

A Novel Method of Hyperbranched Poly(amide-ester) Modifying Nano-SiO₂ and Study of Mechanical Properties of PVC/Nano-SiO₂ Composites

Hui Zhao,^{1,2} Ruimin Sun,¹ Yunjun Luo,² Jie Li²

¹Research Center of Functional Materials, Kaifeng University, Kaifeng 475001, People's Republic of China

²School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, People's Republic of China

A new method of surface chemical modification of nano-SiO₂ was proposed in the paper. In the presence of catalyst, the active hydroxyl groups on the surface of nano-SiO₂ reacted with AB₂-type monomer (*N,N*-dihydroxyethyl-3-amino methyl propionate) by one-step polycondensation. And the product's Fourier transform infrared graphs and transmission electron microscopy (TEM) images proved that hyperbranched poly(amine-ester) (HPAE) was grafted from nano-SiO₂ surface successfully. Moreover, polyvinyl chloride (PVC)/modified nano-SiO₂ composites were made by melt-blending. The composites' structures and mechanical properties were characterized by TEM, scanning electron microscopy, and electronic universal testing machine. The results showed that nano-SiO₂ grafted by HPAE increased obviously in dispersion in PVC matrix, and mechanical properties of PVC were effectively improved. Additionally, it was found that mechanical properties of PVC/nano-SiO₂ composites reached the best when weight percent of nano-SiO₂ in PVC matrix was 1%. Compared with crude PVC, the tensile strength of HPAE grafted nano-SiO₂/PVC composite increased by 24.68% and its break elongation, flexural strength, and impact strength increased by 15.73, 4.07, and 184.84%, respectively. POLYM. COMPOS., 29:1014–1019, 2008. © 2008 Society of Plastics Engineers

INTRODUCTION

Nano-SiO₂ plays an important role in nature, science and technical applications due to its special physical and chemical properties [1–4]. However, nano-SiO₂ is easy to aggregate and difficult to disperse in solvent and polymer matrix because of its high specific surface area and sur-

face energy, it is necessary to modify its surface prior to use. The grafting of polymers onto nano-SiO₂ is one of the effective methods to improve the surface properties because the grafted polymer chains on the surface interfere with the aggregation of these particles and increase remarkably the affinity of the surface for solvent and polymer matrix [5–7]. And the surface modification of nano-SiO₂ by polymer grafting and application of the polymer-grafted nano-SiO₂ has become of major interest lately. Murota et al. reported that the radical, cationic, and anionic graft polymerization of various polymers onto ultrafine silica surface initiated by peroxyester [8] or azo [9], acylium perchlorate [10], and potassium carboxylate groups [11] introduced onto the surface, respectively. Mori et al. grafted hyperbranched (meth)acrylates grafted onto SiO₂ surface by one-step self-condensing atom transfer radical polymerization [12]. Chen and Armes functionalized ultrafine silica surface using a polyelectrolytic macroinitiator [13]. And Bagwe et al. studied surface modification of silica nanoparticles to reduce aggregation and nonspecific binding [14].

In this paper, hyperbranched poly(amine-ester) was grafted from nano-SiO₂ surface by one-step polycondensation, which can be regarded as a novel and convenient method towards the preparation of smart interfaces. And the product's Fourier transform infrared (FTIR) graphs proved that hyperbranched poly(amine-ester) (HPAE) was grafted on nano-SiO₂ surface successfully. And then, the resulting modified nano-SiO₂ was blended with polyvinyl chloride (PVC) to improve its properties and processing. It was found that HPAE grafted nano-SiO₂ (HPAE-*g*-SiO₂) increased obviously in dispersion in PVC matrix by transmission electron microscopy (TEM) pictures, showing it has good compatibility with PVC matrix. And, mechanical properties studies showed that tensile strength, break elongation, bending modulus, and bending strength of PVC were effectively improved after HPAE-*g*-SiO₂ was added.

Correspondence to: Hui Zhao; e-mail: kfsrm@yahoo.com.cn

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EXPERIMENTAL SECTION

Materials

Nano-SiO₂ with 25 ± 5 nm particle size and 160 m²/g specific surface area was purchased from Zhoushan Mingri nano-material Co., Zhejiang Province of China, and dried in vacuum oven at 110°C prior to use; Methyl acrylate was available from Beijing Chemical Factory, and distilled under reduced pressure to remove the inhibitors before use; diethanolamine was purchased from Beijing Chemical Factory, and has been vacuum dried for 6 h under the temperature of 30°C. *N,N*-Dihydroxyethyl-3-amino methyl propionate was synthesized according to the procedure in [15]. PVC was purchased from Shandong petrochemical Co., and used without further purification; other chemical agents were all available from Beijing Chemical Factory and were used without further purification.

Characterization and Instrumentation

FTIR spectra were measured on a Nicolet 8700 spectrometer using KBr disks. TEMs were conducted on a Hitachi H-700 electron microscope at 100 kV, and the samples of grafted and ungrafted nano-SiO₂ for TEM measurements were sonicated in ethanol for 30 min, respectively, and then one drop of each sample was placed on copper grids coated with carbon; Ultrathin sections (about 80 nm) were cut from the samples of the composites' standard bar specimens by an ultramicrotome (RMC MT-X, RMC Instruments Corp., USA), and then the degree of dispersion for nano-SiO₂ in PVC was directly observed using the TEM. The morphologies of the materials' tensile and impact fracture surfaces were observed by Japan JEOL JSM-35C scanning electronic microscopy (SEM). WD-4005 Electronic universal testing machine was used to test materials' tensile and bending properties according to international standard GB/T1040-92. XJJ-50 Impact testing machine was used to test notch impact properties of the materials.

Synthesis

1 g nano-SiO₂ (there are about 0.0234 mol hydroxyl group on its surface), 0.0702 g *N,N*-dihydroxyethyl-3-amino methyl propionate, and 0.07 g paratoluenesulfonic acid (catalyst) were mixed in four-neck flask. The system was stirred vigorously for 10 h under the protection of nitrogen at 120°C. And then, the products were diluted with methanol and centrifugated to remove unreacted monomer and ungrafted HPAAE. The solid was dispersed in methanol and centrifugated again, and then 200 mL of methanol was washed the deposition several times, the dispersion, centrifugating, and washing steps were repeated until unreacted monomer and ungrafted HPAAE in filtering

solution could not be tested by TCL. Finally, the grafted nano-SiO₂ products were dried under vacuum for 6 h at 30°C.

Preparation of Standard Bar Specimens for Testing Mechanical Properties

Unmodified nano-SiO₂ and nano-SiO₂ modified with KH550 synthesized according to reference [16] and grafted with HPAAE were respectively premixed with PVC according to weight percent of 0.5, 1, 2, 3% of nano-SiO₂. The mixture were then dried in air blowing dryer for 6 h at 30°C. The final materials were then extruded using Germany Brabender double-screw extruder ($L/D = 30$), and temperatures of each heating region: 1st region was 145°C; 2nd region was 155°C; 3rd region was 155°C; 4th region was 150°C; and 5th region was 150°C respectively and the screw rotational speed was 80 r/min. And then, in order to prepare standard shape samples for testing tensile strength, break elongation, flexural strength, impact strength, the materials were injected into HU-90 automatic plastic injection machine (made by Dalian Huada mechanical Co.), and The temperatures of each heating region: 1st region was 150°C; 2nd region was 155°C; 3rd region was 160°C; 4th region was 155°C respectively. Injection pressure preparing standard bar specimens for testing tensile strength and break elongation was 50 MP and kept for 15 s at room temperature; Injection pressure preparing standard bar specimens for testing flexural strength and impact strength was 60 MP and kept for 30 s at room temperature.

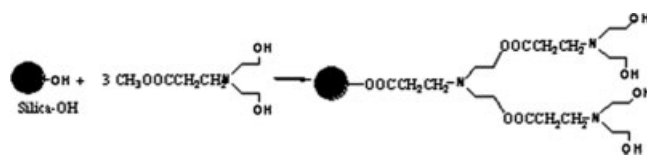
RESULTS AND DISCUSSION

Hyperbranched Poly(amine-ester) Grafting From Nano-SiO₂

The schematic representation of hyperbranched poly(amine-ester) grafting from nano-SiO₂ is shown in Scheme 1.

In the reaction system, in the presence of the catalyst of paratoluenesulfonic acid, silica-OH as the core initiated *N,N*-dihydroxyethyl-3-amino methyl propionate to polymerize. Thus, hyper-branched poly(amine-ester) was grafted from nano-SiO₂ surface by one-step polycondensation. And the FTIR spectra of the samples (grafted and ungrafted nano-SiO₂) are shown in Fig. 1.

From the FTIR spectra in Fig. 1, compared with the curve of ungrafted nano-SiO₂, in the curve of grafted



SCHEME 1. Schematic representation of hyperbranched poly(amine ester) grafting from nano-SiO₂.

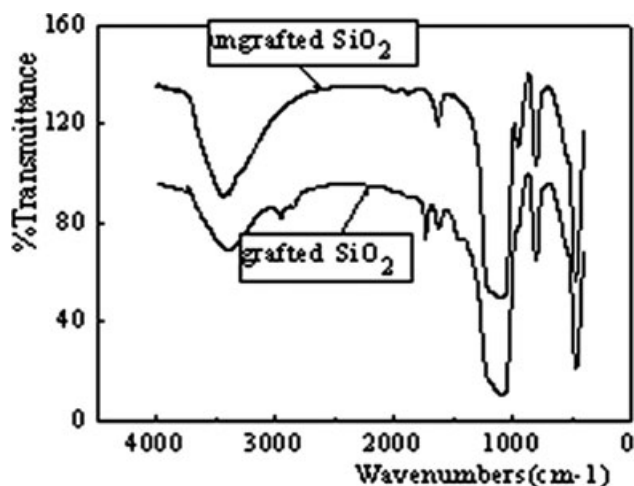


FIG. 1. FTIR spectra of grafted and ungrafted nano-SiO₂.

nano-SiO₂, new peaks appeared at 1720 cm⁻¹ ascribing to C=O of —COO— and 2920 cm⁻¹ and 2850 cm⁻¹ ascribing to C—H stretch mode, which are the evidences of successful grafting HPAAE from nano-SiO₂ by one-step polycondensation.

Effect of Reaction Temperature and Time on Conversion Rate and Grafting Rate

The percentage of conversion rate and grafting rate were defined as the following equations [17]: conversion rate(%) = $\frac{g+u}{m} \times 100\%$; grafting rate(%) = $\frac{h-n}{n} \times 100\%$; where *g* (g) was the weight of grafted polymer; *u* (g) the weight of ungrafted polymer; *m* (g) the weight of the monomer; *h* (g) the weight of the product of HPAAE grafted nano-SiO₂; *n* (g) the weight of nano-SiO₂; And the effects of reaction temperature and time on grafting rate and conversion rate are shown in Tables 1 and 2, respectively.

From Table 1, it can be seen that, both grafted rate and conversion rate are very low when the temperature is below 100°C, and with temperature increasing, both values reach the maximum at 120°C, and then, both of them begin to decrease. The reasons may be that excessively high temperature can cause the decomposition of

TABLE 1. Effect of reaction temperature on grafting polymerization.

Reaction temperature (°C)	Grafted composition (g)	Conversion rate (%)	Grafting rate (%)
80	0.0231	33.79	2.31
100	0.0863	36.56	8.63
120	0.1610	67.25	16.10
130	0.1204	42.88	12.04
140	0.1020	37.49	10.20

1 g of nano-SiO₂, 0.0734 mol of monomer, and 0.07 g catalyst were mixed and reacted for 10 h in all experiments in this table.

TABLE 2. Effect of reaction time on grafting polymerization.

Reaction time (h)	Grafted composition (g)	Conversion rate (%)	Grafted rate (%)
4	0.0035	38.14	0.35
6	0.0481	49.04	4.81
8	0.1302	64.17	13.02
10	0.1610	67.25	16.10
12	0.1616	71.56	16.16

1 g of nano-SiO₂, 0.0734 mol of monomer, and 0.07 g catalyst were mixed and reacted at 120°C in all experiments in this table.

monomer (monomer decomposes at 140–150°C) and accelerate self-polycondensation of monomer. Therefore, the best reaction temperature is 120°C.

From Table 2, it can be suggested that both grafted rate and conversion rate increase with reaction time increasing. However, increase extent is not obvious after reaction for 10 h. Therefore, it is the best appropriate and economical to react for 10 h.

TEM Analysis

TEM pictures of nano-SiO₂ in ethanol are shown in Fig. 2. 2-1 picture that is a TEM image of ungrafted nano-SiO₂ suggested that ungrafted nano-SiO₂ tended to agglomerate and it was difficult to disperse in the solvent; 2-2 picture that is a TEM image of HPAAE grafted nano-SiO₂ suggested that HPAAE grafted nano-SiO₂ dispersed evenly and its particle diameter is nanometer grade, indicating HPAAE grafted nano-SiO₂ tends to disperse in solution more easily and can exist stably.

2-3, 2-4, and 2-5 TEM pictures are that of the composites PVC/SiO₂, PVC/KH-550-SiO₂, and PVC/HPAAE-g-SiO₂, in which weight percent of nano-SiO₂ in PVC matrix is 1%. From the TEM pictures, it can be seen that there are many agglomeration in the PVC/SiO₂ and PVC/KH-550-SiO₂ composites; and there are a little less agglomeration in the PVC/KH-550-SiO₂ composites than that in the PVC/SiO₂ composites. However, in the PVC/HPAAE-g-SiO₂ composites, nano-SiO₂ particles appear excellent dispersion, showing there is good compatibility between HPAAE-g-SiO₂ and PVC matrix.

SEM Analysis

SEM pictures of impact fracture surface and tensile fracture surface of the samples were taken, and are shown in Figs. 3 and 4, respectively.

In Fig. 3, the pictures from 3-1 to 3-4 are SEM pictures of impact fracture surface of the composites PVC, PVC/SiO₂, PVC/KH-550-SiO₂, and PVC/HPAAE-SiO₂ respectively, and in the composite, weight percent of SiO₂ in PVC matrix is 1%. From the pictures, it can be seen that, compared with the other composites, pure PVC has a smooth impact fracture surface and some fine cracks,

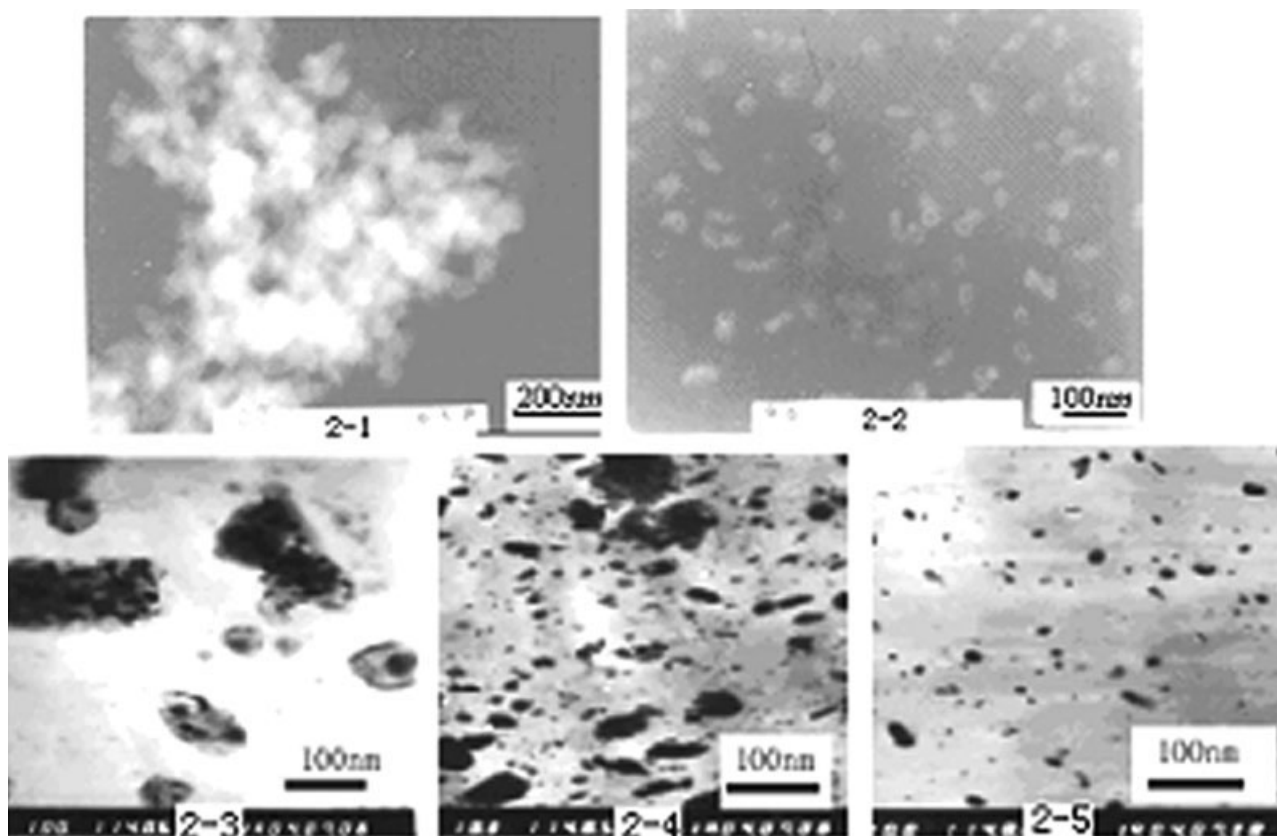


FIG. 2. 2-1 and 2-2 are TEM pictures of grafted and ungrafted nano-SiO₂ in ethanol; 2-3, 2-4, and 2-5 are TEM pictures of the composites PVC/nano-SiO₂, PVC/KH-550-SiO₂, and PVC/HPAE-g-SiO₂, respectively.

which is classic brittle fracture. However, after added nano-SiO₂, the impact fracture surfaces become rougher. Especially, after HPAE-g-SiO₂ added in the PVC matrix, there appears multiple crazing on the fracture surface of the composites, which is classic ductile fracture.

In Fig. 4, the pictures from 3-1 to 3-4 are SEM pictures of tensile fracture surface of the composites PVC, PVC/SiO₂, PVC/KH-550-SiO₂, and PVC/HPAE-SiO₂ respectively, and in the composites, weight percent of SiO₂ in PVC matrix is 1%. From the SEM pictures, it can be seen that tensile fracture surface of pure PVC has no conglutination and has obvious cracks, which suggested that the material had bad mechanical properties. However, there exists conglutination in the tensile fracture surface of the samples added SiO₂, which indicates that there are intramolecular forces between nano-SiO₂ and PVC matrix and

can form physical entanglement. Thus, it is favorable to transfer tensile stress and improve the matrix to produce yielding and plastic deformation. These suggested that the composites with this kind interface structure might have good mechanical properties. Moreover, the PVC/HPAE-g-SiO₂ composites have the most conglutination than the other samples. There has excellent interface structure between HPAE and PVC matrix, so the mechanical properties of the composites should increase greatly.

Mechanical Properties of PVC/Nano-SiO₂ Composites

Tensile Strength, Break Elongation, and Bending Modulus of PVC/SiO₂ Composites. Mechanical properties for PVC/SiO₂ composites as a function of nano-SiO₂ weight percent in PVC matrix were shown in Fig. 5.

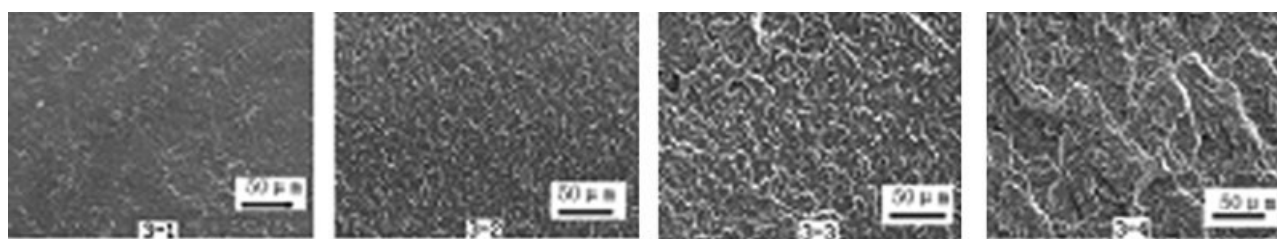


FIG. 3. SEM pictures of the impact fracture surface of the samples.

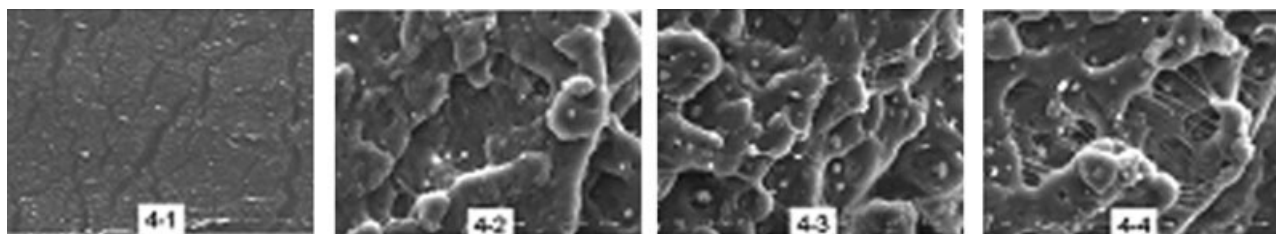


FIG. 4. SEM pictures of the tensile fractures surface of the samples.

As is shown in Fig. 5, it can be seen that mechanical properties of the three kinds of composites varied similarly with weight percent of nano-SiO₂ increasing and all reached maximum values at about 1 wt% of nano-SiO₂ in PVC matrix, and mechanical properties of PVC composites were obviously enhanced after modified nano-SiO₂ was added. Compared with crude PVC, (PVC/HPAE-*g*-SiO₂) composites' maximum tensile strength, break elongation, and impact strength increased by 24.68, 15.73, and 184.84% respectively.

It may be considered that nano-SiO₂ particles acted as physical crosslink points in PVC matrix, and the PVC molecules were linked together through "point" and "point" by a certain pattern. Nano-SiO₂ particles could play a role of scattering multidirectional load when the pull was given to the sample bar, and could prevent molecule chains slipping. Thus, PVC mechanical properties were improved. However, when amount of nano-SiO₂ added was too more (more than ~1%), there were too much crosslink points in PVC matrix, and mobile molecular units decreased and the movement of molecule chains were blocked badly, leading to tensile strength decrease. Additionally, if weight percent of nano-SiO₂ added was much more, stress effect was found, resulting in larger fine cracks occurring and then the material's toughness decreasing.

From Fig. 5, it was also seen that mechanical properties of PVC/HPAE-*g*-SiO₂ composites were better than that of the other two PVC composites. There may be two reasons as follows. Firstly, after nano-SiO₂ was grafted

by hyperbranched poly(amine-ester), its surface energy decreased. As a result, HPAE-*g*-SiO₂ could disperse well in PVC matrix; secondly, solubility parameters of PVC and HPAE are $\delta_{\text{PVC}} = 19.5$ and $\delta_{\text{HPAE}} = 20.0$; therefore, the compatibility between HPAE modified nano-SiO₂ and PVC matrix increases, and there are many physical entanglements (including hydrogen-bonding) between the two. These above make the interaction of HPAE-*g*-SiO₂ and PVC matrix increase, resulting that the stress can be transferred to nano-SiO₂ [18] and mechanical properties of the composites increase efficiently. However, in the case of silane coupling agent KH-550, after alkoxy groups at the end of KH-550 molecule chain hydrolyze, the polar functional groups can only produce weak force with surface active groups of SiO₂, which, although, can improve nano-SiO₂ surface activity, increase its dispersion, and advance the composite's mechanical properties, the increase extent in mechanical properties is not higher than that of PVC/HPAE-*g*-SiO₂. As for PVC/nano-SiO₂ composites, its increase extent in mechanical properties is the lowest due to the bad dispersion of SiO₂ (seen 2-3 picture in Fig. 2).

Bending Strength and Bending Modulus of PVC/SiO₂ Composites. Bending strength and modulus of the composites (1 wt% of SiO₂ in PVC matrix) are shown in Table 3.

As is shown in Table 1, all the composites added SiO₂ have higher bending strength and bending modulus values than the pure PVC sample. Additionally, the values of the

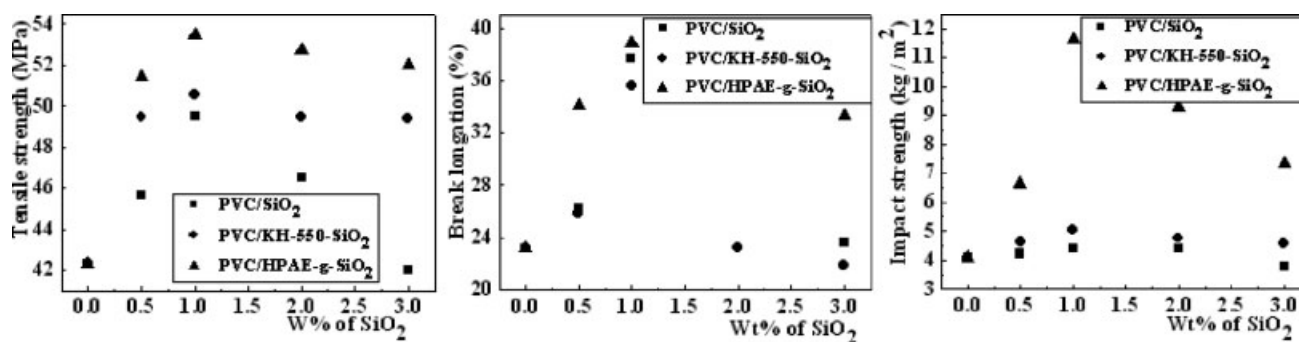


FIG. 5. Mechanical properties for PVC/SiO₂ composites as a function of nano-SiO₂ weight percent in PVC matrix.

TABLE 3. Bending strength and bending modulus of PVC/nano-SiO₂ composites.

Sample	Flexural strength (MPa)	Flexural modulus
PVC	65.30	2354.26
PVC/SiO ₂	65.65	2396.11
PVC/KH-550-SiO ₂	67.70	2516.42
PVC/HPAE-g-SiO ₂	67.93	2569.83

PVC/HPAE-g-SiO₂ composite are the highest, showing that the compatibility between HPAA and PVC is the best, which can make the two produce many physical entanglements that can form network structure, and the stress can be transferred quickly through chain segments, so its bending strength and bending modulus increase greatly. However, the values of the PVC/KH-550-SiO₂ composite are a little lower than that of the PVC/HPAE-g-SiO₂ composite, the reasons of which are that, chain segments of KH-550 are short, interfacial force of KH-550 and PVC is very weak and is easy to yield when external force is given to the composites, so its bending strength and bending modulus increase less.

Processing of the Composites

When PVC/SiO₂ and PVC/KH-550-SiO₂ composites were extruded using a double-screw extruder, it could be found that the viscosity increased and extrusion time prolonged obviously compared with pure PVC. And the more nano-SiO₂ was added, the more the viscosity increased, and the more extrusion time took, the less smooth the surface of the extruded product had. On the contrary, during PVC/HPAE-g-SiO₂ processing, the viscosity decreased and extrusion time became little, and the surface of the extruded product was the smoother. The reasons may be that hyperbranched poly(amine-ester) has three-dimensional structure, which can penetrate into the chains of linear polymer and weaken the entanglement of PVC chain segments, sequentially, the viscosity of the composites decreases, namely, hyperbranched poly(amine-ester) could act as a lubricant during processing of the composites [19]. The experimental results indicate that some HPAA-g-SiO₂ are added the PVC matrix, the composites' processing can improve to a certain extent.

CONCLUSIONS

1. Hyperbranched poly(amine-ester) was successfully grafted from nano-SiO₂ surface using A₂B monomer *N,N*-dihydroxyethyl-3-amino methyl propionate by one-step polycondensation. And grafted rate reached the highest when

reaction carried out for 10 h at 120°C, TEM pictures showed that hyperbranched poly(amine-ester) grafted nano-SiO₂ had excellent dispersion stability in ethanol.

2. The dispersibility of nano-SiO₂ increased greatly in PVC matrix after hyperbranched poly(amine-ester) was grafted from nano-SiO₂.
3. The composites' mechanical properties were improved after nano-SiO₂ was added into PVC matrix, and PVC/HPAA-g-SiO₂ composites' mechanical properties increased greater than that of PVC/KH-550-SiO₂ and PVC/SiO₂ composites though that of the three kinds of composites all reached maximum values at about 1 wt% of nano-SiO₂ in PVC matrix.
4. Compared with pure PVC, PVC/HPAA-g-SiO₂ composites' processing improved to a certain extent.

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