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Synthesis of polyethylene glycol-polystyrene core-shell structure particles in a plasma-fluidized bed reactor

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Abstract−Particles with core-shell structure with polystyrene (PS) core and polyethylene glycol (PEG) grafted on the surface were synthesized in a plasma-fluidized bed reactor. The virgin, plasma-treated, and grafted powders were characterized by the DPPH method, UV-vis spectrophotometer, NMR, FT-IR and SEM. The plasma-treated PS powders have well formed peroxide on the surface. By PEG grafting polymerization, PEG is well grafted and dispersed on the surface of the plasma-treated PS powders. The PEG-g-PS powder exhibits the core shell structure in the cross-sectional SEM image, and it can be claimed that well dispersed PEG grafting polymerization on PS surface can be achieved in the plasma fluidized bed reactor.

Key words: Fluidized Bed, Plasma, Surface Treatment, Polyethylene Glycol, Polystyrene

INTRODUCTION

Modifying particle surface property with a special functional group can provide many useful applications in the fields of biomedical, cosmiceutical, pharmaceutical and polymerization materials. There are two basic approaches for surface modification: wet methods [1-4] and dry methods such as plasma or radiation treatment [5-12]. The former requires additional processes such as washing and drying, and yields an inhomogeneous modified surface. The surface modification by plasma treatment is a clean process that modifies the surface of the material without any damage within a short reaction time [5]. However, most of the developed reactors for plasma treatment to date are suitable only for films [13] and only few reactors are capable for modifying a powder surface [8,14-19]. The reactors for powder treatment can be classified into three types: static bed [14,15], moving bed [8], and fluidized bed [16-19] reactors. Among these reactors, the fluidized bed has shown the particular features since powders are suspended while the plasma is generated in the upper part of the reactor. This method also has many advantages including homogeneous mixing between powders and the reactive gas, easily controlled continuous operation, maintaining isothermal condition throughout the reactor, and the amenability to large scale operation.

Polyethylene glycol (PEG) has non-toxic, odorless, neutral, nonvolatile, nonirritating and water-soluble properties that have led to use of PEG in various pharmaceutical products [20]. Moreover, PEG is well-known as its extraordinary ability to resist protein adsorption resulting from its hydrophilicity, large exclude volume and unique coordination with surrounding water molecules in aqueous molecules [21], while polystyrene (PS) powder is non-porous, non-toxic and hydrophobic having good physical and chemical properties. Therefore, this core-shell PEG-g-PS structure can be utilized as a support in synthesis of the biomaterials and antifouling matter [2,22].

In this work, particles with core-shell structure with PS core and PEG grafted on the surface (PEG-g-PS) were produced using the plasma-fluidized bed reactor. The effects of treatment time and plasma power on surface modification of PS powder were determined as a function of the peroxide concentration on PS powder in the plasma-fluidized bed reactor. In addition, the optimum operation condition in the plasma-fluidized bed reactor for large amount of powders in fluidizing state was determined, which is different from that in the reactor for film types. Thus, the PEG-g-PS particle with mono-dispersed PEG shell was successfully synthesized using the plasma-fluidized bed reactor in the optimum operation condition.

EXPERIMENTAL

1. Materials

Polystyrene powder (d_p=237 μm, ρ_s=105 kg/m^3) was supplied by Kumho Petrochemical Inc. To form the active species, argon gas (99.999%) was used as a plasma gas, and then air was used to convert from active species to peroxides on the surface of PS powder. Poly(ethylene glycol) methacrylate (M_n=360, Aldrich) was used as a grafting material.

2. Plasma Fluidized Bed Reactor

Formation of the peroxides on the surface of PS powders was carried out in a plasma-fluidized bed reactor (41 mm-ID×900 mm-heig; Pyrex) as shown in Fig. 1. The plasma reactor is composed of plasma matching network, Radio Frequency (RF, 13.56 MHz) power generator, vacuum pump, and gas inlet port. To generate the plasma, an inductively coupled plasma type electrode (44 mm-ID, 6 turns, copper tube) was used that was located in the freeboard of the reactor. The flow rate of fluidizing gas was regulated by a mass flow controller at a constant pressure for fluidizing powders for surface reactions. The exit of the filter was connected to a vacuum pump.

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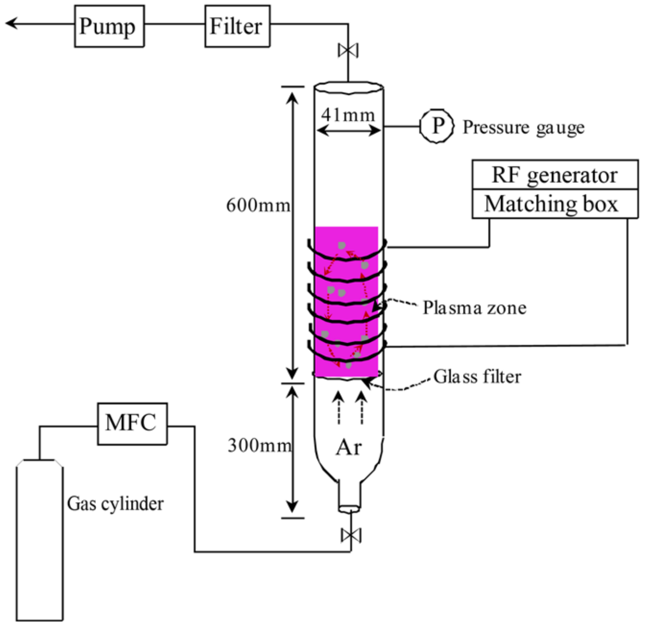

Fig. 1. Schematic diagram of the experimental apparatus.

The pressure of the reactor was monitored by using a vacuum gauge (Granville-Phillips) and the reactor pressure was maintained at 0.5 torr during the plasma treatment.

3. Experimental Procedure

Fig. 2 shows the mechanism of peroxide formation. In the PEG grafted on the surface of PS powder, active radicals from the argon-plasma treatment in a plasma-fluidized bed reactor were converted to peroxides by continuous treatment with air. The peroxides were then used to initiate graft polymerization of PEG onto PS surface to yield PEG-g-PS. The grafting of PEG was limited to the surface region of the PS powder. The peroxides formed on the PS surface and the final PEG-g-PS were characterized by the DPPH (1,1-diphenyl-2-picrylhydrazyl) method, FT-IR and SEM.

The surface-modified PS powder was produced by the following two treatment processes. First, 160 g of PS powder was loaded into the plasma-fluidized reactor, and then Ar gas ($1.5u_{mf}$, minimum fluidizing velocities [23]) was introduced into the bottom of the reactor at 1 torr. At this stage, PS powders act fluid-like over u_{mf}, which can provide intimate and homogeneous mixing between the powders and the reactive gas to improve the reaction rate for a uniform treated surface [17]. Then, the fluidized PS powder was vigorously mixed with the argon-plasma from the rf power generator in the free board region of the fluidized bed to make the surface-activated PS powder. This powder was then exposed to dry air in order to form the peroxide species on the powder surface for 10 min. Second, the peroxide-modified PS powder was loaded into a reactor for polymerization with distilled water and PEG methacrylate monomer (10 v/v %). Before the polymerization, the reactor was purged by Argon gas to remove the residual air. By grafting polymerization on the surface of peroxide-modified PS powder with PEG methacrylate in Argon gas at the appropriate temperature, the PEG-g-PS powder was synthesized. The obtained PEG-g-PS powder was then washed with distilled water, ethanol and methanol to remove residual monomer, and dried at 30 °C for 12 hr in a vacuum oven.

4. Characterization

The total amount of peroxides per unit mass of the plasma-treated PS powder was measured by the DPPH (1,1-diphenyl-2-picrylhydrazyl) method [7]. DPPH is a stable free radical that has a characteristic absorption at 520 nm. When DPPH reacts with a free radical, it becomes colorless; therefore, the consumption of DPPH can be monitored by examining the intensity of a peak at 520 nm by UV-vis spectrophotometer. In this study, the total amount of radicals was measured by dispersing the samples in DPPH solution at 70 °C for 24 h under dry argon gas and monitoring the peak at 520 nm by UV-vis spectrophotometer. The contact angle of the powder was determined by using a wicking meter. The samples were loaded into a cylindrical column holder that was vertically fixed at a balance, one end of which was sealed with a glass filter and in contact with the water surface in a beaker. As a result, water penetrated up into the column by the capillary attraction. Weight of water penetrating into the holder was automatically recorded [19]. Meanwhile, morphologies of the samples were observed directly by using SEM (Leo 1455VP). The peroxides and functional groups by the plasma treatment and polymerization reaction were analyzed by Fourier transform infra-red spectroscopy (FTIR, Bomen MB500) and ^{1}H nuclear magnetic resonance (NMR, FT500).

RESULTS AND DISCUSSION

The hydrodynamic properties in the plasma fluidized bed reactor at low pressures were determined in our previous study [24] from which the optimum operation condition to make plasma state stable in the fluidized bed is a gas flow rate of $1.5u_{mf}$ (0. 216 m/s) at 0.5 torr.

It has been known that the operating parameters such as rf power, gas flow rate and treatment time are the important factors in the plasma surface treatment condition [17]. Therefore, the effects of plasma power and treatment time at a gas velocity of $1.5u_{mf}$ are determined

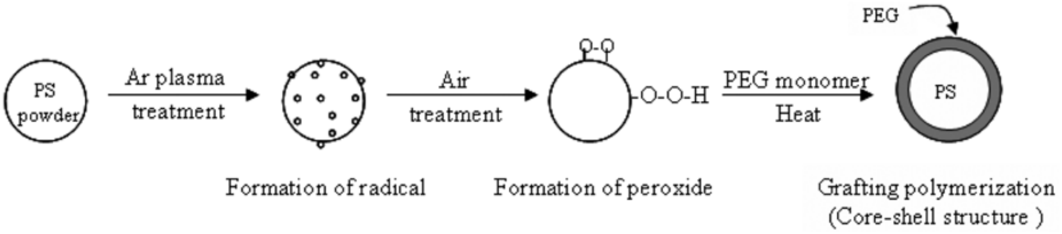

Fig. 2. Schematic diagram of the mechanism of peroxide formation.

by the amount of peroxides formed on PS powder. The effect of plasma-treatment time on the total amount of peroxides on PS powder at 100 W under 0.5 torr is shown in Fig. 3. As can be seen, the total amount of peroxides exhibits a maximum value (3.2 μmol/g) at a treatment time of 5 min and then it decreases up to 10 min. The total amount of peroxides reaches about 2.4 μmol/g after 10 min that may represent the equilibrium reaction condition.

The effect of plasma power on the peroxide concentration with 5 min plasma treatment time is shown in Fig. 4. The total amount of peroxides has a maximum value at 100 W because generation and activation of the active species by plasma is insufficient under the treatment time of 5 min at less than plasma power of 100 W, while the etching effect predominates over the formation rate of radicals at the plasma power over 100 W.

Non-porous film has a maximum value of the peroxide concentration within a few seconds [6] and, at the same time, porous film has it within 30-40 s [25]. Given that it is for the treatment of only one side of small film-type samples, less than 1 min is sufficient to have a maximum value of the peroxide concentration. However, the maximum value can be obtained around 5 min with the powders rather than film in this study. This longer time is inevitable since

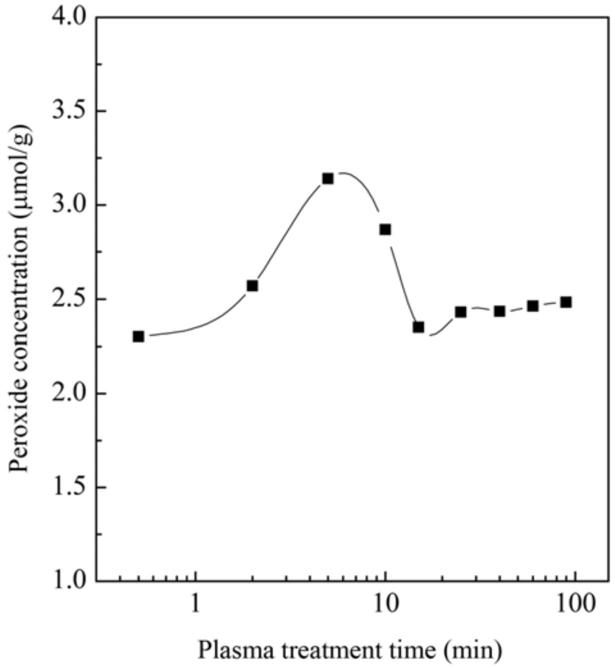

Fig. 3. Effect of plasma treatment time on the amount of peroxide.

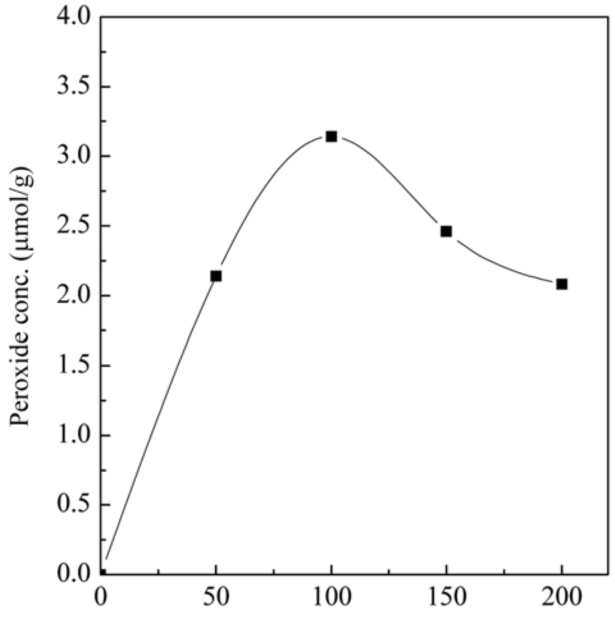

Fig. 4. Effect of plasma power on the peroxide concentration.

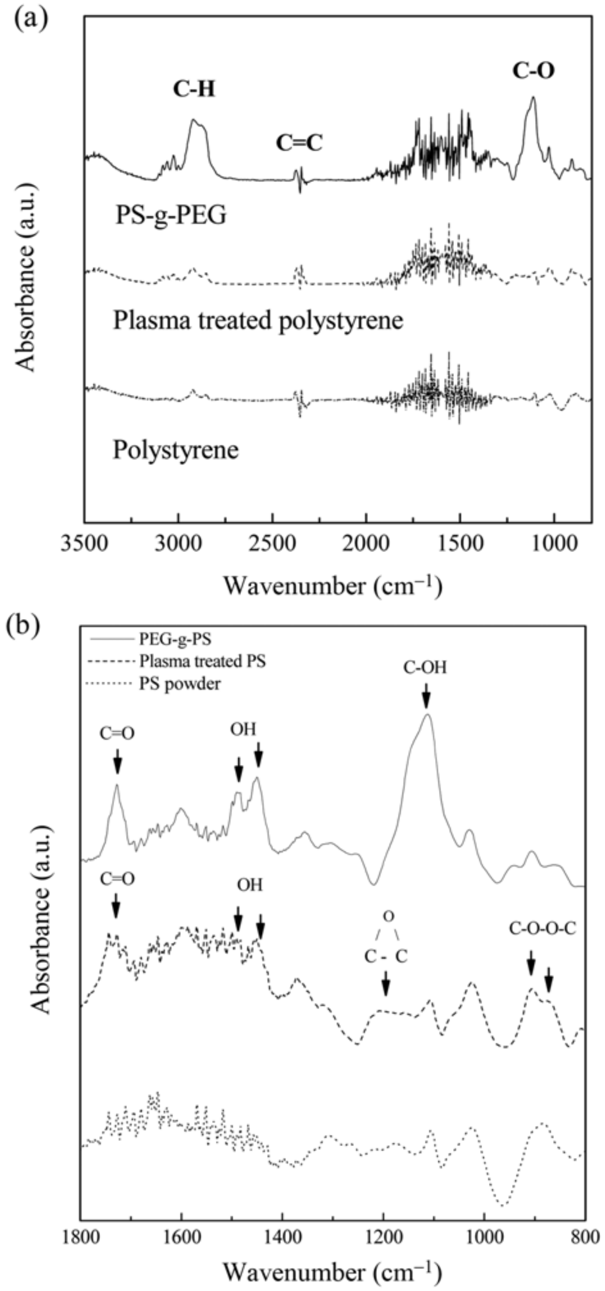

Fig. 5. FT-IR spectra of raw PS, peroxide-functionalized PS and PEG-g-PS at (a) wide and (b) low wave-number.

the surface area of a large amount of powders (160 g) in fluidizing state is much larger than that of film type samples.

From our previous study, the optimum operating pressure is 0.5 torr and the plasma power of 100 W and a treatment time of 5 min in the present plasma-fluidized reactor.

The FT-IR spectra of raw PS, peroxide-functionalized PS and PEG-g-PS powders at the wide and low wave-numbers are shown in Fig. 5. The absorption bands at 1,030 cm^{-1}, 2,900-3,000 cm^{-1} and 3,030 cm^{-1} are assigned to the C-O, C-H and C-H of aromatic (C-$H_{aromatic}$), respectively. In case of PS-g-PEG sample, two strong adsorption bands are observed at 2,900-3,000 cm^{-1} from C-O band and at 1,030 cm^{-1} from C-H, as can be seen Fig. 5(a). This result indicates that the PEG groups are dispersed on PS powder. However, the spectra of PS and plasma-treated PS have no noticeable difference because the amount of the peroxides generated on the surface of PS powder is very small, compared with that of the whole bulk of PS powder. Therefore, the detailed magnified spectra at 800 and 1,800 cm^{-1} are shown in Fig. 5(b). The absorption bands at 900-850 cm^{-1}, ~1,110 cm^{-1}, ~1,450 cm^{-1} and ~1,730 cm^{-1} are assigned to the peroxide group, alcoholic group, hydroxyl group and carbonyl group, respectively. For the plasma-treated PS powder, however, two adsorption bands can be observed, one at 900-850 cm^{-1} from peroxide species and the other at 1,450 cm^{-1} from the hydroxyl group. These findings confirm that the plasma-treated powders followed by the exposure to air creates peroxides and hydroxyl groups on the particle surface. The FTIR spectrum of the final PEG-g-PS powder exhibits various absorption bands. For the PEG-g-PS powder, the adsorption band of carbonyl group is assigned at ~1,730 cm^{-1} and the hydroxyl groups are assigned at ~1,110 and ~1,450 cm^{-1}. All these adsorption bands come from the grafted PEG. These results indicate that the reactant (poly ethylene glycol methacrylate) is polymerized by grafting with free radicals that come from the peroxide species. Thus, the FTIR analysis confirms that the surface of the PS powder is changed by the plasma treatment, and then the modified surface of the PS powder undergoes grafting polymerization with the precursor of PEG.

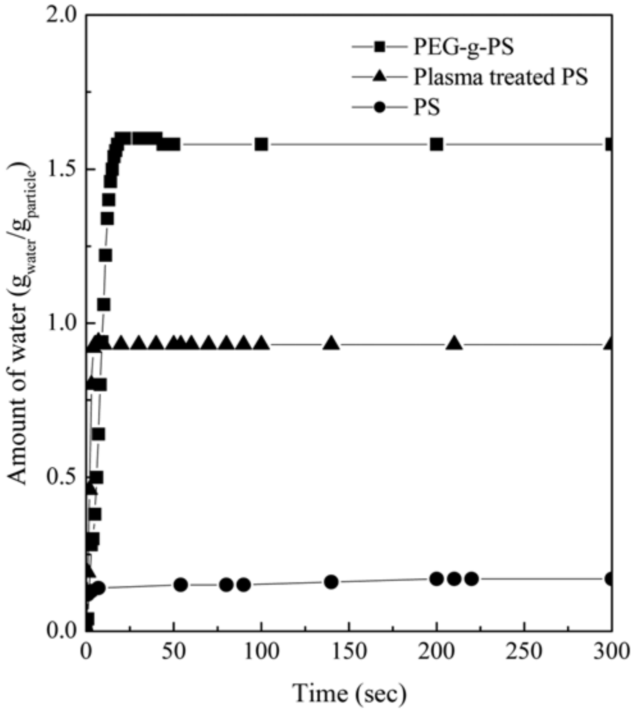

Fig. 6. Comparison of the water penetration of raw PS, peroxide-functionalized PS and PEG-g-PS.

The weight of water that penetrated into a column packed of the raw PS, peroxide-functionalized PS and PEG-g-PS particles determined by the wicking meter is shown in Fig. 6. In case of the untreated PS particles, the weight of penetrating water is very small due to the hydrophobic property of PS powder. By contrast, the peroxide-functionalized PS and PEG-g-PS powders absorb a much larger quantity of water due to the hydrophilic property of peroxides and PEG groups on the PS powder formed by the plasma treatment and grafting polymerization. Specifically, the peroxide-functionalized powder sample takes up water more than 90% of its own weight, and the PEG-g-PS powder absorbs water over 160% of its own weight. These results indicate that PS powder has highly hydrophobic surface, whereas the peroxide-functionalized PS and PEG-g-PS powders are highly hydrophilic. Moreover, the weight of penetrating water in the PEG-g-PS powder (160%) indicates that the PEG-g-PS powder is swelled by the penetrated water.

The quantitative analysis used the grafting frequency of the PEG-g-PS as determined by the area of benzene peak (6-7 ppm) as a functional group of polystyrene and that of PEG peak (CH_2-CH_2, 3.6 ppm) as a functional group of PEG divided by the number of each H atom. The final value of PEG is divided by that of PS, which indicates the grafting number of PEG per PS unit, a grafting frequency by our definition in this study.

The grafting frequency increases and then levels off with increasing the grafting time at 70 °C (Table 1) because the number of active radicals converted by the peroxide groups on PS surface increases with the grafting time and the PEG monomers reacted on many active radicals on PS surface. Meanwhile, the grafting frequency increases and then is maintained due to steric hindrance, which prevents from PEG monomer's reacting with PEG grafted on the surface PS, with PEG chain increasing. Also, Table 1 shows the grafting frequency as a function of reaction temperature. The peroxides rapidly decompose and are converted to active radicals with increasing temperature. Thus, temperature is an important factor to convert peroxides into the active radicals. The half-life of decomposition time of peroxides is 3 h at 70 °C and 840 s at 110 °C [26].

SEM images of morphology of PS and PEG-g-PS powders are shown in Fig. 7. The surface of raw PS powders is smooth but that

Table 1. Effect of grafting time and temperature on the grafting frequency

[a]Grafting time (h)	Grafting frequency (PEG unit/PS unit)	[b]Grafting temperature (°C)	Grafting frequency (PEG unit/PS unit)
5	13.5×10^{-4}	50	3.0×10^{-4}
8	19.0×10^{-4}	70	19.5×10^{-4}
12	21.4×10^{-4}	80	19.0×10^{-4}
22	20.0×10^{-4}	90	58.0×10^{-4}

[a]Reaction was carried out at 70 °C and Monomer conc.: 10 v/v%
[b]Reaction was carried out for 8 h and Monomer conc.: 10 v/v%

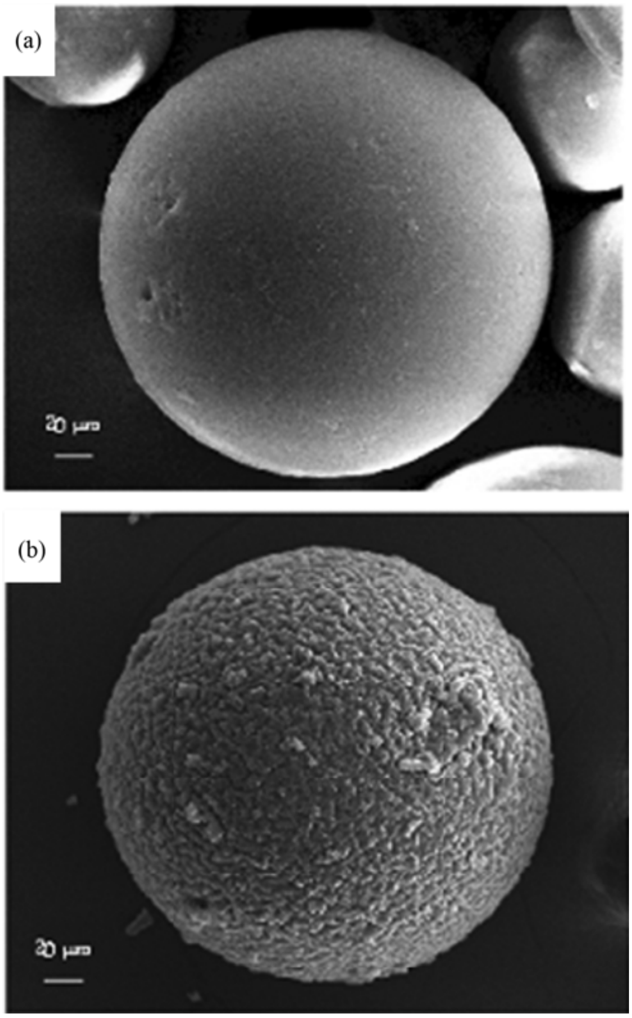

Fig. 7. SEM images of (a) PS and (b) PEG-g-PS particles (Magnification of 350 times).

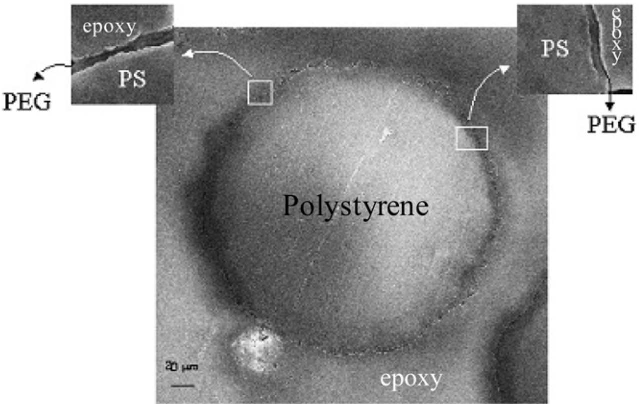

Fig. 8. SEM image of the cross-section of a PEG-g-PS particle (Magnification of 350 and 4000 times).

of PEG-g-PS powders is rough, which is consistent with roughening the powder surface when PEG is grafted onto PS to form PEG-g-PS.

A cross-sectional image of PEG-g-PS powder is shown in Fig. 8. As can be seen, almost uniform thickness of the PEG layer on PS powder is formed around 4 μm thickness. Therefore, well dispersed PEG grafting polymerization on PS surface can be achieved successfully in the plasma fluidized bed reactor.

CONCLUSIONS

Synthesis of core-shell structure of PEG-g-PS powder was carried out in a plasma-fluidized reactor with the radical-grafting polymerization. The physical and chemical structures were analyzed after each step by using the DPPH method, UV-vis spectrophotometer, FT-IR, NMR and SEM. Under the optimum condition at the operating pressure 0.5 torr, plasma power 100 W and treatment time 5 min, the total amount of peroxides exhibits a maximum value of 3.1 μmol/g. Based on the data obtained by FTIR analysis and the wicking method, the plasma treatment creates free radicals on the surface of PS powder, which are characterized by peroxide species, and PEG is well grafted on the plasma-treated PS powder with a well developed core-shell structure as observed in the SEM analysis of morphology of the PEG-g-PS powders.

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