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A SIMPLE PROCESS FOR COVALENT HYBRID OF CORE-SHELL AlOOH-POLYGLYCOL

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Abstract

Core-shell AlOOH-polyglycol (APG) was synthesized by refluxing polyglycol with AlOOH nanoparticles in toluene in the presence of *p*-toluene sulphonic acid. The effects of solvent amount on the core-shell structure have been investigated. The morphology and thermal stability of the products were characterized by means of transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The TEM images showed a clarified AlOOH-polyglycol core-shell structure with a diameter of about 200nm. While the infrared spectra (IR) revealed that polyglycol molecules grafted onto AlOOH nanoparticle's surface through covalent combination. A possible formation mechanism of the AlOOH-polyglycol core-shell composites was also proposed. Moreover, APG exhibited excellent mechanical performance in poly (ethylene-co-vinyl acetate) matrix (EVA).

Keywords and phrases: core-shell, AlOOH, polyglycol, graft.
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1. Introduction

Fabrication of core-shell materials with tailored surface properties have attracted extensive attention because their curious structures and fascinating physical, chemical, and mechanical properties [1-5]. Recently, organic shell coating inorganic nanomaterials has been conducted to overcome aggregation and incompatibility between inorganic filler and polymer matrix [6-9]. However, most conventional coatings on AlOOH nanoparticles by way of physisorption and chemisorption are easily peeled off when they encounter violent variation of stresses in polymer matrix [10-12]. Covalent grafting of ethylene glycol into brucite motivated us to probe the possibility of obtaining core-shell nanostructure based on polycondensation between AlOOH and organic molecule through covalent hybrid [13]. In contrast, covalent hybrid core-shell AlOOH-polyglycol (APG) has been rarely reported, in particular, performance of inorganic core and organic shell as an integral whole in polymer matrix remains unknown [14, 15]. Herein, we report the synthesis of core-shell AlOOH-polyglycol (APG) through covalent combination by refluxing polyglycol with AlOOH nanoparticles in toluene in the presence of *p*-toluene sulphonic acid. Meanwhile, the mechanical properties of hybrid nanoparticles are evaluated in EVA. It is expected that one tail of polyglycol grafting onto AlOOH through covalent combination and the other tail anchoring to EVA matrix through physical entanglements and van der Waals interactions would promote mechanical properties of composites [16].

2. Experimental Section

Polyglycol (PEG) 400, *p*-toluene sulphonic acid, toluene and acetone were purchased from Sigma-Aldrich Corporation (analytical grade). Ethanol of analytical grade was purchased from Shenyang Chemical Agents Corporation (China). Aluminum oxide hydroxide with the size ranged from 50nm to 200nm was prepared according to a reported sol-gel process [17]. Deionized water was used throughout the experiments.

AlOOH colloidal solution was prepared by adding 2g AlOOH nanoparticles and appropriate *p*-toluene sulphonic acid into 30mL toluene in ultrasonic at room temperature. And 0.2g polyglycol (MW = 400) was added dropwise into 10ml toluene at room temperature (total amount of toluene is 40ml). And then both of them were mixed together and heated to reflux with stirring for 3h. The water generated from polycondensation between aluminum hydroxide and polyglycol was removed by way of dehydrator. The yielding APG was filtrated and dried in a vacuum oven at 60°C for 12h. To compare the effects of solvent amount, the above-mentioned process was also carried out by using different toluene amount from 10ml to 80ml. The case below 30ml is called as low ratio of solvent and the case above 60ml is called as high ratio of solvent. EVA/APG composites with different loading amount of PG were prepared by melting mixture in a Haake internal mixer at 140°C for 15 min. The composites were molded into sheets of 1mm in thickness for next test.

The morphology of particles was carefully examined under high-resolution transmission electron microscopy (HRTEM, Tecnai G^2-20). Powder X-ray diffraction (XRD) patterns of the particles were recorded on a Rigaku D/max 2400 system using CuKα radiation at 2θ values ranging from 10° to 80°. Thermal analysis was performed on a Mettler-Toledo TGA/SDTA 851e thermal analyzer at a heating rate of 10°C/min from room temperature to 800°C under a static air atmosphere. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-460 plus spectrometer using a KBr disc method. Tensile tests were conducted on a JSL-5000N testing machine (Jiangdu Jingyi Test Instruments Co., Ltd., Jiangsu Province, China) at an extension rate of 200mm/min at room temperature following the GB/T 1040-92 standard. The tensile strength (refers to the peak stress) and elongation at break were recorded. Before testing, the specimens were conditioned at room temperature at least 24h. The test results were the average values of at least ten die-cut dumbbell specimens (1mm thickness).

3. Results and Discussion

The X-ray diffraction (XRD) patterns of both samples (Figure 1) showed that all the Bragg peaks could be indexed to orthorhombic AlOOH (JCPDS Card No. 21-1307). No peaks from other phases can be observed. Compared with raw material (Figure 1(a)), the diffraction intensity of core-shell APG was decreased as seen in Figure 1(b), which could be attributed to the coating of polyglycol onto the AlOOH.

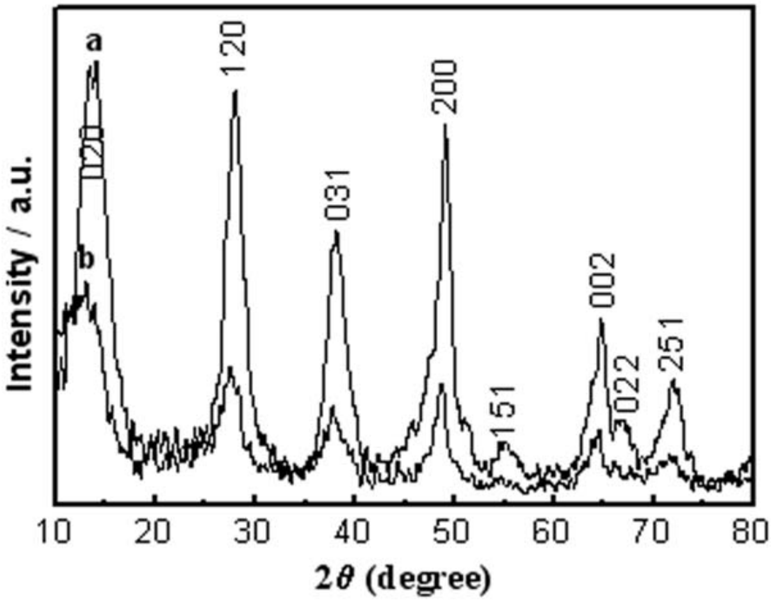
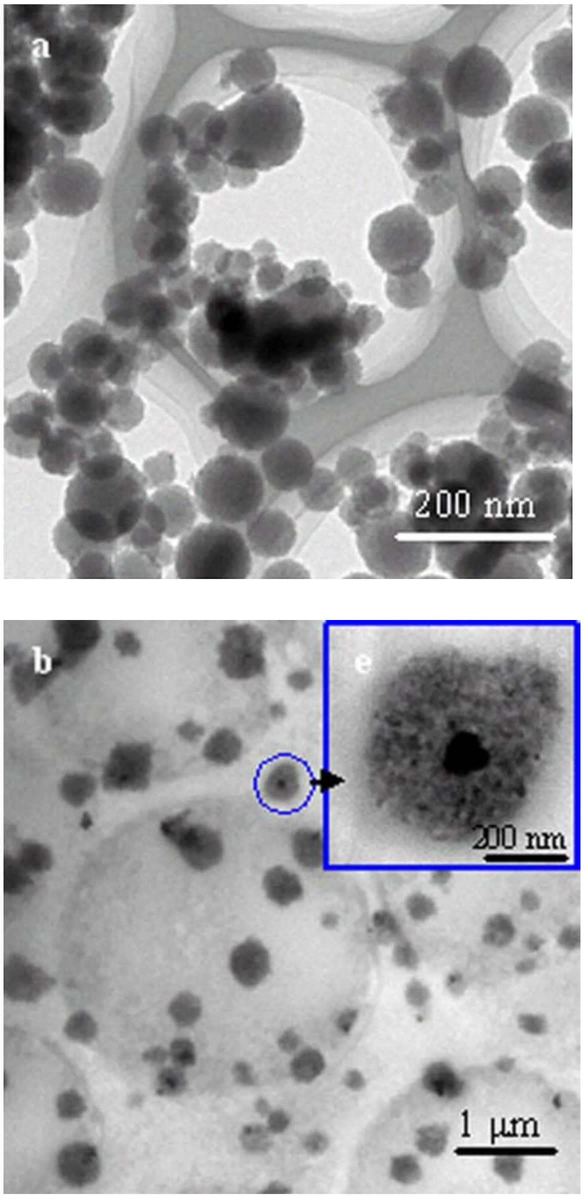


Figure 1. XRD pattern of (a) the raw AlOOH and (b) the core-shell APG.

Typical transmission electron microscopy (TEM) image of raw AlOOH nanospheres is shown in Figure 2(a). We can see that the as-synthesized AlOOH display homogeneous nanospheres with a diameter of 50-100nm. The abundant hydroxyl groups on the surface of AlOOH particles played paramount role on covalent bonding with organic molecules. When the hydroxyl of polyglycol approached to the hydroxyl of AlOOH in toluene molecular cage, polycondensation was about to take place in the presence of *p*-toluene sulphonic acid. As expected, well-dispersed core-shell nanoparticles with an organic shell of about 50nm in thickness were observed in Figure 2(b) and Figure 2(e). Based on the thickness of organic shell, it was supposed that polycondensation would proceed not only between hydroxyl groups of polyglycol and the surface hydroxyl of AlOOH but also among polyglycol themselves. Otherwise, the organic shell might be quite thin. Figure 2(c) and Figure 2(d) show the typical TEM images of the APG samples obtained in low ratio of solvent and high ratio of solvent, respectively. We found that the amount of solvent (toluene in this contribution) is the key factor to achieve the core-shell APG structure. When the amount of solvent was high ratio, the polycondensation between hydroxyl groups of polyglycol would be dominating, leading to the formation of flocculent product separated from AlOOH nanosphere. Intact coating of polyglycol on AlOOH had not been observed in Figure 2(c). On the contrary, the polycondensation among hydroxyl groups of polyglycol and AlOOH proceeded so fast that aggregation of APG nanoparticles was formed when the amount of solvent was low ratio. The results mentioned-above indicate the reaction processes could be facilely controlled by solvent amount constructing appropriate molecular cage.


a
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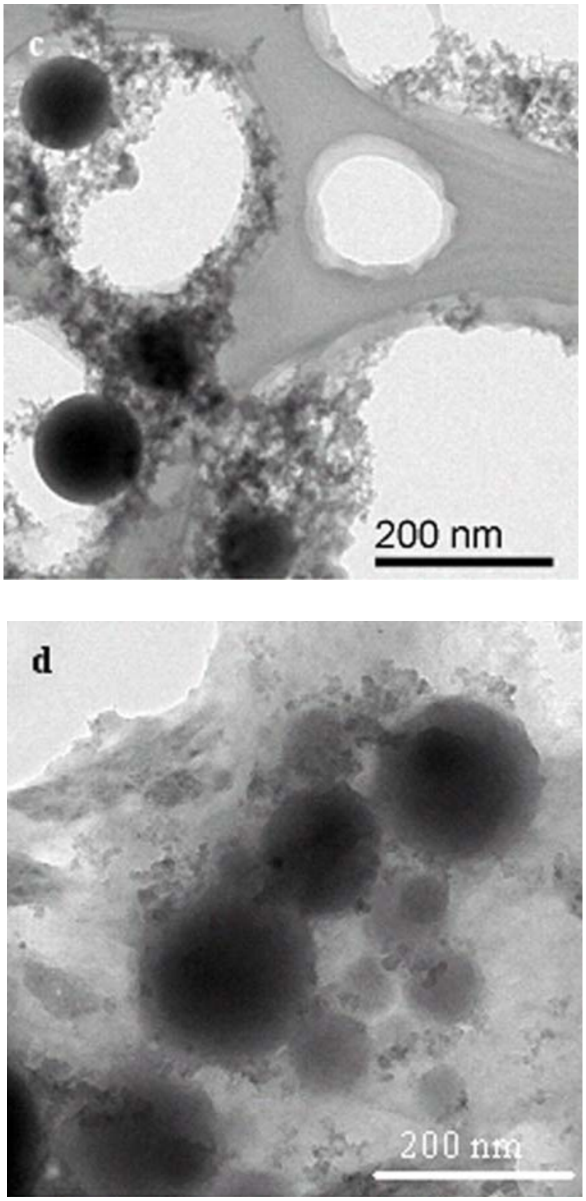

Figure 2. TEM images of (a) the raw AlOOH nanoparticles, (b) the core-shell APG, (c) the sample obtained in high ratio of solvent, and (d) the sample obtained in low ratio of solvent. The inset (e) is a magnification of a single core-shell APG in (b).

The FTIR spectra of raw AlOOH and the APG are shown in Figure 3. AlOOH displays typical hydroxyl stretch band at $3698\mathrm{cm}^{-1}$ and an extended band centered at $3453\mathrm{cm}^{-1}$ relative to hydroxyl stretching of water molecules in various states [18]. Low frequency band at $870\mathrm{cm}^{-1}$ and $986\mathrm{cm}^{-1}$, respectively, assigned to Al–O lattice vibrations. Moderate intensity bands were also observed at $1416\mathrm{cm}^{-1}$, $1517\mathrm{cm}^{-1}$, and $1636\mathrm{cm}^{-1}$ (surface-absorbed/co-intercalated water). APG shows almost the same characteristic bands with AlOOH at $870\mathrm{cm}^{-1}$, $1517\mathrm{cm}^{-1}$, $1636\mathrm{cm}^{-1}$, and $3453\mathrm{cm}^{-1}$. The most important difference between the spectra of raw AlOOH and APG is that two C-H stretching bands of CH_2 groups at $2920\mathrm{cm}^{-1}$ (antisymmetric) and $2857\mathrm{cm}^{-1}$ (symmetric) were formed [19, 20]. One moderate band was observed at $1387\mathrm{cm}^{-1}$, which may be correspondent to oxyethylene units $(\mathrm{O-CH_2-CH_2-O})$. Absorption bands at $1030\text{-}1100\mathrm{cm}^{-1}$, typically attributed to Al–O–C and C–C–O bonds in gibbsite, have been observed at $1042\mathrm{cm}^{-1}$, $1126\mathrm{cm}^{-1}$, and $1179\mathrm{cm}^{-1}$ for APG [21, 22]. The FTIR spectra indicated that polyglycol grafted onto AlOOH' surface through covalent bond interaction.

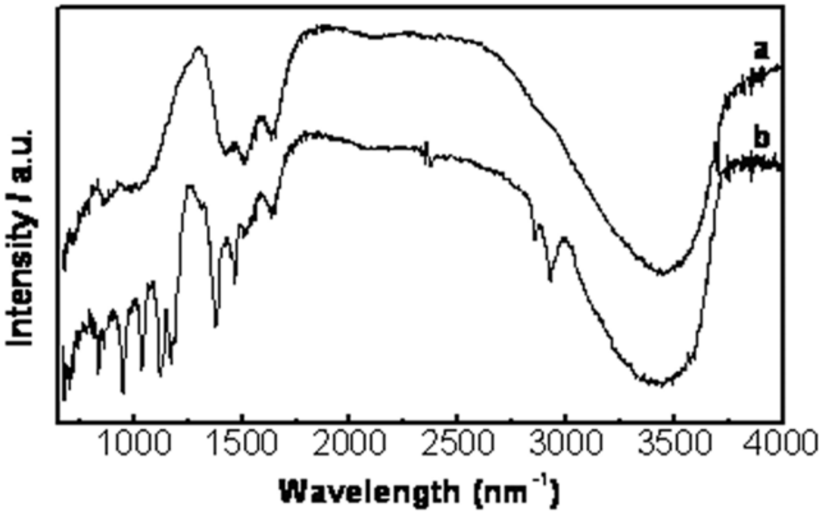

Figure 3. IR spectra of (a) the raw AlOOH and (b) the core-shell APG.

The TG curves of raw AlOOH and the APG are illustrated in Figure 4. The TG curve of the core-shell APG shows that the APG was decomposed through three successive processes at 219ºC, 319ºC, and 525ºC, respectively. The first stage indicates the decomposition of polyglycol, while the others correspond to dehydroxylation or/and the removal of residual organics. In contrast with TG curve of AlOOH (Figure 4(a)), the weight loss stage of APG sample (Figure 4(b)) suggested that polyglycol grafted onto AlOOH. It is thus expected that both thermal and mechanical stabilities of the APG are higher than those based on weak adhesion.

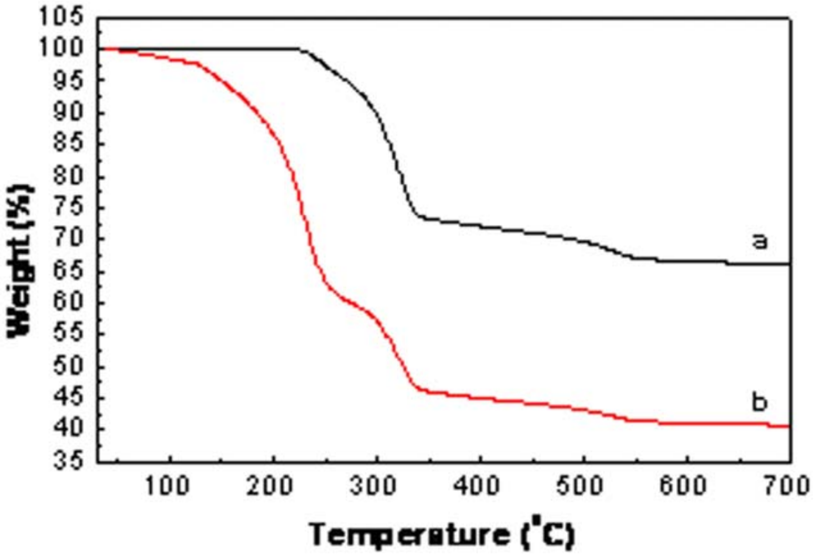

Figure 4. The TG curves of (a) the raw AlOOH and (b) the core-shell APG.

According to our experimental results, a plausible formation process for the core-shell hybrid is shown schematically in Figure 5. Aluminum oxide hydroxide particles with the diameter of 50 ~ 200nm are generated by hydrolysis of aluminum isopropoxide. The hydroxyl groups on surface of aluminum oxide hydroxide react with the hydroxyl groups of polyglycol through polycondensation ①. Meanwhile, similar reaction ② would also take place among polyglycol themselves, which results in the thickness increase of organic shell. Therefore, polyglycol shell with about 50nm in thickness covalently bonded onto aluminum oxide hydroxide to construct core-shell nanostructure.

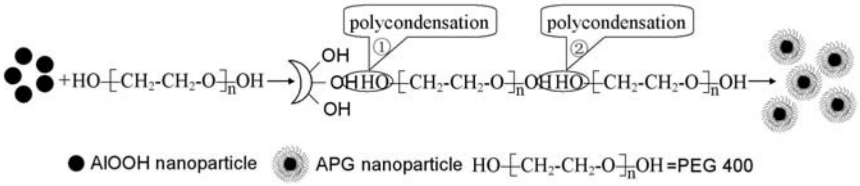

Figure 5. Formation mechanism of core-shell APG.

The test of tensile strength and elongation at break is widely used to evaluate the mechanical performance of as-synthesized core-shell materials in EVA [23]. It can be seen that the tensile strength values of EVA blends decrease gradually with increasing the content of APG as shown in Figure 6. In comparison with the case of untreated AlOOH, however, the tensile strength of EVA blends arrives up to 12.6MPa when the content of APG nanoparticles is 50 wt%. Meanwhile, the elongation at break of composites was promoted from 170% to 190%. One tail of polyglycol grafting onto AlOOH through covalent combination and the other tail anchoring to EVA matrix through physical entanglements and van der Waals interactions would be responsible for better mechanical properties of composites.

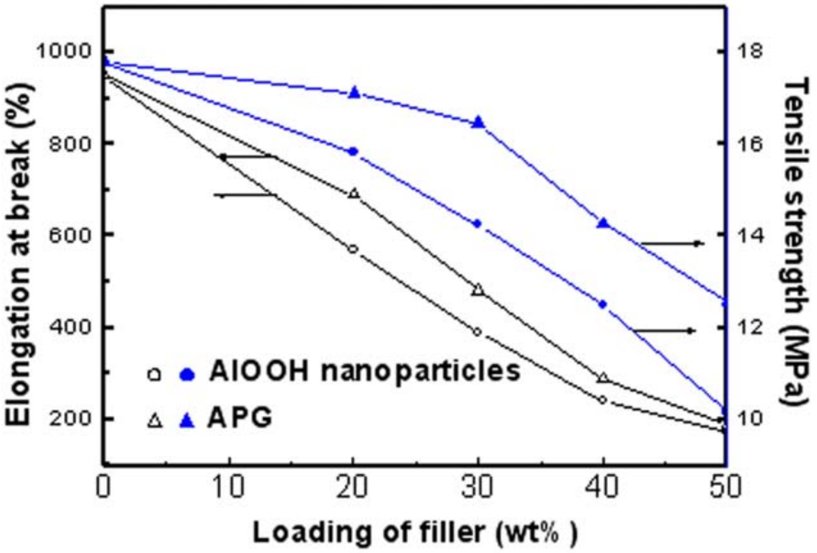

Figure 6. Effect of loading of (a) the raw AlOOH and (b) the core-shell APG on the mechanical properties of EVA composite.

4. Conclusion

A novel core-shell inorganic-organic APG composite has been successfully fabricated through polyglycol grafting onto AlOOH nanoparticles' surface. It is verified that covalent bonds are formed between AlOOH colloid particles and polyglycol chains. The solvent amount has significant influence on core-shell nanostructure of samples. The TEM images showed nanostructured APG with an organic shell of about 50nm in thickness. Moreover, APG exhibited better tensile strength and higher elongation at break in EVA composites.

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