

Surface Modification of Nano-Sized Silicon Nitride with BA-MAA-AN Tercopolymer

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Received 9 November 2006; accepted 27 February 2007

DOI 10.1002/app.26563

Published online 24 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this work, a macromolecular coupling agent (BA-MAA-AN tercopolymer) was used for surface modification of native nano-sized silicon nitride (Si_3N_4) powder. This modification strategy was designed for preparing nano- Si_3N_4 /NBR composites. The structure and surface properties of modified nano- Si_3N_4 were systematically investigated by FTIR, XPS, TGA, TEM, Size Distributions Analyzer, and Contact Angle Measurement. It was found that, the optimum loading of BA-MAA-AN tercopolymer coated on the surface of nano-sized Si_3N_4 is 10% of nano- Si_3N_4 . According to the spectra of FTIR, XPS and TGA, it can be inferred that this macromolecular coupling agent covalently bonds on the surface of nano-sized Si_3N_4 particles

and an organic coating layer is formed. The contact angle experiments show that the hydrophobic property of nano-sized Si_3N_4 modified with macromolecular coupling agent is improved obviously. TEM reveals that modified nano- Si_3N_4 possesses good dispersibility and the average diameter in NBR is less than 100 nm. It has also been found that the oil resistance of NBR based nanocomposites is improved greatly due to the modified nano- Si_3N_4 . © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 562–570, 2008

Key words: macromolecular coupling agent; nano-sized silicon nitride (Si_3N_4); surface modified; nanocomposite; oil resistance

INTRODUCTION

Silicon nitride (Si_3N_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. Chen⁶ chose β - Si_3N_4 as inorganic filler [treated with γ -(methacryl)oxylpropyl-trimethoxysilane KH-570] to prepare Si_3N_4 /polyol acrylate composite material. This material could effectively used in oral clinical which owns high compression strength, Brinell hardness, and low coefficient of thermal expansion. Zhang⁷ reported the good friction and wear properties of silicon nitride/PTFE (polytetrafluoroethylene) composite. Si_3N_4 can increase the friction coefficient of PTFE while reduce the wear of PTFE effectively. In addition, the friction and wear properties of Si_3N_4 /PEEK, Si_3N_4 /epoxy, Si_3N_4 /bis-

maleimide composites^{8–11} were investigated. Our research group has prepared nano- Si_3N_4 /NBR composites that exhibit unique hybrid properties including good heat-resistance, good wear-resistance, and good dynamic mechanical properties.¹²

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 nanoparticle agglomerates and for 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. Some metal oxides such as MgO, Al_2O_3 , Y_2O_3 , and Re_2O_3 have been used as sintering additives to obtain a high-density Si_3N_4 .^{13,14} The liquid formed via the chemical reactions between these additives and the initial powder could enhance the diffusivity of the atoms during sintering. Coating with alumina on the nano- Si_3N_4 will improve the interface combination strength.¹⁵ Kramer¹⁶ also modified the surface of silicon nitride with alcohol (octanol, dodecyl alcohol, octadecyl alcohol), the new group comes into being on the surface of silicon

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Contract grant sponsor: Chinese Ministry of Science and Technology; contract grant number: 2005BA316C.

Contract grant sponsor: The Key Laboratory of Environment-Friendly Polymer Materials of Anhui Province.

Journal of Applied Polymer Science, Vol. 107, 562–570 (2008)

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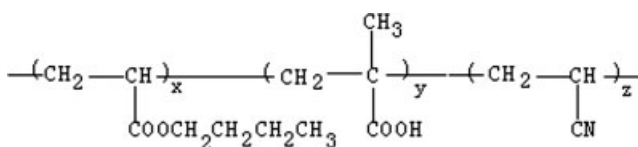


Figure 1 Chemical structure of BA-MAA-AN tercopolymer.

nitride particle due to alkylation reaction. Wang¹⁷ studied a surface modification process of silicon nitride with γ -glycidochloropropyl methyl trimethoxy silane (KH-560). When the nano- Si_3N_4 powder was modified with KH-560, the coupling agent will bond on the surface of nano- Si_3N_4 . This modification method can be applied in preparing nano- Si_3N_4 /polymer composite.

In this study, a novel surface modification strategy with macromolecular coupling agent for Si_3N_4 was developed so that the modified nano- Si_3N_4 can be added to the NBR matrix for improving their compatibility and nanoparticles' dispersibility. A tercopolymer butyl acrylate (BA)- α -methacrylic acid (MAA)-acrylonitrile (AN) was designed and synthesized to modify the surface of silicon nitride nanopowder. Figure 1 shows the chemical structure of BA-MAA-AN. On the one hand, carboxyl groups in the tercopolymer can react with amidocyanogen group and hydroxy group that are on the surface of the nano- Si_3N_4 . When several groups on each BA-MAA-AN macromolecular chain are chemical bonded with the surface of nano- Si_3N_4 particle, an arch like chain structure will form on the surface, as shown in Figure 2. Covered with this arch like chain structure, the nanoparticles' coating area is much larger when compared with that modified with small molecular coupling agent. On the other hand, a strong interaction will come into being between $-\text{CN}$ group of tercopolymer and $-\text{CN}$ group of NBR, at the same time the entanglements between the long chains of tercopolymer and the main rubber matrix will substantially enhance the interactions between nano- Si_3N_4 particles and NBR matrix and improve the compatibility between them. This article will attempt to characterize the interaction between macromolecular modifier (BA-MAA-AN tercopolymer) and surface of nano- Si_3N_4 particles and determine its effect on the interparticle potential. The modification effect on nano- Si_3N_4 particles' dispersion and the nano- Si_3N_4 /NBR composite's oil resistance are also investigated.

EXPERIMENTAL

Materials

Silicon nitride used for this study was a commercial ultrafine amorphous powder (Hefei Kaier Nanometer

Technology and Development Co., Hefei, China) with the following characteristics: average particle diameter 15 nm, specific surface area $115 \text{ m}^2/\text{g}$. Butadiene-acrylonitrile rubber (NBR-26) was supplied by Japan Synthetic Rubber Co., Ltd., Tokyo, Japan.

Commercial monomers: butyl acrylate (Tianjin Bodi Chemicals Co., Tianjing, China); α -methacrylic acid (Shanghai Wulian Chemicals Co., Shanghai, China), purified by vacuum distillation; acrylonitrile (China National Pharmaceutical Group Shanghai Chemical Reagent Co., Shanghai, China), distilled under normal pressure.

Dodecyl mercaptan and acetone were obtained from Shanghai Zhenxing Chemicals Co.; 2,2-azobisisobutyronitrile (AIBN) was purchased from Shanghai No.4 Reagent and H. V. Chemical Co., Shanghai, China.

Synthesis of BA-MAA-AN tercopolymer

In a 4-mouth flask holding a nitrogen inlet, mechanical stirrer, reflux-condenser, constant-pressure funnel, and thermometer, optimum acetone is added. At 50°C , butyl acrylate (BA), α -methacrylic acid (MAA), acrylonitrile (AN), 2,2-azobisisobutyronitrile (AIBN), dodecyl mercaptan, and acetone are slowly added into the flask in a definite proportion through the constant-pressure funnel. The reaction mass is heated to 75°C at which the reaction continues for 2 h to yield a viscous tercopolymer solution. The residual monomers are removed from the product by the method of vacuum drying. The solid content of the tercopolymer solution is about 32.02% by mass fraction and the monomer conversion is 96.07%.

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 (5–20% of total mass) the macromolecular coupling agent (tercopolymer BA-MAA-AN) was added into the

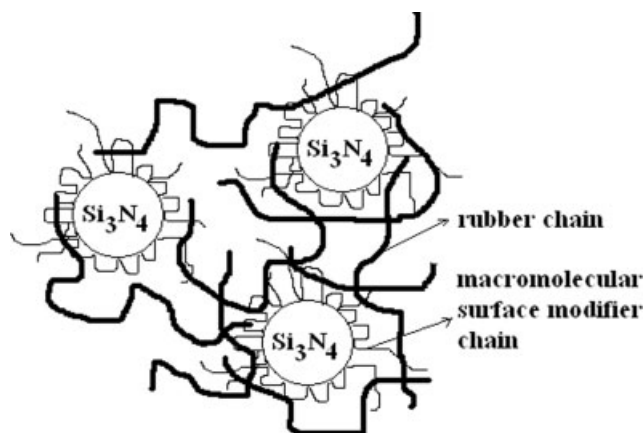


Figure 2 Schematic drawing of the possible structure of modified nano- Si_3N_4 dispersed in NBR matrix.

flask, mixing round with high speed at 45°C for 2.5 h, then vacuum drying for 10 h.

Preparation of nano-Si₃N₄/NBR composite

The nanocomposites in our experiments contain 100 phr NBR-26, 80 phr high wearable carbon black, 5.0 phr zinc oxide, 1.0 phr octadecanoic acid, 0.5 phr sulfur, 1.0 phr nano-size Si₃N₄, 2.0 phr antioxidant, and 1.8 phr accelerant.

Nano-Si₃N₄/NBR composites were masticated in an internal mixer (K1 MK4, Francis Shaw Co., Ltd., Manchester, England) and were cured at 175°C for optimum cure time (*t*₉₀).

Characterization of tercopolymer, nanoparticles, and nanocomposites

The structure of tercopolymer was characterized by FTIR (Neuxs-830, Nicolet, USA). The molecular weight of tercopolymer was determined using a gel permeation chromatograph (GPC-244 WATERS, USA). And the element analysis was carried out by using Elementar Vario EL III (Elementar, Germany).

Native nano-Si₃N₄ and modified nano-Si₃N₄ were investigated by FTIR (Neuxs-830, Nicolet); TGA (Pyris-1, PerkinElmer Corp., USA); TEM (JEM-100SX, TEOL, Japan); XPS (ESCALAB-MK-II, VG Scientific, England. X-ray source: MgK_α); and Size Distributions Analyzer (3000HS', Malvern, England).

The morphology of nano-Si₃N₄/NBR composites were investigated by H-800-1 transmission electron microscope (Hitachi Co., Japan) at 120 KV with ultra-thin cryosectioning technique. To observe the dispersion state of nano-Si₃N₄ in rubber matrix clearly, we chose peroxide DCP as vulcanizer to prepare the nano-Si₃N₄/NBR composite samples for TEM, not adding any other fillers into rubber except for nano-Si₃N₄ powders.

The contact angle and surface free energy were investigated using contact angle measuring instrument, (KRUSS GmbH, Germany) at room temperature. The experiments of oil resistance were carried out according to GB/T 1690-92. For tensile tests an Instron 1122 tensile tester (Instron Co., England) was used at a strain rate of 500 mm/min, and the testing temperature is 25°C.

RESULTS AND DISCUSSION

Characterization of nano-Si₃N₄ and macromolecular coupling agent by FTIR

The macromolecular coupling agent that was applied for modification of nano-Si₃N₄ was synthesized with a certain mass ratio of butyl acrylate (BA); α-methacrylic acid (MAA); acrylonitrile (AN) by radical

copolymerization. Fourier transform infrared spectroscopy (FTIR) was utilized to characterize the tercopolymer BA-MAA-AN (Number-average Molecular Weight is about 6000~9000, CN% = 2.94%) and the changes in the nano-Si₃N₄ surfaces, as shown in Figure 3. The surface modified nano-Si₃N₄ was analyzed by FTIR after being washed with acetone in Soxhlet extractor for 72 h. Figure 3 (curve a) shows the spectrum of nano-Si₃N₄. For a comparison the spectra of modified nano-Si₃N₄ (curve b) and of the tercopolymer BA-MAA-AN (curve c) are also reported.

Silicon nitride is strongly reactive when exposed to air. So the surface region of commercial Si₃N₄ powder has a significant amount of Si₂-NH, Si-NH₂, and Si-OH groups.¹ In Figure 3(a), νOH (hydrogen bonded)¹⁸ +νNH combination band can be seen at 3422 cm⁻¹. The detection of absorption at 1064 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 SiO₂.¹⁹ The band at 1633 cm⁻¹ is assigned to the N-H shear vibration, 974 cm⁻¹ is assigned to the backbone vibrations of Si-N-Si and 1385 cm⁻¹ is attributed to the bending mode of hydroxyl groups.²⁰

For the modified nano-Si₃N₄, In Figure 3(b), the peak at 1741 cm⁻¹ is related to C=O stretching vibration mode, and the peak at 2968 cm⁻¹ is related to -CH₂, -CH₃ asymmetric stretching mode. The band appears at 2240 cm⁻¹ is correspond to the stretching mode of -C≡N. These three peaks are the characteristic peak of BA-MAA-AN tercopolymer [as shown in Fig. 3(c)]. This proved that the macromolecular coupling agent tightly absorbed at the surface of nano-Si₃N₄ by chemisorption and it is still exist in the modified powders even after being extracted by Soxhlets extractor in acetone.

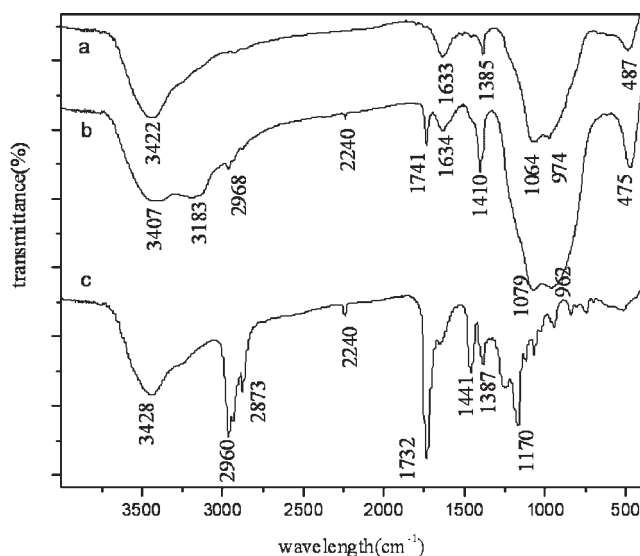


Figure 3 IR spectra of (a) nano-Si₃N₄, (b) modified nano-Si₃N₄, (c) BA-MAA-AN tercopolymer.

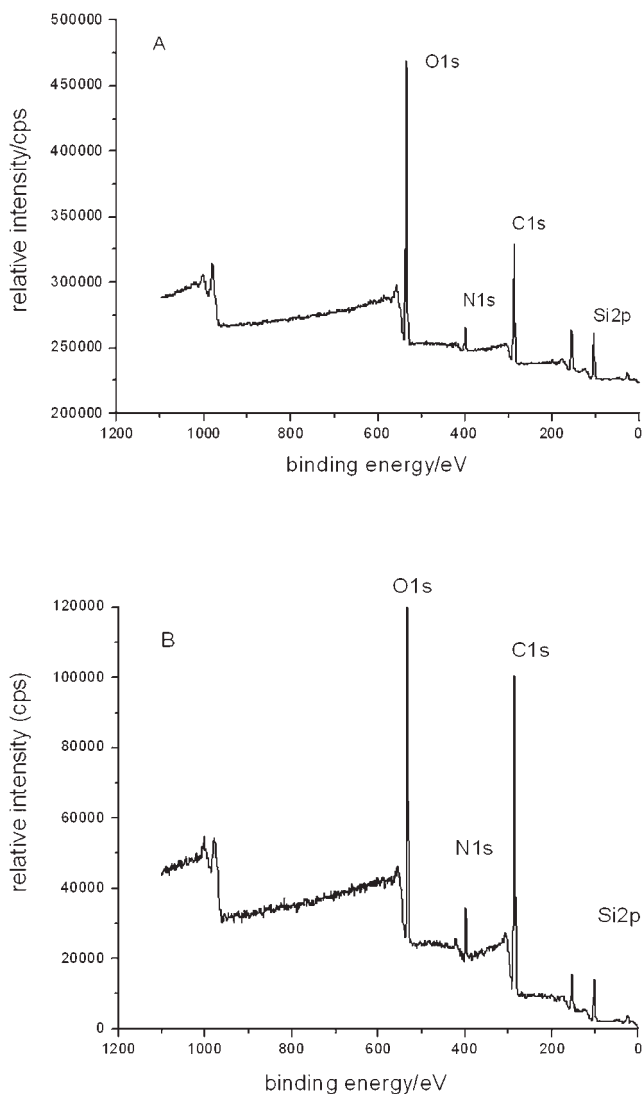


Figure 4 XPS survey scan spectra of nano-Si₃N₄ and modified nano-Si₃N₄ (A) unmodified, (B) modified.

Moreover, the double peak 3407 cm⁻¹ and 3183 cm⁻¹ in the Figure 3 (curve b) is assigned to N—H stretching vibration of primary amide, and 1410 cm⁻¹ could be related to ν_{C—N} of primary amide. This suggests that Si—NH₂ group on the surface of nano-Si₃N₄ has combined with —COOH group of macromolecular coupling agent forming —NH—CO—. The Si—O—C absorption bands are observed with IR (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 nano-powder at 900–1100 cm⁻¹ is broader and stronger than that of the native nano-Si₃N₄ powder. This indicates that the surface group of nano-Si₃N₄ has changed from Si—OH to Si—O—C.²¹ The —COOH groups of macromolecular coupling agent were subject to dehydrating condensation with the —OH groups. According to these, we can suggest that macromolecular coupling agent is bonded on the surface of nano-sized Si₃N₄ particles and an organic coating layer is formed.

Photo-electron spectroscopy

XPS is an important analytical technique for surface characterization of solid materials. It provides qualitative and quantitative information relating to the outermost atom or molecule layers. The depth of information or the thickness of the analyzed surface layer ranges from 1 to 3 nm. It provides a direct insight into chemical bonding parameters (chemical shift). For the further determination of chemical composition changes of nano-Si₃N₄, XPS measurements were performed to characterized the surface compositions of native nano-Si₃N₄ and nano-Si₃N₄ modified with 10 wt % tercopolymer (BA-MAA-AN). The surface chemical compositions of the samples analyzed by XPS are measured within a range of binding energies of 0–1000 eV. C1s, O1s, N1s, and Si2p spectra are measured and shown in Figure 4. For a better quantitative comparison, the integrated peak areas were divided by the appropriate atomic sensitivity factors. The atomic sensitivity factors were provided by Physical Electronics. The atomic concentration ratio of C/Si, O/Si, and N/Si are listed in Table I.

According to Figure 4 and Table I, the effective coverage with macromolecular modifier (BA-MAA-AN tercopolymer) results in a strong increase of the carbon signal (from 42.05% to 60%) and a corresponding decrease in both the silicon (from 12.74% to 6.49%) and oxygen signal intensities (from 40.71% to 29.42%). The atomic ratio of C/Si for the modified nano-Si₃N₄ is almost three times higher than that of the unmodified nanopowder. The atomic ratio of O/Si does not change drastically from 3.19 to 4.53 due to carboxyl groups and ester groups involving in the long chains of macromolecular coupling agent. The

TABLE I
Electron Binding Energies and Surface Composition

Sample	X _{AT} /%				Atomic ratio		
	C1s	O1s	N1s	Si2p	C/Si	O/Si	N/Si
Native nano-Si ₃ N ₄	42.05	40.71	4.50	12.74	3.30	3.19	0.35
Modified nano-Si ₃ N ₄	60.00	29.42	4.09	6.49	9.24	4.53	0.63

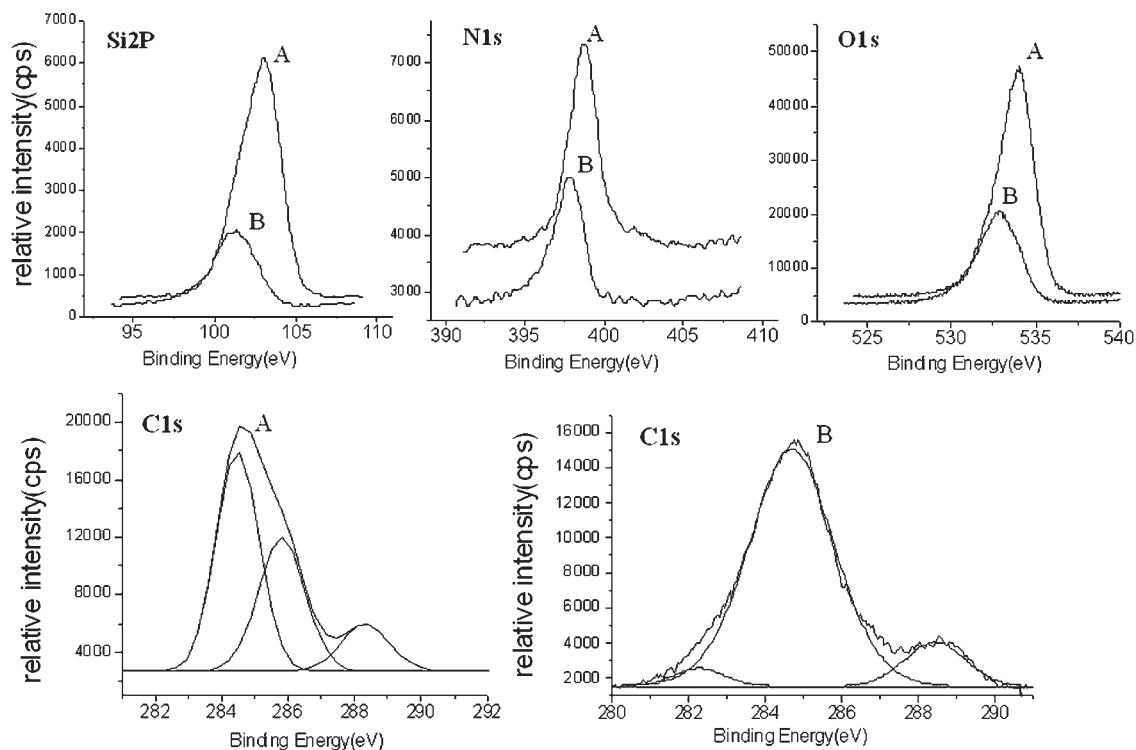


Figure 5 Si2p, O1s, N1s, and C1s core level spectra of nano-Si₃N₄ sample (A) unmodified, (B) modified.

atomic ratio of N/Si also increases further indicating that the surface of silicon nitride was covered with macromolecular coupling agent.

Figure 5 shows the Si2p, O1s, and N1s peak and the simultaneous splitting of C1s core levels spectra, it can be found that after being modified, the Si2p, O1s, N1s, and C1s peak area (content of carbon element), peak shape and position are changed which reflecting the chemical interaction between nano-Si₃N₄ and tercopolymer BA-MAA-AN. From Figure 5, it can be seen that the Si2p, O1s, and N1s spectrum include only one peak. The typical O1s spectrum (at 533.9 eV) indicates that there are Si—OH bonds in the unmodified nano-Si₃N₄ samples. After having modified, the binding energy of the O1s peak changes from 533.9 to 532.9 eV for Si—O—C. The binding energy of the Si2p peak changes from 103.04 (Si—O) to 101.35 eV (Si—C). The binding energy of the N1s peak change from 398.68 to 397.4 eV, these can be explained as because of a change in the chemical environment of the nitrogen, due to the formation of —NH—CO groups.

Compared with native nano-Si₃N₄ and corresponding modified nano-Si₃N₄, at the surface of native nano-Si₃N₄, C1s peak at 288.31 eV (CO₂), 284.53 eV (C—C, C—H), and 285.89 eV (C—O). After a surface coverage with macromolecular coupling agent, a low BE peak at 282.27 eV is observed and it is thought to be C—Si binding configuration.²²

All data of XPS suggested that macromolecular coupling agent covalently bonds to the surface of nano-sized Si₃N₄ particles and an organic coating layer is formed. This result is agreement with that obtained from FTIR.

Characterization of nano-Si₃N₄ and macromolecular coupling agent by TGA

Thermal stability of nano-Si₃N₄, modified nano-Si₃N₄, and tercopolymer BA-MAA-AN were measured by dynamic thermogravimetric analysis (TGA). The surface modified nano-Si₃N₄ sample was analyzed after being washed with acetone in Soxhlet extractor for 72 h. Figure 6 is TG and DTG curve of nano-Si₃N₄, modified nano-Si₃N₄ and tercopolymer BA-MAA-AN (the heating rate was monitored at 20°C/min, and the flow rate of N₂ of 60 mL/min). As shown in the TG curve (a), the thermal decomposition of native nano-Si₃N₄ begins at about 60°C, and the continuous mass loss can be seen from 60°C to 550°C. This is likely due to 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, and etc. from the surface of nano-Si₃N₄ with increasing temperature results in the continuous mass loss.²³ As presented in Figure 6 (curve a), in 60–180°C stage, native nano-Si₃N₄'s mass loss is 7.5% with a high decomposition rate

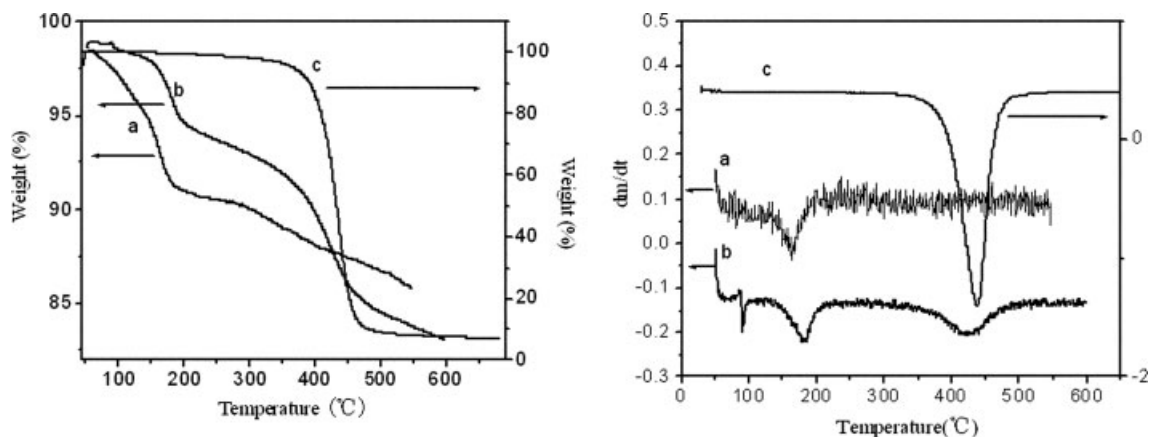


Figure 6 TG-DTG curves of (a) nano-Si₃N₄, (b) modified nano-Si₃N₄, (c) BA-MAA-AN tercopolymer.

while in 180–550°C the mass loss is only 5% with a low decomposition rate. In contrast with only one peak on the DTG curve(a), the thermal decomposition process of modified nano-Si₃N₄ can be divided into three stages from 50 to 500°C, as predicted by the DTG curve(b). And there are mass losses with maximum rate at 90.94°C, 186.02°C, and 422.24°C in this curve. The first stage started from 85 to 105°C with a mass loss at 0.4%. The second stage is in the range of 135–220°C with the mass loss of 4.1%. The third stage of decomposition is in the 370–475°C temperature range with a mass loss of 6.2%. This stage is identical with the main thermal decomposition stage of tercopolymer BA-MAA-AN. Thus, we consider that most of the macromolecular coupling agent coats on the surface of nano-Si₃N₄ particles and strong chemical bonding establishes between tercopolymer BA-MAA-AN and nano-Si₃N₄. It can be seen from Table II that the remnant mass percentage of native nano-Si₃N₄ is 91.4% at 180°C, compared to which, the remnant mass percentage of modified nano-Si₃N₄ falls to 91.3% only when heating to 370°C. That is to say, at the same temperature below 370°C, the remnant mass percentage of native nano-Si₃N₄ is less than that of modified nano-Si₃N₄. This result also indicates that owing to the strong chemical bonding, the decreasing number of —NH₂ and —OH group on the surface of modified nano-Si₃N₄ results in the reduction of gas desorption quantity on the surface of modified nano-Si₃N₄ below 370°C. The thermal stability of modified nano-Si₃N₄ has been proved.

TABLE II
TGA Data of Nano-Si₃N₄ and Terpolymer

Sample	Weight (%)			
	150°C	180°C	370°C	475°C
(a) Native nano-Si ₃ N ₄	94.4%	91.4%	88.7%	87.1%
(b) Modified nano-Si ₃ N ₄	97.8%	96.0%	91.3%	85.1%
(c) Terpolymer			94.4%	10.6%

Analysis of nanoparticle size and distribution

On the basis of dynamic light scattering (DLS) principle, the number average diameter and size distribution of nano-Si₃N₄ suspension were analyzed using Size Distributions Analyzer (3000HS, Malvern, England), as shown in Figure 7 and Table III. The nano-Si₃N₄ suspension in 95% alcohol was prepared through ultrasonic dispersion²⁴ for 30 min using ultrasonic cleaner SB5200 (Shanghai Branson Ultrasonics Co., China). According to the result, the average diameter of native nano-Si₃N₄ is about 50–60 nm while that of modified nano-Si₃N₄ decreased obviously. It was suggested that the dispersing effect of nano-Si₃N₄ in 95% alcohol be improved obviously after modified with macromolecular coupling agent.

The native nano-Si₃N₄ particles were dispersed poorly in alcohol and the serious agglomerations were formed due to the existence of Si—OH group on the surface of the native nano-Si₃N₄ powders.

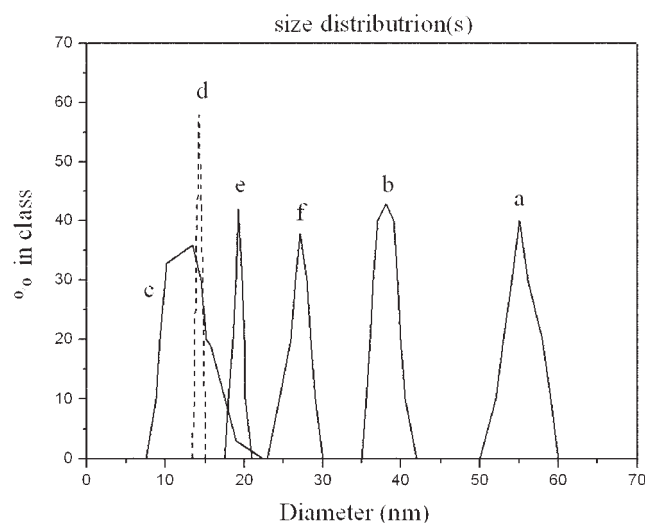


Figure 7 Size distribution of nano-Si₃N₄ modified with different percentage of macromolecular coupling agent (a) 0%, (b) 5%, (c) 7.5%, (d) 10%, (e) 15%, (f) 20%.

TABLE III
Average Diameter and Size Distribution of Nano-Si₃N₄ (by Number)

Coupling agent (%)	0	5	7.5	10	15	20
Average diameter (nm)	55.0	38.2	12.5	14.3	19.0	26.8
Size distribution (nm)	50–60	35–42	7.5–22.5	13.4–15.1	17.5–21	23–30

TABLE IV
Contact Angle and Surface Free Energy of Nano-Si₃N₄ and NBR-26 at 20°C

Sample	Contact angle (°)		Surface free energy (J/M ²)		
	Water	Glycol	γ_D (J/M ²)	γ_P (J/M ²)	γ_T (J/M ²)
Native nano-Si ₃ N ₄	23.6	34.4	131.79	2.78	129.01
Modified nano-Si ₃ N ₄	56.1	40.1	55.18	1.73	53.45
NBR-26	84.3	71.5	22.06	6.78	15.27

Compared with the native powders, the nano-Si₃N₄ modified with BA-MAA-AN tercopolymer showed good dispersibility in alcohol. Because of the new chemical bond's forming between macromolecular coupling agent and nano-particles, the interaction among nano-particles was broken down and the agglomeration was controlled effectively. With the increasing loading of the macromolecular coupling agent, the average diameter of nano-Si₃N₄ decreased gradually, but when the loading of macromolecular coupling agent exceed 10%, the average diameter

increased again. This may be because when the loading of BA-MAA-AN tercopolymer is insufficiency, the uncoated nano-Si₃N₄ will be likely to agglomerate together. While if the loading is superabundance corresponding to the mass of nano-Si₃N₄, the average diameter of modified nano-Si₃N₄ may increase again because of the thickening of the macromolecular coupling agent coating layer and the entanglement between long and flexible chain of macromolecular coupling agent. On the other hand, the —CN group on the chain of BA-MAA-AN tercopolymer enhance

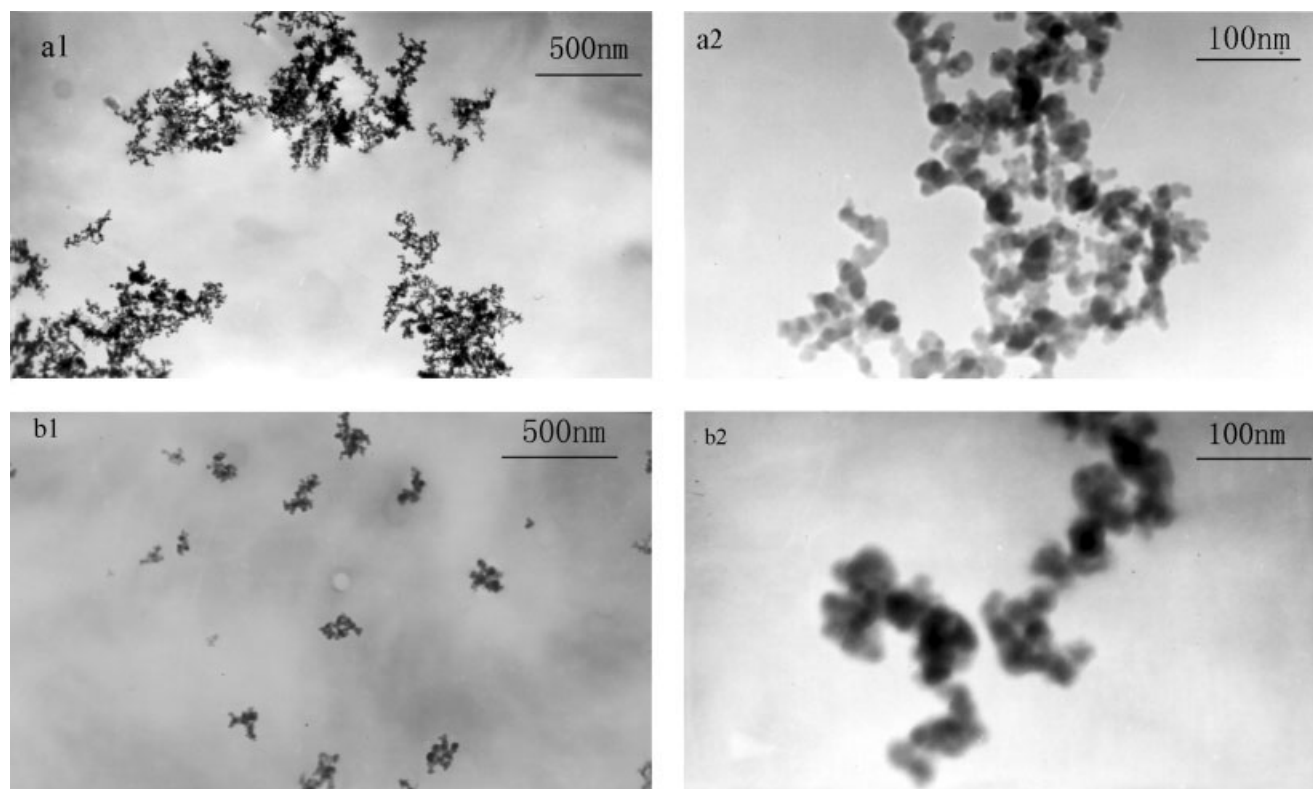


Figure 8 TEM micrographs of (a) nano-Si₃N₄, (b) modified nano-Si₃N₄, showing different morphologies.

the polarity and interaction, so the agglomeration between nano-Si₃N₄ particles will be aggravated.

Contact angle and surface free energy

The change of surface hydrophilicity was investigated by contact angle measurements. Surface free energy of nano-Si₃N₄ and NBR were calculated by corresponding contact angle. Table IV shows an obvious change of contact angle after modifying nano-Si₃N₄ surfaces with 10 wt % BA-MAA-AN tercopolymer. After the surface modification, the contact angle increased from 23.6° to 56.1°, suggesting increased surface hydrophobicity. These changes are likely due to the carbon backbone of tercopolymer, which is hydrophobic. After modification with tercopolymer (BA-MAA-AN), the surface free energy of nano-Si₃N₄ decreased sharply from 131.79 to 55.18 J/m², which was much closer to that of NBR-26. Thus, we can conclude that the nano-Si₃N₄ modified with BA-MAA-AN tercopolymer can be dispersed in NBR matrix more easily than native nano-Si₃N₄ powder.

Comparison of nano-Si₃N₄ and modified nano-Si₃N₄'s dispersion

TEM morphology of nano-Si₃N₄

Figure 8 displays the TEM photographs of native nano-Si₃N₄ and modified nano-Si₃N₄ suspensions in 95% 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-Si₃N₄ [Fig. 8(a1,a2)] while a better dispersion can be seen in the photograph of modified nano-Si₃N₄ [Fig. 8(b1,b2)]. In the TEM photographs of Figure 8(b2), the tercopolymer coating layers are clearly shown as the gray area, it coated on the surface of nano-Si₃N₄ particles and reduced the agglomerations. This suggests that physical bonding or chemical bonding should occur between the polar —CN bond and reactive group (—COOH) of BA-MAA-AN tercopolymer and —OH, —NH₂ group on the surface of nano-Si₃N₄. The molecular chains of macromolecular coupling agent that connect with the surface of nano-Si₃N₄ particles brought mutual exclusion and steric hindrance effect, thus the surface free energy reduced correspondingly and the agglomeration was controlled. This was also confirmed by surface free energy values in Table IV.

The dispersion of nano-Si₃N₄ in NBR matrix

The dispersion states of native and modified nano-Si₃N₄ in the Si₃N₄/NBR nanocomposites were investigated by transmission electron microscopy (TEM). Low

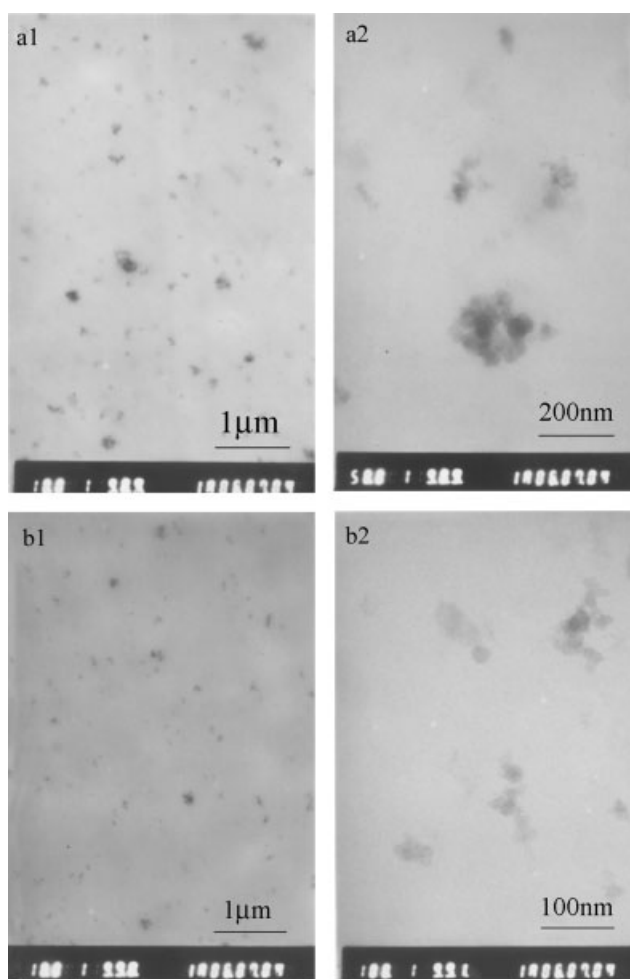


Figure 9 TEM micrographs of nano-Si₃N₄/NBR composite (a) dispersion of unmodified nano-Si₃N₄ in NBR matrix, (b) dispersion of nano-Si₃N₄ modified with BA-MAA-AN tercopolymer in NBR matrix.

magnification TEM photographs [Fig. 9(a1)] clearly display that several bigger aggregates (about 200 nm) exist in native nano-Si₃N₄/NBR composite, while modified nano-Si₃N₄ dispersed more finely and homogeneously in the NBR matrix [Fig. 9(b1)], their dispersed dimension is much smaller than that of native nano-Si₃N₄. The high-magnification TEM image [Fig. 9(b2)] reveals that modified nano-Si₃N₄ can disperse with nano-sized grade (<100 nm) in NBR matrix.

Oil resistance of nano-Si₃N₄/NBR modified with BA-MAA-AN tercopolymer/NBR composite

The prepared nanocomposites exhibit outstanding mechanical performances¹² and improved oil resistance properties, which are likely attributed to the nanometer scale dispersion and good compatibility between nano-particles and rubber matrix. The effect of tercopolymer on the oil resistance of composite was studied after immersing them in the oil (No.3

TABLE V
Influence of Macromolecular Coupling Agent on the Oil Resistance
of Nano-Si₃N₄/NBR Composite

	Modified nano-Si ₃ N ₄ /NBR	Native nano-Si ₃ N ₄ /NBR	NBR
Length change (%)	8.36	10.97	9.84
Width change (%)	6.85	5.96	5.34
Mass change (%)	17.83	19.04	18.39
Shore A hardness change (°)	-13	-16	-15
Tensile strength (MPa)			
Before (in oil)	11.88	10.67	11.31
After (in oil)	3.35	2.99	2.53
Elongation at break (%)			
Before (in oil)	330.66	278.13	267.90
After (in oil)	114.33	111.22	82.16

standard oil) at 125°C for 70 h. It can be found that the native nano-Si₃N₄ could not improve the NBR's oil resistance, it may even worsen it. When the nano-Si₃N₄ was modified with tercopolymer BA-MAA-AN, the NBR vulcanizate showed much better oil resistance. As shown in Table V, nearly all the performances of modified nano-Si₃N₄/NBR vulcanizate enhanced distinctly including the change rate of dimension, change rate of mass and Shore A hardness, tensile strength, elongation at break. This reveals that due to the introduction of —CN side groups on the tercopolymer's chain, not only the compatibility between modified nano-Si₃N₄ particles and NBR matrix is enhanced but the NBR vulcanizate's oil resistance can be improved, which is needed for producing oil sealing product.

CONCLUSIONS

The BA-MAA-AN tercopolymer can be used as a macromolecular coupling agent to modify the nano-Si₃N₄ powder, which is applied to prepare the nano-Si₃N₄/NBR composite. The optimal loading of this macromolecular modifier is 10 wt % as that of nano-Si₃N₄. Via modification, an organic coating layer formed on the surface of nano-Si₃N₄ powder, and chemical bond combination happens between BA-MAA-AN tercopolymer and nano-Si₃N₄ powder surface. Homogenous dispersion of modified nano-Si₃N₄ particles in NBR matrix is likely owing to the increased surface hydrophobicity and decreased surface free energy.

The nano-Si₃N₄/NBR composite's oil resistance can be improved distinctly when nano-Si₃N₄ modified with the BA-MAA-AN tercopolymer.

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