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Synthesis of Poly (Methyl Methacrylate-Co-Butyl Acrylate)/Perfluorosilyl Methacrylate Core-Shell Nanoparticles: Novel Approach for Optimization of Coating Process

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Abstract: In this study, the coating order of two monomers in the shell polymerization process of core-shell nanoparticles was altered to facilitate easy coating and optimize the properties of the coated surface to simplify the additional coating formulation process. To obtain a glass transition temperature suitable for coating, a core was synthesized by the copolymerization of an acryl monomer. A perfluoro monomer and silane monomer were additionally added to synthesize nanoparticles exhibiting both water-oil repellency and anchoring properties. In order to realize various surface properties, the nanoparticles underwent surface modification and cellulose fiber was introduced. Through the various data described in this text, the surface properties improved with the order of introduction of the two monomers.

Keywords: Core-shell nanoparticles; Optimization; Surface properties; Perfluorosilyl methacrylate.

1. Introduction

Fluorinated acrylate emulsions have attracted increasing research attention because the various films fabricated from these nanoparticles not only maintain their original properties, such as good matrix adhesion [1], but also exhibit unique properties, such as high thermal and chemical resistance [2-4], water repellency, good oxidation resistance, and strong fluorine electronegativity. However, they are limited in some applications; for example, the fluorinated films exhibit a poor anti-fouling property in seawater because when perfluoroalkyl-containing polymers contact with water, the perfluoroalkyl groups on the surface migrate toward the polymer, reducing their interfacial free energy, while the non-fluorinated groups migrate toward the interface. This will cause the copolymers to possess surface free energy [5-8]. In addition, some products of poly(perfluoroalkyl acrylate) with long perfluoroalkyl groups (more than seven carbons), such as perfluorooctanoic acid and perfluorooctanesulfonic acid (PFOS), have been found to resist degradation [9,10]. Therefore, short perfluoroalkyl groups with seven or fewer carbon atoms play an important role in practical applications because studies involving non-human primates and human tissues indicate that the short perfluoroalkyl groups have substantially shorter half-lives and are less toxic than long perfluoroalkyl groups [11].

Currently, fluorinated acrylate polymers with various structures, such as random [12] and hybrid nanocomposites [13], grafts, and core-shell nanoparticles [14-16], are synthesized by emulsion polymerization, suspension-emulsion-combined polymerization, seeded emulsion polymerization, and other synthetic polymerization methods. A core-shell fluorinated silyl methacrylate latex prepared via

semi-continuous seeded emulsion polymerization is particularly attractive because of its advantage in film formation compared to general emulsion, especially the latex consisting of a fluorine-free acrylate core and fluorine-containing acrylic shell. During the film-forming process, the fluorine-containing acrylic shell preferentially migrates toward the surface and provides the materials with excellent surface properties.

However, some distinct drawbacks in conventional fluorinated acrylate latex may restrict the utilization of particular advantages of fluorinated acrylate copolymer emulsion, e.g., residue emulsifier in conventional emulsion, which could easily migrate to the interface between the polymer and solid substrate, leading to a poor adhesion of the polymers on the substrates, while the fluoroalkyl groups would migrate toward the inside of the film when placed in water, causing the latex film to perform poorly. It is thus imperative to develop new methods for preparing fluorinated acrylate copolymer emulsion and introduce new functional monomers to improve the properties of the emulsion and its latex film. To address the issue mentioned above, an increasing number of studies have been conducted on the soap-free emulsion polymerization method [17-26] using reactive emulsifiers, because the reactive emulsifier can react with monomers and become part of the polymers, decreasing the negative effects of general emulsifiers on the nature of the latex film. In addition, self-crosslinking functional monomers, which can copolymerize with other vinyl monomers to form fluorinated acrylate copolymer latexes, but also form a reticular polymer matrix during the film-forming process to restrict the fluoroalkyl groups from migrating inside, have attracted gradually increasing interest.

Thus, the purpose of this study can be divided into two major categories. First, to control the content of the monomer with low and high glass transition temperatures, the core was polymerized so it could easily be coated at the optimum temperature on the desired substrate. Second, 1H,1H,2H,2H-tridecafluoro-n-octyl acrylate (TFOA) and trimethoxysilyl propyl methacrylate (TPM) were injected sequentially or mixed in the shell polymerization process to reduce the additional coating formulation process. As a result, the roughness of the coated surface was uniform when the two monomers were added sequentially.

2. Materials and methods

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), 4-styrenesulfonic acid sodium salt hydrate (NaSS), ammonium persulfate (APS), and TPM were purchased from Sigma-Aldrich (MO, USA). TFOA was purchased from Tokyo Chemical Industry Co., (TCI, Japan). Cellulose fiber (CF) was purchased from Nycon Materials Co., LTD (FIF 400, Korea). All chemicals were used as received without further purification. Deionized (DI) water was used in all experiments.

2.2. Synthesis of poly(methyl methacrylate-co-butyl acrylate) (PMBA) nanoparticles

The PMBA nanoparticles were prepared in a 300-mL double-jacketed glass reactor equipped with a mechanical stirrer and three inlets. First, NaSS (0.25 g, 1.12 mmol) was dissolved in 100-mL DI water. Next, MMA (6 g, 59.9 mmol) and BA (4 g, 31.2 mmol) were added into the reactor. Then, after APS (0.2 g, 1.1 mmol) was dissolved in 5-mL DI water, APS solution was slowly added into the reactor at a rate of 2.6 ml/h for 2 h. The combined solutions were stirred at 70 °C.

2.3. Synthesis of PMBA/perfluorosilyl methacrylate (PMBA-PFSM) core-shell nanoparticles

In the previously synthesized P(MMA-co-BA) nanoparticles, we synthesized P(MMA-co-BA) PFSM core-shell nanoparticles by mixing or sequentially injecting TPM and TDFOA into the reactor. Here, the TPM (1.35 g, 5.4 mmol), TDFOA (2 g, 4.8 mmol), and mixed monomer (TPM + TFOA [3.35 g]) were slowly added into the reactor at a rate of 1.56, 0.705, and 1.133 ml/h for 2 h, respectively. Then, the resultant mixture was stirred for 3 h at 300 rpm.

2.4 Characterization

PMBA/PFSM core-shell nanoparticle morphologies were observed by field-emission scanning electron microscopy (FE-SEM; JSM 7001F, JEOL, Japan) and transmission electron microscopy (TEM; JEM-F200, JEOL, Japan). The samples for FE-SEM and TEM analysis were prepared by mounting diluted samples onto a silicon wafer and copper grids, respectively. FT-IR analysis was performed within a wavenumber range of 600–4000 cm^{-1} at room temperature using a PerkinElmer Spectrum 100 (USA). Solid-state NMR experiments were acquired with a Bruker Avance II⁺ 400 MHz NMR system (in Korea Basic Science Institute [KBSI] Seoul Western Center). The thermal properties of these samples were measured by differential scanning calorimetry and thermogravimetric analysis (TGA) under an N_2 atmosphere. The heating and cooling ranges were -100 – 100 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. The heating range was from 30 to 800 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. The static and dynamic contact angles were measured using a drop shape analyzer.

The surface chemical composition of the PMBA/PFSM nanocomposite coatings was studied using an XPS instrument (K-alpha, Thermo Scientific, VG, U.K.). XPS spectra were recorded with a $400\text{-}\mu\text{m}$ spot size and monochromatic Al X-ray sources (1486.6 eV). The X-ray source was operated at a power of 250 W and the high voltage was maintained at 140 kV with a take-off angle of 90° . All spectra were calibrated by the C1s peak of the C–C bond at 285 eV. After that, different functional groups were assigned using the reported C1s chemical shifts.

The surface topography of the films was investigated by atomic force microscopy (AFM, JPK Instruments) in tapping mode with a scan size of $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ at 25 $^{\circ}\text{C}$.

3. Results and discussion

3.1. Effects of change of input order on fluorinated monomer (TFOA) and comonomer (TPM)

Figure 1 shows a schematic of the PBMA/PFSM core-shell nanoparticles prepared by polymerizing the core nanoparticles with the MMA and BA monomer, followed by TFOA and TPM in a second shot using the delayed addition method. First, the reason for using a NaSS, a reactive surfactant, residue emulsifier in conventional emulsion, which could easily migrate to the interface between the polymer and solid substrate, is that it leads to a poor adhesion of the polymer on the substrate. In addition, to optimize the coating temperature at room temperature, when the core was polymerized, the weight ratio of MMA and BA was set to $1.5 : 1$ ($6.6\text{ g} : 4.4\text{ g}$) because the glass transition temperatures of poly(methyl methacrylate) and poly(butyl acrylate) are 105° and -49° , respectively. When the core was polymerized for 2 h, a conversion of about 80% was achieved, while the remaining 20% of the MMA and BA monomers existed at the core interface. In this case, TFOA and TPM were mixed or sequentially injected to form a core-shell structure by reacting double bonds with the BA and MMA monomers present at the core interface. Here, when TFOA and TPM were mixed, it was difficult to prove the optimization of the surface properties of the PMBA/PFSM core-shell nanoparticles because of their random arrangement at the core interface. In addition, there may be an uncertainty in whether shell parts were formed in the core-shell morphology. In contrast, when TFOA and TPM were sequentially added, TFOA was present primarily in the shell, and they were independently present in the shell part to ensure that the characteristics could clearly be confirmed. PMBA/PFSM core-shell nanoparticles were synthesized by sequentially injecting TFOA and TPM to realize easy coating with the substrate and a higher contact angle. In other words, the probability of the presence of TPM on the surface of the core-shell nanoparticles increased, making the coating easier.

Figure 1. Schematic diagram of PMBA/PFSM core-shell nanoparticle using delay addition method

3.2. Chemical structure of PMBA/PFSM core-shell nanoparticles

Figure 2 presents FT-IR spectra of the PMBA/PFSM core-shell nanoparticles by the change of the input order and ratio of the shell materials. Let Figures 2 (a), (c), and (e) be “A,” which are the samples prepared by mixing TFOA and TPM, and Figures 2 (b), (d), and (f) be “B,” which are the samples prepared by sequentially injecting TFOA and TPM. In the spectrum, the peak at 1730 cm^{-1} is assigned to the stretching vibration of $\text{C}=\text{O}$. The peaks at 1440 and 1388 cm^{-1} represent the symmetrical and asymmetrical vibration of CH_3 , respectively. Moreover, after the core was polymerized, because of the formation by the reaction of unreacted acrylate monomers and TFOA at the core interface, the absorption peak at 1150 cm^{-1} may be the carboxyl group. Comparing A and B, we can see that the OH stretching vibration represents A at 3250 cm^{-1} because TFOA and TPM are mixed and injected owing to the formation of OH groups via the reaction between TFOA and TPM.

Figure 2. FT-IR spectra of PMBA/PFSM core/shell nanoparticles by the change of input order and ratio of shell materials: (a) TCR-1, (b) TCR-2, (c) TCR-3, (d) TCR-4, (e) TCR-5, (f) TCR-6

Figures 3 (a) and (b) present a ^1H MAS NMR spectrum of the TCR-1 sample for the confirmation of hydrolysis. Here, the purpose of confirming the hydrolysis of the TCR-1 sample was to react the CF through the surface modification of the TCR-1 sample to investigate the surface characteristics after coating. Comparing the results before and after hydrolysis, the peak in the range from 6 to 7 ppm in Figure 3 (a) disappears in Figure 3 (b), indicating hydrolysis.

Figure 3. ^1H MAS NMR spectra of TCR-1 sample [(a) before hydrolysis, (b) after hydrolysis].

Next, Figure 4 presents the solid-state ^{29}Si CP/MAS NMR analysis results, performed to determine whether the hydrolyzed TCR-1 sample reacts with the silane series (aerosol). Generally, the degree of reaction in ^{29}Si CP/MAS NMR analysis can be seen from the peaks in the T and Q series groups. The related chemical structure is also displayed in Figure 4 [27]. Six signals are observed in the spectrum that can be assigned to different Si groups in the material. The Q^4 group [$\text{Si}(\text{OSi})_4$] exhibits a resonance at about -110 ppm, while the Q^3 group [$\text{Si}(\text{OSi})_3\text{OH}$] exhibits a resonance at -100 ppm. Additionally, a small resonance for the Q^2 [$\text{Si}(\text{OSi})_2\text{OHR}$] groups is observed at -90 ppm. The T^3 [$\text{Si}(\text{OSi})_3\text{R}$] and T^2 [$\text{Si}(\text{OSi})_2(\text{OH})_2$] groups appear at -59 and -50 ppm, respectively. Therefore, it can be confirmed that the hydrolyzed TCR-1 sample and aerosol reacted well.

Figure 4. ^{29}Si CP/MAS NMR spectra for TCR-1 sample by aerosol contents (cf. Chemical structure of T and Q series)

3.4. Morphologies of PMBA/PFSM core-shell nanoparticle and nanocomposite

Figure 5 presents TEM images of the PMBA/PFSM core-shell nanoparticles and the PMBA/PFSM + CF nanocomposite reacting with the hydrolyzed CF. In Figure 5 (a), the average size of the PMBA/PFSM core-shell nanoparticles is about 200 nm, and we can clearly see the boundary between the core and shell. Figure 5 (b) shows a sample obtained by surface modification between the PBMA/PFSM nanoparticle and CF. As shown in Figure 5 (b), the existence of the PMBA/PFSM nanoparticle at the CF interface indirectly indicates that the surface modification of the CF was successful.

Figure 5. TEM images of (a) PMBA/PFSM core-shell nanoparticles, and (b) PMBA/PFSM + CF nanocomposite react with hydrolysis cellulose fiber

3.5. Physical and thermal properties of PMBA/PFSM core-shell nanoparticles

Table 1 presents the values of the particle size and contact angle (water/hexadecane [HD]) of PMBA/PFSM core-shell nanoparticles according to the order and amount of addition of TFOA and TPM. Let us set the TC-1, 3, and 5 sample groups to "A" and TCR-2, 4, and 6 sample groups to "B." First, when the TFOA content increases, the particle size increases. Similarly, the contact angles increase in both water and HD. This is because the core is first polymerized in the PMBA/PFSM core-shell nanoparticle and added for shell formation. As the content of TFOA increases, the repulsive force of water and HD on the surface coated with the fluorinated group of TFOA increases. Therefore, the contact angles increase.

Table 1. The physical properties of PMBA/PFSM core-shell nanoparticles

Sample	TFOA/TPM weight ratio (g)	Diameter (nm)	Contact Angle (°) [Water/HD]	
TCR-1		123.7	130.5	72.8
TCR-2	2(15%)/1.35(10%)	130.1	135.1	74.9
TCR-3		186.3	138.6	77.6
TCR-4	2.7(20%)/1.35(10%)	190.1	135.1	76.3
TCR-5		270.5	135.1	92.1
TCR-6	4.87(30%)/1.35(10%)	256.3	142.4	101.4
TCR-A1	2.7(20%)/4.05(30%)	-	102.1	-
TCR-A2	2.7(20%)/2.7(20%)	-	106.2	-
TCR-A3	2.7(20%)/0.675(5%)	96.91	141.4	86.7
TCR-B1	4.87(30%)/4.05(30%)	-	107.1	-
TCR-B2	4.87(30%)/2.7(20%)	-	123.1	-
TCR-B3	4.87(30%)/0.675(5%)	106.3	140.3	97.9

In the TCR-A & B series, the content of TPM was controlled. At 20% and 30%, the measurement of the particle size is impossible with increasing viscosity. However, it is possible at 5% TPM and the highest values of the contact angle are 30% for TFOA and 5% for TPM. It was found that this condition is the optimum condition with the highest contact angle value.

Next, the thermal stability of TFOA and TPM by injection order is illustrated in Figure 6 through TGA analysis. From the comparison of the pyrolysis start temperatures of TCR-1 and TCR-2, it can be seen that the temperature increases from about 400 to 550 °C. This is because the TCR-2 sample has a cross-linked density that completely reacts with the shell part of the core-shell nanoparticles by sequentially injecting TFOA and TPM.

Figure 6. Thermal stability of PMBA/PFSM core-shell nanoparticles to the order of injection

3.6. Surface chemical composition of PMBA/PFSM nanocomposite coatings

The chemical states of the TCR-1 and 2, and TCR + CF nanocomposite samples were investigated by XPS measurements, and the corresponding wide-scan spectra are plotted in Figure 7. For all samples, because of the PMBA/PFSM cellulose-based components, C1s and O1s species are the dominant signals and occur at binding energies (BEs) of 285.0 and 531.88 eV, respectively. Fluorine and silicon peaks are also found at about 688.0 and 105.0 eV. The chemical compositions of the TCR-1 and 2, and TCR + CF nanocomposite samples are listed in Table 2. The BEs of all the peaks have been corrected relative to the reference peak (C–C, 285.0 eV). In Table 2, when comparing the TCR-1 and TCR-2 samples, there is almost no difference compared to the other elements, but the “Si” content increases. As shown in Figure 7 (b), compared to Figure 7 (a), both “O” and “Si” increase because TPM is present at the core-shell nanoparticle interface by sequentially injecting TFOA and TPM. In the case of the TCR sample and CF nanocomposite, the number of –OH bonds at the CF interface increases because of the surface modification of the particles.

Figure 7. XPS survey spectra of (a) TCR-1 and TCR-2, (b) TCR-1, 2 + CF nanocomposites

Table 2. Chemical composition of TCR-1, 2 and TCR + CF nanocomposite sample determined by XPS analysis (atom %)

Sample	Concentration, % at wt			
	C1s	O1s	F1s	Si2p
TCR-1	73.37	23.06	2.59	0.99
TCR-2	73.19	21.75	2.67	2.38
TCR-1+CF	72.14	23.07	3.52	1.26
TCR-2+CF	62.72	29.45	1.35	6.49

Next, Figure 8 shows the fitted peaks in the region of the carbon BE of the TCR and TCR + CF nanocomposite sample. The C1s spectrum reveals the presence of two different types of carbon atoms (functional groups). Considering that the peak located at 285.0 eV represents aliphatic C–C/C–H, the

other peak appearing at about 288.0 eV can be linked to carbon atoms belonging to C=O -based functional groups (Figure 8 [a]). Moreover, in Figure 8 (b), the peak at about 288.0 eV shifts to the right because the hydrolysis of PBMA/PFSM nanoparticles results in the formation of OH functional groups

in the TCR + CF nanocomposite sample.

Figure 8. High-resolution XPS spectra with peak-fitting in the region of carbon-binding energy:
(a) TCR-1, TCR-2, (b) TCR-1, 2 + CF nanocomposites

3.7 Surface topography of PMBA/PFSM nanocomposite coatings

The surface topography of the coatings is presented in Figures 9 and 10. As shown in Figure 9, when comparing groups "A" and "B", it can be seen that group B is more uniform than group A. In addition, the arithmetic average roughness (R_a) and root mean square (R_q) values are smaller than group A. The detailed values are listed in Table 3. The reason for the lower R_a and R_q values in group B is that TFOA and TPM are mixed in group A when the PBMA/PFSM coating solution is synthesized, and TFOA and TPM are sequentially introduced in group B. Therefore, the dispersion stability in group B increases, and the values of R_a and R_q are low. Figure 8 presents AFM images of the sample obtained by reacting the CF with the hydrolyzed TCR sample. The overall behavior is similar to Figure 7, but the values of R_a and R_q are higher. Both R_a and R_q are calculated using Eqs. (1) and (2), respectively:

$$R_a = \frac{1}{n} \sum_{i=1}^n |\gamma_i|, \quad \text{---OH} \quad (1)$$

$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n \gamma_i^2}, \quad (2)$$

where n is the number of equally spaced measuring points along the trace and γ represents the vertical distance from the mean line.

Table 3. Calculated values of the arithmetic average roughness (R_a), the root mean squared roughness (R_q) for the TCR series and TCR + CF nanocomposite sample

Figure 9. AFM height images of the TCR series sample (a) TCR-1 film, (b) TCR-2 film, (c) TCR-3 film, (d) TCR-4 film, (e) TCR-5 film, and (f) TCR-6 film

Figure 10. AFM height images of the TCR series + CF nanocomposite sample (a) TCR-1, (b) TCR-2, (c) TCR-3, (d) TCR-4, (e) TCR-5, and (f) TCR-6.

4. Conclusions

PMBA/PFSM core-shell nanoparticles were prepared by synthesizing PMBA nanoparticles as a core through delayed addition and then injecting TFOA and TPM. By the sequential addition of 30% TFOA and 5% TPM, the highest contact angle achieved was 142.4° and 101.4°, respectively, because if more than 5% of TPM was added, the viscosity of the PMBA/PFSM latex would increase and the particle shape would no longer be maintained. In addition, the thermal properties of the TFOA and TPM were investigated, and it was found that the pyrolysis temperature increased by about 150 °C.

To investigate the coated surface properties, solid-state ²⁹Si NMR was analyzed to verify the reactivity of the prepared particles with CFs by surface modification. In addition, XPS analysis indicated that the PMBA/PFSM latex and PMBA/PFSM latex + CF nanocomposite were coated well on the substrate. Finally, the order of addition of TFOA and TPM and the roughness of the CF nanocomposite sample were investigated. The *R_a* values of TFOA and TPM were found to decrease, while the CF nanocomposite sample exhibited identical behavior.

In this approach, it was found that the thermal, physical, and surface characteristics of the PMBA/PFSM core-shell nanoparticle synthesis process improved by sequentially injecting TFOA and TPM rather than mixing them together. In other words, we found that the order and content of TFOA and TPM constituting the shell material in the PMBA/PFSM core-shell nanoparticle synthesis process significantly influenced the optimization of the coating conditions. Further, based on the data presented above, it is believed that the PMBA/PFSM core-shell nanoparticle will be fully utilized as a paper coating material.

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Figures and tables

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