

Preparation and Characterizations of C₆₀/Polystyrene Composite Particle Containing Pristine C₆₀ Clusters

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Fullerene/polystyrene (C₆₀/PS) nano particle was prepared by using emulsion polymerization. Styrene and fullerene were emulsified in aqueous media in the presence of poly(*N*-vinyl pyridine) as an emulsion stabilizer, and polymerization was initiated by water soluble radical initiator, potassium persulfate. The obtained nano particles have an average diameter in the range of 400-500 nm. The fullerene contents in the nano particle can be controlled up to 15 wt % by varying the feed ratio, which was confirmed by thermogravimetric analysis (TGA) and elemental analysis (EA). The structure and morphologies of the C₆₀/PS nano particles were examined by various analytical techniques such as dynamic light scattering (DLS), scanning electron microscope (SEM), transmission electron microscope (TEM), electron diffraction (ED) pattern, X-ray powder diffraction (XRD), and UV spectroscopy. Unlike conventional C₆₀/PS particles initiated by organic free radical initiators, in which the fullerene is copolymerized forming a covalent bond with styrene monomer, the prepared C₆₀/PS nano particles contain pristine fullerene as secondary particles homogeneously distributed in the polystyrene matrix.

Key Words : Fullerene, Polystyrene, Nanoparticle, Emulsion polymerization

Introduction

Fullerene (C₆₀) is a widely studied material due to its unique optical, electrical, and chemical properties.¹⁻³ However, one of the key issues in the practical application of C₆₀ comes from its extremely low solubility in organic solvents. Besides, C₆₀ tends to form aggregated clusters, which hinder the homogeneous dispersion in the molecular level. Therefore, much of efforts have been devoted to disperse C₆₀ particles. Zhang *et al.* prepared C₆₀-containing microemulsions in the hydrophobic oil core and an aqueous bulk phase with sodium dodecyl sulfate (SDS).⁴ The colloidal dispersions of C₆₀ in the polymer micelles and/or emulsion particles prepared from the supramolecular self-assembly of amphiphilic block copolymers were also reported.^{5,6} Chemical modifications of C₆₀ molecules by attaching polymer chains were attempted to improve the solubility.^{7,8} Encapsulated particles consisting of an organic or inorganic functional material and a polymer can make advanced applications with better control of optical properties, charge carrier mobility, surface chemistry, stability, and etc.

There have been many efforts to prepare C₆₀/polymer composite particles. Firstly, the polymerizations of vinyl monomers in the presence of C₆₀ have been widely studied. Generally, copolymerization of vinyl monomers such as styrene and methyl methacrylate with C₆₀ is initiated by organic free radical initiators such as 2,2'-azobis(2-methylpropionitrile) (AIBN) or dibenzoyl peroxide (BPO).⁹⁻¹⁴ Due to the high susceptibility of C₆₀ toward free radicals (> 10⁵ times higher than vinyl monomers),⁹ however, C₆₀ molecules are incorporated in the polymer chain with a covalently

bonded structure resulting in a copolymerization with styrene, which consequently changes the spectroscopic and electronic properties of C₆₀. Liao *et al.* investigated the self-organized supramolecular aggregates obtained from spraying the solution of fullerenes grafted with linear polymer chains by light-scattering and fluorescence spectroscopy.¹⁵ More recently, a C₆₀/polymer composite particle was prepared by a one-step seed dispersion polymerization in supercritical carbon dioxide (scCO₂).¹⁶ C₆₀ was initially dissolved in styrene monomer with initiator (AIBN) and stabilizer, and was then injected into scCO₂. Because scCO₂ acted as an antisolvent, C₆₀ precipitated and dispersed in scCO₂. The resulting particles then acted as the seeds for the dispersion polymerization of styrene in scCO₂, leading to the formation of the polystyrene-C₆₀ composite microparticles. However, it was revealed that the intrinsic properties of C₆₀ were altered in these C₆₀/polymer composite particles. After extensive analyses including transmission electron microscope (TEM), powder X-ray diffraction (XRD), UV absorption and fluorescence spectroscopy, the authors concluded that the one-step seed dispersion polymerization of styrene using C₆₀ in scCO₂ resulted in the copolymerized product in which C₆₀ molecules are covalently bound in the polystyrene (PS) chain as in the case of copolymerization of vinyl monomers with C₆₀.

To our knowledge, there has been no report concerning the preparation of C₆₀/polymer composite particles by emulsion or dispersion polymerization in which C₆₀ molecules are incorporated in their pristine form. Preserving the intrinsic properties of C₆₀ in the composite particle is crucial for its utilization in the practical application. For example, alteration

of HOMO/LUMO energy levels and band gap of C₆₀ molecule would result in different cell performances such as photo-current efficiency (PCE) and open-circuit voltage (V_{OC}) in organic photovoltaic application. In this paper, we report the first preparation of C₆₀/polymer composite particles containing pristine C₆₀ clusters in the PS matrix, which was successfully obtained by using water-soluble radical initiator, potassium persulfate (KPS) instead of organo-soluble initiators such as AIBN or BPO. In addition, the resulting particles were characterized by comparing the optical and physical properties with those obtained by the conventional copolymerization method. The results enable us to utilize the intrinsic properties of C₆₀ without any perturbation. Also, the high content of C₆₀ in the particles will find many applications such as in photovoltaic and organic semiconductors area.

Experimentals

Reagents. C₆₀ (+99+%) was obtained from MER Corporation, and used without purification. Potassium persulfate (KPS), divinyl benzene (DVB), and styrene monomer were purchased from Aldrich Chemical Co., and styrene monomer was purified prior to use by washing with 10 wt % NaOH aqueous solution several times followed by drying and vacuum distillation to remove polymerization inhibitor. Dispersion stabilizer, poly(*N*-vinylpyrrolidone) (PVP), was obtained from Showa Chemical Co. For the emulsion polymerizations, deionized (DI) water was obtained from double distilled water by using Eyela Still Ace SA-2100E1 system equipped with ion-exchange membranes. 2,2'-Azobis(2-methylpropionitrile) (AIBN) was obtained from Sanyo Chem. Co., and recrystallized in methanol prior to use. Dichlorobenzene was purchased from TCI Chem. Co., and distilled under low pressure.

Preparation of C₆₀/PS Nanoparticles. Typical procedure for the preparation of C₆₀/polymer composite nanoparticles is listed below: To 1.182 g of styrene monomer and 0.237 g of DVB were added and dispersed by ultrasonication for 1 h. To a 5 mL of 0.1 wt % aqueous PVP solution, 1.182 g of C₆₀ was added and dispersed by ultrasonication for 1 h. Both solutions were, then, mixed, ultrasonicated for 1 h, and transferred to a reactor equipped with mechanical stirrer. The reaction mixture was stirred for 15 min at 300 rpm under N₂ atmosphere, and 0.03 g of KPS dissolved in 2 mL of DI water was added. The temperature was slowly raised to 75 °C and kept for 24 h with stirring at the same speed. After the polymerization, the reaction mixture was cooled to room temperature, and repeatedly washed with methanol and DI water followed by filtering to remove unreacted chemicals and oligomers. The filtered particles were dried in vacuum oven at room temperature for 24 h.

Preparation of C₆₀-styrene Copolymer. To compare with the chemical structure of C₆₀/PS nanoparticles, C₆₀-styrene copolymer (C₆₀-PS copolymer) was prepared by solution polymerization of styrene and C₆₀ in dichlorobenzene with AIBN according to literature.⁹ 0.025 g of C₆₀ was dissolved

in 5 mL of dichlorobenzene and placed in a polymerization ampoule containing 0.028 g of AIBN and 1 g of styrene. The ampoule was degassed by using three freeze-thaw cycles followed by flame-sealing under vacuum, and placed in the oven at 65 °C for 37 h. The polymer solution was repeatedly precipitated into methanol and the resulting powder was dried in a vacuum oven at 40 °C for 24 h.

Instruments and Measurements. Fourier transform infrared (FT-IR) spectra were taken to investigate the existence of C₆₀ and the chemical structure of C₆₀ and PS in the C₆₀/PS composite particles by JASCO Model 300E FT-IR spectrometer. The nanoparticles were ground with KBr to prepare a sample pellet. Thermal stability of particles was measured by using thermogravimetric analyses (TGA) on TGA 2050 (TA Instruments) under nitrogen atmosphere at a heating rate of 10 °C/min up to 600 °C. The amount of C₆₀ in the C₆₀/PS particle was estimated from the elemental analyses (VarioEL, Elementar). Size of prepared particles was measured by particle size analyzer (ELS-600, Zeta-potential and particle size analyzer, Otsuka, Japan) after dispersing the sample in ethanol. The shape and size of particles were also investigated with scanning electron microscope (SEM, S-4800, Hitachi). To observe the internal structure of the particles, transmission electron microscope (TEM, H-7650, Hitachi Co.) was used. The samples were spread onto carbon coated mica, and the carbon layer was floated on a water surface, and recovered to copper grids. Electron and X-ray diffraction patterns were obtained by using JEM-2010 (JEOL Co.) and MAX III A (Rigaku Co.), respectively. UV-vis spectra was measured on a Scinco Model UV-3100S spectrophotometer in toluene solution.

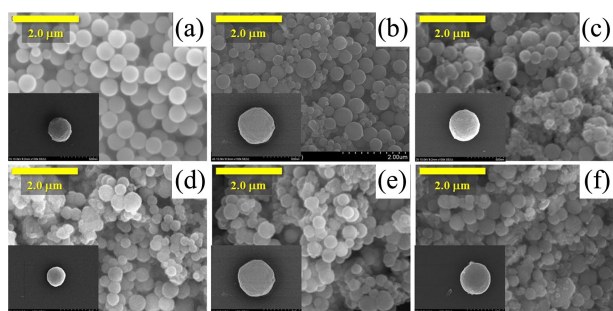
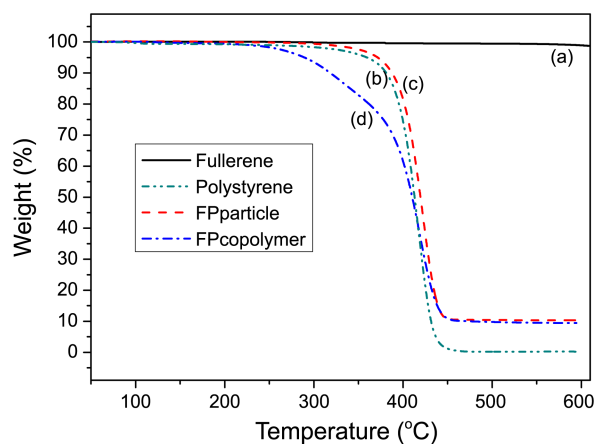
Results and Discussion

In Table 1, recipes of emulsion polymerization of C₆₀/PS particles were listed. Instead of using organo-soluble free radical initiators such as AIBN or BPO, which generally result in the copolymerization of C₆₀ and styrene, we employed an aqueous radical initiator, KPS. The resulting C₆₀/PS particles were obtained as brown colored powder. In Figure 1, SEM images of various C₆₀/PS particles were displayed. In the insets of Figure 1, the shapes of single particles were shown in large magnification. The surface of the particle was rough compared to that of general PS particles prepared by emulsion polymerization techniques. The average particle shapes were spherical with a diameter of 300-600 nm. When the particle size was measured by electrophoretic particle size analyzer (ELS-600), the average particle size was ranged from 400 to 550 nm as listed in Table 1. The size of particles was slightly increasing with increasing C₆₀ amount in the feed, though the tendency was not strict. This can be attributed to the decreased relative amount of dispersion stabilizer as well as the increase of total solid contents.

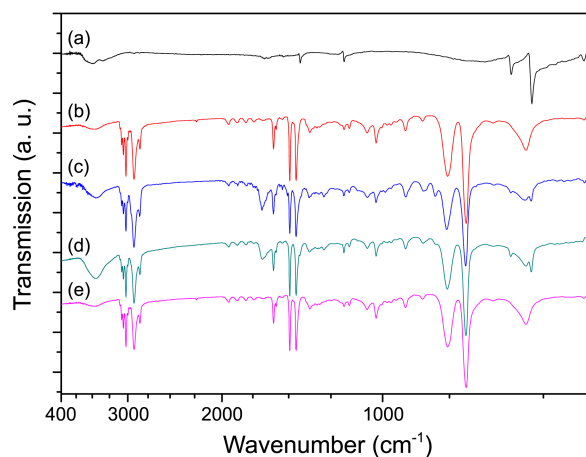
The content of C₆₀ in the particle was estimated by using TGA and elemental analyses data. In Figure 2, TGA thermogram of C₆₀/PS particle (FP-1) was compared with those of C₆₀, PS, and C₆₀-PS copolymer. Pristine C₆₀ was stable up to

Table 1. Recipes for emulsion polymerization of fullerene/polystyrene particle

Sample	C ₆₀ (g)	Styrene (g)	PVP (g)	DVB (g)	KPS (g)	DI water (ml)	C ₆₀ Content (wt %)		Avg. particle size (nm)
							EA	TGA	
FP-1	0.10	1.18	0.05	0.24	0.03	12	10.5	10.3	433.3
FP-2	0.13	1.18	0.05	0.24	0.03	12	10.4	15.3	536.0
FP-3	0.30	1.18	0.05	0.24	0.03	12	17.6	23.6	555.3
FP-4	0.51	1.18	0.05	0.24	0.03	12	29.7	32.6	397.2
FP-5	0.79	1.18	0.05	0.24	0.03	12	42.5	44.3	556.1
FP-6	1.18	1.18	0.05	0.24	0.03	12	56.1	57.3	533.4
Co-FP	-	-	-	-	-	-	11.8	9.5	-

**Figure 1.** SEM images of fullerene/polystyrene nano particles. Insets are magnified SEM images of single particles. (a) FP-1, (b) FP-2, (c) FP-3, (d) FP-4, (e) FP-5 and (f) FP-6. I.**Figure 2.** TGA thermograms of (a) C₆₀, (b) PS, (c) C₆₀/PS particle (PF-1), and (d) C₆₀-PS copolymer.

600 °C without almost any weight loss, while the pure PS decomposed rapidly at 313 °C (at 2.0 wt % loss) with 0% char yield. The above result was utilized as a basis of calculation of C₆₀ contents in the C₆₀/PS particle. As shown in Figure 1(c), C₆₀/PS particle decomposed initially at 343 °C (at 2.0 wt % loss) showing slightly higher initial decomposition temperature than pure PS, and then exhibited a similar decomposition behavior to that of PS. On the other hand, C₆₀-PS copolymer prepared by radical polymerization with AIBN showed completely different behavior. It began to decompose at much lower temperature (256 °C at 2.0 wt % loss) with two-step decomposition mode. The char yields of C₆₀/PS particle and C₆₀-PS copolymer at 600 °C

**Figure 3.** FT-IR absorption spectra of (a) C₆₀, (b) PS, (c) C₆₀/PS particle (PF-1), (d) physical blend of C₆₀ and PS, and (e) C₆₀-PS copolymer.

were 10.3 and 9.42%, respectively. From the above results, the contents of C₆₀ in the C₆₀/PS particles were estimated, and the data were compared with those obtained from the elemental analyses as listed in Table 1. From the elemental analyses data, C and H contents was used to calculate the amounts of C₆₀ in the C₆₀/PS particles assuming that only styrene and DVB contribute C and H ratio and the amount of other components such as PVP is negligible. As shown in Table 1, the estimated C₆₀ contents from TGA and elemental analyses data showed consistent values with each other. We were able to obtain C₆₀/PS particles with maximum C₆₀ content up to > 56% (FP-6) when increasing the amount of C₆₀ in the feed. Preparation of C₆₀/PS particles having higher C₆₀ content was not successful due to the agglomeration of produced particles.

To further characterize the chemical structure of C₆₀/PS particles, FT-IR absorption spectra were compared to those of C₆₀, PS, C₆₀-PS copolymer and physical blend of C₆₀ and PS as shown in Figure 3. Pristine C₆₀ (Figure 1(a)) displayed 4 characteristic vibrational bands at 1429, 1181, 576, and 527 cm⁻¹.^{17,18} In the IR spectrum of PS (Figure 1(b)), C-H aromatic stretching vibration was monitored at 3059 and 3026 cm⁻¹, and C-H stretching vibration was observed at 2924 and 2850 cm⁻¹. Absorption bands at 1450, 1492.5 and 1600.8 cm⁻¹ are corresponding to the phenyl ring stretching vibration. Ring in phase C-H stretching vibration and ring

out-of-plane bend were displayed at 1027 and 699 cm⁻¹, respectively. In Figure 1(c) and 1(d), FT-IR absorption spectra of C₆₀/PS particle and the physical blend of C₆₀ and PS were shown, respectively. For both of the samples, the characteristic vibrational bands of C₆₀ at 576 and 527 cm⁻¹ were clearly found together with the characteristic absorption bands of PS, implying that C₆₀ is incorporated in the pristine form without any structural change such as a covalent bond formation. On the other hand, C₆₀-PS copolymer (Figure 1(e)) exhibited no such characteristic vibrational bands of C₆₀, indicating that C₆₀ is no longer in its pristine form and covalently bonded to the growing PS chain. Such covalent incorporations of C₆₀ during the polymerization of styrene initiated by organic radical initiators were also reported by many researchers,^{10,11,16} and, in this case, the original chemical characteristics and physical properties of C₆₀ should be lost after the incorporation. From the above results, it was evident that C₆₀ was incorporated in the C₆₀/PS particles in its pristine form under our preparation conditions, which is favorable for the utilization of chemical or physical properties of C₆₀.

Comparison of X-ray powder diffractions of C₆₀, PS, C₆₀/PS particle (PF-1), and C₆₀-PS copolymer revealed more evidently that the nature of C₆₀ in the C₆₀/PS particle was completely different from that of C₆₀-PS copolymer as shown in Figure 4. Both PS and C₆₀-PS copolymer samples showed broad amorphous hollow centered at 2θ = 19.4° and 19.68°, respectively.¹¹ In contrast, C₆₀/PS particle exhibited smaller but all the characteristic diffraction peaks of pristine C₆₀^{19,20} in addition to the characteristic amorphous hollow of PS as shown in Figure 4(d). This result also clearly indicated that C₆₀ existed in the amorphous PS domain of C₆₀/PS particle with the same crystalline structure as its pristine form.

To investigate the distribution of C₆₀ inside the particle, TEM images of single particles were taken for various C₆₀/PS samples. However, we were not able to observe any noticeable C₆₀ domains in the single C₆₀/PS particle even at the high magnification (× 250 K).²¹ Furthermore, the electron diffraction experiment taken for the same TEM image area

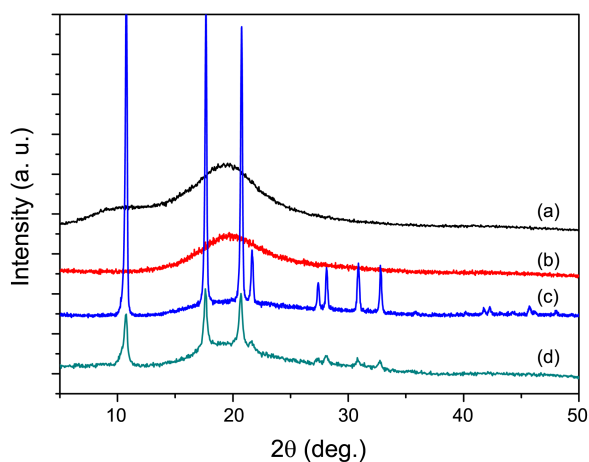


Figure 4. X-ray powder diffraction diagrams from (a) PS, (b) C₆₀-PS copolymer, (c) C₆₀, and (d) C₆₀/PS particle (PF-1).

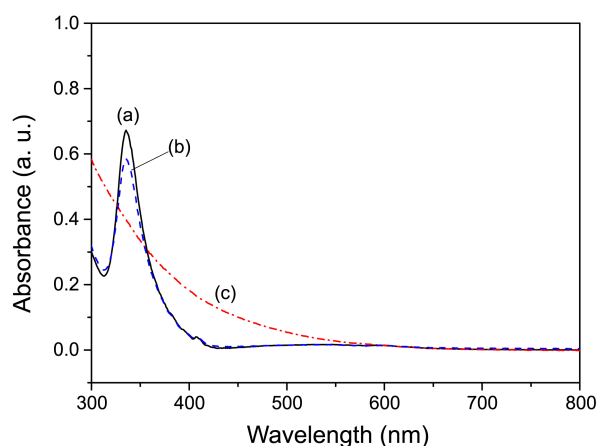


Figure 5. UV-vis absorption spectra of the (a) C₆₀, (b) C₆₀/PS particle (PF-1), and (c) C₆₀-PS copolymer.

also displayed no appreciable diffraction patterns. These results are presumably attributed to the homogeneous distribution of C₆₀ micro-clusters in the C₆₀/PS particle.

In Figure 5, UV-vis absorption spectra of C₆₀, C₆₀/PS particle (PF-1), and C₆₀-PS copolymer in toluene were compared. As reported,^{9,10} pure C₆₀ exhibited two absorption maxima at 335 and 408 nm corresponding to the π-π transitions, while the C₆₀-PS copolymer showed no such absorption peaks due to the covalently bonded structure of C₆₀.²² Nayak *et al.*²² ascribed this featureless curves tailing beyond 500 nm to incorporation of substituents onto C₆₀ molecules as a result of polymerization. On the contrary, C₆₀/PS particles in this work exhibited almost identical absorption spectra to that of pristine C₆₀. The electronic absorption spectral data, therefore, also supports the homogeneous incorporation of C₆₀ in the C₆₀/PS particle in its pristine form.

Conclusion

In conclusion, we demonstrated a new method to prepare C₆₀/polymer composite particles containing pristine C₆₀ clusters in the PS matrix, which could enable us to utilize the intrinsic properties of C₆₀ without any perturbation. The C₆₀/polymer composite particles were prepared by *in situ* emulsion technique by using a water-soluble radical initiator, potassium persulfate (KPS). The shape and sizes of resulting particles were investigated by using SEM, ELS, and TEM. The C₆₀ contents in the particle were up to 56 wt % as measured by TGA experiments and elemental analyses. We proved that the C₆₀ was incorporated in its pristine form by comparing its optical and physical characteristics with those of covalently incorporated C₆₀ by using TGA, FT-IR and UV-vis spectroscopies, and XRD. Various effects of stabilizers, solid contents, and initiator concentrations on the preparation of C₆₀/polymer composite particles were also investigated, which will be reported elsewhere in the future. The mechanism of the PS polymerization in the presence of C₆₀ should require further extensive investigations. Nonetheless, the new C₆₀/polymer composite particles containing pristine C₆₀ with high C₆₀ contents may find many appli-

cation areas such as organic photovoltaics, biomedical imaging probes and antioxidants.

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