Study on Organic Modification of Lanthanum Oxide

Yunhan SUN¹, Xiaoning Wang¹, Qingxiu JIA¹*, Jian YANG²

¹ School of Materials Design and Engineering, Beijing Institute of Fashion Technology, Beijing, China 100029;
² Beijing Beihua New Rubber Special Material Technology Co., Ltd, Beijing, China 100029

*Corresponding author’s e-mail: jiaqingxiu@163.com

Abstract—In this paper, lanthanum oxide was modified by silane coupling agent (KH560), titanate coupler NDZ-201 and dopamine hydrochloride (DP). The microstructure and chemical structure of modified La₂O₃ were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), and the dispersion of modified lanthanum oxide in polypropylene (PP) was investigated. The results show that the three modifiers can improve the organic properties of lanthanum oxide, and the interfacial compatibility between dopamine modified La₂O₃ and PP is better than the other two modifiers.

1. Introduction

Rare earth has a special 4f electron layer structure, which can absorb energy particles from 38.9kev to 63kev, and can effectively compensate the lead in the weak energy absorption region. It is a good radiation protection material. A variety of rare earth/polymer radiation protection materials have been developed, such as rare earth/NR composite[1-2], rare earth / PP composite fibers[3-5], and rare earth doped barium tellurate glass[6].

As inorganic materials, the interface between rare earth and organic polymers is very poor, resulting in poor mechanical properties of the composites. Therefore, organic modification of rare earth is needed to improve the compatibility, interfacial strength and dispersion between rare earth and polymer matrix. Acrylic acid, methacrylic acid and silane coupling agent are generally used for organic modification of rare earth [1-6]. However, the structure and modification methods of these modifiers are relatively simple, and the effects of modifier types on the structure and properties of rare earth and its dispersion in polymers have not been studied in detail.

In this paper, silane coupling agent KH560, titanate coupler NDZ-201 and dopamine were used as modifiers to investigate the effects of different modifiers on the structure and properties of rare earth lanthanum oxide and its dispersion in polypropylene matrix. The results can provide a reference for the preparation of rare earth / polymer composites.

2. EXPERIMENTAL

2.1. Materials

Polypropylene (PP), spinning grade, density 0.9g/cm³, melt index 25g/min(235℃,2.16kg), Sinopec Group; Lanthanum oxide (nano grade, ≥99.99%), China Beijing Nonferrous Metals Research Institute; dopamine hydrochloride (analytical purity, ≥99.9%), titanate coupler NDZ-201 (analytical purity,
≥99%), and KH560 (analytical purity, ≥98%), Beijing Chemical Reagent Company. All other reagents used are commercially available.

2.2. Organic modification of La$_2$O$_3$

First, the modifier and the organic solvent were mixed in a certain ratio to obtain a solution, the pH value was adjusted, and then lanthanum oxide was added to the above solution, and ultrasonic treatment was performed for a certain period of time to carry out sufficient organic modification. Then, the modified lanthanum oxide was put into a blast drying oven and dried at 40°C to remove the solvent, and finally lanthanum oxides modified with different modifiers were obtained. The solution ratio and experimental conditions used in three modification processes are shown in Table 1.

| Modifier                        | Solution                      | Weight ratio of modifier to La$_2$O$_3$ | pH value          | Time of ultrasonic processing | Blast drying conditions |
|---------------------------------|-------------------------------|-----------------------------------------|-------------------|-------------------------------|-------------------------|
| silane coupling agent (KH560)   | absolute ethanol: deionized water: KH560: acetone=70:28:1:1 (v:v) | 1:25                      | 3–5 adjusted with acetic acid | 0.5 h                      | 40 °C, 24h              |
| dopamine hydrochloride (DP)     | absolute ethanol: deionized water: dopamine=50:49:1 (v:v)        | 1:25                      | 8 adjusted with trimethylol aminomethane | 0.5 h                      | 40 °C, 24h              |
| titanate coupler NDZ-201 (NDZ201)| ethanol:NDZ201=99:1 (w:w)          | 1:25                      | 7                 | 0.5 h                      | 40 °C, 24h              |

2.3. Preparation of modified La$_2$O$_3$ blends with PP

The modified lanthanum oxide and PP were added to the twin-screw Haake extruder at a mass ratio of 30:100, blended for 10 minutes under the conditions of 210 °C and 100 r/min, and extruded to obtain a modified lanthanum oxide/PP composite.

2.4. Characterization

**Scanning electron microscopy (SEM)** Surface observation of rare earth particles and composite fibers before and after modification was carried out using a Japan Electron JSM-7500F type field emission scanning electron microscope, and the surface gold spraying method was used to prepare the observation samples with a thickness of about 10 nm.

**X-ray photoelectron spectroscopy (XPS)** The relative content of La2O3 powder elements was measured using a Model 250 X-ray photoelectron spectrometer manufactured by Excalab.
3. Results and Discussions

3.1. Morphology of La$_2$O$_3$ particles

The micro morphology of La$_2$O$_3$ before and after modification is shown in Figure 1. It can be seen that the shape of unmodified La$_2$O$_3$ particles is irregular, the particle size is about 1 ~ 2 μ m, and some particles agglomerate. After modification with KH560 and DP, the particle size of La$_2$O$_3$ is less than 1 μ m, and there is no agglomeration between particles. This may be due to the grafting of modifier molecules on the surface of La$_2$O$_3$, which increases the molecular spacing of modified particles and reduces particle agglomeration. Although the particle size of NDZ201 modified Lanthanum oxide decreased, some particles still agglomerated, but the particle size of the agglomerated lanthanum oxide was smaller than that of unmodified La$_2$O$_3$.

3.2. XPS analysis

Figure 2 shows the total XPS spectrum of modified La$_2$O$_3$ obtained using different modifiers, and Table 2 shows the XPS elemental content of modified La$_2$O$_3$. From Figure 2 and Table 2, it can be seen that C, O and La elements were detected in the unmodified La$_2$O$_3$, with the highest content of O elements, followed by the content of C elements and the lowest content of La elements. The presence of carbon elements may be due to the presence of La$_2$O$_2$(CO$_3$) in the system. The KH560 modified La$_2$O$_3$, the DP modified La$_2$O$_3$ and the NDZ201 modified La$_2$O$_3$ have more Si elements, N elements, and P elements compared with the unmodified La$_2$O$_3$, indicating that the modifier KH560, dopamine, and NDZ201 have been successfully grafted to La$_2$O$_3$ surface.
Table 2 XPS elemental content of modified La$_2$O$_3$

|                     | C 1s(%) | O 1s(%) | La 3d(%) | Si 2p(%) | N 1s(%) | P 2p(%) |
|---------------------|---------|---------|----------|----------|---------|---------|
| unmodified La$_2$O$_3$ | 26.67   | 36.02   | 10.65    | —        | —       | —       |
| KH560 modified La$_2$O$_3$ | 12.44   | 21.31   | 5.61     | 60.64    | —       | —       |
| DP modified La$_2$O$_3$   | 35.42   | 48.9    | 12.82    | —        | 2.86    | —       |
| NDZ201 modified La$_2$O$_3$ | 29.18   | 44.76   | 13.63    | —        | —       | 12.34   |

Fig. 3 XPS spectra of unmodified La$_2$O$_3$ (a) C 1s high-resolution XPS spectrum; (b) O 1s high-resolution XPS spectrum; (c) La 3d high-resolution XPS spectrum

The elemental high fraction XPS spectra of unmodified La$_2$O$_3$, KH560 modified La$_2$O$_3$, DP modified La$_2$O$_3$ and NDZ201 modified La$_2$O$_3$ are shown in Fig. 3, 4, 5, and 6, respectively. In the C 1s spectrum of La$_2$O$_3$ shown in Fig. 3(a), the 284.8 eV peak originates from the indeterminate carbon in chalcocite, while 289.7 eV corresponds to La$_2$O$_2$(CO$_3$) in La$_2$O$_3$; in the O 1s spectrum of La$_2$O$_3$ shown in Fig. 3(b), the 530.9 eV and 531.3 eV correspond to La$_2$O$_3$ and La(OH)$_3$, respectively; in La 3d spectra of La$_2$O$_3$ shown in Fig. 3(c), 835.9 eV, 839.5 eV, and 852.7 eV correspond to La$_2$O$_3$, La(OH)$_3$, and La(III) in La$_2$O$_3$, respectively.
The O 1s spectrum of KH560 modified La$_2$O$_3$ was fitted to the split peaks and the results are shown in Fig.4(b). From Fig.4(b), it can be seen that the fitted O 1s spectrum has only one peak, which is located at the binding energy of 530.8 eV. It is known that this place is O in the structure of La(OH)$_3$. A split-peak fit to the Si 2p spectrum of KH560 modified La$_2$O$_3$ is shown in Fig.4(d). From Fig. 4(d), it can be seen that the fitted Si 2p spectrum has three peaks located at binding energies of 101.3 eV, 104.5 eV, and 107.6 eV, respectively. Among them, the peak at 101.3eV is Si with Si-O-Si structure; the peak at 104.5eV is Si with Si-O-OH structure; and the peak at 107.6eV is Si with Si-O-C structure. From the structure of KH-560, there is only one chemical state of element Si, i.e., Si-O-C structure; the appearance of Si-O-Si structure, further surface KH 560 has chemically reacted with the surface of La$_2$O$_3$ to generate new chemical bonds.
Fig. 5 XPS spectra of DP modified La$_2$O$_3$ (a) C 1s high-resolution XPS spectrum; (b) O 1s high-resolution XPS spectrum; (c) La 3d high-resolution XPS spectrum; (d) N 1s high-resolution XPS spectrum

The C 1s spectrum of DP modified La$_2$O$_3$ was fitted to the split peaks and the results are shown in Fig. 5(a). From Fig. 5(a), it can be seen that the fitted C 1s spectrum has three peaks located at binding energies of 284.8 eV, 286.1 eV, and 289.6 eV, respectively. Among them, the peak at 284.8 eV is C in the C-H/C-O structure; the peak at 285.9 eV is C in the -C-O structure; and the peak at 289.1 eV is C in the -C=O structure. The N 1s spectrum of DP modified La$_2$O$_3$ was fitted to the split peaks, and the results are shown in Fig. 5(d). From Fig. 5(d), it can be seen that the fitted N 1s spectrum has one peak located at the binding energy of 399.6 eV. It is known that this location is the N in the R-NH2-R structure. The appearance of the N 1s peak spectrum further proves that dopamine chemically reacted with the surface of La$_2$O$_3$ and successfully grafted on the surface of La$_2$O$_3$. 
Fig. 6 XPS spectra of NDZ201 modified La$_2$O$_3$ (a) C 1s high-resolution XPS spectrum; (b) O 1s high-resolution XPS spectrum; (c) La 3d high-resolution XPS spectrum; (d) P 2p high-resolution XPS spectrum

The C 1s spectrum of NDZ201 modified La$_2$O$_3$ was fitted to the split peaks and the results are shown in Fig. 6(a). From Fig. 6(a), it can be seen that the fitted C 1s spectrum has three peaks located at binding energies of 284.8 eV, 286.1 eV, and 289.6 eV, respectively. Among them, the peak at 284.8 eV is C in the C-H/C-O structure; the peak at 286.1 eV is C in the -C-O structure; and the peak at 289.6 eV is C in the -C=O structure. The P 2p spectrum of KR-La$_2$O$_3$ was fitted to the split peaks, and the results are shown in Fig. 6(d). From Fig. 6(d), it can be seen that the fitted P 2p spectrum has three peaks located at the binding energy of 129.4 eV, 133.4 eV, and 136.6 eV, respectively. Among them, the peak at 129.4 eV is the P in the P 2p orbital; the peak at 133.4 eV is the P in the LaPO$_4$ structure; and the peak at 136.6 eV is the P in P$_2$O$_5$. The comparative analysis with the elemental spectrum of La$_2$O$_3$ further proves that the phthalate coupling agent reacted chemically with the surface of La$_2$O$_3$ and successfully grafted on the surface of La$_2$O$_3$.
3.3. Morphology and modified La$_2$O$_3$/PP composites

Fig.7 SEM micrographs of (a) KH560 modified La$_2$O$_3$/PP composite; (b) DP modified La$_2$O$_3$/PP composite; (c) NDZ201 modified La$_2$O$_3$/PP composite; (d) unmodified La$_2$O$_3$/PP composite

Figure 7 shows the SEM micrographs of La$_2$O$_3$/PP composites modified by different modifiers. Unmodified La$_2$O$_3$ agglomerates seriously in polypropylene matrix (Fig. 7 (d)), and many particles precipitate from the matrix. The interfacial bonding and filler dispersion of three modified La$_2$O$_3$/PP composites are obviously better than those of unmodified La$_2$O$_3$/PP composite. Compared with three kinds of modified Lanthanum oxide, NDZ201 modified La$_2$O$_3$ still has agglomeration, and the dispersed particle size is relatively large. KH560 modified La$_2$O$_3$ is well blended with PP matrix, and the dispersed particle size decreases significantly. In DP modified lanthanum La$_2$O$_3$/PP composites, rare earth is evenly dispersed without aggregation, and the cross-section of the composite is very smooth which means a good interface bonding between La$_2$O$_3$ and matrix.

4. Conclusion
Modification of La$_2$O$_3$ by silane coupling agent (KH560), titanate coupler NDZ-201 and dopamine hydrochloride (DP) and the dispersion of modified rare earth in PP matrix were investigated. The three modifiers can improve the organic properties of lanthanum oxide and the interfacial bonding between lanthanum oxide and PP. Among them, DP has the best modification effect on lanthanum oxide. The DP modified La$_2$O$_3$ can disperse evenly in PP matrix with good interface bonding. KH560 also can improve the dispersion of La$_2$O$_3$ in PP. However, the dispersion of NDZ201 modified La$_2$O$_3$ in the matrix is still poor. In general, dopamine and KH560 can effectively improve the interfacial bonding between lanthanum oxide and polymer, and improve its dispersion in polymer matrix, which is conducive to high-performance lanthanum oxide/polymer composites or fiber materials.

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