Preparation of Hyperbranched Polyamidoamine Polymer–Ultrafine Silica Hybrid Composite

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ABSTRACT: Grafting of hyperbranched polyamidoamine (PAMAM) polymer onto ultrafine silica was prepared. First, an initiating site was incorporated into silica surface by treating silica particle with 3-aminopropyltriethoxysilane producing amino functionalized silica. Then grafting of hyperbranched PAMAM was performed by repetitive reactions between Michael addition of silica amino groups to methyl acrylate (MA) and amidation of the resulting terminal methyl ester groups with ethylenediamine (EDA). Excessive amounts of MA and EDA present in each step were removed by a rotary evaporator and dialysis separation, respectively. FT-IR analysis was employed to monitor the propagation of hyperbranched PAMAM on silica which was carried out until reaching the generation of 3.0. The yellowish liquid product was obtained. Amino group content in each generation was determined which was found significantly lower than theoretical value due to unavoidable side reactions. Laser light scattering and SEM results revealed that the particulate agglomerate was disaggregated into finer particle size as hyperbranched PAMAM generation increased. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3230–3237, 2008

Key words: hyperbranched PAMAM polymer grafted ultrafine silica; organic/inorganic hybrid

INTRODUCTION

Recently, nanometer-sized particles have attracted considerable interest because of their novel functionalities. For example, polyamidoamine (PAMAM) dendrimers which are the starburst polymers having highly branch monodisperse structures in nanometer scale as well as hyperbranched PAMAM polymer (analogous to PAMAM dendrimers) are of great interest as nanoscopic containers, nanoreactors, host-guest encapsulation, and delivery devices.[1–8] Furthermore, PAMAM dendrimers' terminal groups could be modified to obtain different functionalities such as acetamid, hydroxyl, carboxyl, or quaternary ammonium, leading to an increase in the versatile applicability of these materials.[9–13] Also, inorganic nanoparticles particularly such as carbon black and silica are of considerable interest due to their promising properties enhancer as nanofillers for rubber and plastics. However, a good and uniform dispersion of these types of extremely fine particles in polymer matrix is very difficult to achieve due to agglomeration problem. It is fortunate that surface modification of nanoparticle fillers could help improve the nanoparticle dispersibility. Several approaches have been proposed including treatment with coupling agents and polymer grafting.[14–17] The grafting of hyperbranched PAMAM polymer onto inorganic particle surface is one possibility.[8,18–22] The grafted polymer effectively prevents agglomerate formation, resulting in the stability of ultrafine nanoparticles in colloidal state or dispersibility in polymer matrix.

In this work, hyperbranched PAMAM polymer was grafted onto ultrafine silica surface as follows: First, the amino groups were introduced into the silica surface by reacting silica silanol group with amino functional group containing organosilane (APTES). Grafting reaction and propagation of hyperbranched PAMAM polymer from the silica surface were achieved by reiterative two step reaction sequences; a) an exhaustive alkylation of primary amine (Michael addition) with methyl acrylate (MA), and b) amidation of amplified ester groups with large excess of EDA to produce primary amine terminal groups. Grafting effect on silica particle disaggregation was studied using SEM and laser light scattering techniques.

EXPERIMENTAL

Materials and chemicals

Fumed silica (AEROSIL 200) having an average particle size of 14 nm and surface area of 200 m^2/g was

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purchased from JJ Degussa (Thailand), Co. Methyl acrylate (MA), Ethylene diamine (EDA), and 3-Aminopropyltriethoxysiliane (APTES) from Fluka (France) were used without purification. Toluene and methanol were distilled before use. Dialysis membrane with the molecular weight cut-off of 6000–7000 Da was bought from Membrane Filtration Products.

Incorporation of amino groups into ultrafine silica particle

The attachment of amino groups onto the silica surface was achieved by the condensation reaction between surface silanol groups and 3-aminopropyltriethoxysilane. Into a 600 mL flask, 15.0 g of fumed silica and 500 mL of 10% v/v toluene solution of 3-aminopropyltriethoxysilane were charged, and the fumed silica particles were homogenously dispersed by a magnetic stirrer for 30 min. Then 50 mL of methanol: water (4 : 1 or 2 : 1) was added to the mixture and stirred for 72 h. After that, the modified silica particles were filtrated and extracted with toluene for 24 h using soxhlet extractor to remove unreacted 3-aminopropyltriethoxysilane. The APTES treated silica was dried in an oven at 60°C for 24 h and stored in autodehumidity desiccators [yields: 44.07% (2 : 1) and 33.44% (4 : 1)].

Grafting of polyamidoamine polymer from silica surface

The Michael addition was carried out as follows: a 1000 mL flask containing 20.0 g APTES treated silica was added drop by drop with 600 mL of methanol having methyl acrylate with the concentration of 10 times higher than the amino content found in treated silica. The mixture was stirred at room temperature for 48 h, producing G0.5 PAMAM grafted silica. The methanol and unreacted methyl acrylate were evaporated by reduced pressure evaporator.

The amidation of terminal ester groups from the Michael addition step was carried out as follows: the whole amount (34 g) of ester terminated silica obtained from Michael addition step was put into a 1000 mL round bottom flask. Then, 500 mL of methanol was added. A solution containing 45 mL of EDA and 100 mL of methanol was added. The mixture was vigorously stirred at room temperature for 72 h. G1.0 hyperbranched PAMAM grafted silica was produced. The solvent and unreacted EDA were removed by a rotary evaporator performing at the temperature no higher than 40°C. The unreacted EDA was hardly evaporated under such condition. Separation of EDA was further achieved using dialysis membrane. Complete removal of EDA present in the product was followed up by monitoring the pH value of dialysate solution.

The propagation for second and third generations was carried out by repeating the two step reactions: Michael addition and amidation. The second generation (G2.0) was synthesized as follows: the G1.0 hyperbranched PAMAM grafted silica from the above reaction was reacted with MA (two times higher concentration than MA used from the synthesis of G0.5) in 100 mL of methanol. The mixture was stirred at room temperature for 48 h, leading to G1.5 hyperbranched PAMAM grafted silica. Then the solvent and unreacted MA was evaporated. After that, the resulting grafted silica was reacted with EDA (two times higher concentration than used in the synthesis of G1.0) in 100 mL of methanol. After 72 h, the solvent was removed by a rotary evaporator. The excess EDA was again separated from the product using dialysis membrane. The third generation (G3.0) was followed the second generation preparation.

Determination of amino group content on PAMAM grafted silica

The amino group content of hyperbranched PAMAM grafted silica was determined by titration technique. Into a 125 mL flask, 0.1000 g of grafted silica and 25 mL of 0.01*M* hydrochloric acid aqueous solution were charged. The mixture was stirred at room temperature for 2 h. Then, the mixture was filtrated and titrated with a standardized aqueous solution of sodium hydroxide using phenolphthalein as an indicator.

Determination of percent grafting

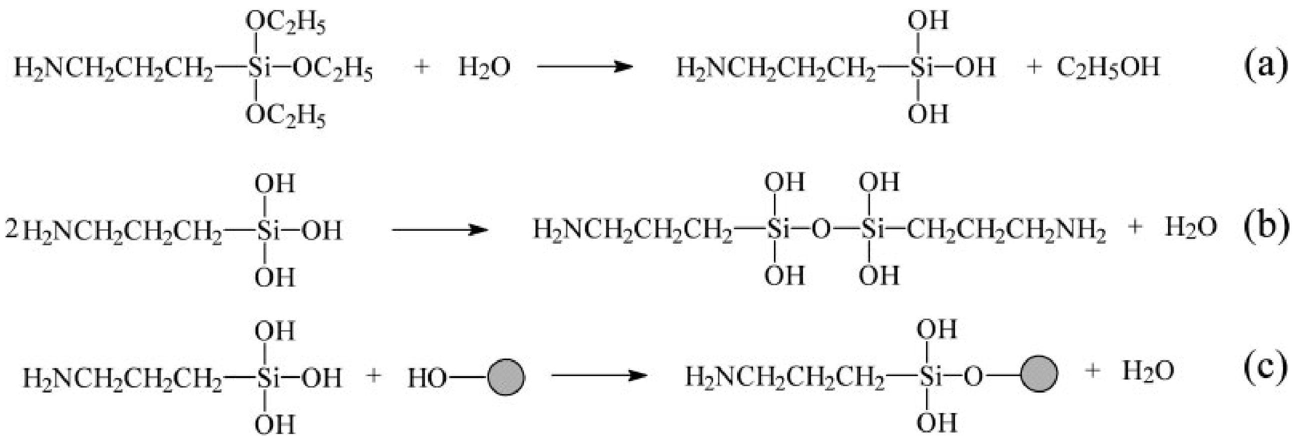
The weight of PAMAM grafted onto the silica surface was determined by weight loss when PAMAM grafted silica was heated to 800°C by TGA (Mettler Toledo STARe System DCS822e Module). The percentage of grafting was calculated by the following equation.[13]

$$\text{Percentage of grafting} = (A/B) \times 100$$

where A, weight of PAMAM grafted (g) and B, silica charged (g).

Characterizations

The morphology of hyperbranched PAMAM grafted silica was observed by scanning electron microscopy (SEM; Model JSM-5410LV, JEOL, Tokyo, Japan) operated at 15 kV accelerating voltage. The particle size distribution was analyzed using laser light scattering (Mastersizer 2000, Malvern Instruments). FTIR spec-



Scheme 1 Equation of hydrolysis reaction from alkoxysilanes (a) and self condensation reaction (b) or (c) condensation reaction between APTES and silica.

troscopy taken on KBr pellet samples was recorded on a Nicolet Fourier transform spectrophotometer (Nicolet Impact 400D). Proton NMR spectra of the samples were recorded on Bruker DPX-300 spectrometer. TGA was performed using Mettler Toledo STARe System DCS822e Module.

RESULTS AND DISCUSSION

Introduction of amino groups into the silica surface

The surface functionalization of silica particles was carried out by the condensation reaction of silica silanol group with 3-aminopropyltriethoxysilane(APTES), resulting in silica particle containing amino groups on the surface which acted as the initiator sites for PAMAM grafting. There are several treatment methods concerning APTES grafting onto silica surface including graftings in acid-aqueous solution and in anhydrous solution.[23] In this study, the condensation reaction was base-catalyzed and APTES amine groups were self-catalyzed component. The mechanism involved the hydrolysis of APTES triethoxy groups by water, generating silanol groups. Then condensation reaction between APTES silanol group and silica silanol group took place on silica surface as shown in Scheme 1. Self-condensation of APTES also occurred, resulting in undesirable products. The amount of water present in the system significantly influenced the hydrolysis reaction of triethoxy groups which then determined the condensation reaction on silica surface.

The rate of hydrolysis and condensation reaction was controlled by using a mixture of water and methanol. In this study, the methanol to water ratios of 4 : 1 and 2 : 1 were used. The measured amino contents on silica plotted against reaction times are shown in Figure 1. As can be seen, the amino group content increases with an increase in the amount of water and reaction time. Water was consumed to convert APTES triethoxy groups to silanol groups (hydrolysis reaction). The amount of water, hence, determined the rate of hydrolysis. Consequently, the more silanol groups produced the higher the rate of subsequent silanol condensation reaction. In this work, amino-functionalized silica for PAMAM grafting was prepared as follows: a 2 : 1 ratio of methanol to water was used and the surface functionalization of silica particles was allowed to occur for 3 days.

As a result of silanization reaction, the amino functionalized silica was produced. An FTIR analysis was further employed to provide the evidence of the attachment of APTES on silica. Figure 2 compares FTIR spectra between APTES grafted silica, virgin silica, and APTES. Silica which is an inorganic substance in nature exhibits the strong absorption

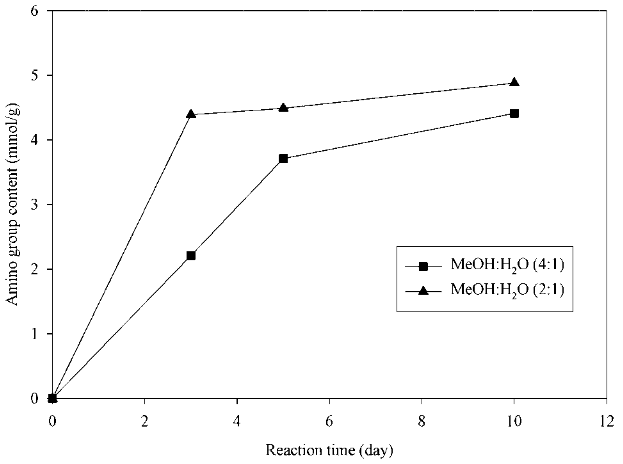


Figure 1 Amino group content measured on APTES treated silica versus reaction time.

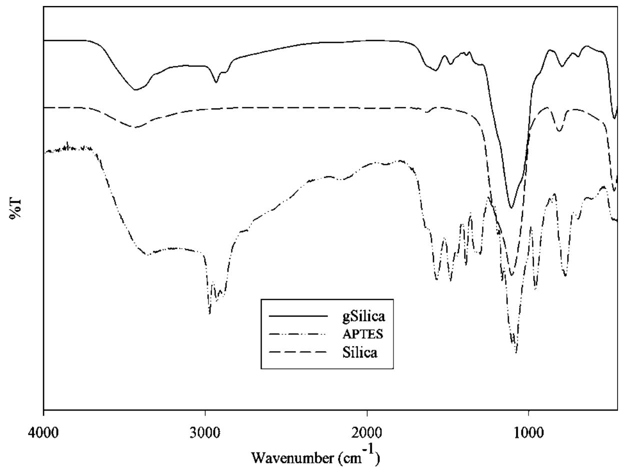


Figure 2 FTIR spectra of silica, APTES and APTES grafted silica.

band of siloxane (Si—O—Si) bonding at ~1200 cm^{-1} and the silanol OH band in the range of 3200~3400 cm^{-1}. When considering the APTES silica, organo-functionalized silica, its spectrum exhibits new absorption frequencies at 2932 cm^{-1} and 1640 cm^{-1}. These bands are associated to C—H stretching and primary amine (—NH$_2$) stretching absorptions, respectively. Also, these bands are found corresponding with the absorption characteristics of APTES spectrum. These results indicate that APTES is incorporated into silica particles. The silica surface modification is further confirmed by change observed in spectrum pattern in the region of silanol OH band (3200–3400 cm^{-1}) due to new interhydrogen bonding interaction among amino silica particles.

Grafting of hyperbranched PAMAM from silica surface

After the introduction of primary amine functional groups was successful and yielded amino initiating sites, grafting of hyperbranched PAMAM onto the surface of amino-functionalized silica was carried out by repeating two processes, Michael addition and amidation which were used in the same manner

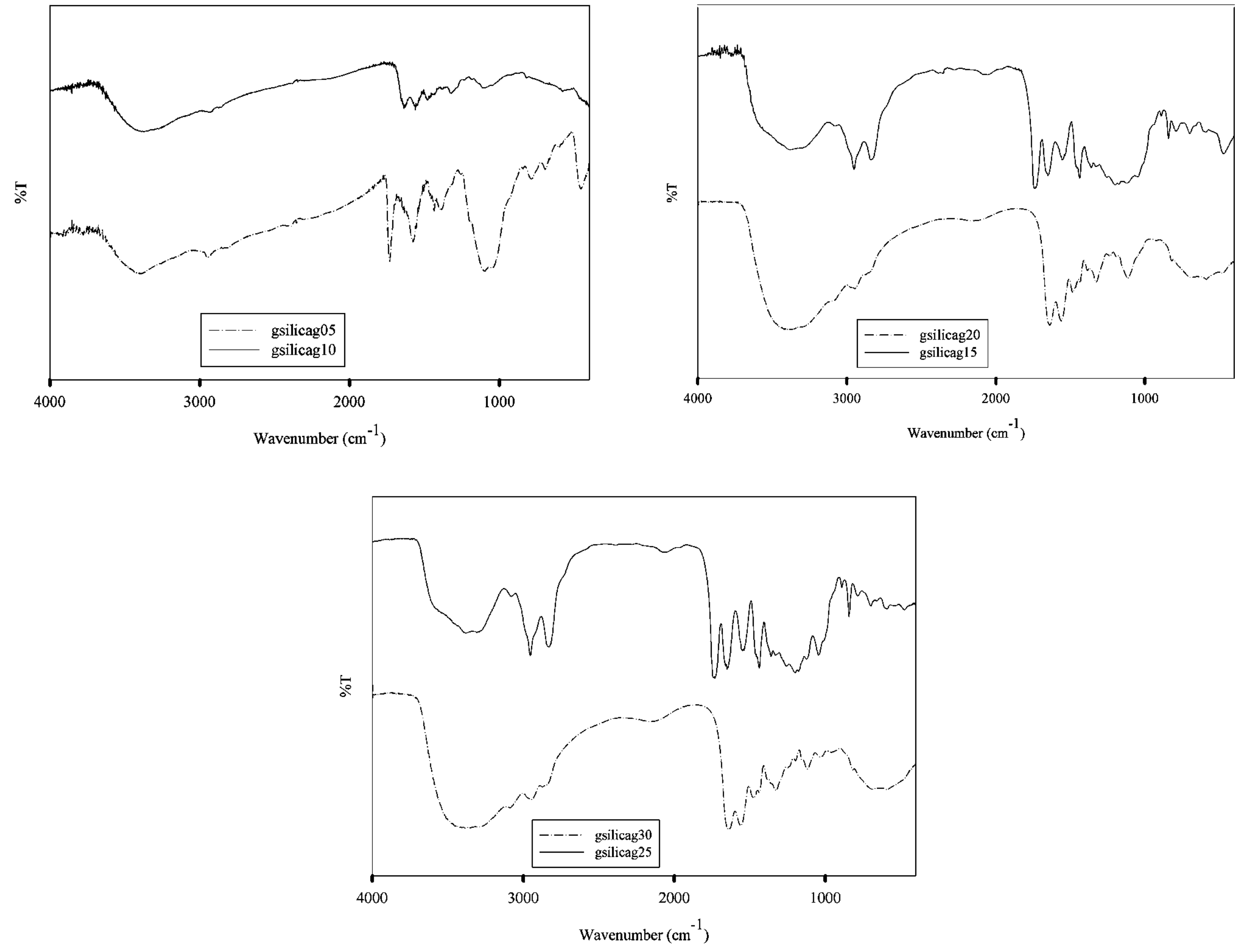
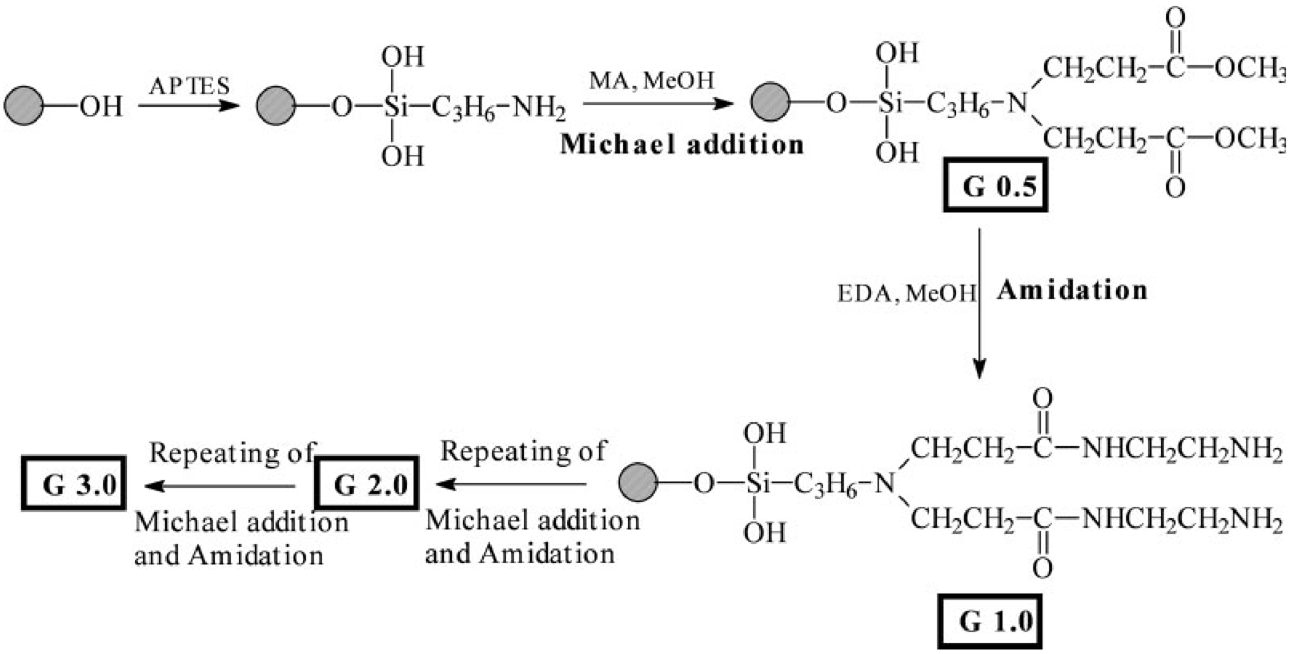


Figure 3 FTIR spectra of G0.5 – G 3.0PAMAM grafted silicas.



Scheme 2 The theoretical synthesis of PAMAM grafted silica.

as in the synthesis of PAMAM dendrimers. A removal of excessive MA and EDA in each reaction step was necessarily performed during grafting reaction. In the Michael addition step, excessive amount of MA was easily removed from the reaction product by reduced pressure evaporator due to its low boiling temperature. On the other hand, excessive amount of EDA left in the amidation step was hardly removed by a typical rotary evaporator. In this work, EDA was therefore separated from the reaction product using dialysis membrane. The purified products were analyzed by FT-IR analysis which is a useful tool for monitoring the Michael addition and amidation reaction. FT-IR results are shown in Figure 3. In the Michael addition step, the terminal methyl ester group of G0.5, G1.5, and G2.5 products shows a strong and distinguishable band at 1740 cm^{-1}. This peak completely disappears from the spectra of G1.0 and G2.0 as a result of the amidation reaction. In this step, the terminal amine group was obtained which corresponds to the appearance of the strong absorption intensity of the N—H band in the region of 3000–3350 cm^{-1}. Its absorption intensity remarkably increases with an increase in PAMAM generation, reflecting that the number of terminal amine groups also significantly increases. When considering G3.0 hyperbranched PAMAM grafted silica, the absorption peaks at 1649 cm^{-1} and 1568 cm^{-1} are found, indicating the characteristics of C=O stretching and N—H bending. In addition, the absorption peaks at 3281 cm^{-1} and 3086 cm^{-1} are correspondent to N—H antisymmetric stretching and N—H symmetric stretching of primary amine, respectively. In accordance, the C—H band at 2900 cm^{-1} which shows up strongly in the spectra of G0.5 and G1.5 becomes less dominant due to suppressing influence by the surrounding N—H band. The theoretical reaction scheme is shown in Scheme 2.

Proton NMR analysis was also performed. The ^{1}H NMR spectrum of ester terminated PAMAM grafted silica is shown in Figure 4. The signal which indicates the presence of terminal methyl ester group (CH_3—O—) appears at ~3.8 ppm. When comparing with the ^{1}H NMR spectrum of free amine terminated PAMAM grafted silica shown in Figure 5 it is seen that the signal of methyl proton completely disappears due to the amidation reaction. Again, the sig-

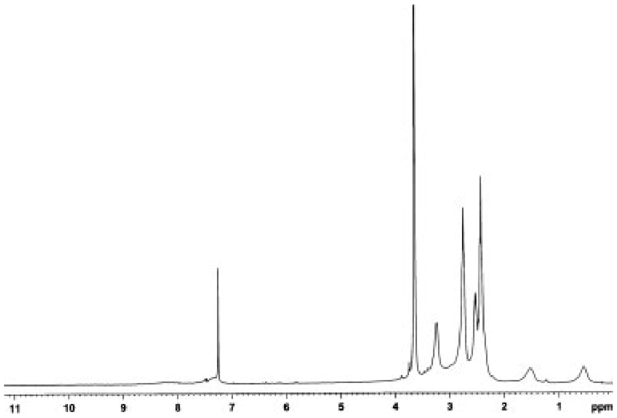


Figure 4 ^{1}H NMR spectrum of G1.5 hyperbranched PAMAM grafted silicas.

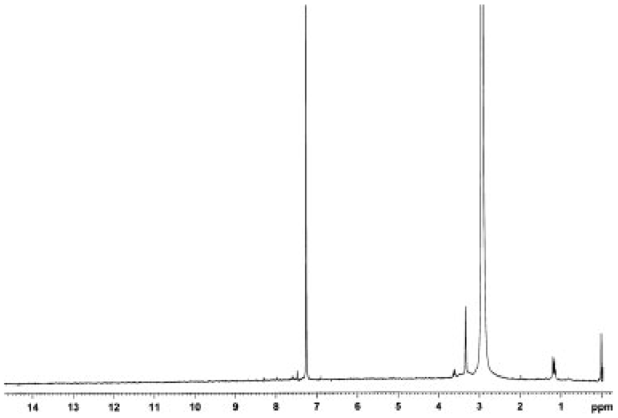


Figure 5 ^{1}H NMR spectrum of G2.0 hyperbranched PAMAM grafted silicas.

nal peak at ~3.8 ppm shows up strongly in the NMR spectrum of G2.5 hyperbranched PAMAM grafted silica (not present). The results obtained from FT-IR and ^{1}H NMR lead to a conclusion that grafting of PAMAM polymer onto silica particle was successful.

The TGA thermograms of hyperbranched PAMAM grafted silicas from G0.5 to G3.0 are shown in Figure 6. From the thermogram curves, percent graftings were calculated and their results are also given in Figure 7. As seen, percent grafting increases when PAMAM generation grows as a result of PAMAM propagation from the silica surface amine groups. For example, percent grafting obtained from G1.0, G2.0, and G3.0 are 74%, 342%, and 1332%, respectively. As observed, percent grafting trend exponentially increases due to the characteristics of PAMAM synthesis. The amino group contents were expected to increase in a similar manner to percent grafting. Also from Figure 5, the amino group contents of G1.0, G2.0, and G3.0 are 14.62, 23.26, and 60.21 mmol/g of silica, respectively. However, the measured amounts are much lower than the theoretical value. Based on the reaction chemistry, there were two main reasons why the theoretical value was hardly to achieve. One was the effect of steric hindrance arising from congestion of end groups; the higher the reaction step the more the congestion effect. As a result, the propagation of PAMAM branches was blocked. The second drawback suppressing an increase in amino content occurred in the amidation step; the side reaction of one EDA with two molecule ester groups to form intra- and intergroup crosslink products as shown in Scheme 3, decreased the amount of ester groups available for the next step reaction.[24]

SEM analysis and particle size analysis

By nature, the as-received fumed silica nanoparticles powder aggregated and formed micron-sized nanoclusters. Typically, physical interaction among nanoparticles is too strong to separate them by mechanical agitation means into individual particles due to its large surface area characteristic. In this study, the effect of hyperbranched PAMAM dendrimer grafted onto silica surface on particle disaggregation and its stability was examined using SEM and particle size analysis. SEM images are shown in Figure 8. As found in SEM, as-received fumed silica particles are tightly packed and adhered together in agglomerate form. It is understandable that physical force such as hydrogen bonding is solely responsible for particle aggregation. After grafting, changes in particle distribution behavior as well as the agglomerate size were observed and the results are also shown in Figure 9. The results indicate that hyperbranched PAMAM grafting onto silica has been proven to be successful in dispersing particle agglomeration. This achievement was due to the steric role of grafted hyperbranched PAMAM. In addition, as observed in SEM images, the grafted hyperbranched PAMAM resulted

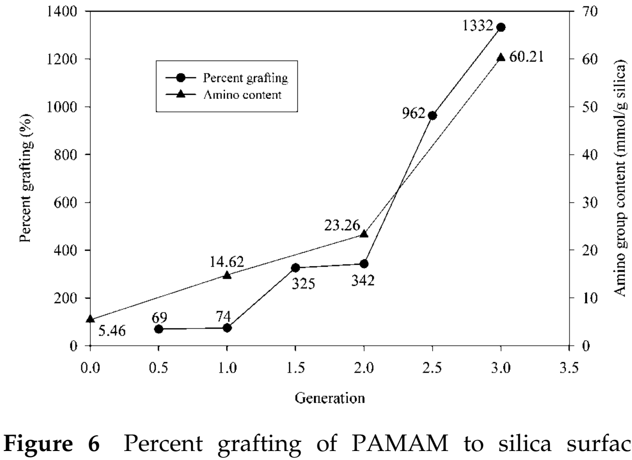


Figure 6 Percent grafting of PAMAM to silica surface and amino group content.

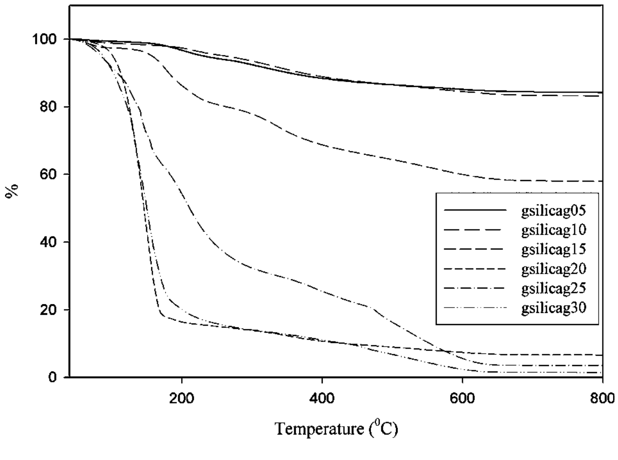
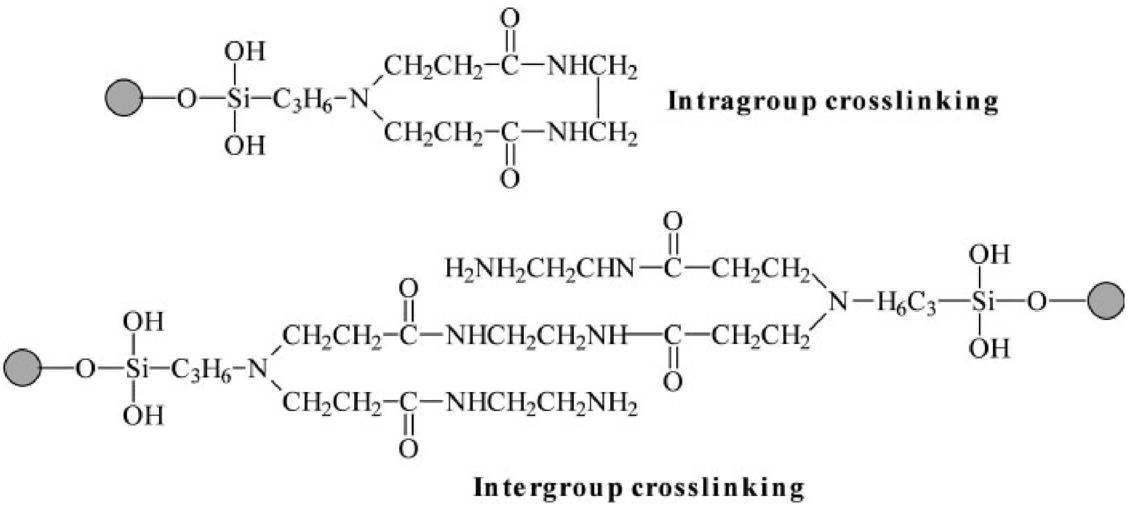


Figure 7 TGA thermograms of G0.5–G3.0 PAMAM grafted silicas.



Scheme 3 Intra- and intergroup reaction of terminal amine group and terminal ester group of PAMAM grafted silica.

in reducing the agglomerate size. The particle size of sample was further measured with laser light scattering. Figure 9 shows the particle size distribution comparison between as-received fumed silica, G0.5, G1.5, and G2.5 hyperbranched PAMAM graft silicas. In this experiment, G1.0, G2.0, and G3.0 hyperbranched PAMAM graft silicas were excluded due to the fact that the attractive force among agglomerates is pH dependent. In case of free amino terminated silicas, pH value was higher than pH 10. Therefore, the silica silanol groups started becoming deprotonated and repulsive force took effect on particle size measurement. In case of ester terminated PAMAM grafted silicas, their pH values were mildly basic (pH < 9). As can be seen, the particle sizes before treatment are in an average size of

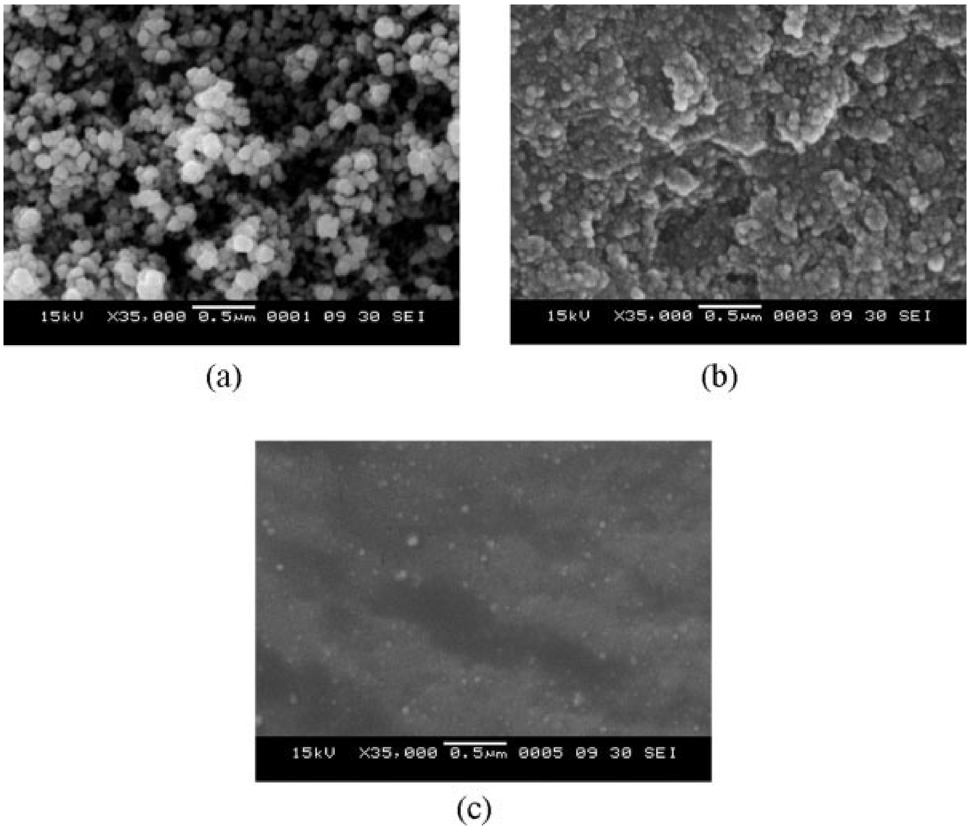
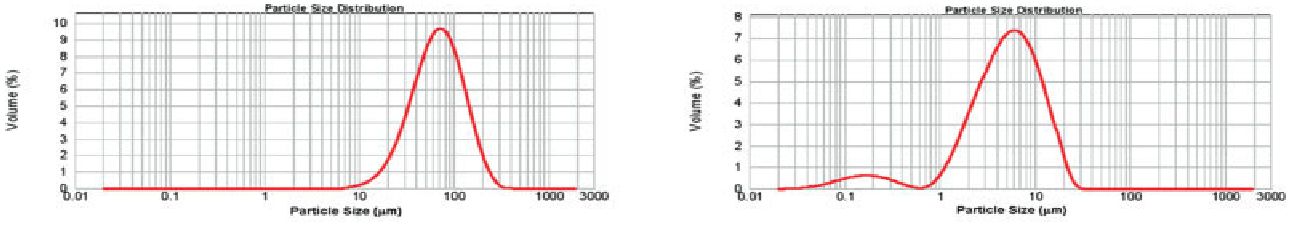
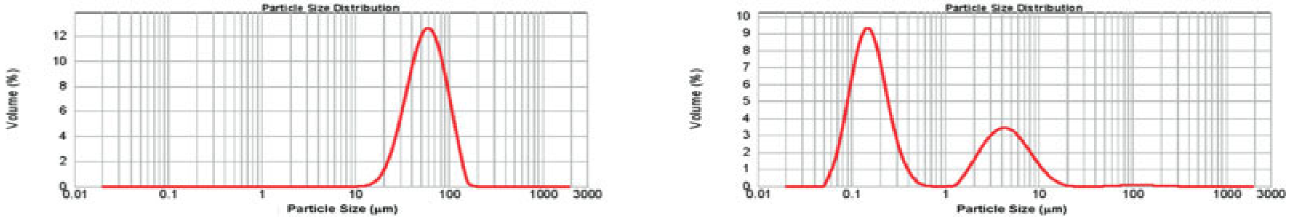


Figure 8 The SEM images of (a) silica, (b) G0.5 PAMAM grafted silica, and (c) G1.0 PAMAM grafted silica.



(a) Virgin silica **(c) gsilicag05**



(b) Grafted silica **(d) gsilicag15**

Figure 9 The particle size distribution of (a) virgin silica, (b) grafted silica, (c) G0.5 PAMAM grafted silica, and (d) G1.5 PAMAM grafted silica. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

∼100 microns. The average size of G0.5 PAMAM silica particles decreases to ∼10 microns and then after PAMAM propagation reaching G2.5 the particle sizes decrease to ∼100 nm.

CONCLUSIONS

The grafting of hyperbranched PAMAM polymer onto amino groups functionalized silica was successfully achieved by repetitive reactions between Michael addition of silica amino group to methyl acrylate and amidation of resulting terminal methyl ester group with ethylenediamine. A series of silicas grafted with hyperbranched PAMAM up to generation 3 were produced. Percent graftings calculated from TGA were 74, 342, and 1332 for G1, G2, and G3, respectively. While the amino group contents of G1, G2, and G3 were 14.62, 23.26, and 60.21, respectively, which exhibited an increasing trend in similar manner with percent grafting. However, the measured amounts were much lower than theoretical values due to the effect of steric hindrance and the intra- and intergroup crosslinking. Grafted hyperbranched PAMAM played the steric hindrance and the intra- and intergroup crosslinking, leading to well dispersion of nanoparticles. As a result, the agglomerate size found in average size of ∼100 microns before grafting was significantly reduced to nanometer range of ∼100 nm after grafting.

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