Synthesis of Tercopolymer BA–MMA–VTES and Surface Modification of Nano-Size Si$_3$N$_4$ with this Macromolecular Coupling Agent

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ABSTRACT: A new macromolecular coupling agent butyl acrylate (BA)-methyl methacrylate (MMA)-vinyl triethoxy silane (VTES) tercopolymer was synthesized using solution polymerization initiated by free radical initiator benzoyl peroxide (BPO) and dicumyl peroxide (DCP). Dodecylthiol is choosed as the chain transfer to control the molecule weight of this tercopolymer. The terpolymer's molecular structure was confirmed by FTIR and NMR, and its average molecular weight was determined by GPC. In this work, the tercopolymer BA–MMA–VTES is used for surface modification of silicon nitride (Si$_3$N$_4$) nanopowder. The structure surface properties and thermal stability of modified nano-Si$_3$N$_4$ were systematically investigated by FTIR, TGA, TEM, and size distribution analyzer. The results show that the macromolecular coupling agent bonds covalently on the surface of nano-sized Si$_3$N$_4$ particles and an organic coating layer is formed. The optimum loading of this macromolecular coupling agent BA–MMA–VTES tercopolymer is 5% (wt %) of nano-sized Si$_3$N$_4$. TEM also reveals that modified nano-Si$_3$N$_4$ possesses good dispersibility. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1100–1107, 2008

Key words: macromolecular coupling agent; nano-size silicon nitride (Si$_3$N$_4$); surface modification

INTRODUCTION

Silicon nitride (Si$_3$N$_4$) is an important ceramic material used for various applications because of its high strength, high fracture toughness, high thermal-shock resistance, low coefficient of thermal expansion, and good wear resistance.[1–5] It has been proved to be an effective filler for the improvement of mechanical properties, and in particular the wear resistance, of polymeric materials, such as PTFE, PEEK, epoxy, bismaleimide composites,[6–9] and so on.

It has a strong tendency of nanoparticles to agglomerate because of its high surface energy. So a homogeneous dispersion of nanoparticles in a polymer matrix especially in rubber matrix is a very difficult task. The so-called nanoparticles filled polymers sometimes contain a number of loosened clusters of particles and exhibit properties even worse than conventional particle/polymer systems. To break down the nanoparticles agglomerates and improving the dispersivity of nanosized particles in polymer matrix, the technology of surface-modification is used for producing nanostructural composites.

There are several methods to modify the surface of silicon nitride in literatures. Coating with alumina on the nano-Si$_3$N$_4$ will improve the interface combination strength.[10] Kramer[11] also modified the surface of silicon nitride with alcohol (octanol, dodecyl alcohol, octodecyl alcohol) the new group come into being on the surface of silicon nitride particle because of alkylation reaction. Wang Jun[12] studied a surface modification process of silicon nitride with γ-glycidochloropropyl methyl trimethoxy silane (KH-560). When the nano-Si$_3$N$_4$ powder was modified with KH-560, the coupling agent will bond on the surface of nano-Si$_3$N$_4$. This modification method can be applied in preparing nano-Si$_3$N$_4$/polymer composite.

In our previous work, a tercopolymer butyl acrylate (BA)-α-methacrylic acid (MAA)-acrylonitrile (AN) was synthesized to modify the surface of silicon nitride nanopowder which was applied to prepare nano-Si$_3$N$_4$/NBR composites. Because of the strong interface action, this nanocomposite we prepared exhibit unique hybrid properties including good heat-resistance, good wear-resistance, and good dynamic mechanical properties.[13,14]

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Vinyl triethoxy silane(VTES), as a silane coupling agent, is often used to modify the fillers such as Mg(OH)$_2$,[15] Al(OH)$_3$,[16] attapulgite,[17] glass beads,[18] and so on. When the modified fillers were filled into a certain polymer matrix, the interface adhesion between inorganic fillers and polymer matrix can be enhanced obviously. It was reported by Zhou Xiaodong[19] that two block copolymers polystyrene(PP)-polybutadiene(PB)-polyvinyltriethoxysilane(PVTES) and polystyrene (PP)-polyisoprene(PIP)-polyvinyltriethoxysilane (PVTES) were synthesized as a macromolecular coupling agent.

In this study, a novel macromolecular coupling agent tercopolymer BA–MMA–VTES is designed for ceramic nanopowder/weak polarity rubber composite. The side group —Si(OC$_2$H$_5$)$_3$ on this tercopolymer's main chain may react with —OH, >NH—, and —NH$_2$ which are on the surface of the nitride ceramic nanopowder containing active hydrogen (such as nano-Si$_3$N$_4$ and nano-AlN). When several groups on each BA–MMA–VTES macromolecular chain are chemical bonded with the surface of nano-Si$_3$N$_4$ particle, an arch like chain structure will form on the surface, as shown in Figure 1(a). Covered with this arch
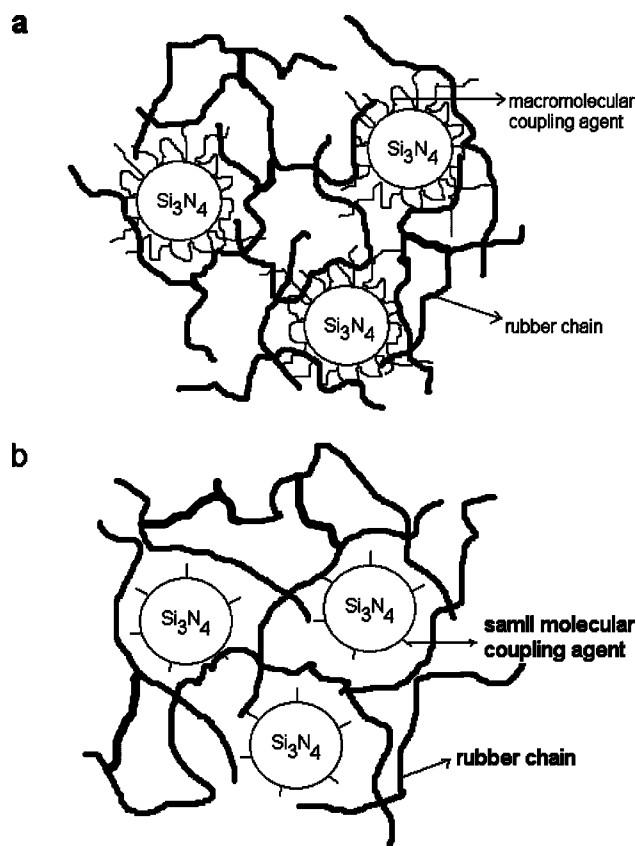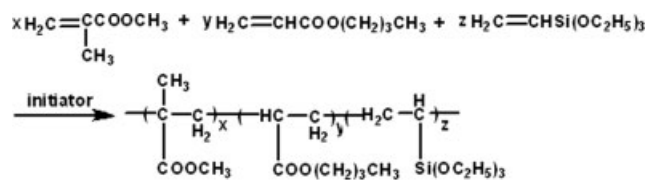

Figure 2 The polymerization course of tercopolymer BA–MMA–VTES.

like chain structure, the nanoparticles' coating area is much larger compared with that modified with small molecular coupling agent [shown in Fig. 1(b)].

On the other hand, the quite similar structure or polarity between alkyl group on the ester side group and natural rubber, styrene–butadiene rubber and ethylene–propylene rubber, etc. provide them with good compatibility. Also, when the macromolecular coupling agent bridged nanopowder with rubber matrix, the entanglements between the long chains of tercopolymer and the main rubber matrix will substantially enhance the interactions between nitride ceramic nanoparticles and rubber matrix which we mentioned earlier and improve the compatibility between them (as shown in Fig. 1). As a result, the rubber nanocomposite will achieve some good properties that nitride ceramic nanopowders possess. The previous experiments revealed that nano-Si$_3$N$_4$ which was treated with tercopolymer BA–MMA–VTES can improve the heat-resistance, wear-resistance, and dynamic mechanical properties of rubber nanocomposites.

The macromolecular coupling agent tercopolymer BA–MMA–VTES is synthesized by solution copolymerization. The polymerization course is shown in Figure 2. This article will attempt to characterize the structure of BA–MMA–VTES and the interaction between macromolecular coupling agent (BA–MMA–VTES tercopolymer) and surface of nano-Si$_3$N$_4$ particles.

Figure 1 Schematic drawing of the possible structure of modified nano-Si$_3$N$_4$ dispersed in rubber matrix (a. nano-Si$_3$N$_4$ modified with BA–MMA–VTES tercopolymer/rubber matrix nanocomposites. b. Nano-Si$_3$N$_4$ modified with small molecular coupling agent/rubber matrix nanocomposites).

EXPERIMENTAL

Materials

Silicon nitride used for this study is a commercial ultrafine amorphous powder (Hefei Kiln Nanometer Technology, Heifei, China,) with the following characteristics: average particle diameter <20 nm, specific surface area 115 m^2/g.

Commercial monomers: butyl acrylate (Tianjin Bodi Chemicals Co., Tianjing, China); α-methyl methacrylate (China National Pharmaceutical Group Shanghai Chemical Reagent Co., Shanghai, China) Vacuum distillation; vinyl triethoxy silane (Shandong Qufu Wanda Chemicals Co., Shandong, China), Vacuum dehydration; benzoyl peroxide (Beijing Beijiao Fine Chemical Factory, Beijing, China); dicumyl per-

oxide (Sinopec Shanghai GaoQiao petrochemical Corporation, Shanghai, China); Dodecyl mercaptan and acetone were obtained from Shanghai Zhenxing Chemicals Co., Shanghai, China.

Synthesis of BA–MMA–VTES tercopolymer

In a four-mouth flask holding a nitrogen inlet, mechanical stirrer, reflux-condenser, constant-pressure funnel, and thermometer, optimum toluene is added. Then butyl acrylate (BA), methyl methacrylate (MMA), vinyl triethoxy silane (VTES), benzoyl peroxide (BPO), dodecylthiol, and excess toluene are slowly dropped into the flask in a definite proportion through the constant-pressure funnel. The reaction kettle is heated in oil bath keeping temperature at 80°C for 2 h. After that, another initiator Dicumyl peroxide (DCP) is added into the reaction kettle after dropping about 2/3 mixture (monomers, initiator, and chain transfer) and the resulting mixture was heated to 115°C at which the reaction continues for 2 h to yield a viscous tercopolymer solution. The solid content of the tercopolymer solution is about 30% by mass fraction and the monomer conversion is 93%.

Surface modification of nano-size Si_3N_4

The native nano-Si_3N_4 powders were dispersed in acetone(in N_2 atmosphere), and a certain amount of macromolecular coupling agent (tercopolymer BA–MMA–VTES) was added into the flask, mixing round with high speed at 60°C for 3 h, and then vacuum drying for 10 h.

Characterization of tercopolymer and nanoparticles

The structure of tercopolymer BA–MMA–VTES was characterized by FTIR (Neuxs-830, Nicolet, USA) and ^{1}HNMR (Bruke CAV400, Switzerland). The molecular weight and distribution of tercopolymer was determined using a gel permeation chromatograph (GPC-244 WATERS, USA). Monomer conversion is determined by gravimetric method.

Nano-Si_3N_4 and modified nano-Si_3N_4 were investigated by FTIR (Neuxs-830; Nicolet, USA), TEM (JEM-100SX; TEOL, Japan), TGA (Pyris-1; PE, USA) and Size Distributions Analyzer (3000HS, Malvern, England).

RESULTS AND DISCUSSION

Characterization of nano-Si_3N_4 and macromolecular coupling agent by FTIR

The tercopolymer BA–MMA–VTES was applied for modification of nano-Si_3N_4 as a macromolecular coupling agent. Fourier transform infrared spectroscope (FTIR) was utilized to characterize the tercopolymer (BA–MMA–VTES) and the changes in the nano-Si_3N_4 surfaces, as shown in Figure 3.
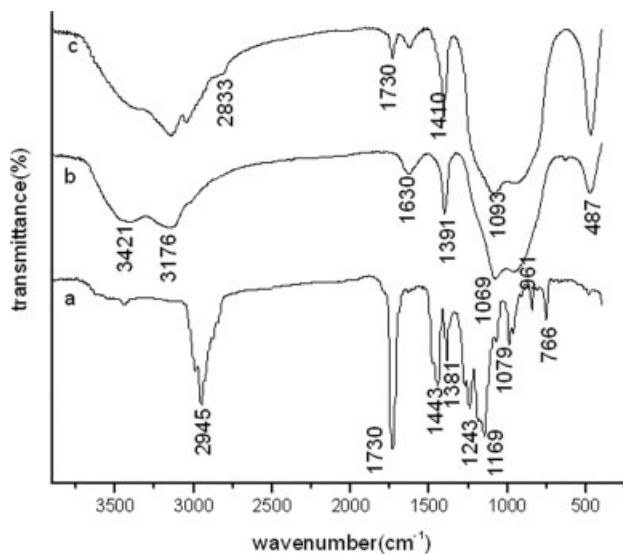
Figure 3 IR spectra of (a) BA–MMA–VTES, (b) native nano-Si_3N_4, and (c) modified nano-Si_3N_4.

It can be seen from Figure 3(a) that the peak at 1730 cm^{-1} is related to C=O stretching vibration mode, and the peak at 2945 cm^{-1} is related to —CH_2, —CH_3 asymmetric stretching mode. The band appears at 1079 cm^{-1} corresponds to the stretching mode of —Si—O—C—. These peaks are the characteristic peaks of tercopolymer (BA–MMA–VTES) synthesized.

The surface modified nano-Si_3N_4 was analyzed by FTIR after being washed with acetone in Soxhlet extractor for 72 h. Figure 3(c) shows the spectrum of nano-Si_3N_4 modified with the tercopolymer BA–MMA–VTES.

Silicon nitride is strongly reactive when exposed to air. So the surface region of commercial Si_3N_4 powder has a significant amount of Si_2—NH, Si—NH_2, and Si—OH groups.[1] In Figure 3(b), νOH[20] + νNH combination band can be seen at 3421 and 3176 cm^{-1}. The detection of absorption at 1069 cm^{-1} as well as of a broad and weak band at 487 cm^{-1} in our sample, is probably indicative of the presence of SiO_2.[21] The band at 1630 cm^{-1} is assigned to the N—H shear vibration, 961 cm^{-1} is assigned to the backbone vibrations of Si—N—Si and 1391 cm^{-1} is attributed to the bending mode of hydroxyl groups.[22]

For the modified nano-Si_3N_4, in Figure 3(c), the peak at 1730 cm^{-1} is related to C=O stretching vibration mode, and the peak at 2833 cm^{-1} is related to —CH_2, —CH_3 asymmetric stretching mode. The band appears at 1093 cm^{-1} is corresponded to the stretching mode of —Si—O—Si—. These peaks are the characteristic peak of tercopolymer (BA–MMA–VTES). This proved that the macromolecular coupling agent tightly absorbed at the surface of nano-Si_3N_4 by chemisorption and it is still exist in the modified
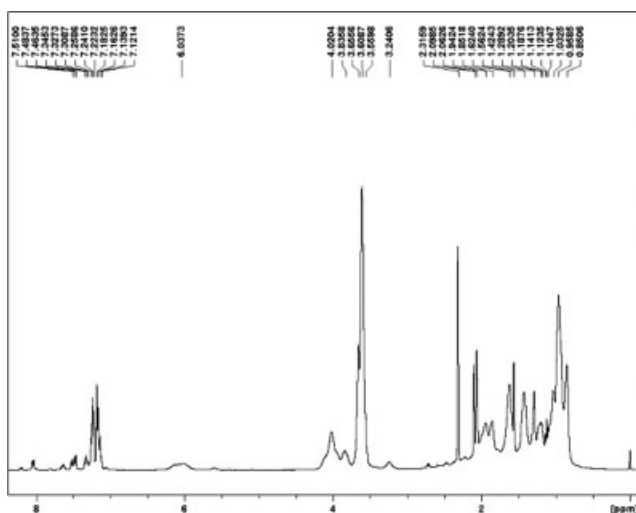
Figure 4 ^{1}HNMR spectrum of BA–MMA–VTES.

powders even after being extracted by Soxhlets extractor among acetone. What's more, the Si—O—Si absorption bands are observed at 1100–1050 cm^{-1}, these are overlapped by the Si—O and Si—N absorption (800–1100 cm^{-1}) and thus could not be confirmed by the Si—N and Si—O absorption area, but it can be found that the peak of surface modified silicon nitride nanopowder at 900–1100 cm^{-1} is broader and stronger than that of the native nano-Si$_3$N$_4$ powder. This indicates that the surface group of nano-Si$_3$N$_4$ has changed from Si—OH to Si—O—Si. From these, we can suggest that macromolecular coupling agent is bonded on the surface of nano-sized Si$_3$N$_4$ particles and an organic coating layer is formed.

^{1}HNMR analysis

^{1}HNMR spectra of the tercopolymer BA–MMA–VTES (as shown in Fig. 4) was obtained on an AVANCE 400 nuclear magnetic resonance spectrometer, using TMS as internal reference and deuterated acetone (CD$_3$COCD$_3$) as solvent. ^{1}H band for Si—O—CH$_2$— is 3.84 ppm and ^{1}H band for —CH$_3$ in —Si—O—CH$_2$CH$_3$ is 1.10–1.14 ppm, which indicates the existence of VTES structural unit in the tercopolymer product. The methylene protons which is in the main chain resonate at 1.62 ppm, the methyl protons which is in side group —COOCH$_2$CH$_2$CH$_2$CH$_3$ resonate at 1.42 ppm and —CH$_3$ side group which is in MMA structural unit absorb in the chemical shift range from 0.85 to 0.96. ^{1}H band for CH$_3$—O— is 3.56–3.66 ppm. δ = 4.02 is assigned to ^{1}H band for —CHCO— which is in BA structural unit. The ^{1}HNMR results further demonstrate that the synthesized product is tercopolymer BA–MMA–VTES, which is consistent with the FTIR results.

Molecular weight and distribution BA–MMA–VTES tercopolymer

The molecular weight of BA–MMA–VTES tercopolymer could be controlled by the loading of initiators (BPO, DCP) and chain transfer agent (dodecylthiol). As a macromolecular coupling agent, number-averaged molecular weight of this tercopolymer is controlled at the range of 3000–10,000 to modify the ceramic nanopowders. The molecular weight of BA–MMA–VTES tercopolymer has been analyzed through THF-eluted gel permeation chromatography (GPC). Data and chromatogram of synthesized tercopolymer obtained are shown in Figure 5. Weight-averaged molecular weight is 30,900; number-averaged molecular weight is 9400 and polydispersity is 3.29. This indicates that the tercopolymer BA–MMA–VTES synthesized can be used to modify the ceramic nanopowders.

Analysis of nanoparticles' size and distribution

The nano-Si$_3$N$_4$ suspension in acetone was prepared through ultrasonic dispersion[23] for 30 min using ultrasonic cleaner SB5200 (Shanghai Branson Ultrasonics Co., Shanghai, China). On the basis of dynamic light scattering (DLS) principle, the number average diameter and size distribution of nano-Si$_3$N$_4$ suspension was analyzed using size distributions analyzer (3000HS, Malvern, England) (as shown in Fig. 6 and Table I).

According to the result, the native nano-Si$_3$N$_4$ particles were dispersed poorly in acetone and the serious agglomerations were formed because of the existence of Si—OH group on the surface of the native nano-Si$_3$N$_4$ powders. Its average diameter is about 350–2600 nm. Compared with the native powders, the nano-Si$_3$N$_4$ modified with BA–MMA–VTES tercopolymer showed good dispersibility in acetone,
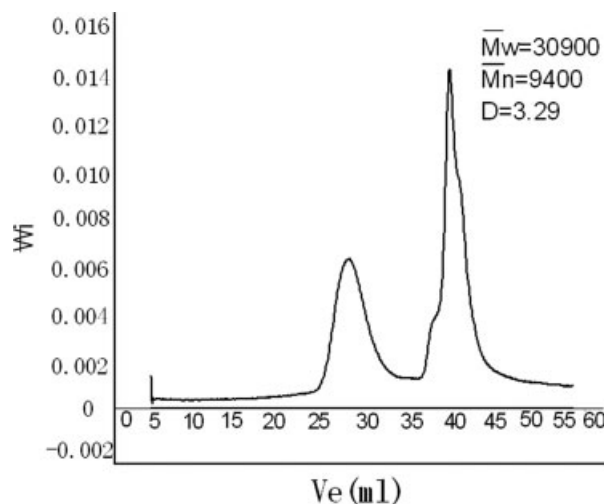

Figure 5 Molecular weight and distribution of BA–MMA–VTES tercopolymer.
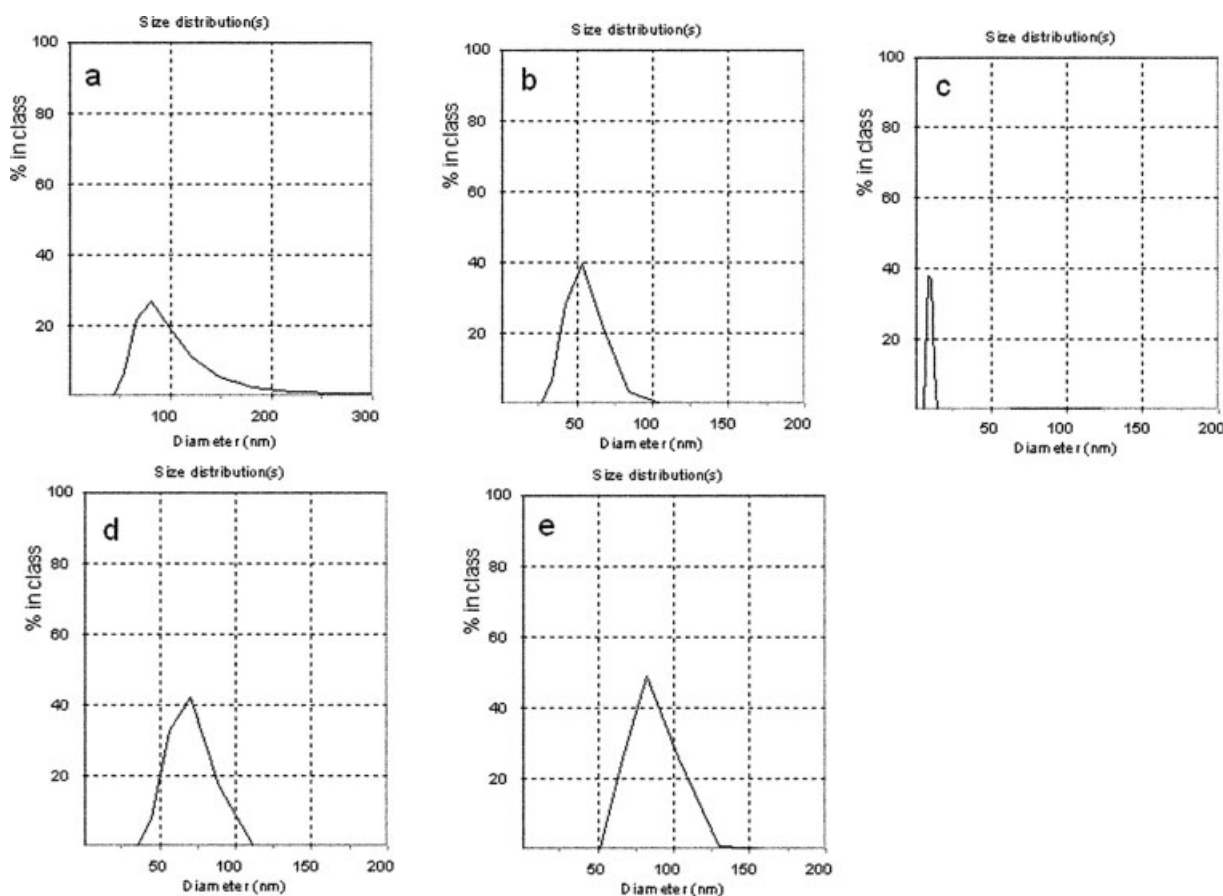
Figure 6 Size distribution of nano-Si_3N_4 modified with different percentage macromolecular coupling agent (a) 0%, (b) 3%, (c) 5%, (d) 7%, (e) 10%.

especially the sample which modified with 5 wt % tercopolymer [as shown in Fig. 6(c)]. It was suggested that the dispersing effect of nano-Si_3N_4 in acetone can be improved after being modified with macromolecular coupling agent. Because of the new chemical bond's forming between macromolecular coupling agent and nanoparticles, the interactions among nanoparticles were broken down and the agglomeration was controlled effectively. With the increasing loading of the macromolecular coupling agent, the average diameter of nano-Si_3N_4 decreased gradually, but after the loading of macromolecular coupling agent exceed 7 wt %, the average diameter increased again. This may because when the loading of BA–MMA–VTES tercopolymer is insufficiency, the uncoated nano-Si_3N_4 will be likely to agglomerate together. While if the loading is superabundance corresponding to the mass of nano-Si_3N_4, the average diameter of modified nano-Si_3N_4 maybe increased again because of the thickening of the macromolecular coupling agent coating layer and the entanglement between long and flexible chain of macromolecular coupling agent.

Thermal mechanical properties

Thermal stability of nano-Si_3N_4, modified nano-Si_3N_4, and tercopolymer BA–MMA–VTES were measured by dynamic thermogravimetric analysis (TGA). Figure 7 is TG and DTG curve of nano-Si_3N_4, modified nano-Si_3N_4, and tercopolymer BA–MMA–VTES (the heating rate was monitored at 20°C/min, and the flow rate of N_2 of 30 mL/min).

The TGA thermogram of BA–MMA–VTES tercopolymer in nitrogen is shown in Figure 7(1). The BA–MMA–VTES tercopolymer showed a slight weight loss before 280°C for its low molecular weight. A much greater weight loss (75.6 wt %) occurs at the temperature range 280–500°C.

TABLE I
Average Diameter and Size Distribution of Nano-Si_3N_4 (By Number)

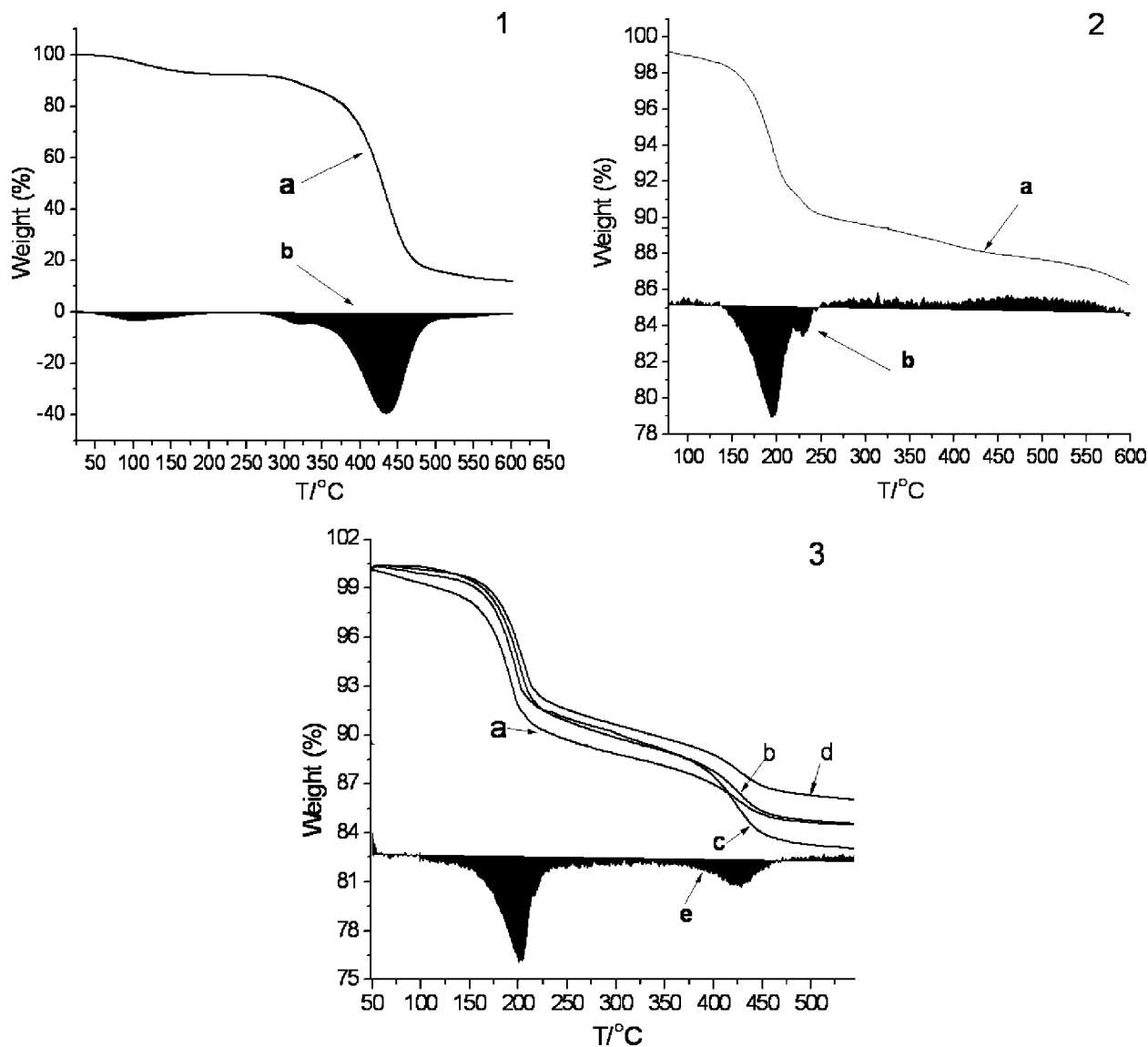| Coupling agent(%)	0%	3%	5%	7%	10%
Average diameter (nm)	105.8	52.9	11	64.5	84.0
Width	56.2	29.8	4.1	35.7	39.3

Figure 7 1. Native nano-Si₃N₄ (a. TGA curve of native nano-Si₃N₄, b. DTG of native nano-Si₃N₄). 2. BA–MMA–VTES ter-copolymer (a. TGA curve of BA–MMA–VTES b. DTG of BA–MMA–VTES). 3. Modified nano-Si₃N₄ (a. 3%, b. 5%, c. 7%, d. 10%, e. DTG of modified nano-Si₃N₄ of 5% coated).

As shown in the Figure 7(2), the thermal decomposition of native nano-Si₃N₄ begins at about 60°C and the continuous mass loss can be seen from 60°C to 500°C. This is likely because of a series of chemical reactions happening on the surface of nano-Si₃N₄ between surface groups or some physical and chemical adsorption substances, then the desorption of H₂O, NH₃, etc. from the surface of nano-Si₃N₄ with increasing temperature results in the continuous mass loss.[24] As presented in its DTG curve, native nano-Si₃N₄'s mass loss is 8.5% with a high decomposition rate in 125–250°C stage while in 250–500°C stage the mass loss is only 2.5% with a low decomposition rate.

The surface modified nano-Si₃N₄ sample was analyzed after being washed with acetone in Soxhlet extractor for 72 h. The thermal degradation curves of nano-Si₃N₄ modified with different percentage BA–MMA–VTES tercopolymer are shown in Figure 7(3).

TABLE II
TGA Data of BA–MMA–VTES and Nano-Si₃N₄

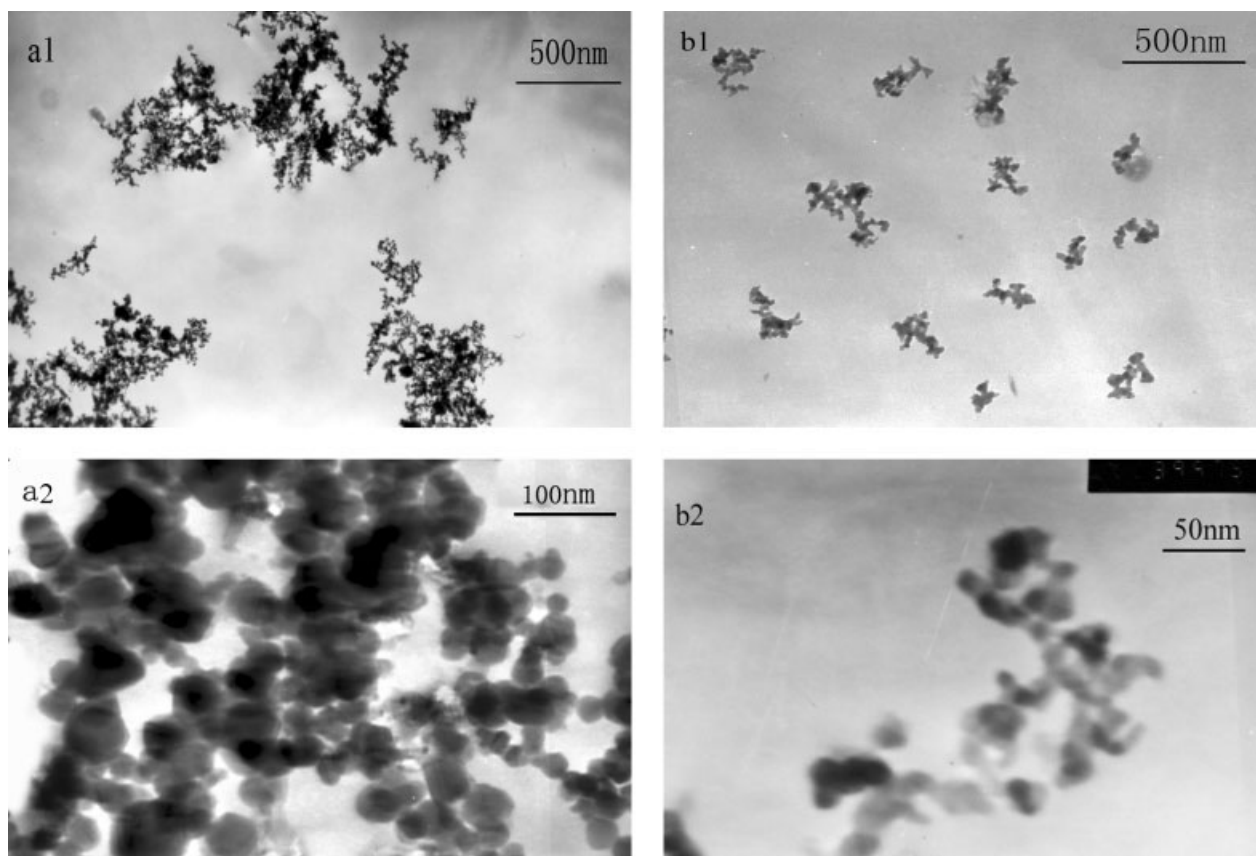| Sample	Char yield (%)			
	50°C	125°C	325°C	500°C
BA–MMA–VTES	99.7	91.7 (280°C)	88.3	16.1
Native nano-Si₃N₄	99.5	98.7	89.5	87.7
Modified nano-Si₃N₄				
3% tercopolymer	100.1	100	88.5	84.6
5% tercopolymer	100.1	98.9	89.4	84.8
7% tercopolymer	100.1	100	89.6	83.2
10% tercopolymer	100.3	99.6	90.2	86.3

Figure 8 TEM micrographs of (a) nano-Si$_3$N$_4$, (b) modified nano-Si$_3$N$_4$, showing different morphologies.

We can find that all curves are similar with Figure 7(2) before 325°C, which is assigned to the loss of nano-Si$_3$N$_4$. According to Figure 7(1), the weight loss from 325°C to 500°C is attribute to the degradation of BA–MMA–VTES tercopolymer. The thermal stability of modified nano-Si$_3$N$_4$ is enhanced with the increase of macromolecular coupling agent's loading, as shown in Table II. In contrast with sample b(nano-Si$_3$N$_4$ modified with 5% BA–MMA–VTES), sample d(nano-Si$_3$N$_4$ modified with 10% BA–MMA–VTES) show less weight loss (3.92%) from 325°C to 500°C than that of sample b(4.65%). This indicates that the excess tercopolymer in the sample which could not bond on the surface of nano-Si$_3$N$_4$ had been extracted by Soxhlet extractor.

TEM morphology of nano-Si$_3$N$_4$

Figure 8 displays the TEM photographs of native nano-Si$_3$N$_4$ and modified nano-Si$_3$N$_4$ suspensions in alcohol which were prepared with ultrasonic vibrating method. To represent detailed morphological information of the specimens, different magnifications were utilized for various samples. The obvious agglomeration can be seen in the photograph of native nano-Si$_3$N$_4$ [Fig. 8(a)] and the homogeneous dispersion can be seen in the photograph of modi-

fied nano-Si$_3$N$_4$ [Fig. 8(b)]. In the TEM photographs of Figure 8(b2), the tercopolymer layers are clearly shown as the gray area, it coated on the surface of nano-Si$_3$N$_4$ particles and reduced the agglomerations. This suggests that physical bonding or chemical bonding have been modified successfully by BA–MMA–VTES tercopolymer. The molecular chains of macromolecular coupling agent which connect with the surface of nano-Si$_3$N$_4$ particles brought mutual exclusion and steric hindrance effect, thus the surface free energy reduced correspondingly and the agglomeration was controlled.

CONCLUSIONS

A novel macromolecular coupling agent BA–MMA–VTES tercopolymer was synthesized and it can be used to modify the nano-Si$_3$N$_4$ powder which is applied to prepare the nano-Si$_3$N$_4$/rubber composite. The results show that the optimum mass fraction of macromolecular coupling agent coated on the surface of nano-sized Si$_3$N$_4$ is 5%. Some organic coating layer formed on the surface of nano-Si$_3$N$_4$ powder, and chemical bond combination happens between BA–MMA–VTES tercopolymer and nano-Si$_3$N$_4$ powder surface at modified nano-Si$_3$N$_4$ possesses good dispersibility by modification.

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