Preparation and Characterization of Monodisperse Polystyrene-Silica Nanocomposites

Eunhye Kim[2], Sooyeon Kim[2], and Sung Soo Kim*[,1,2]

[1]*Department of Chemical Engineering, Kyung Hee University, Gyeonggi 446-701, Korea*
[2]*Regional Innovation Center, Kyung Hee University, Gyeonggi 446-701, Korea*

Abstract: Polystyrene-silica nanocomposites were successfully prepared by UV-induced graft polymerization of styrene onto a silica surface. Composites were prepared by batch and continuous-circulation reactions, and results indicated that polystyrene was successfully grafted onto inorganic silica particles for both reactions. Scanning electron microscopy and thermogravimetry analyses of the composites indicated 45% volume increase and 37% polymer content after an optimal reaction time of 30 minutes, respectively, for the batch reaction. For the continuous-circulation reaction, the corresponding results were 63% volume increase and 42% polymer content after 140 min of reaction time. Fourier Transform-Raman spectroscopy analysis of composites showed the characteristic peaks of both silica and polystyrene thus confirming the successful graft-polymerization for both reactions. Disappearance of C-H and C=C ring stretching bands at 3070 and 1578 cm^{-1} in composites after their optimal reaction times for both reactions indicated a possible ring opening mechanism due to prolonged exposal to the UV light source. For the batch reaction, composites showed new vibration bands at 1052 and 812 cm^{-1} for asymmetric and symmetric Si-O-C stretching, respectively, indicating a covalent bond between the grafted polymer and silica surface. X-Ray photoelectron spectroscopy (XPS) analysis showed an increase in the elemental concentration of carbon from 5 to 46% for 30 minute composites in batch reaction. XPS analysis also indicated that the relative OH group content of the surface of the silica particles determines the effectiveness of the graft-polymerization of styrene.

Keywords: organic-inorganic nanocomposites, UV-induced graft polymerization, polystyrene, silica.

Introduction

Polymer-silica hybrid nanocomposites are being fabricated and studied enormously in recent years due to the beneficial synergism of properties these composites possess. For instance, Pu *et al*. reported an improvement of mechanical and optical properties of polymethylmethacrylate (PMMA) by incorporating silica nanoparticles into the polymer matrix.[1] It also has been proven that surface modification of silica nanoparticles by vinyl monomers significantly enhanced the stability of silica and dispersions in polymer solvents by increasing the affinity of the surface for organic substances.[2] These nanocomposites can be used for many applications including coatings,[3] electronic devices,[4] and biosciences.[5] Among many methods reported for the fabrication of the polymer-silica hybrid composites, graft polymerization of monomers onto inorganic silica particles have attracted much attention lately.[6-9]

The successful graft-polymerization of monomers onto silica nanoparticles were reported by conventional free radical polymerization,[10] surface-initiated free radical polymerization,[11-13] controlled/living radical polymerization[14-16] and *in situ* radical transfer addition polymerization of mercaptopropyl-modified silica.[9] During graft-polymerization, the surface of the inorganic silica particles is modified to render the properties required for the specific application. The selection of the monomer is determined by the final properties the composites must possess. However, graft polymerization of silica particles often occurs in clusters since the particles possessing high surface energy tend to agglomerate. In our previous work we have proved that UV-induced grafting of methylmethacrylate (MMA) onto silica nanoparticles to be a more effective preparation method for monodisperse PMMA/silica composites with much less agglomeration of the particles and homopolymerization of the monomer.[17] We also indicated by the grafting mechanism that the presence of reactive hydroxyl groups is a prerequisite for successful UV-induced graft-polymerization of MMA.

For the present study, we also employed UV-induced grafting for the preparation of polystyrene-silica nanocomposites. Fabrication of polystyrene (PS)-silica composite particles of micron-scale by UV-induced graft-polymerization has been previously studied by our group for the applications as back-

*Corresponding Author. E-mail: sungkim@khu.ac.kr

light unit diffusing particles and as adhesive spacer particles in liquid crystal displays, and results were published elsewhere.[18,19]

In attempt to further reduce the agglomeration of the pure silica particles during the reaction and for the mass production of the composites, continuous-circulation reactions were also implemented for UV-induced grafting of styrene as well as previously employed batch reactions. The volume increase of the particles after grafting was investigated by scanning electron microscopy (SEM) and compared with the grafted-polymer content of composites obtained by thermogravimetry (TGA). X-Ray photoelectron spectroscopy (XPS) analysis was performed to correlate the carbon content of the polystyrene-silica composites with the polymer content by TGA. Fourier Transform (FT)-Raman experiment was also carried for the chemical structural analysis to confirm successful grafting of the polymer and whether the graft-polymerization occurred with a covalent bond between the silica surface and polymer chains. We also present here a criterion for selecting the reactive silica particles for the successful fabrication of polystyrene-silica composites *via* XPS analysis of silica particles.

Experimental

Materials and Reagents. Monomer styrene were purchased from Aldrich Chemical Co., and used after removing the inhibitor using inhibitor-remover column also purchased from Aldrich. Methanol, ethanol and benzophenone were also purchased from Aldrich and used as received.

The spherical silica nanoparticles were prepared by sol-precipitation method using tetraethyl orthosilicate (TEOS) as the main reactant as described in the previously published work.[20] To precipitate the particles, the colloidal suspension was centrifuged at 5,000 rpm for 5 min. The silica precipitate was dispersed in ethanol and centrifuged repeatedly. The final precipitate was dried in vacuum at 100 °C for 24 h before use.

UV-induced Graft Polymerization *via* Batch Reactor. Into a shallow glass Petri dish with a 150 mm diameter, 2.5 g of silica, 25 g of ethanol and 0.05 g of benzophenone (BP) was charged. The Petri dish was placed under a UV lamp and irradiated for 20 min at room temperature. A 350 W high-pressure mercury lamp from Oriel Co. (London, UK) was used for UV-induced graft polymerization. Its wavelength ranged from 200 to 500 nm. The distance between the reaction mixture and the light source was 25 cm. BP having optimum absorption wavelength about a range of 240~350 nm was used as an initiator of UV-induced reaction. Experimental conditions, such as the amount of the initiator and distance between the reaction mixture and the light source, had been optimized.

The reaction mixture was stirred with a magnetic stirrer under dry nitrogen at room temperature during the irradiation. After irradiation, 2.5 g of styrene was charged into the reaction mixture and again irradiated for a set of different times. A small amount of the reaction mixture was taken out at each specified time for analyses. The reaction mixture was centrifuged at 5,000 rpm for 5 min in ethanol, which led to sedimentation of the polymer-grafted silica particles. The supernatant, which contained unreacted monomer and residual initiator, was discarded. The particulate sediment was redispersed in methanol and centrifuged two more times. To remove the ungrafted polymer, the precipitate was dispersed in tetrahydrofuran (THF) and centrifuged repeatedly. The off-white polymer-grafted silica was collected and dried in vacuum at 100 °C for 24 h before characterization.

UV-Induced Graft Polymerization *via* Continuous-Circulation Reactor. In attempt to reduce the formation of ungrafted polymer particles as well as the agglomeration of the pure silica particles during the reaction, continuous-circulation reactions were implemented for UV-induced grafting of the monomer. Continuous-circulation reactors also can be used for the mass production of the composites. Apparatus for continuous-circulation reactions consists of an Aldrich 130 mL glass vacuum trap with straight inlet connected to Masterpump Model 7523-35 (Barnant Co.) with L/S™ 16 Masterflex silicon tubing and a 10 or 20 mL glass reactor exposed to UV lamp. The reaction mixture is deoxygenated by bubbling with nitrogen for 30 min before the UV experiment, and being pumped at 80 mL/min and continuously circulated throughout the reaction. As with the batch reactions, monomer is introduced after 20 min of UV-irradiation for better adsorption of initiator onto the surface of silica. About 5 mL of the reaction mixture is taken out from the end of the reactor by a stopcock valve at a specified interval for analysis.

Particle Chracterizations. Particle size analysis of the silica particles and the polymer-grafted silica particles was performed with SEM (Leica Stereoscan 440, England). Average particle sizes were obtained using image analysis software (Image-Pro Plus). The amount of grafted polymer on the silica particle surface was assessed by TGA (Perkin-Elmer TGA-7). FT-Raman Spectroscopy (RFS-100/S, Bruker, Germany) analysis was performed to study the chemical structure of polystyrene (PS)-grafted composites. XPS (ESCA 2000, VG MicroTech) analysis was carried out in order to determine the surface compositions of the pure and polystyrene-grafted silica particles.

Results and Discussions

Batch Reactions. As can be seen in Figure 1, both pure silica particles and polymer-grafted composites are spherical and the coefficient of variation (C.V.), an index for the accuracy of the particle diameter, is small. The coefficient of variation of the particle diameter is defined as the standard deviation divided by the mean particle diameter. Hisamitsu *et al.* reported that polymer-silica composites in micron-scale require C.V. of the particle diameter less than 10%, preferably less than 6% for application in liquid crystal displays as adhesive spacers. It is shown on the figure that polystyrene-silica composites have C.V. of less than 6%. Also, the surface
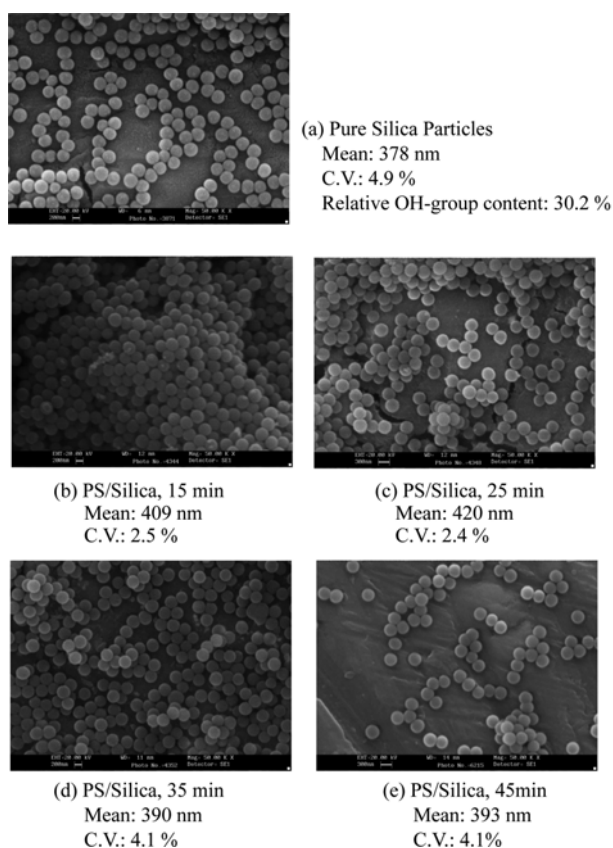
Figure 1. SEM images of (a) pure silica particles, (b) to (e) PS-grafted silica particles after 15 to 45 min of irradiation (PS/Silica), batch reaction.

modification occurred in the form of single particles not clusters. Formation of ungrafted-polymer particles was not observed though presence is possible. A substantial increase in the mean diameter of the particles was observed after irradiation due to the graft polymerization of styrene onto the surface of the silica.

Figure 2 shows the linear increase in diameter with reaction time until about 30 min. A sudden decrease in the diameter was observed after 30 min indicating the presence of optimal reaction time. This phenomenon coincides with results from the preparation of PMMA-silica particles in our previously reported work but decrease was much gradual in the case of PMMA-silica particles. The styrene-silica composites showed a 45% increase in volume of the particles at optimal reaction time, increasing from 378 to 428 nm. In the above mentioned work, PMMA-silica nanocomposites showed much higher volume increase of 78% at optimal reaction time. The smaller increase in polystyrene-silica composites might be due to the possibility that the bulky side group in polystyrene blocks the initiating sites on the silica surface. Results also suggested that a fraction of the polymer chains become detached from the silica surface after the optimal time for monomer styrene. The same trend was observed with monomer MMA. This con-
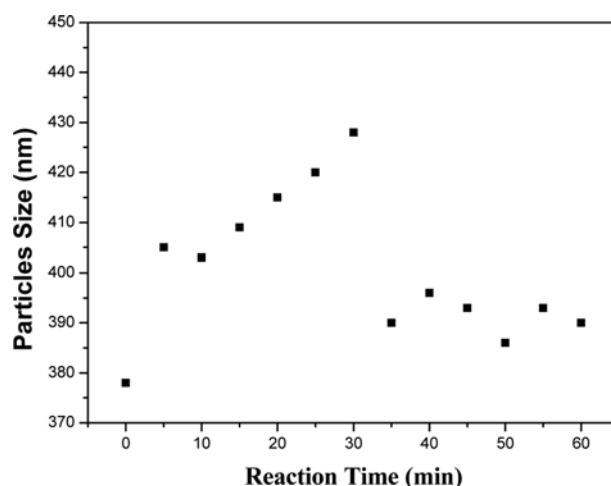

Figure 2. Effect of irradiation time on mean particle diameter of PS-grafted silica particles.

firms the degradation of the grafted polymer chains on silica particles with prolonged exposure to UV irradiation. A study by Kaczmarek *et al.* proved that the polymer chains become shorter as a consequence of breaking C-C bonds during UV degradation.[21]

Polymer Content by Thermogravimetry. Figure 3 shows the weight loss of the polystyrene-grafted silica particles when heated to 700 °C at 20 °C/min in air. Pure polystyrene showed a degradation temperature around 380 °C as expected. 30 min particles showed the largest weight lost of 37%. 40 to 60 min particles showed a weight loss less than the 30 min particles, indicating the degradation of polymer chains. From these results, we conclude that grafted-polymer contents of the composites are in good agreement with mean size increase of the composites from SEM images.

Mechanism of Grafting. We believe the mechanism of UV-induced grafting of styrene on silica nanoparticles would be
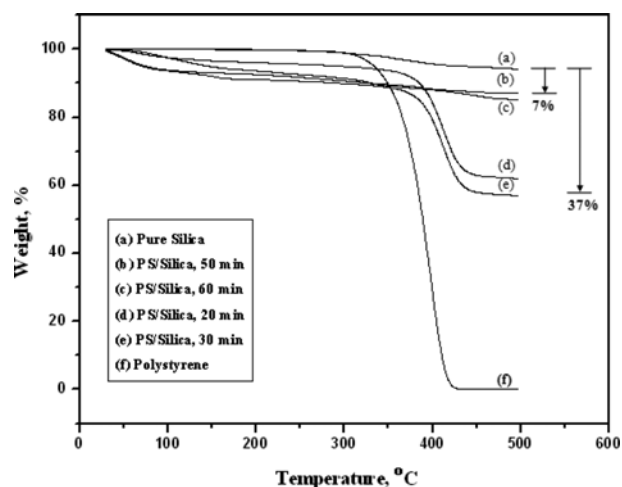

Figure 3. Weight loss of the PS-grafted silica particles when heated to 700 °C at 20 °C/min.
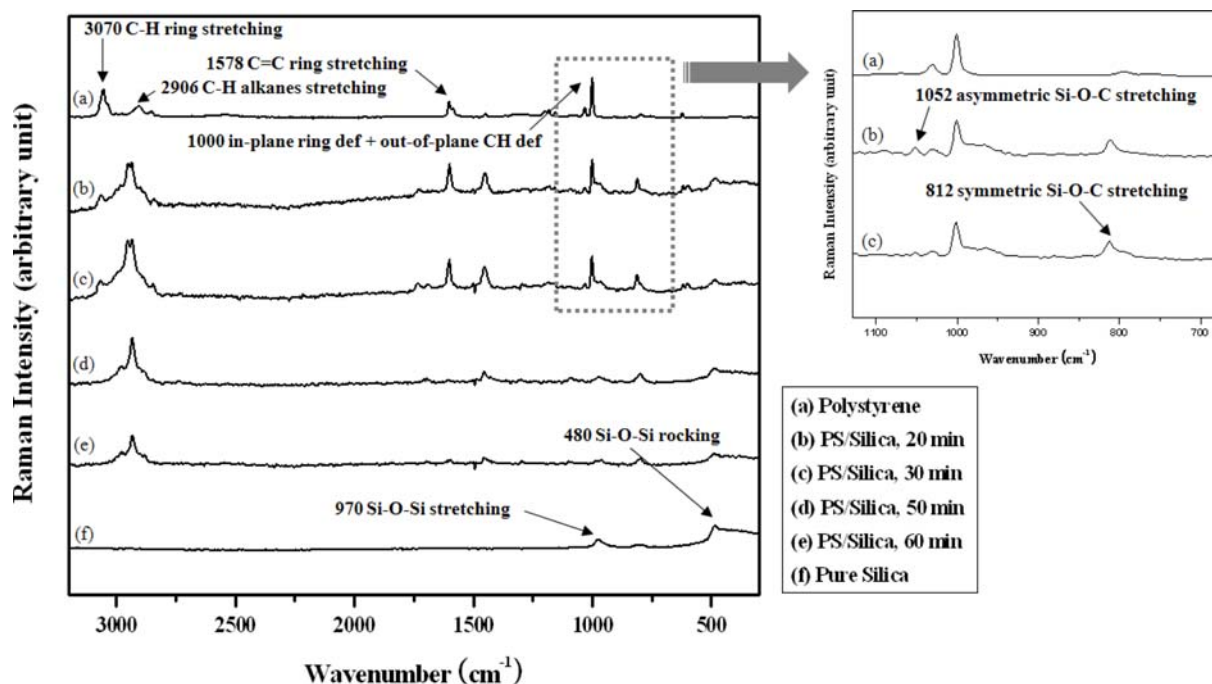
Figure 4. Raman spectra of PS-grafted silica particles with pure silica particles for comparison. Enhanced FT-Raman spectra of PS-grafted silica particles showing new vibration peaks.

the same as with grafting of MMA previously studied. The photo-initiator, benzophenone absorbs in the far UV spectrum near 250 nm and forms free radical that abstracts hydrogen from the silica surface. The radical formed on the silica surface reacts with styrene monomer, which initiates the growth of a grafted chain. Thus a new covalent bond, Si-O-C, is formed on the surface of silica. This formation of a covalent bond between functional organic layer and inorganic silica by UV-induced grafting will overcome the problems of phase separation or leaching of the polymer-silica hybrid composites.

Chemical Structure Analysis of Polystyrene-Grafted Particles. The Raman spectra for PS-grafted silica composites are shown in Figure 4. The pure silica particle shows vibration peaks at 480 and 970 cm^{-1} contributed to rocking and stretching of Si-O-Si as expected in Figure 4. 20 and 30 min particles showed the characteristic peaks of both silica and polystyrene thus confirming the successful graft-polymerization. It is worthwhile noting the disappearance of C-H and

C=C ring stretching bands (at 3070 and 1578 cm^{-1}) in 50 and 60 min composites. This can be explained with the possible ring-opening mechanism during UV degradation. Figure 4 shows the enhanced FT-Raman spectra of 20 and 30 min composites with polystyrene spectrum to confirm the formation of a covalent bond between silica surface and polymer. Composites show the new vibration peaks at 1052 and 812 cm^{-1} for asymmetric and symmetric Si-O-C stretching, respectively.[22] Thus spectral analysis supports the proposed mechanism of UV-induced graft polymerization of styrene monomer onto the surface of silica particles by a covalent bond.

Surface Composition Analysis. In X-ray photoelectron spectroscopy experiments the Si$_{2p}$ signal accounts for the silica particles and most of the C$_{1s}$ signal is due to the surface-grafted polymer chains. Besides the expected peaks, a C$_{1s}$ peak was observed in pure silica particle sample. This C$_{1s}$ signal might be due to the ubiquitous adsorption of hydrocarbon impurities during sample preparation. The C/Si atomic ratios

Table I. Summary of the Mean Diameter, Volume Increase, Polymer Content, C/Si Atomic Ratio of Silica and PS-Grafted Silica

Sample Description	Mean Diameter by SEM (nm)	Volume Increase by SEM (%)	Polymer Content by TGA (wt%)	Atomic Concentration (%) by XPS Si/C/O	C/Si Atomic Ratio by XPS
Pure Silica	378			31.91/5.11/62.98	0.16
PS/Silica, 20 min	415	32	32	18.04/45.15/36.81	2.50
PS/Silica, 30 min	428	45	37	17.32/46.29/36.39	2.67
PS/Silica, 40 min	396	15	10	28.65/11.46/59.89	0.40
PS/Silica, 50 min	386	7	7	29.94/10.50/59.26	0.35

(a) Pure Silica Particles
Mean: 330 nm
C.V.: 4.0 %

(b) PS/Silica, 80 min
Mean: 377 nm
C.V.: 3.2%

(c) PS/Silica, 100 min
Mean: 384 nm
C.V.: 3.8%

(d) PS/Silica, 120 min
Mean: 387 nm
C.V.: 2.9 %

(e) PS/Silica, 140min
Mean: 388 nm
C.V.: 2.8%

(f) PS/Silica, 160 min
Mean: 386 nm
C.V.: 3.4%

(g) PS/Silica, 180 min
Mean: 386 nm
C.V.: 2.9 %

(h) PS/Silica, 200 min
Mean: 376 nm
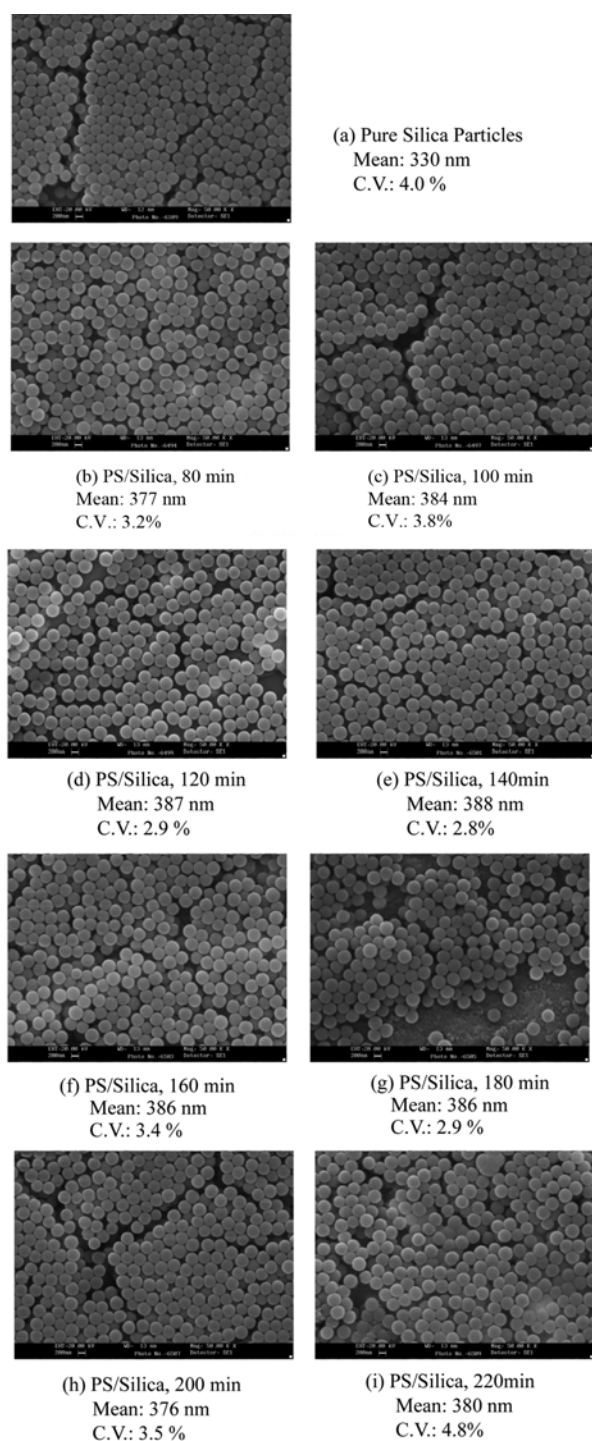C.V.: 3.5%

(i) PS/Silica, 220min
Mean: 380 nm
C.V.: 4.8%

Figure 5. SEM images of (a) pure silica particles, (b) to (i) PS-grafted silica particles after 80 to 220 min of irradiation (PS/Silica), continuous-circulation reaction.

are summarized in Table I along with the mean diameter and polymer content of the particles by TGA for PS-grafted silica composites. Increased mean diameter leads to increase in the C/Si atomic ratio, as expected. Carbon element content increased from 5 to 46% when the polystyrene chains were

grafted to the silica surface, and the silicon atomic concentration decreased to 17% from 32%. For 40 and 50 min composites, the carbon concentration was less than 30 min composites but greater than pure silica particles. These results correlate very well with the mean size increased by SEM. Therefore, we conclude that these XPS results confirm the successful grafting of MMA on the silica surface.

Continuous-Circulation Reactions. Figure 5 shows the SEM photographs of PS-grafted composites *via* continuous-circulation reaction. We only reported the mean particle diameters of composites after 80 min of UV-irradiation since the size increase before 80 min was negligible. This is due to the fact that actual exposal time of the reaction mixture to UV light source is much less in the continuous-circulation reaction than in batch reaction. These PS-grafted silica composites also showed a significant increase in mean diameter as shown in Figure 6, increasing from 330 to 388 nm for 140 min composites for a volume increase of 63%. Continuous-circulation reaction also indicated the presence of an optimal reaction time. The composites also showed degradation of polymer chains, resulting in decrease of the mean diameter, after the optimum reaction time as with the batch reaction. When compared with the batch reaction composites, the decrease in mean particle diameter after the optimal time was more gradual in continuous-circulation reaction. This is possible since the degradation of the polystyrene chains due to UV-irradiation is less since the reaction mixture is being circulated and only a portion of the reaction mixture is exposed to UV at one time, thus less exposal time.

FT-Raman spectra for these composites are shown in Figure 7. The composites particles showed characteristic peaks for both polystyrene and silica, indicating successful graft polymerization of styrene. Whether the grafting occurred with a covalent bond is not evident at this point of the research, but the possibility should not be ignored. Disappearance of the C-H ring stretching band at 3070 cm^{-1} indicates a possible
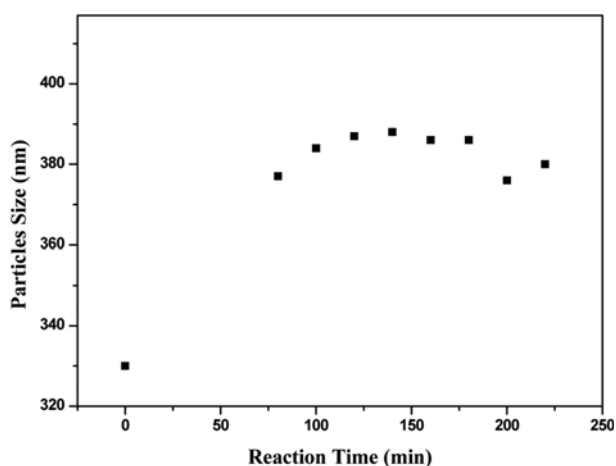

Figure 6. Effect of irradiation time on mean particle diameter of PS-grafted silica particles *via* continuous-circulation reaction.
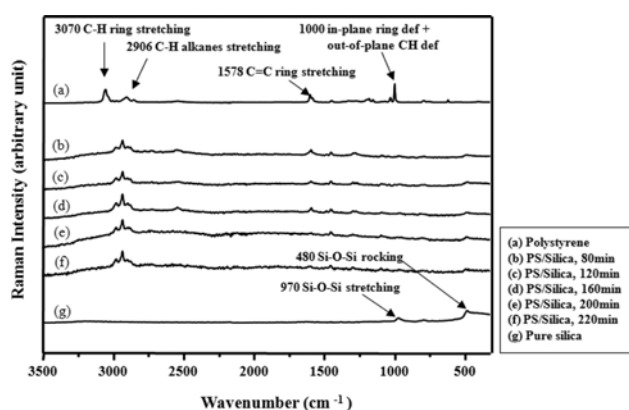
Figure 7. Raman Spectra of PS-grafted silica particles with pure silica particles for comparison, continuous-circulation reaction.

Figure 8. Terminal groups on the surface of silica.

ring-opening reaction occurring during chain propagation as well as degradation. This phenomenon was previously observed for batch reaction as well. TGA analysis shows the grafted-polymer content ranging from 24 to 29 wt%. Results are summarized in Table II. Composites near the optimal time of 140 min showed the largest weight loss of 29% thus confirming that polymer-layer thickness can be controlled and the optimum thickness of the polymer can be obtained by continuous-circulation reaction as well as the batch reactions. From these characterization analyses, we can safely conclude that the continuous-circulation reaction can be used for the mass production of polystyrene-silica nanocomposites while reducing agglomeration of particles.

Effect of OH Group Content on the Grafted-Polymer Layer Thickness. To study the effect of relative hydroxyl group content of pure silica particles on the grafted-polymer layer thickness, XPS measurements were performed on eight silica samples. XPS is widely used in the analysis of the surface functional groups, since it can determine the binding energy of the atomic orbitals, which shifts according to the surrounding ato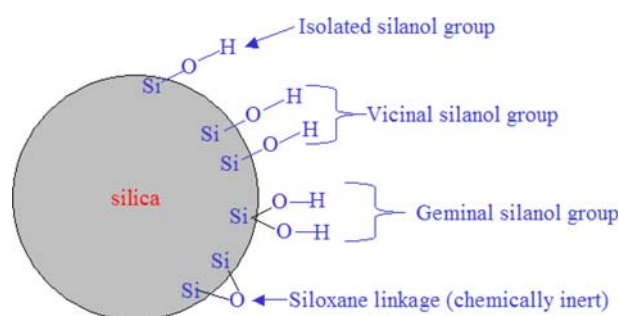ms. The presence of the OH group on the silica surface is a prerequisite in the surface-initiated graft-polymerization; therefore, the relative concentration of the OH group will affect how well the grafting reaction occurs. At the silica surface, the structure terminates in either siloxane group (Si-O-Si) with the oxygen atom on the surface, or one of the three forms of silanol groups (Si-OH) as shown in Figure 8.

Figure 9 shows the O_{1s} curve fittings for three pure silica samples. These curve fittings of the O_{1s} peak was carried out with a non-linear least-squares curve fitting program using a combination of Gaussian and Lorentzian functions (70:30%). The binding energies were referenced to the C_{1s} binding energy of 285.0 eV. These peak fittings show the presence of two oxygen components which are attributed to Si-O at 531.8 eV and Si-O-H at 533.8 eV.[23] The peak of O_{1s} spectrum can be decomposed into two component peaks. The first component peak is the Si-O bond at 531.8 eV, and the second component peak is the Si-OH bond at 533.8 eV. The percentages of the two bonds are calculated from peak area measurements. As with increasing Si-OH percentage, the peak broadens and the O_{1s} peak shifts to the higher energy from 532.46 to 532.78, then to 532.82 eV.

Table III shows the effect of OH (hydroxyl) group content of the pure silica particles on the grafted-polymer layer thickness. From the eight silica samples, we obtained the relative

Table II. Summary of the Mean Diameter, Volume Increase and Polymer Content of PS-Grafted Silica Particles, Continuous-Circulation Reaction

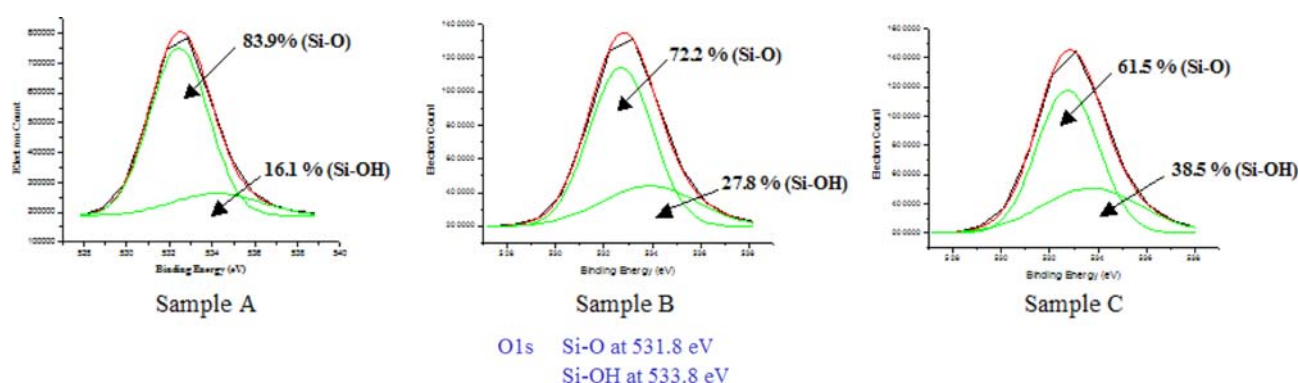| Sample Description	Mean Diameter by SEM (nm)	Volume Increase by SEM (%)	Polymer Content by TGA (wt%)
Pure Silica	330		
PS/Silica, 80 min	377	49	25
PS/Silica, 100 min	384	58	25
PS/Silica, 120 min	387	61	27
PS/Silica, 140 min	388	63	29
PS/Silica, 160 min	386	60	29
PS/Silica, 180 min	386	60	27
PS/Silica, 200 min	376	48	24
PS/Silica, 220 min	380	53	24

Figure 9. O_{1s} curve-fittings for three pure silica samples.

Table III. Mean Particle Diameter Increase in % After UV-Induced Grafting of Styrene onto Eight Silica Samples with Their Relative OH Group Content by XPS

Mean Particle Size of Pure Silica in nm (C.V. in %)	Relative Hydroxyl Group Content by XPS (%)	Mean Particle Size of Composites in nm (C.V. in %)	Volume Increase by SEM (%)
486 (2.8)	15.8	503 (3.4)	10.87
498 (3.6)	16.1	508 (2.4)	6.15
380 (3.6)	16.4	391 (4.2)	8.94
484 (3.3)	20.1	491 (3.3)	4.40
395 (3.9)	27.8	413 (3.9)	14.30
378 (4.9)	30.2	420 (2.4)	37.17
376 (3.7)	33.4	441 (4.3)	38.38
464 (2.6)	38.5	518 (3.4)	39.13

content of OH group ranging from 16 to about 40%. For all eight reactions, the optimal time of 25 min was used. The results indicated that the volume increase in particles does not have a linear relationship with the OH group content. It is observed that at least 30% or more of the OH group is needed for significant volume increase. This indicated that the relative content of reactive hydroxyl group on the surface of silica should be more than 30% for the graft-polymerization of styrene to be successful. Even though the particles with less than 20% showed increase in the volume, the thickness of the grafted polymer was much smaller than particles with 30% or more of OH group. This XPS surface analysis renders us a criterion for selecting the reactive silica particles for the fabrication of polystyrene-silica composites.

Conclusions

Polystyrene was successfully grafted onto inorganic silica particles by UV-induced graft polymerization in both batch and continuous-circulation reaction modes. The radical formed on the silica surface reacted with styrene monomer to form a new covalent bond, Si-O-C, which provided the formation of a covalent bond between functional organic layer and inorganic

silica particle. For batch reactions, 45% volume increase and 37% polymer content increase were attained at an optimal reaction time of 30 min. For continuous-circulation reactions, the results were 63% volume increase and 42% polymer content at 140 min of reaction time. Prolonged exposal to the UV light source after optimal reaction times for both reactions caused degradation by possible ring opening mechanism to result in the decreases of volume and polymer content. Disappearance of C-H and C=C ring stretching bands at 3070 and 1578 cm^{-1} in composites supported the degradation. XPS analysis indicated that the relative OH group content of the surface of the silica particles determines the effectiveness of the graft-polymerization of styrene, and the relative content of reactive hydroxyl group on the surface of silica should be more than 30% for the graft-polymerization of styrene to be successful. The continuous-circulation reaction can be used for the mass production of polystyrene-silica nanocomposites while reducing agglomeration of particles.

References

(1) Z. Pu, J. E. Mark, J. M. Jethmalani, and W. T. Ford, *Chem. Mater*., **9**, 2442 (1997).

(2) Y. Shirai and N. Tsubokawa, *React. Funct. Polym*., **32**, 153 (1997).

(3) C. C. Chen, D. J. Lin, T. M. Don, F. H. Huang, and L. P. Cheng, *J. Non-Cryst. Solids*, **354**, 3828 (2008).

(4) M. J. Bawden and S. R. Turner, in *Electronic and Photonic Applications of Polymers, Advances in Chemistry Series*, Vol. 218, ACS, Washington, DC, 1988.

(5) B. J. Ratner, *Biomed. Mater. Res.*, **27**, 837 (1993).

(6) T. von Werne and T. E. Patten, *J. Am. Chem. Soc.*, **121**, 7409 (1999).

(7) T. von Werne and T. E. Patten, *ACS PMSE Prepr.*, **82**, 294 (2000).

(8) C. Y. Hong, X. Li, and C. Y. Pan, *Eur. Polym. J.*, **43**, 4114 (2007).

(9) P. Liu, W. M. Liu, and Q. J. Xue, *Eur. Polym. J.*, **40**, 267 (2004).

(10) J. Ueda, S. Sato, A. Tsunokawa, T. Yamauchi, and N. Tsubokawa, *Eur. Polym. J.*, **41**, 193 (2005).

(11) B. Rånby, *Int. J. Adhes. Adhes.*, **19**, 337 (1999).

(12) N. Tsubokawa and H. Ishida, *J. Polym. Sci., Part A: Polym. Chem. Ed.,* **30**, 2241 (1992).

(13) N. Tsubokawa and H. Ishida, *Polym. J.*, **24**, 8, 809 (1992).

(14) D. A. Shipp, J. L. Wang, and K. Matyjaszewski, *Macromolecules*, **31**, 8005 (1998).

(15) J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, **117**, 5614 (1995).

(16) A. K. Mallik, M. M. Rahman, M. Czaun, M. Takafuji, and H. Ihara, *J. Chromatogr. A*, **1187**, 119 (2008).

(17) S. Y. Kim, E. H. Kim, S. S. Kim, and W. S. Kim, *J. Colloid Interface Sci.*, **292**, 93 (2005).

(18) S. S. Kim, S. Y. Kim, and E. H. Kim, Korea Patent, 10-0823830 (2008).

(19) E. H. Kim, S. Y. Kim, and S. S. Kim, *Mol. Cryst. Liq. Cryst.*, **464**, 217 (2007).

(20) K. S. Kim, J. K. Kim, and W. S. Kim, *J. Mater. Res.*, **16**, 2, 545 (2001).

(21) H. Kaczmarek, M. Swiatek, and A. Kaminska, *Polym. Degrad. Stab.*, **83**, 35 (2004).

(22) M. H. Nayfeh, E. V. Rogozhina, and L. Mitas, in *Synthesis, Functionalization and Surface Treatment of Nanoparticles*, M. I. te Baratón, Ed., American Scientific Publishers, Stevenson Ranch, 2003.

(23) J. Viard, E. Beche, D. Perarnau, R. Berjoan, and J. Durand, *J. Eur. Ceram. Soc.*, **17**, 2025 (1997).