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Al₂O₃ Nanoparticles Modified by the Hyper-Branched Polyester Via One-Pot Polycondensation Process

Jifang Fu*, Yinglin Xiao, Liyi Shi*, Liya Chen, Yi Chen, Qingdong Zhong

Abstract: The surface grafting of hyperbranched aliphatic polymer onto Al₂O₃ nanoparticles were successfully obtained in the work. The hyperfunctional Al₂O₃ was prepared by the one-pot polycondensation of the AB₂-type monomer 2, 2-bis (hydroxymethyl) propionic acid (bis-MPA), from the surfaces of the amino group modified Al₂O₃ nanoparcles (amino-Al₂O₃) with p-toluenesulfonic acid (p-TSA) as catalyst. The whole processes were contained two steps: (i) introduce the amino group onto the surface of Al₂O₃ nanoparticles; (ii) Hyperfunctional Al₂O₃ nanoparticles was prepared by grafting of hyperbranched aliphatic polyester onto the surface of the amino group modified Al₂O₃ nanoparticles. The composition of the hyperbranched aliphatic polyester grafted Al₂O₃ (HAPE-Al₂O₃) was characterized by Fourier transform infrared (FTIR) spectrum, transmission electron microscope (TEM), thermogravimetric analysis (TGA) and X-Ray Fluorescence (XRF). The crystal structure of the HAPE-Al₂O₃ was characterized by X-ray diffraction (XRD).

Keywords: Hyperbranched polymer; Nanoparticles; Al₂O₃; Surface treatment

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Introduction

In recent years, much research attention has been paid to ceramic powders such as silicon carbide (SiC), aluminum nitride (AlN) and aluminum oxide (Al₂O₃). Especially Al₂O₃ nanoparticles were used and applied as the most common inorganic solid additives in the polymer composites [1-5], due to its excellent thermal and mechanical stability, good wear resistance and cheap cost. Considering the strong agglomeration among nanoparticles particles due to their high surface energy, and the poor adhesion between nanoparticles and polymer matrix, surfactants [5], small molecular coupling agent [6], macromolecular coupling agent [7] were often selected to modify the particles, since

chemical treatment of filler surface has become the most successful method to improve polymer-filler and reduce filler-filler interactions. Surface-grafting modification and macromolecular coupling agent are more effective; because the organic coating layer on the modified nanoparticles by macromolecular coupling agent is thicker than that by surfactants and small molecular coupling agent and bring about more strong electrostatic and steric stabilization. The surface functionalization of nanomaterials by grafting of polymer is expected to play important roles in the chemical modification of the surface of nanocomposite materials [6-8]. A great interest has been focused on "dendrimer", because the dendrimers have the fundamental building blocks, controlled molecular weight, con-

trolled branching and versatility in modification of terminal groups [10]. Many researchs have reported the surface modifications of nanomaterials by the grafting of hyperbranched polymer, such as carbon nanotubes, silica and carbon black. For example, Feng QP has reported that the surface grafting of hyperbranched aromatic polyamideimide onto the multiwalled carbon nanotubes was successfully achieved [9]. Liu P has reported that the hyperbranched polymer had been successfully grafted onto the surfaces of SiO₂ nanoparticles [10-11]. And Taniguchi Y has reported the surface modifications of carbon black by grafting of hyperbranched polyester [12]. However there are few literature examples of the hyperbranched polymer grafted aluminum oxide nanoparticles.

In the present work, we report the effective preparation of hyperbranched aliphatic polyester grafted Al₂O₃ nanoparticles via a melt polycondensation of 2, 2-bis(hydroxymethyl) propionic acid (bis-MPA) with the catalysis of p-tolueneSulfonic (p-TSA). And the product's Fourier transform infrared (FTIR) graphs proved that hyperbranched poly was successfully grafted onto Al₂O₃ nanoparticles surface.

Experimental

Raw material and reagents

α-Al₂O₃ nanoparticles with the average diameter of 150 nm was provided by Dalian Luming Nanometer Material CO., LTD. γ-aminopropyltriethoxysilane (APTES) was obtained from Shanghai Yaohua Chemical Plant and was used without further purification. 2,2-bis(hydroxymethyl) propionic acid (bis-MPA) was analytical grade, and used as received from Quzhou Mingfeng Chemical CO., LTD. Acetone, ammonia solution, ethanol, p-toluenesulfonic (p-TSA) and N, N-Dimethylformamide (DMF) were all analytical grade and used as received from Sinopharm Chemical Reagent Co., Ltd.

Characterization and Instrumentation

FTIR spectra were recorded on AVATAR 370 series Fourier Transform infrared spectrophotometer using KBr disks. Morphology of nanoparticles was observed with a JEOL 2000FX TEM (JEOL, Japan) at an activation voltage of 200 kV.

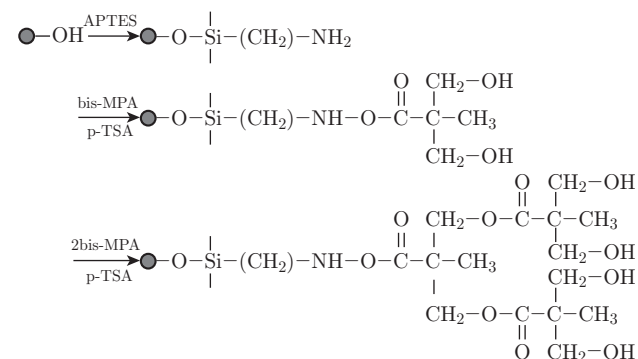
X-Ray Fluorescence (XRF) analysis was carried out with a XRF-1800 analyzer with aperture 10.0 in vacuum. Thermogravimetric analysis (TGA) was carried out with a TGA Q5000 Thermal analyzer at a scan rate of 10°C/min in N₂ atmosphere. X-ray diffraction (XRD) analysis was carried out with a D/MAN-RB X-ray diffraction analyzer, operated at 40 kV and 20 mA over the range 10<2θ<90°.

Melt polycondensation

The mechanism of the introduction of amino and hyperbranched polymer onto α-Al₂O₃ nanoparticles surface was shown in Scheme 1.

The introduction of amino onto Al₂O₃ nanoparticles surface was achieved by the treatment of surface silanol groups with APTES. The example was as follows: into a 500 ml three-necked round-bottom flask with a reflux condenser, 10.0 g of Al₂O₃ nanoparticles, 10.0 mL APTES, 10.0 mL ammonia solution, and 40 mL ethanol were added. The mixture was irradiated ultrasonically for 30 min and then agitated at 500 rpm at 80 °C for 4 h. Next the mixture was heated to 120°C and stirred at temperature for additional 2 h. After ethanol was completely removed, the product was triturated in mortar, and then agitated at 500 rpm at room temperature for 12 h to get tiny particles. The sample was dried in a furnace at 120°C for 1 day.

The AB₂ monomer, bis-MPA, was melt polycondensated according to the method reported previously [10]. The example was as follows: 5.0 g amino-Al₂O₃, 2.5 g bis-MPA and 0.25 g p-TSA were triturated in mortar to achieve a well proportioned mixture. The mixture were added into a three-necked flask with a reflux condenser and agitated at 500 rpm at 200°C for 1 hour, and 40 ml DMF was added into the flask. After that the mixture cooled to room temperature. The mixture was irradiated ultrasonically for 30 min and washed throughout with DMF and next with deionized water until no polymer was found in the filtrate, and then dried in a furnace at 120°C.



Scheme 1. Preparation procedure for the HAPE-Al₂O₃ nanoparticles.

Resusts and discussion

FTIR characterization

Figure 1 shows the infrared spectra of bare Al₂O₃ (a), amino-Al₂O₃ (b), and HAPE-Al₂O₃ (c). The infrared spectrum of amino-Al₂O₃ showed some new absorption appear at 2931.95 cm⁻¹ ascribing to C-H stretching vibration, and 1139.54 cm⁻¹ ascribing to C-N stretching

vibration, which were characteristic of APTES. This suggested that amino group was introduced onto the Al_2O_3 surface. The infrared spectrum of HAPE- Al_2O_3 showed new absorption peak appear at 1734.72 cm^{-1} ascribing to $\text{C}=\text{O}$ of $-\text{COO}-$ stretching vibration, which was characteristic of bis-MPA. This suggested that hyperbranched polymer was successfully grafted onto the amino- Al_2O_3 nanoparticles surface.

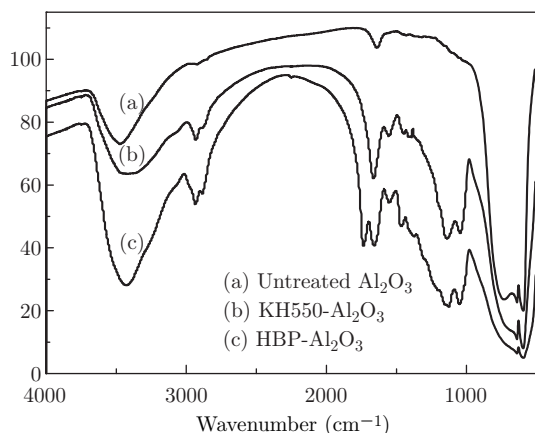


Fig. 1 Shows FTIR spectrum of bare Al_2O_3 (a), amino- Al_2O_3 (b), and HAPE- Al_2O_3 (c).

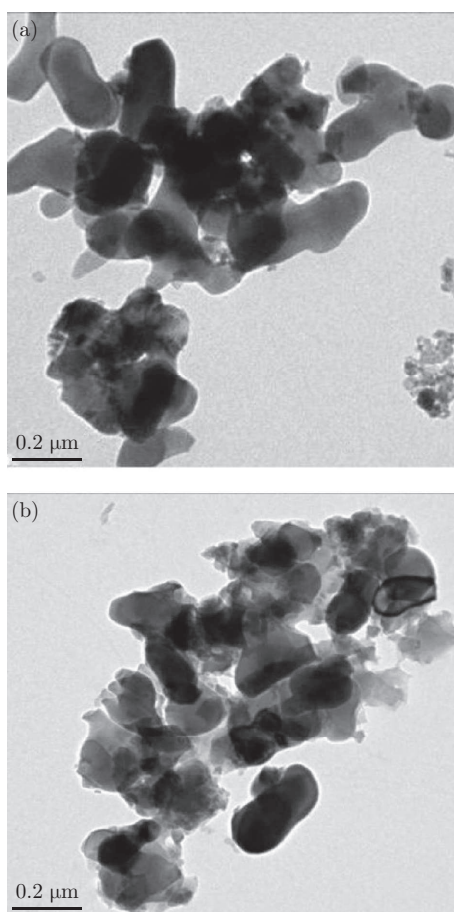


Fig. 2 TEM of Al_2O_3 (a) and Al_2O_3 -HMPA (b)

TEM analysis

Figure 2 shows the TEM of untreated Al_2O_3 and Al_2O_3 -HMPA nanoparticles. There are large bulks in Fig. 2(a), which indicate the untreated Al_2O_3 nanoparticles agglomerated seriously. There are single dispersed nanoparticles, which are surrounded by organic layers to form a thin film in Fig. 2(b), which indicate that HMPA were successfully grafted onto nanoparticles; those agglomerated particles were successfully separated by the strong inorganic-organic interactions.

TGA analysis

Figure 3 Shows the TGA curves of the bare a- Al_2O_3 and HAPE- Al_2O_3 . The bare Al_2O_3 lost weight of 1.7% from 50°C to 800°C in nitrogen atmosphere and the HAPE- Al_2O_3 lost weight of 17.3% in the same condition. In the curve of the bare Al_2O_3 , the weight loss at nearly 100°C could be assigned to the release of solvent adsorbed, and the weight loss at 200°C to 600°C was assigned to the release of the structure water of Al_2O_3 . In the curve of the HAPE- Al_2O_3 , The main weight losses at 200°C were assigned to the release of the thermal degradation of the grafted hyperbranched aliphatic polyester [11]. Comparing these results, it could be concluded that hyperbranched polymer was grafted onto the Al_2O_3 nanoparticles surface.

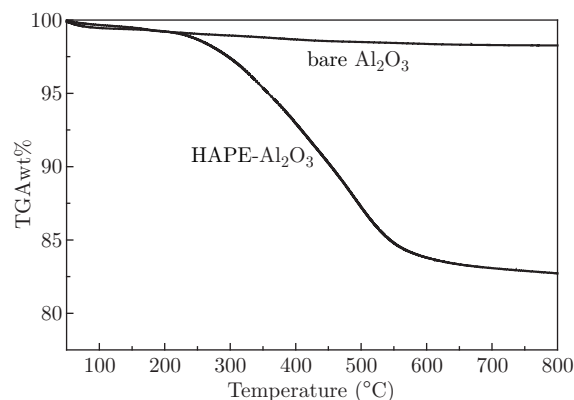


Fig. 3 Shows TGA curves of the bare Al_2O_3 and HAPE- Al_2O_3 .

XRF analysis

The changes of the Al, Si, O, and C element content were demonstrated in the analyses of the bare Al_2O_3 , amino- Al_2O_3 , and HAPE- Al_2O_3 by X-Ray Fluorescence (XRF) analysis (Table 1). It also validates the surface grafting of the hyperbranched aliphatic polyester had been successfully grafted onto the surfaces of Al_2O_3 . The Al content decreased all through the two fabrication steps because both of the surface modified compounds do not contain Al element. And the O element content decreased after the assembly of

the functional silane and the melt polycondensation because the O content of functional silane was lower than that of Al_2O_3 , and the O content of the grafted hyperbranched aliphatic polyester was lower than that of amino- Al_2O_3 . The Si element contents increased after the assembly of the functional silane and then decreased after the melt polycondensation because of the silane contains Si and the monomer does not contain it. The C element content increased through all the two fabricating steps because the C content of the functional silane was higher than Al_2O_3 , and the grafted hyperbranched aliphatic polyester was higher than amino- Al_2O_3 .

Table 1 the compositional data from XRF

XRF analysis (at.%)	Bare Al_2O_3	Amino- Al_2O_3	HAPE- Al_2O_3
Al	52.7281	35.0301	28.5302
O	47.2261	43.0114	41.4008
Si	0.0358	10.4404	7.0702
C	0.0100	11.5182	22.9988

XRD analysis

Figure 4 shows that all the diffraction peaks of bare Al_2O_3 (a), amino- Al_2O_3 (b), and HAPE- Al_2O_3 (c). There was no change of the XRD patterns of the Al_2O_3 after surface modification with the silane and the hyperbranched aliphatic polyester, except for the changes of their intensities, implying that Al_2O_3 was stable enough to experience the surface modification with silane and the hyperbranched aliphatic polyester. On the other hand, no novel diffraction peak appeared after reactions indicated that the highly branched polymers on the surface of Al_2O_3 existed in a form of noncrystalline state [13].

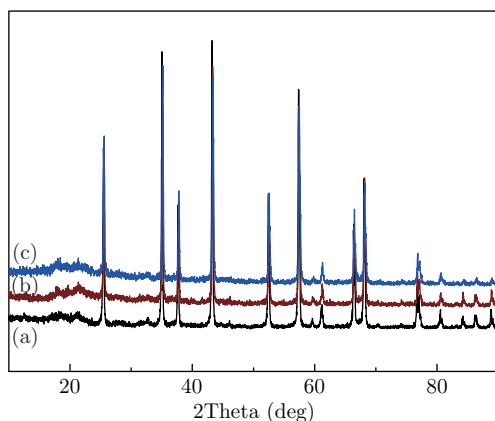


Fig. 4 Shows that all the diffraction peaks of bare Al_2O_3 (a), amino- Al_2O_3 (b), and HAPE- Al_2O_3 (c).

Conclusion

It was concluded that the grafting of hyperbranched polyester onto Al_2O_3 nanoparticles surface was achieved by the one-pot polycondensation of the AB_2 -type monomer bis-MPA, from the surfaces of the amino- Al_2O_3 with p-TSA as catalyst. The grafting technique would provide a facile route to prepare hyperfunctional aluminum oxide having terminal hydroxyl groups. And the products are expected to be used as reactive fillers for polymer composites.

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