



Surface Modification of Nano-Sized Silicon Nitride with HFMA-MMA-VTMS Tercopolymer and their dispersion in FKM Composites

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In this work, a new macromolecular coupling agent HFMA-MMA-VTMS tercopolymer was synthesized using solution polymerization. The terpolymer's molecular structure was confirmed by FTIR and ¹H NMR and GPC. The HFMA-MMA-VTMS tercopolymer was used for surface modification of silicon nitride (Si₃N₄) nanopowder. The structure surface properties and thermal stability of modified nano-Si₃N₄ were systematically investigated by FTIR, size distribution analyzer, TGA, TEM and nano-Si₃N₄/FKM composite was investigated by SEM. The results show that the macromolecular coupling agent bonds covalently on the surface of nano-sized Si₃N₄ particles and an organic coating layer was formed. The optimum loading of this macromolecular coupling agent HFMA-MMA-VTMS tercopolymer was 12 % (wt %) of nano-sized Si₃N₄. TEM also reveals that modified nano-Si₃N₄ possesses good dispersibility. SEM reveals that modified nano-Si₃N₄ dispersed more finely and homogeneously in the FKM matrix.

Key Words: Macromolecular coupling agent, Nano-size silicon nitride (Si₃N₄), Surface modification, FKM composite.

INTRODUCTION

During the past few years, much research attention had been paid to surface modification of nanoparticles, because nano-particles have a strong tendency to agglomerate due to its high surface energy and weak combination with the polymer matrix. Their novel optical, electronic and chemical properties absent in bulk materials were considered which have great application prospects in the composite materials. The crux lies in the fact how to well disperse inorganic nano-particles in organic polymer matrices and how to improve their interfacial interaction. Nano-sized silicon nitride (Si₃N₄) 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 resistance¹⁻⁵. Nano-sized Si₃N₄ had also been proved to be an effective filler for the improvement of mechanical properties and in particular the wear resistance of polymeric composites, such as PTFE, epoxy, PEEK, bismaleimide composites, NBR⁶⁻¹⁰, etc.

There were two ways to modify the surface of nano-particles, such as dry processing and wet processing, which had been reported¹¹⁻¹³. In previous work, molecular coupling agent, such as macromolecule BA-MAA-AN, BA-MMA-VTES were synthesized to modify nano-sized silicon nitride (Si₃N₄), which was applied to prepare nano-particles/NBR composites. The result show *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 to the increased surface hydrophobicity and decreased surface free energy. The nano-Si₃N₄/NBR composite's oil resistance can be improved distinctly^{14,15}. It was also reported by Xiaodong¹⁶ that two block copolymers polystyrene (PS)-polybutadiene (PB)-polyvinyltrieth-oxysilane (PVTES) and polystyrene (PS)-polyisoprene (PIP)-polyvinyltriethoxysilane (PVTES) were synthesized as a macromolecular coupling agent. Silane coupling agent, is often used to modify the fillers such as CaCO₃, TiO₂, silica nanocomposite, Fe₃O₄, etc. As the modified fillers were filled into a certain polymer matrix, the interface adhesion between inorganic fillers and matrix can be enhanced obviously¹⁷⁻¹⁹. The previous work proved the effect of modified nano-particles modified by macromolecules better than modified by small molecule in the composites especially rubber matrix. That is because the entanglements between the long chains of macromolecule and the main rubber matrix will substantially enhance the interactions between nano-particles and matrix and improve the compatibility between them.

In this study, a novel macromolecular coupling agent tercopolymer HFMA-MMA-VTMS was designed for ceramic nanopowder/FKM composite. The side group -Si(OCH₃)₃ on this tercopolymer's main chain may react with -OH, -NH-

and -NH_2 , which were on the surface of the nitride ceramic nanopowder containing active hydrogen. When several groups on each HFMA-MMA-VTMS macromolecular chain were chemical bonded with the surface of nano- Si_3N_4 particles, an arch like chain structure will form on the surface. This article will attempt to characterize the structure of HFMA-MMA-VTMS and the interaction between macromolecular coupling agent (HFMA-MMA-VTMS tercopolymer) and surface of nano- Si_3N_4 particles and the dispersion of nano- Si_3N_4 in FKM matrix²⁰⁻²³.

EXPERIMENTAL

Silicon nitride (Si_3N_4) used for this study is a commercial ultrafine amorphous powder (Hefei Kiln Nanometer Technology, Hefei, China,) whose average particle diameter < 20 nm, specific surface area $115 \text{ m}^2/\text{g}$. Methyl methacrylate (China National Pharmaceutical Group Shanghai Chemical Reagent Co., Shanghai, China) vacuum distillation; vinyltrimethoxysilane (VTMS) (Nanjing Shuguang Silane Chemical Co., Ltd); dodecyl mercaptan (Shanghai Zhenxing Chemicals Co., Shanghai, China); 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFMA); ethyl acetate and methenyl chloride were obtained from Shanghai Suyi Chemical Reagent Co., Shanghai, China. Benzoyl peroxide (Shanghai Shanpu Chemicals Co., Shanghai, China), which was purified by recrystallization from acetone.

In a 4-mouth flask, holding a nitrogen inlet, mechanical stirrer, reflux-condenser, constant-pressure funnel, ethyl acetate was added. Then 2,2,3,4,4,4-Hexafluorobutyl methacrylate (HFMA), methyl methacrylate (MMA), vinyltrimethoxysilane (VTMS), benzoyl peroxide (BPO), dodecylthiol and excess ethyl acetate were slowly dropped into the flask in a definite proportion through the constant-pressure funnel. After dropping about 3/4 of benzoyl peroxide, the reaction kettle was heated on an oil bath keeping temperature at 80°C for 2 h. After that, another 1/4 benzoyl peroxide was added into the 4-mouth flask and the resulting mixture was heated at 80°C for another 2 h to yield a viscous tercopolymer solution. The solid content of the tercopolymer solution was about 25.1 %.

The native nano- Si_3N_4 powders were dispersed in chloroform and a certain amount of macromolecular coupling agent (tercopolymer HFMA-MMA-VTMS) was added into the flask, mixing round with high speed at 80°C for 3 h and then vacuum drying for 24 h.

Detection method: The structure of tercopolymer HFMA-MMA-VTMS, native nano- Si_3N_4 and modified nano- Si_3N_4 (Fig. 1) were investigated by Fourier transform infrared spectra (Nicolet Co.,Nexus-870,USA). The content of intercalated polymer was determined by thermogravimetric analysis (TGA) on thermal analyzer (Netzsch Co., TG 209, Germany) Samples were heated to 700°C from room temperature at the speed of $30^\circ\text{C min}^{-1}$. The mean size and size distribution of nano-particles was determined by particle size distributions analyzer (3000HS, Malvern, England). The morphology analysis was performed on scan electron micrograph analyzer (S-4800; Hitachi, Japan); transmission electron micrograph analyzer (Jeol 100CX-II JAPAN).

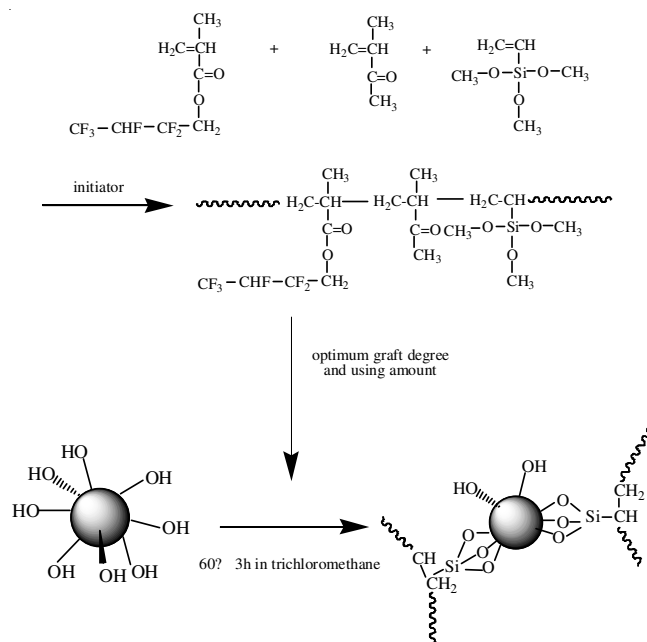


Fig. 1. Schematic representation for the modification of nano- Si_3N_4 particles with a new macromolecular coupling agent (HFMA-MMA-VTMS)

RESULTS AND DISCUSSION

Characterization of nano- Si_3N_4 and macromolecular coupling agent

FTIR: It can be seen from Fig. 2. that the peak at 1730 cm^{-1} was related to $\text{C}=\text{O}$ stretching vibration mode and the peak at 2945 cm^{-1} was related to -CH_2 , -CH_3 asymmetric stretching mode. The band appears at $845\text{-}750 \text{ cm}^{-1}$ corresponds to the stretching mode of -Si-Me . $1400\text{-}1000 \text{ cm}^{-1}$ was the range peak of C-F . These peaks were the characteristic peaks of tercopolymer (HFMA-MMA-VTMS) synthesized. The double bond absorption peak $1650\text{-}1600 \text{ cm}^{-1}$ does not appear, indicating there was no single product existed, terpolymers as expected products.

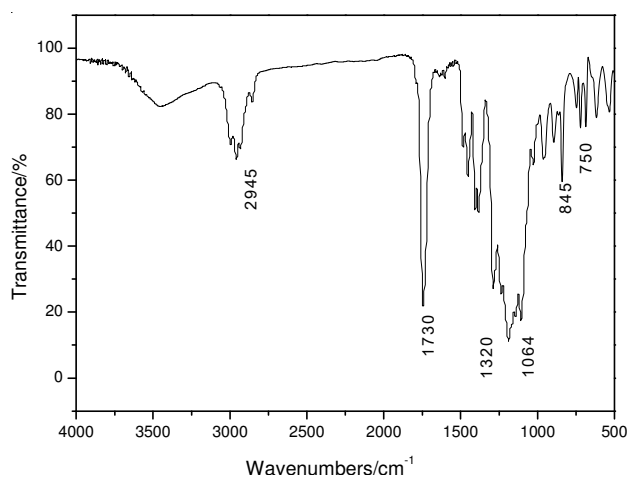


Fig. 2. IR spectra of HFMA-MMA-VTMS

The surface modified nano- Si_3N_4 was analyzed by FTIR after being washed with acetone in Soxhlet extractor for 12 h. For the modified nano- Si_3N_4 , in Fig 3(b), the peak at 1742 cm^{-1}

was related to C=O stretching vibration mode and the peak at 2806 cm^{-1} was related to $-\text{CH}_2$, $-\text{CH}_3$ asymmetric stretching mode. These peaks were the characteristic peak of terpolymer (HFMA-MMA-VTMS). It was proved that the macromolecular coupling agent tightly absorbed at the surface of nano- Si_3N_4 by chemisorption and it was still exist in the modified powders even after being extracted by Soxhlets extractor. The Si-O-Si absorption bands were observed at $1100\text{--}1050\text{ cm}^{-1}$, these were overlapped by the Si-O and Si-N absorption ($1100\text{--}800\text{ cm}^{-1}$) 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 $1100\text{--}900\text{ cm}^{-1}$ was broader and stronger than that of the native nano- Si_3N_4 powder. This indicates that the surface group of nano- Si_3N_4 has changed from Si-OH to Si-O-Si. From these, we can suggest that macromolecular coupling agent was bonded on the surface of nano-sized Si_3N_4 particles and an organic coating layer was formed.

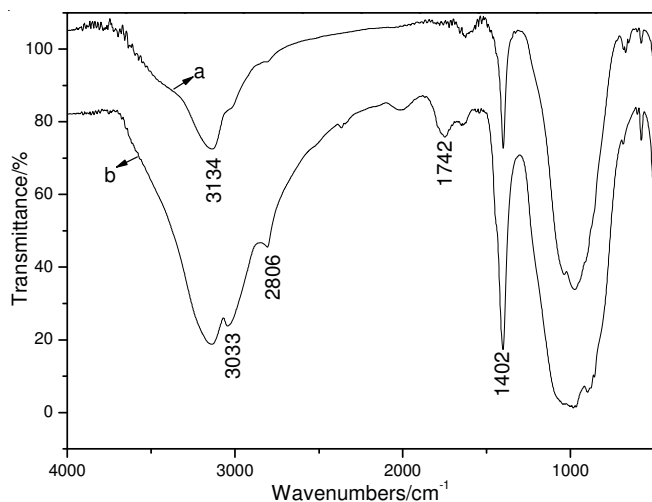


Fig. 3. IR spectra of (a) unmodified nano- Si_3N_4 (b) modified nano- Si_3N_4 by LMPB-GMA

^1H NMR analysis: ^1H NMR spectra of the terpolymer HFMA-MMA-VTMS (Fig. 4) was obtained on an AVANCE 400 nuclear magnetic resonance spectrometer, using TMS as internal reference and deuterated acetone (CD_3COCD_3) as solvent. H band for $-\text{Si}-\text{O}-\text{CH}_3$ in $-\text{O}-\text{CH}_3$ was 3.605 ppm , which indicates the existence of VTMS structural unit in the terpolymer product. And H band for $-\text{CF}_2-\text{CHF}-\text{CF}_3$ absorb in the chemical shift range from 4.904 to 5.006 ppm and $-\text{O}-\text{CH}_3$ group which was in MMA structural unit absorb in the chemical shift range from $4.093\text{--}4.146\text{ ppm}$. The ^1H NMR results further demonstrate that the synthesized product was terpolymer HFMA-MMA-VTMS, which was consistent with the FTIR results.

Molecular weight of HFMA-MMA-VTMS terpolymer: The molecular weight of HFMA-MMA-VTMS terpolymer could be controlled by the loading of initiators (BPO) and chain transfer agent (dodecylthiol). As a macromolecular coupling agent, number-averaged molecular weight of this terpolymer was controlled at the range of $3000\text{--}10,000$ to modify the silicon nitride. The molecular weight of HFMA-MMA-VTMS terpolymer has been analyzed through

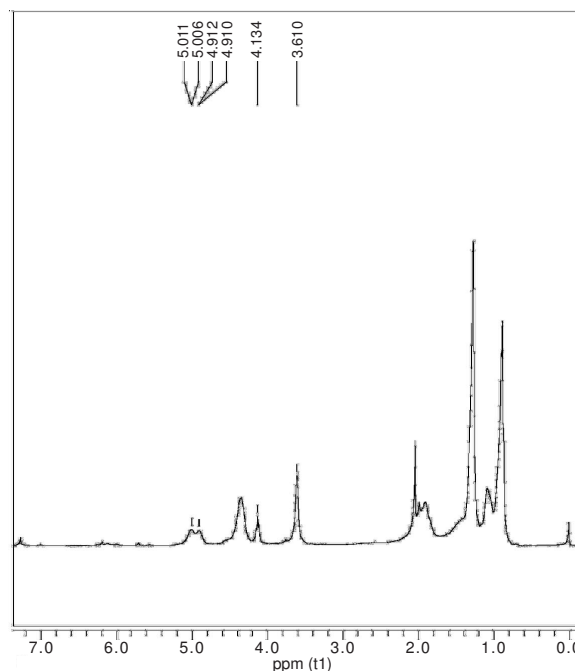


Fig. 4. ^1H NMR spectra of HFMA-MMA-VTMS

THF-eluted gel permeation chromatography (GPC). Data and chromatogram of synthesized terpolymer obtained. Weight-averaged molecular weight was 23700 ; number-averaged molecular weight was 18400 and polydispersity was 1.288 . This indicates that the terpolymer HFMA-MMA-VTMS synthesized can be used to modify the ceramic nanopowders.

Stability of nano- Si_3N_4 particle dispersion in trichloromethane: The separation of the free HFMA-MMA-VTMS from the HFMA-MMA-VTMS anchored to nano- Si_3N_4 particles was achieved by dialysis. Typically, 100 mL trichloromethane dispersion of 0.1 g modified nano- Si_3N_4 particles was allowed to stand at room temperature. After a definite time, 5 mL of dispersion liquid was taken out with a pipette and the content of nano- Si_3N_4 particles dispersed was determined. The stability of dispersion was estimated from percentage of dispersed nano- Si_3N_4 particles after standing by the following equation²⁴.

$$\text{Nano-}\text{Si}_3\text{N}_4\text{ particles dispersed (\%)} = \frac{G}{G_0} \times 100\%$$

where, G (g) and G_0 (g) are the weight of nano- Si_3N_4 dispersed after and before standing, respectively.

The dispersion stability of modified nano- Si_3N_4 particles in methylene chloride was compared with native nano- Si_3N_4 particles (Fig. 5). It can be seen that native Si_3N_4 nano-particles have been completely precipitated for about 3 days, while the modified Si_3N_4 nano-particle modified with 12% (wt %) (HFMA-MMA-VTMS) have a stable colloidal dispersion in trichloromethane.

The hydroxyl groups ($-\text{OH}$) from nano- Si_3N_4 particles can interacted with $-\text{Si}(\text{OCH}_3)_3$ from HFMA-MMA-VTMS to form (HFMA-MMA-VTMS-g- Si_3N_4) complex on the surface of nano- Si_3N_4 particles. Consequently, no matter what reaction occurred, the terpolymer are initially anchored on the surface

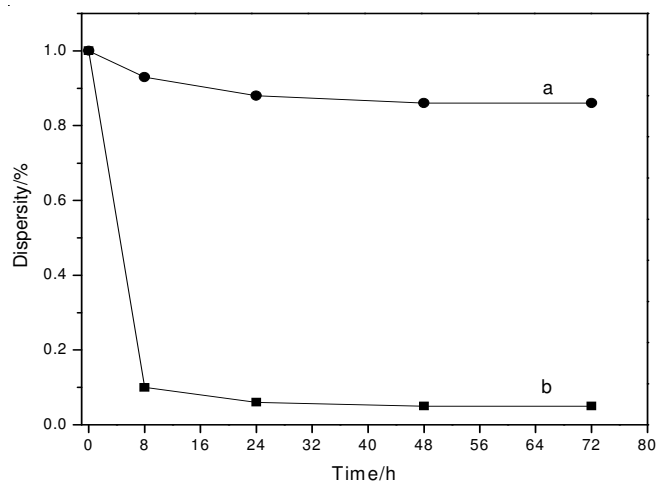


Fig. 5. Stability of nano-Si₃N₄ particle dispersion in trichloromethane: (a) modified nano-Si₃N₄ particle with HFMA-MMA-VTMS (b) unmodified nano-Si₃N₄ particle

of the particles at one or several spots. The other terminal of HFMA-MMA-VTMS was organic polymer chain, which fulfills steric hindrance between inorganic nano-particles. All above factors give rise to the homogeneous dispersion of Si₃N₄ nano-particles in trichloromethane and maintain a stable colloidal dispersion for a long time (Fig. 6). They are the photographs of dispersion stabilized of nano- Si₃N₄ in more intuitionwastic by time.

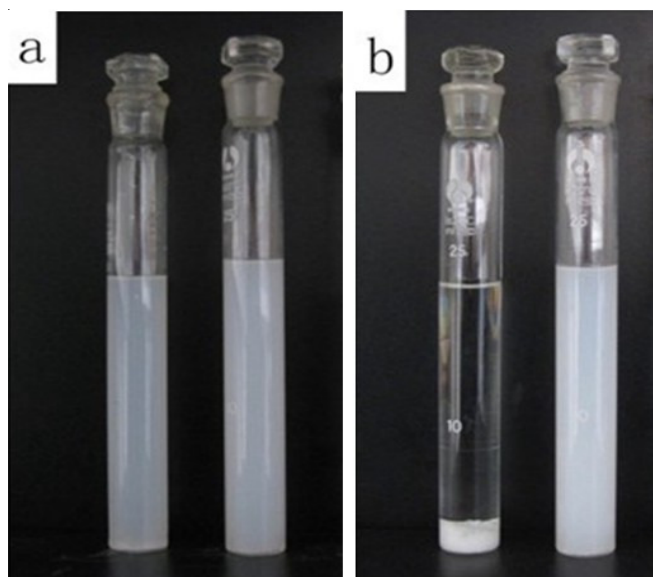


Fig. 6. Photographs of dispersion stabilized of nano-size silicon nitride (Si₃N₄) in trichloromethane solution by time: (a) ultrasonic dispersion samples after 10 min and (b) ultrasonic dispersion samples after 3 days and the left is unmodified silicon nitride sample, the right is modified silicon nitride sample

Analysis of nanoparticles' size and distribution: The nano-Si₃N₄ suspension in trichloromethane was prepared through ultrasonic dispersion for 5 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-Si₃N₄ suspension was analyzed using size distributions analyzer (3000 HS, Malvern, England) (Fig. 7 and Table-1).

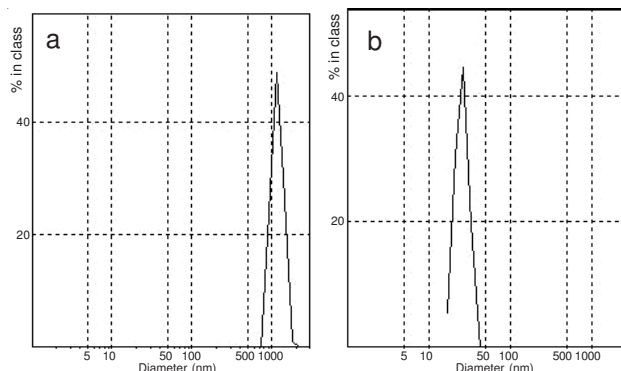


Fig. 7. Size distribution of nano-Si₃N₄ modified with different percentage macromolecular coupling agent (a) 0 %, (b) 12 %

TABLE-1
AVERAGE DIAMETER AND SIZE DISTRIBUTION
OF NANO-Si₃N₄ (BY NUMBER)

Coupling agent (%)	Average diameter (nm)	Width
0	1165.4	549.1
12	25.9	13.1

According to the result, the native nano-Si₃N₄ particles were dispersed poorly in trichloromethane and the serious agglomerations, because of the existence of Si-OH group on the surface of the native nano- Si₃N₄ powders. Its average diameter was about 350-2600 nm. Compared with the native powders, the nano- Si₃N₄ modified with HFMA-MMA-VTMS tercopolymer showed good dispersibility in trichloromethane, the sample which modified with 12 % (wt %) tercopolymer. It was suggested that the dispersing effect of nano- Si₃N₄ in trichloromethane 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.

Analysis of TGA: Thermal stability of nano-Si₃N₄, modified nano-Si₃N₄ and HFMA-MMA-VTMS was measured by dynamic thermo gravimetric analysis as show in Fig. 8.

The thermogram of HFMA-MMA-VTMS in nitrogen was shown in Fig. 8(2a) The HFMA-MMA-VTMS showed a slight weight loss before 280 °C for its low-molecular weight. A much greater weight loss (87.06 wt %) occurs at the temperature range of 280-430 °C, which was more intuitionwastic from the DTG curve Fig. 8(2b).

As shown in Fig. 8(1a), the thermal decomposition of native nano-Si₃N₄ at about 45 °C. This was 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, etc.

The modified nano-Si₃N₄ sample was analyzed before and after being washed with trichloromethane in Soxhlet extractor for 24 h. The thermal degradation curves of nano-Si₃N₄ modified with HFMA-MMA-VTMS are shown in Fig. 8(1b). We can find that both curves were similar, before 250 °C, which was assigned to the loss of nano-Si₃N₄. According to Fig. 8(1b), the weight loss from 280-490 °C was attributed to the degradation of HFMA-MMA-VTMS, which was more intuitionwastic from the DTG curve Fig. 8(1c).

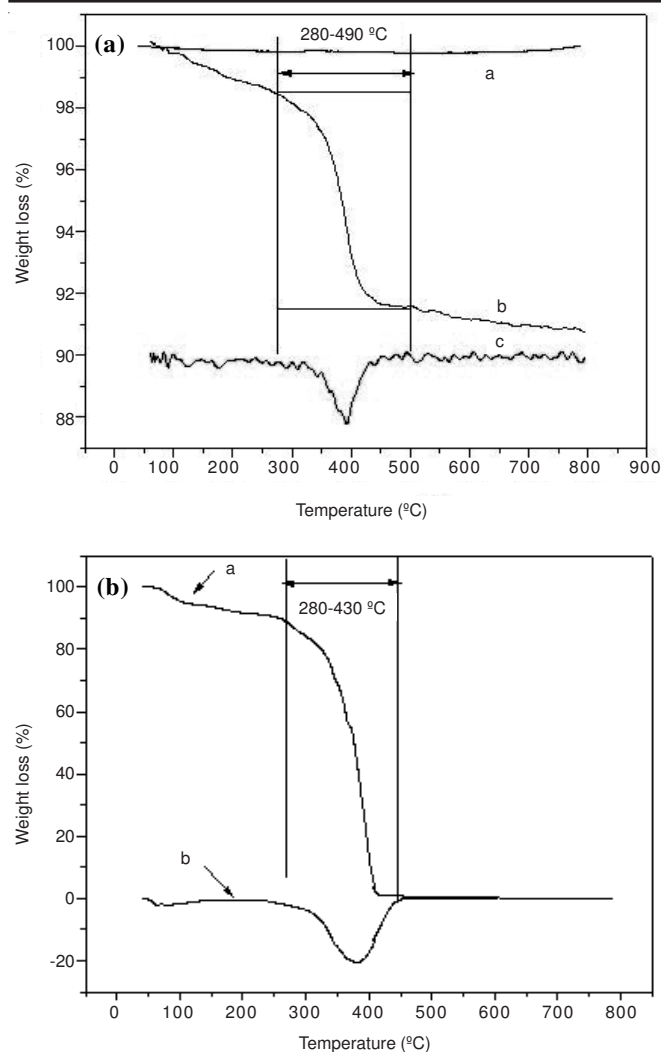


Fig. 8. 1. Native nano-Si₃N₄ (a. TGA curve of native nano-Si₃N₄, b. TGA curve of modified nano-Si₃N₄ c. DTG of modified nano-Si₃N₄). 2. BA-MMA-VTMS tercopolymer (a. TGA curve of HFMA-MMA-VTMS b. DTG of HFMA-MMA-VTMS).

TEM morphology of nano-Si₃N₄: Fig. 9 displays the TEM photographs of native nano-Si₃N₄ and modified nano-Si₃N₄ suspensions in trichloromethane 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. 9(a)] and the homogeneous dispersion can be seen in the photograph of modified nano-Si₃N₄ [Fig. 9(b)]. In the TEM photographs of Fig. 9(b), the tercopolymer layers (HFMA-MMA-VTMS) were 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 have been modified successfully by HFMA-MMA-VTMS tercopolymer. The molecular chains of macromolecular coupling agent which connect with the surface of nano-Si₃N₄ particles brought mutual exclusion and steric hindrance effect, the agglomeration was controlled. All the results above further illustrate that HFMA-MMA-VTMS had played an important role in the dispersion of nano-Si₃N₄ particles.

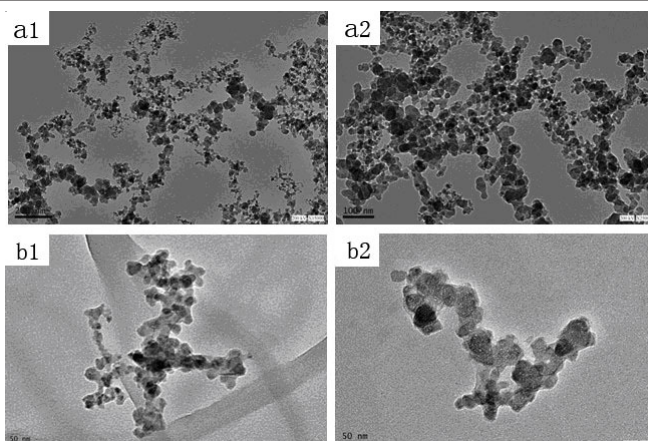


Fig. 9. TEM images for nano-Si₃N₄: (a) untreated particles and (b) modified with HFMA-MMA-VTMS

Dispersion of nano-Si₃N₄ in FKM matrix: FKM without any nano-Si₃N₄ [Fig. 10(a)]. The SEM photographs clearly display that there were no particles exist in the gross rubber before native and modified nano-Si₃N₄ were added in. The dispersion of nano-Si₃N₄ in FKM matrix. The dispersion states of native and modified nano-Si₃N₄ in the Si₃N₄/FKM nanocomposites were investigated by scan electron microscopy (SEM). Low magnification SEM photographs [Fig. 10(b)] clearly display that several bigger aggregates exist in native nano-Si₃N₄/FKM composite, while modified nano-Si₃N₄ was dispersed more finely and homogeneously in the FKM matrix [Fig. 10(c)], their dispersed dimension was much smaller than that of native nano-Si₃N₄. The SEM (Fig. 10) image reveals that modified nano-Si₃N₄ can disperse with nano-sized grade (< 100 nm) in FKM matrix.

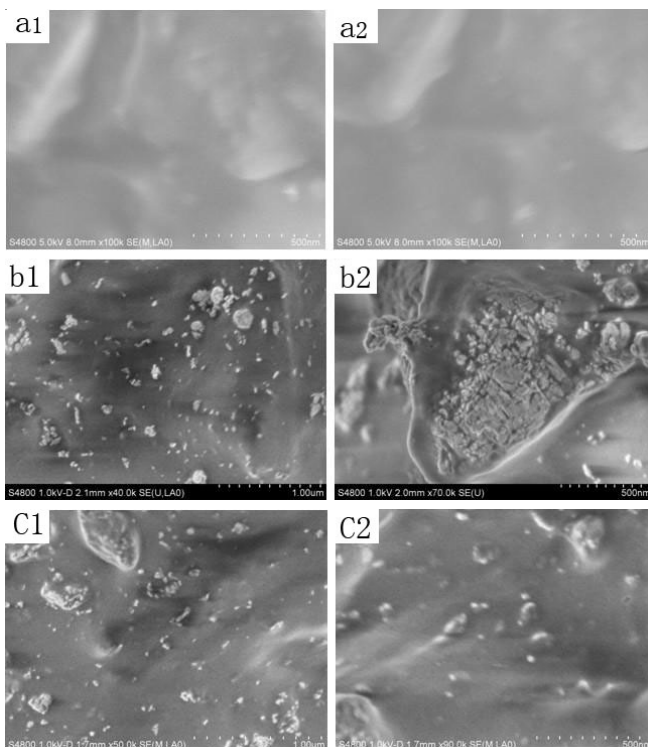


Fig. 10. SEM micrographs of nano-Si₃N₄/FKM composite (a) FKM matrix (b) dispersion of unmodified nano-Si₃N₄ in FKM matrix, (c) dispersion of nano-Si₃N₄ modified with HFMA-MMA-VTMS tercopolymer in FKM

Conclusion

A novel macromolecular coupling agent HFMA-MMA-VTMS tercopolymer was synthesized and it can be used to modify the nano-Si₃N₄ powder, which was applied to prepare the nano-Si₃N₄/FKM composite. The results show that the optimum mass fraction of macromolecular coupling agent coated on the surface of nano-sized Si₃N₄ was 12 % (wt %). Some organic coating layer formed on the surface of nano-Si₃N₄ powder and chemical bond combination happened between HFMA-MMA-VTMS tercopolymer and nano-Si₃N₄ powder surface at modified nano-Si₃N₄ possesses good dispersibility by modification. Homogenous dispersion of modified nano-Si₃N₄ particles in FKM matrix.

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