assignments based on Fourier-transform infrared spectra of the particles obtained by seeded emulsion polymerization of nBA or tBMA at 40°C

Wavelength (cm^{-1})	Characteristic band	Polymer assignments
972, 973	CH$_3$ asymmetric rocking vibrations C–C asymmetric stretching vibrations	PP
1376, 1377	CH$_3$ symmetric deformation vibrations	PP
1724, 1737	C=O stretching vibrations of carbonyl groups	PnBA, PtBMA
2959, 2960	CH$_3$ asymmetric stretching vibrations	PP

Finally, to clarify the advantages of preparing composite particles from PP and a second polymer, tensile strength of the film prepared from PP/PnBA composite emulsion obtained by seeded emulsion polymerization at 90°C (Figure 5). In this tensile test, an emulsion blend system with the same PP/PnBA weight ratio as the composite emulsion was used for comparison. The blend emulsion was prepared by mixing of emulsions of the seed PP particles and PnBA particles (D_w 0.48 nm, C_v 5.7%) prepared by emulsifier-free emulsion polymerization. The tensile strength of the film prepared with PP/PnBA composite particles at 22°C was 5.2 MPa, which was stronger than the emulsion blend system (3.4 MPa). In a tensile test performed at 60°C, both films showed similar tensile strength, but the toughness was clearly greater for the film prepared from the PP/PnBA composite emulsion. To investigate why the tensile strength and toughness differ between the two films, each film was stained with RuO$_4$ vapor and then the internal morphology was observed by TEM (Figure 6). Sea-island structures consisting of PP (high-contrast phase) and PnBA (low-contrast phase) were observed in the

film prepared from blend emulsions. In contrast, in the film obtained from PP/PnBA composite emulsion, PP and PnBA formed a fine co-continuous structure, and the size of each phase was much smaller than that of the blend emulsion system. The much larger interface between PP and PnBA in the film obtained from composite emulsion than the emulsion blend system must have made a difference in the results of tensile test.
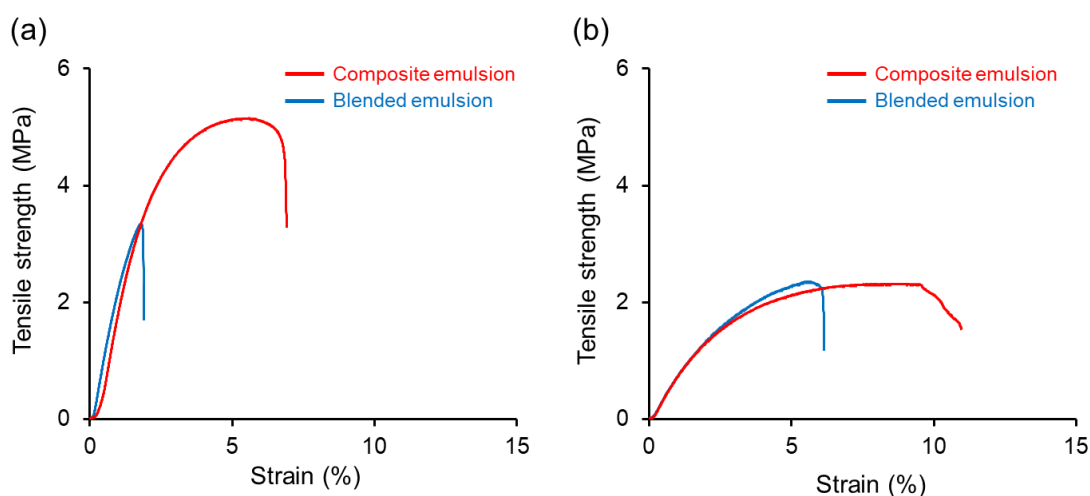

Figure 5. Stress−strain curves of the melt-pressed films prepared from the PP/PnBA composite emulsion or blend emulsion measured at various temperature: (a) 22°C, (b) 60°C.
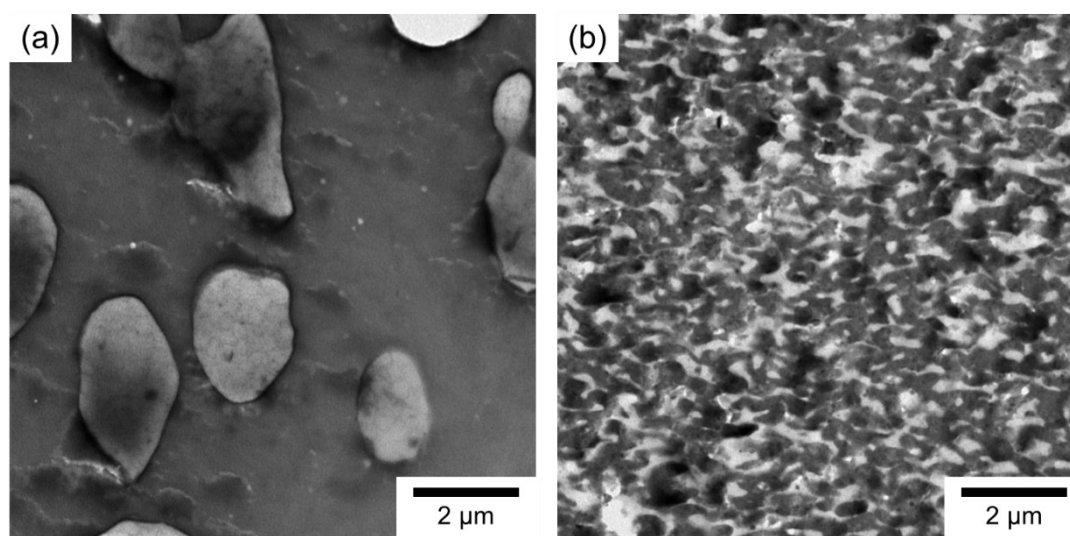

Figure 6. Cross section TEM images of the films prepared by melt-press from the PP/PnBA blend emulsion (a) and composite emulsion (b) after staining with RuO_4 vapor.

Conclusions

The PP composite particles were successfully prepared by seeded emulsion polymerization using three (meth)acrylates (nBA, tBMA and FEMA) as second monomers. The conversion was low for the three (meth)acrylates in the seeded emulsion polymerization at 40°C, but styrene as a comonomer dramatically increased the conversion of FEMA. When the three (meth)acrylates were seeded emulsion homopolymerized at 90°C, an increase in conversion was confirmed for all monomers. These results suggest that the swelling of a second monomer into the seed PP particle, which is the polymerization field, drove the seeded emulsion polymerization with PP as seed particles. The film prepared from PP/PnBA composite emulsion obtained by seeded emulsion polymerization at 90°C had better tensile properties than the film prepared from blend emulsion with the same PP/PnBA weight ratio. The co-continuous structure consisting of PP and PnBA observed in the PP/PnBA composite film is thought to be responsible for the increased strength of the film. The techniques we have developed in this report provide important insights into the fabrication of the composite particles composed of PP and polymers with various structures.

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Concluding remarks

The preparation of novel PP-composite particles was challenged using commercially available PP emulsions as seed particles. It was found that the PP-composite particles could be obtained by general technique on synthesis of polymer particle such as dispersion polymerization and seed emulsion polymerization.

In **Chapter 1**, the PP-composite particles were successfully prepared by dispersion polymerization without a dispersant. Judging from the morphology of the composite particles, the PP particles themselves dispersed the particulates. Appropriate hydrophilicity was essential for the preparation of composites with PP particles. In the presence of styrene, composite particles were not obtained, but when styrene was copolymerized with MMA, a stable emulsion was formed. The surface of the film prepared from PP/PBzMA composite particles was highly hydrophobic. This preparation method for polymer particles without water-soluble dispersants is expected to provide coating materials with new functions.

In **Chapter 2**, preparation of the PP/PS composite particles was achieved for the first time by seeded emulsion polymerization at 40 °C using a cationic initiator. The PP/PS composite particles contained ~60 wt% PP. The composite particles had a unique multilayered structure, in which the PS phase filled the multi-hollow structure of PP seeded particles, and it appeared that the PS chain in the obtained composite particles was partially grafted to the PP backbone. It was revealed that the complicated internal morphology of the PP/PS composite particles was obtained via infiltration of PS into voids in PP seeded particles. The adhesion test showed that the PP/PS composite particle system had advantages over the emulsion blend

system with the same PP/PS weight ratio, indicating that the composite particle would be useful for the development of novel adhesives that bond PP substrates to other materials. Further experiments to clarify the effects of the ionicity of the initiator, monomer types, and other polymerization conditions are in progress and will be discussed in detail in future reports.

In **Chapter 3**, the influence of the intrinsic charge of the azo initiator on the morphology of PP/PS composite particles prepared by seeded emulsion polymerization was investigated. When a cationic or nonionic initiator was used, PP/PS composite particles were obtained in which the PS phase was encapsulated by the PP shell. On the other hand, in PP/PS composite particles derived using an anionic initiator, most of the PS phase was attached to the outer surfaces of seed PP particles. The amount of initiator adsorbed on the seed PP particles depended on the initiator's intrinsic charge. PP/PS composite particles obtained using VA-044, which showed the greatest degree of adsorption on seed PP particles, exhibited a higher PS content than composite particles obtained using either of the other types of initiator. Further analysis suggested that void formation in PP/PS composite particles is due to the infiltration of medium facilitated by the osmotic pressure difference between the interior and exterior of the PP shell. This study provides fundamental mechanistic insights for the development of novel PP-composite materials without volatile organic compounds or surfactants.

In **Chapter 4**, the PP-composite particles were successfully prepared by seeded emulsion polymerization using three (meth)acrylates (nBA, tBMA and FEMA) as second monomers. The conversion was low for the three (meth)acrylates in the seeded emulsion polymerization at 40°C, but styrene as a comonomer dramatically increased the conversion of

FEMA. When the three (meth)acrylates were seeded emulsion homopolymerized at 90 °C, an increase in conversion was confirmed for all monomers. These results suggest that the swelling of a second monomer into the seed PP particle, which is the polymerization field, drove the seeded emulsion polymerization with PP as seed particles. The film prepared from PP/PnBA composite emulsion obtained by seeded emulsion polymerization at 90°C had better tensile properties than the film prepared from blend emulsion with the same PP/PnBA weight ratio. The co-continuous structure consisting of PP and PnBA observed in the PP/PnBA composite film is thought to be responsible for the increased strength of the film. The techniques we have developed in this report provide important insights into the fabrication of the composite particles composed of PP and polymers with various structures.

Knowledge acquired in this study are expected to significantly increase the industrial value of PP. Several novel PP-composite particles have been prepared, but much remains unknown about their properties. Understanding the synergistic effects of PP and other polymers on a microscopic scale will drive the creation of the next generation of high-performance materials.

Publication List

Chapter 1

"Preparation of Polypropylene-Composite Particles by Dispersion Polymerization"

Morimoto, R.; Suzuki, T.; Minami, H.

Langmuir **2021**, 37, 10388−10393.

Chapter 2

"Preparation of Polypropylene/Polystyrene Composite Particles with Multilayered Inner Morphology by Seeded Emulsion Polymerization"

Morimoto, R.; Suzuki, T.; Minami, H.

ACS Appl. Polym. Mater. **2022**, 4, 5619-5625.

Chapter 3

"Morphology of polypropylene/polystyrene composite particles prepared by seeded emulsion polymerization: influence of azo initiator intrinsic charge"

Morimoto, R.; Suzuki, T.; Minami, H.

Polymer Chemistry **2023**, 14, 352-358.

Chapter 4

"Preparation of Polypropylene-Composite Particles by Seeded Emulsion Polymerization of (Meth)acrylates with Different Structures"

Morimoto, R.; Suzuki, T.; Minami, H.

In preparation