

# Phosphonic Acid Functionalization of Hyperbranched Polyamidoamine Grafted Ultrafine Silica to Prepare the Flame Retardant for Cotton Fabric

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## Abstract

Grafting of hyperbranched polyamidoamine (PAMAM) dendrimer onto ultrafine silica followed by the introduction of phosphonic acid groups onto branch ends was carried out. First, an initiating site was incorporated into silica surface by reacting the silica silanol group with 3-aminopropyltriethoxysilane, producing amino-functionalized silica. The free amine group content was controlled by varying ratios of methanol to water in the hydrolysis step of sol-gel reaction. Then grafting of PAMAM was performed by repetitive reactions between Michael addition of silica amino groups to methyl acrylate and amidation of the resulting terminal methyl ester groups with ethylenediamine. Amino group content in each generation was determined. This was found to be significantly lower than theoretical value due to unavoidable side reactions. After the G3.0 hyperbranched PAMAM grafted onto silica was synthesized, phosphonic acids functionalization of the terminal amino groups by the Mannich type reaction was carried out. The phosphorylated hyperbranched PAMAM grafted silica was achieved and its application on cotton fabric to produce phosphonated cellulose was studied.

**Keywords:** polyamidoamine, flame retardant, textile finishing, grafted silica

## 1. Introduction

Polyamidoamine (PAMAM) dendrimers, the starburst polymers with a plurality of terminal functional groups have attracted considerable interest due to their novel functionalities such as nanoscopic containers, delivery devices, ultrafine colloid stabilizers and nanocomposite materials [1-8]. Surface modifications of terminal groups with different functionalities such as acetamide, hydroxyl, carboxyl or quaternized PAMAM dendrimers further increase the versatile applicability of these materials[9-13]. Focused on nanoparticle fillers such as carbon black and silica, these materials are widely used for rubber and plastics. A good uniform dispersion of extremely fine particle size for most of their applications is important. However, these nanoparticles by nature are found in micron sized aggregate whose performance is inferior to those of the nanometer sized form. This problem of nanoparticles having a strong tendency to agglomerate is solved by surface modification[14-17]. The grafting of PAMAM dendrimer onto inorganic particle's surface is one possibility[18-20]. The grafted dendrimer effectively prevents agglomerate formation, resulting in the stability of ultrafine nanoparticles in the colloidal state or dispersibility in the polymer matrix. Nanometer-sized fillers are expected to exhibit the attractive interaction with polymer matrix at very low filler content, resulting in an improved performance of nanocomposite materials. Another interesting effect is that the PAMAM attached on inorganic particles leads to hybrid materials with special characteristics particularly high performance chelating agents[21] and nanoreactors in which metal nanoparticles are stabilized[22]. Other interesting performance concerned with nanocomposites includes reduced gas permeability, increased solvent resistance and reduced flammability. In this study, this type of nanoparticle was specially designed to impart its flame retardancy performance on cotton cellulose. When considering flame retardants for cellulose and cellulose derivatives, phosphorus-based flame compounds have been a major interest because of their environmentally friendly products and their low toxicity, as well as, their low evolution of smoke in fire. These compounds will promote dehydration and char formation.

## 2. Experimental

### 2.1 Materials and reagents

Fumed silica (AEROSIL 200) was purchased from JJ Degussa (Thailand), Co., Ltd. Methyl acrylate (MA), ethylenediamine (EDA), and 3-aminopropyltriethoxysilane (APTES) from Fluka were used without purification. Phosphorus acid was purchased from Aldrich and formaldehyde was obtained from Fluka. Toluene and methanol were distilled before use. Dicyandiamide as a catalyst for

the phosphonic acid and cellulose reaction was bought from Fluka. Dyed knitted industrial cotton fabric was obtained from textile dyeing factory.

## 2.2 Incorporation of amino groups onto 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 homogeneously dispersed by a magnetic stirrer for 30 minutes. Then 50 ml of methanol: water (4:1 or 2:1) was added to the mixture and stirred for 72 hours. After that, the modified silica particles were filtrated and extracted with toluene for 24 hours using soxhlet extractor to remove unreacted 3-aminopropyltriethoxysilane. The APTES treated silica was dried in an oven at 60<sup>0</sup>C for 24 hours and stored in autodehumidity desiccators

## 2.3 Grafting of hyperbranched polyamidoamine dendrimer from silica surface

The Michael addition was carried out as follows: a 1,000 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 hours. 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 hours. The solvent and unreacted EDA were removed by a rotary evaporator performing at the temperature no higher than 40<sup>0</sup>C. The propagation for second and third generations was carried out by repeating the two step reactions, Michael addition and amidation.

## 2.4 Phosphorylation of hyperbranched PAMAM grafted silica

Hyperbranched PAMAM grafted silica (0.2 mole) and crystalline phosphorous acid (0.4 mole) were dissolved in 200 ml of water and concentrated hydrochloric acid (0.6 mole). The mixture was heated to reflux in a three-necked flask fitted with thermometer, condenser and dropping funnel. In the course of ca 1 hour, 40% aqueous formaldehyde solution (0.8 mole) was added by drops, and the reaction was kept at the reflux temperature for an additional hour. The water was evaporated at low

temperature using a rotary evaporator. The concentrated solution was neutralized with concentrated ammonia solution. Finally, the concentrated solution was precipitated in methanol to get yellowish solid gel-like product.

### **2.5 Fixation of phosphorylated hyperbranched PAMAM grafted silica on cotton fabric**

Knitted Cotton fabrics were treated with a solution containing 30% w/w phosphorylated hyperbranched PAMAM grafted silica, 30% w/w urea and 20 g/l dicyandiamide as a catalyst. The application was performed using a pad mangle set a pressure nip at 80 percent wet pick up. The padded fabric was dried at 100°C for 5 min and cured at 170 °C for 3 min to allow the covalent reaction, leading to phosphonated cellulose produced. The treated fabric was washed-off to remove unfixed agents. Then thermal property of the treated fabric was analyzed using TGA analysis.

### **2.6 Determination of amino group content on hyperbranched 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 hours. Then, the mixture was filtrated and titrated with a standardized aqueous solution of sodium hydroxide using phenolphthalein as an indicator.

### **2.7 Determination of percent grafting**

The weight of PAMAM grafted onto the silica surface was determined by weight loss measurement. PAMAM grafted silica was burnt out at 800<sup>0</sup>C using TGA (Mettler Toledo STARe System DCS822e Module). The percentage of grafting was calculated from the difference between percentage of determined original weight of PAMAM grafted silica sample and the percent residual silica.

### **2.8 Characterizations**

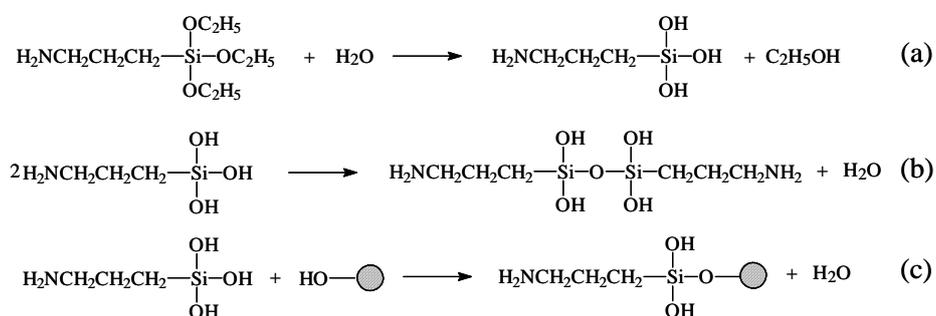
The morphology of hyperbranched PAMAM grafted silica was observed by scanning electron microscopy (JEOL JSM-5410LV) operated at 15 kv accelerating voltage. The particle size distribution was analyzed using laser light scattering (Mastersizer 2000). FTIR spectroscopy taken on KBr pellet samples was recorded on a Nicolet Impact 400D spectrophotometer. <sup>1</sup>H NMR spectra of the samples were recorded on Bruker DPX-300 spectrometer. TGA was performed using Mettler Toledo STARe System DCS822e Module.

### 3. Results and discussion

#### 3.1 Introduction of amino groups onto the silica surface

The treatment of silica with APTES resulted in silica particle containing amino groups on the surface which acted as the initiator sites for PAMAM grafting. The condensation reaction is base-catalyzed and APTES amine groups are self-catalyzed component. The mechanism involved the hydrolysis of APTES triethoxy groups by water, yielding silanol groups. Then condensation reaction between APTES silanol group and silica silanol group took place on silica surface as shown in Figure

1. The amount of water present in the system significantly influenced the hydrolysis reaction of triethoxy groups and the condensation reaction on silica surface [23].



**Figure 1.** Chemical equation of hydrolysis reaction from alkoxy silanes (a) and self condensation reaction (b) or (c) condensation reaction between APTES and silica.

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 2. 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. 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 three days.

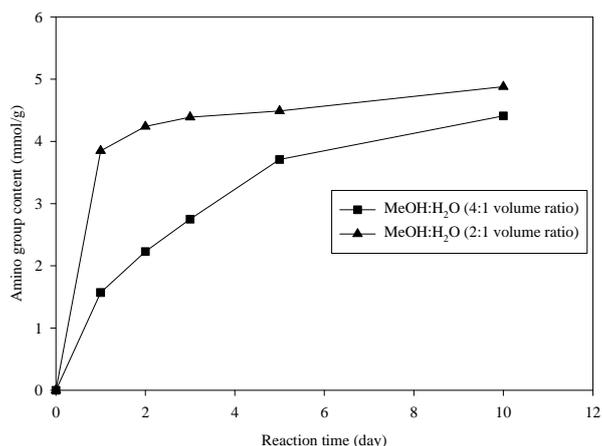


Figure 2 Amino group content measured on APTES treated silica versus reaction time

Figure 3 compares FTIR spectra between APTES grafted silica, virgin silica and APTES. Silica which is an inorganic substance in nature exhibits the strong absorption band of siloxane (Si-O-Si) bonding at  $\sim 1,200\text{ cm}^{-1}$  and the silanol OH band in the range of  $3,200\text{--}3,400\text{ cm}^{-1}$ . When considering the APTES silica, organo-functionalized silica, its spectrum exhibits new absorption frequencies at  $2932\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$ . These bands are associated to C-H stretching and primary amine ( $\text{-NH}_2$ ) stretching absorptions, respectively. Also, these bands are found corresponding with the absorption characteristics of APTES spectrum. These results indicate that APTES was incorporated into silica particles. The silica surface modification is further confirmed by change observed in spectrum pattern in the region of silanol OH band ( $3200\text{--}3400\text{ cm}^{-1}$ ) due to new inter-hydrogen bonding interaction among APTES silica particles.

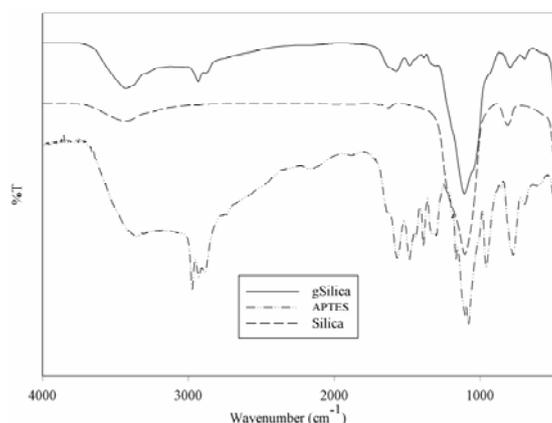


Figure 3 FTIR spectra of silica, APTES and APTES grafted silica

### 3.2 Grafting of hyperbranched PAMAM from silica surface

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 as in the synthesis of PAMAM dendrimers [24]. FTIR results are shown in Figure 4. 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  $1740\text{ cm}^{-1}$ . This peak completely disappears from the spectra of G1 and G2 as a result of the amidation reaction. In this step, the terminal amine group was produced, corresponding to the appearance of the strong absorption intensity of the N-H band in the region of  $3000 - 3350\text{ cm}^{-1}$ . Its absorption intensity significantly increases with an increase in PAMAM generation, reflecting that the terminal amine groups also significantly increases. Focused on G3.0 hyperbranched PAMAM grafted silica, the absorption peaks at  $1649\text{ cm}^{-1}$  and  $1568\text{ cm}^{-1}$  are characteristics of C=O stretching and N-H bending. The absorption peaks at  $3281\text{ cm}^{-1}$  and  $3086\text{ cm}^{-1}$  correspond to N-H antisymmetric stretching and N-H symmetric stretching of primary amine, respectively. In accordance, the C-H band at  $2900\text{ cm}^{-1}$  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.

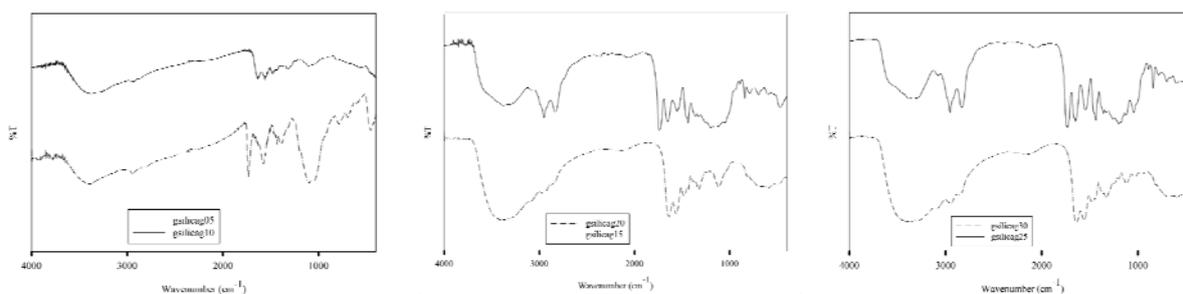


Figure 4 FTIR spectra of G0.5 – G3.0 hyperbranched PAMAM grafted silicas.

From the TGA analysis, percent graftings were calculated and their results are also given in Figure 5. The percent grafting increases when PAMAM generation grows as a result of PAMAM propagation from the silica surface amine groups. The amino group contents were expected to increase in a similar manner to percent grafting.

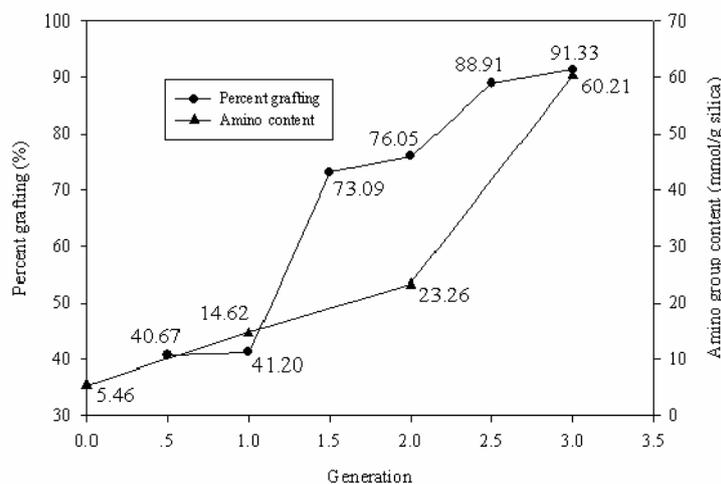


Figure 5 Percent grafting of PAMAM on silica surface and amino group content

### 3.3 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 6. As found in SEM, as-received fumed silica particles are tightly packed and adhered together in agglomerate form. After grafting, changes in particle distribution behavior as well as the agglomerate size were observed and the results are also shown in Figure 7. 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. Figure 7 shows the particle size distribution comparison between as-received fumed silica and hyperbranched PAMAM graft silica. As can be seen, the particle sizes before treatment are in an average size of ~100 microns and then after modification the particle sizes decrease to ~100 nanometers.

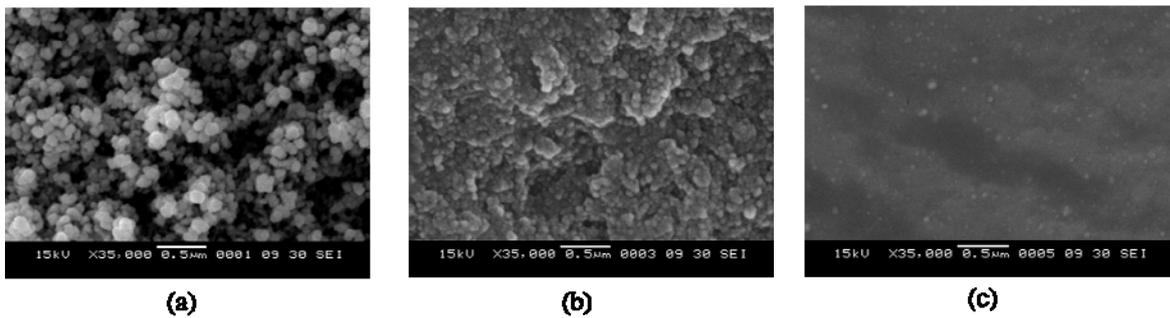
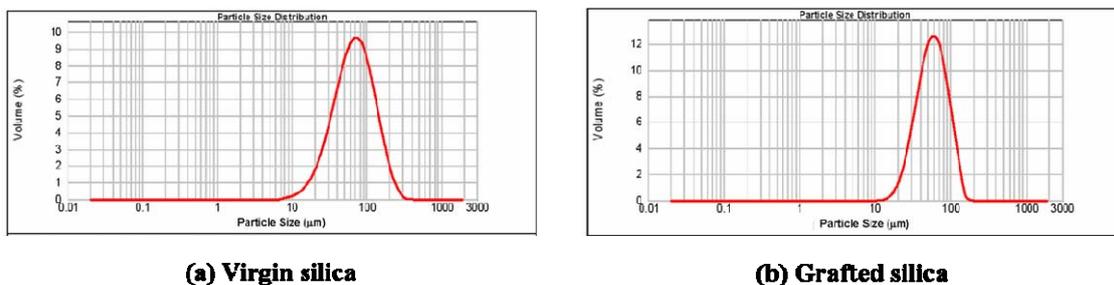


Figure 6 The SEM images of (a) silica, (b) G0.5 PAMAM grafted silica and (c) G1.0 PAMAM grafted silica.



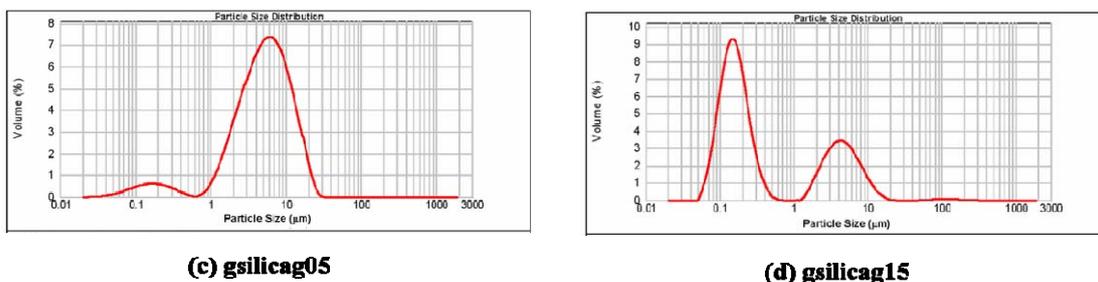


Figure 7 The particle size distribution of (a) virgin silica, (b) grafted silica, (c) G0.5 PAMAM grafted silica and (d) G1.5 PAMAM grafted silica.

### 3.4 Phosphorylation of hyperbranched PAMAM grafted silica

The reaction products were characterized using FTIR analysis and FTIR spectra are shown in Figure 8 (a). When considering the spectrum of the phosphonic acid functionalized silica, new peaks are observed, indicating change occurring in the structure of hyperbranched PAMAM grafted silica. The presence of phosphonic acid moiety is correspondent to the absorption bands at  $1182\text{ cm}^{-1}$ ,  $1078\text{ cm}^{-1}$ ,  $923\text{ cm}^{-1}$  which are the characteristic peaks of (P=O), (P-OH) and (P-O) groups, respectively[25 – 28]. A very broad band extending from  $3,600\text{ cm}^{-1}$  to as low as  $2,500\text{ cm}^{-1}$  is also observed, attributing to the absorption characteristic of the phosphonic acid hydroxyl group (OH). It is noticed that N-H stretching band at  $3500\text{ cm}^{-1}$  in hyperbranched PAMAM grafted silica markedly decreases, reflecting its consumption by Mannich reaction.  $^1\text{H}$  NMR analysis was also performed. In the  $^1\text{H}$  NMR spectrum of phosphonic acids functionalized PAMAM grafted silica in Figure 9 (b), signals indicate the presence of C(1)-H<sub>2</sub> and C(2)-H<sub>2</sub> groups and a methylene group adjacent to phosphorous nucleus are found at 3.6 and 3.7 ppm, respectively.

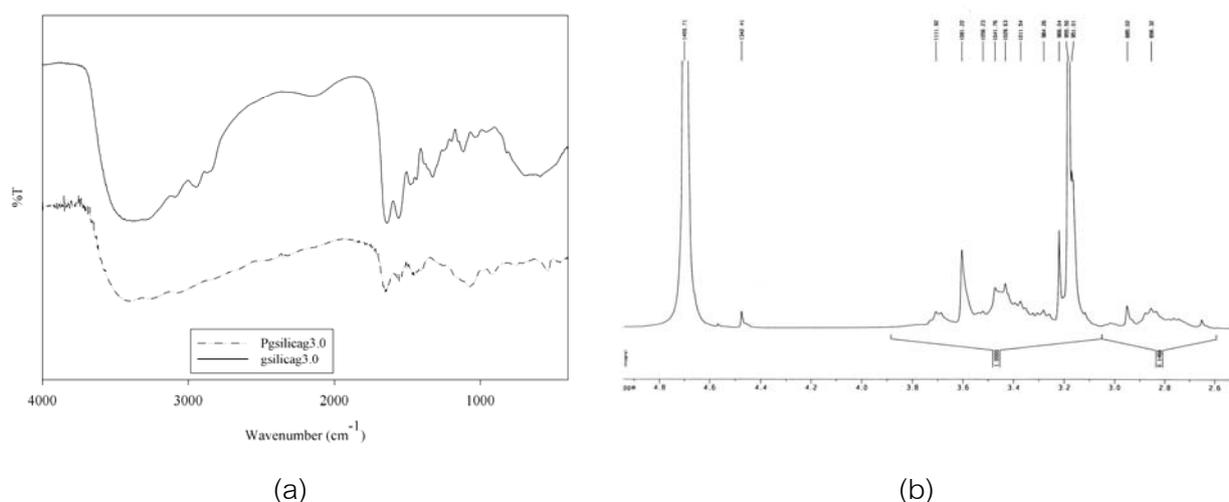


Figure 8 (a) FTIR spectra of hyperbranched PAMAM grafted silica (gsilica 3.0) and phosphorylated hyperbranched PAMAM grafted silica(Pgsilica 3.0), (b)  $^1\text{H}$  NMR spectrum of phosphorylated hyperbranched PAMAM grafted silica

### 3.5 Flame retardancy effect testing

Phosphorylated hyperbranched PAMAM grafted silica potentially offered powerful chelating action and flame retardancy properties. Treatment of cotton with phosphorylated hyperbranched PAMAM grafted silica was expected to render cotton fire resistant. The treated cotton fabric was subject to vertical burning test (Figure 9). Its burning behavior was compared with those of untreated cotton. As observed, the cotton fabric treated with phosphorylated hyperbranched PAMAM grafted silica exhibited fire retardancy property.

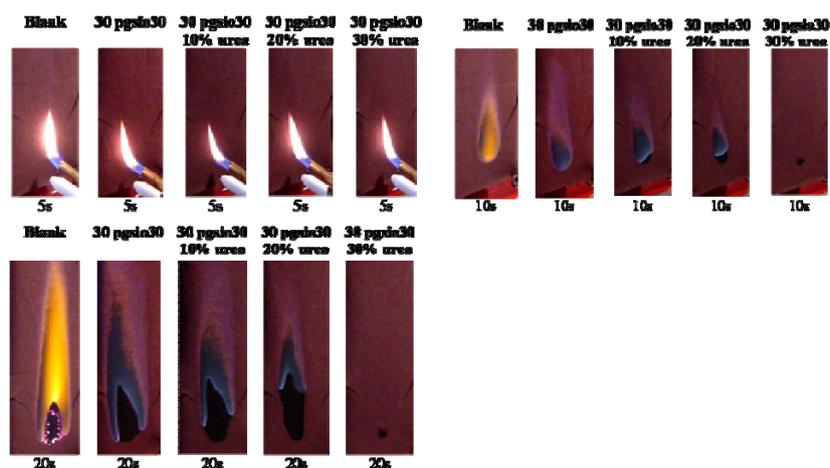


Figure 9 Vertical flammability test of 30 % phosphorylated hyperbranched PAMAM grafted silica treated cotton fabric at various concentrations of urea.

TGA thermograms shown in Figure 10 present the decomposition temperature of treated and untreated cotton fabrics. The untreated fabric starts to decompose at about 300<sup>o</sup>C, continues to reach the 100% weight loss at 350<sup>o</sup>C [29]. In case of treated fabric, the temperature of degradation begins at the relatively lower temperature of 290<sup>o</sup>C. The pyrolysis of flame retardant finished cotton fabric has lower decomposition temperature because of a catalytic dehydration of cellulose by the flame retardant, leading to char forming on fabric surface. The decline of degradation temperature is due to the fact that the phosphorous compounds react with C<sub>6</sub> hydroxyl of the cellulose anhydroglucose unit, blocking the formation of levoglucosan (source of fuel). Then, it will reduce the amount of fuel to the flame and promote char formation. Moreover, its structure contains nitrogen atoms which act synergistically with phosphorus [30]. It is known that nitrogen enhances the electrophilicity of phosphorous thereby making a stronger Lewis acid and also promoting the phosphorylation reaction with C(6) hydroxyl group of anhydroglucose unit.

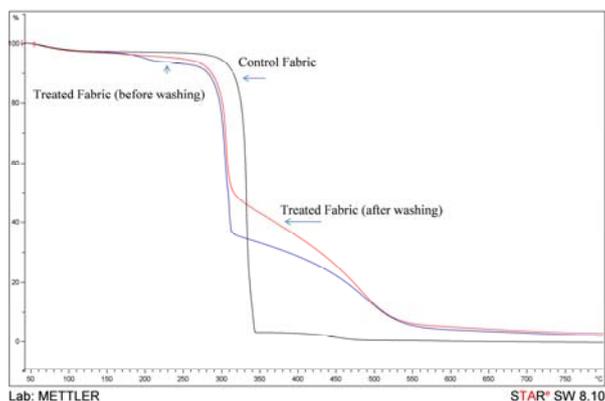


Figure 10. TGA thermograms of treated and untreated cotton fabrics.

#### 4. Conclusions

The grafting of hyperbranched PAMAM dendrimer onto amino groups functionalized silica was successfully achieved by repetitive reactions between Michael addition of silica amino group to methyl acrylate and amidation of the resulting terminal methyl ester group with ethylenediamine. A series of silicas grafted with hyperbranched PAMAM dendrimer up to generation 3 were produced. Percent grafting calculated from TGA results were 41.21, 76.05 and 91.33 for G1.0, G2.0, and G3.0, respectively. The amino group contents of G1.0, G2.0, and G3.0 were 14.62, 23.26, and 60.21 mmol/g silica, respectively, showing an increasing trend which is the same manner as the percent grafting. It was found that grafted hyperbranched PAMAM caused the steric role in dispersing particle agglomeration. The agglomerate size before grafting averaged ~100 microns and after grafting the particle size significantly decreased to a range of ~ 10 nanometer. The phosphorylation of the hyperbranched PAMAM dendrimer terminal amino groups was successfully achieved by Mannich type reaction. The phosphorylated products containing the phosphonic acids exhibited flame retardancy when applied onto flammable cotton fabric.

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#### References

- D.A.Tomalia. 2005 Prog. Polym. Sci. 30. 294-324.
- C.C. Lee, J.A. Mackay, J.M.J. Frechet, F.C. Szoka. 2005. Nat. Biotechnol. 23. 1517 – 1526.
- D.A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S Martin. 1985. Polym. J. (Tokyo) 17. 117-132.
- F. Aulenta, W. Hayes, S. Rannard. 2003. Eur. Polym. J. 39. 1741-1771.

- D.K. Smith, A.R. Hirst, C.S. Love, J.G. Hardy, S.V. Brignell, B.Q. Huang. 2005. *Prog. Polym. Sci.* 30. 220-293.
- B. Pan, F. Gao, L. Ao, H. Tian, R. He, D. Cui. 2005. *Colloid Surf. A.* 259. 89-94.
- A.J. Gong, Y.M. Chen, X. Zhang, H.W. Liu, C.F. Chen, F. Xi. 2000. *J. Appl. Polym. Sci.*, 78. 2186-2190.
- K.D. Demadis, E. Neofotiston. 2007. *Chem. Mater.* 19. 581-587.
- X. Shi, W. Lesniak, M.T. Islam, M.C. Muñiz, L.P. Balogh, J.R. Baker Jr. 2006. *Colloid Surf. A.* 272. 139-150.
- S.M. Ahmed, D.M. Budd, N.B. McKeown, K.P. Evans, G.L. Beaumont, C. Donaldson, C.M. Brennan. 2001. *Polymer.* 42. 889-896.
- I.J. Majoros, B. Keszler, S. Woehler, T. Bull, J.R. Baker Jr. 2003. *Macromolecules.* 36. 5526-5529.
- J.M. Heldt, N.F. Durand, M. Salmain, A. Vessiè, G. Jaouen. 2004. *J. Organomet. Chem.* 689. 4775-4782.
- T. Yoshimaru, S. Abe, K. Esumi. 2004. *Colloid Surf. A.* 251. 141-144.
- H.Y. Li, H.Z. Chen, W.J. Xu, F. Yuan, J.R. Wang, M. Wang. 2005. *Colloid Surf. A.* 254. 173-178.
- K. Bergemann, E. Fanghänel, B. Knackfuß, T. Lühge, G. Schukat. 2004. *Carbon.* 42. 2338-2340.
- S.J. Park, M.K. Seo, C. Nah. 2005. *J. Colloid. Interface Sci.* 291. 229-235.
- R. Qu, Y. Niu, C. Sun, C. Ji, C. Wang, G. Cheng. 2006. *Micro. Meso. Mat.* 97. 58-65.
- N. Tsubokawa, H. Ichioka, T. Satoh, S. Hayashi, K. Fujiki. 1998. *React. Funct. Polym.* 37. 75-82.
- X.Z. Wu, P. Liu, Q.S. Pu, Q.Y. Sun, Z.X. Su. 2004. *Talanta.* 62. 918-923.
- Y. Taniguchi, K. Shirai, H. Saitoh, T. Yamauchi, N. Tsubokawa. 2005. *Polymer* 46. 2541-2543.
- Y. Jiang, Q. Gao, H. Yu, Y. Chen, F. Deng. 2007. *Micro. Meso. Mat.* 103. 316-324.
- N. Perignon, J.D. Marty, A.F. Mingotaud, M. Dumont, I. Rico-Lattes, and C. Mingotaud. 2007. *Macromolecules* 40. 3034 – 3041.
- A. Simon, T. Cohen-Bouhacina, M.C. Porté, J.P. Aimé, C. Baquey. 2002. *J. Colloid. Interface Sci.* 251. 278-283.
- R. Esfand, D.A. Tomalia. 2001. Laboratory synthesis of poly(amidoamine) (PAMAM) dendrimers. In: J.M.J. Fréchet, D.A. Tomalia, editor. *Dendrimers and other dendritic polymers*. Chichester: Wiley, p587-604.
- K.D. Demadis, S.D. Katarachia. 2004. *Phosphorus, Sulfur Silicon Relat. Elem.* 179. 627-648.
- A. Heras, N.M. Rodriguez, V.M. Ramos, E. Agulló. 2001. *Carbohydr. Polym.* 44. 1-8.
- G. Chaplais, J.L. Bideau, D. Leclercq, A. Vioux. 2003. *Chem. Mater.* 15. 1950-1956.
- M.J. Danilich, D.J. Burton, R.E. Marchant. 1995. *Vib. Spectrosc.* 9. 229-234.
- P.Zhu, S. Sui, B. Wang, K. Sun, G. Sun. 2004. *J. Anal. Appl. Pyrolysis.* 71. 645-655.
- S. Gaan, G. Sun. 2007. *J. Anal. Appl. Pyrolysis* 78. 371-377.