Preparation of Yttrium Oxide Hollow Microspheres and Low-Frequency Damping Properties of Their Composite Rubber (Postprint)

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Abstract

Using polymethyl methacrylate (PMMA) microspheres prepared by dispersion polymerization as sacrificial templates, PMMA/yttrium basic carbonate (Y(OH)CO3) composite microspheres were prepared via homogeneous precipitation. After high-temperature calcination, yttrium oxide (Y2O3) hollow microspheres were obtained, which were then compounded with butyl rubber to prepare composite rubber materials with low-frequency high-damping properties. The morphology and structural composition of the Y2O3 hollow spheres were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TG), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The results demonstrated that the Y2O3 hollow spheres consisted of particles with a cubic fluorite structure, featuring an outer hollow diameter of 1 m and a shell thickness of approximately 80 nm. Y2O3/butyl rubber composites were prepared by incorporating Y2O3 hollow microspheres and powder as fillers into butyl rubber, respectively. Compared with the addition of Y2O3 powder, the incorporation of Y2O3 hollow spheres significantly enhanced the damping properties of butyl rubber, exhibiting relatively large loss factors near 8, 18, 28, 50, 65, and 90 Hz.

Full Text

Preamble

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Title: Preparation of Y_2O_3 Hollow Microspheres and Low-Frequency Damping Properties of Rubber Composites Reinforced with Y_2O_3 Hollow Microspheres

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Abstract

Poly(methyl methacrylate) (PMMA) spheres were first prepared through dispersion polymerization. Using these as sacrificial templates, PMMA/yttrium hydroxycarbonate ($Y(OH)CO_3$) composite microspheres were prepared by homogeneous precipitation. Y_2O_3 hollow spheres were then obtained by calcination of the PMMA/$Y(OH)CO_3$ composite at elevated temperature. Finally, Y_2O_3 hollow sphere-reinforced butyl rubber composites were fabricated. The structure and morphology of the Y_2O_3 hollow microspheres were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermogravimetric analysis (TG). The results show that the hollow spheres were composed of Y_2O_3 particles with a face-centered cubic crystallographic structure, with a diameter of approximately 1 m and a thin shell thickness of about 80 nm. Butyl rubber composites were prepared by adding Y_2O_3 hollow microspheres and Y_2O_3 powders as fillers, respectively. The butyl rubber composites with Y_2O_3 hollow spheres exhibited significantly improved damping properties compared to those with Y_2O_3 powders, showing larger loss factors at frequencies of 8, 18, 28, 50, 65, and 90 Hz.

Keywords

composites, polymethyl methacrylate, template, Y_2O_3, hollow spheres, low-frequency damping, butyl rubber

Introduction

Rare earth oxides are functional materials used in applications such as high-efficiency photonic crystals and catalysts. Yttrium oxide (Y_2O_3) is an excellent phosphor host material widely used in fluorescent lamps, field emission displays, and cathode ray tubes, offering good chemical resistance, thermal stability, and low phonon energy. In recent years, Y_2O_3 nanoparticles with various morphologies have been prepared through different methods, including nanoparticles, nanorods, nan powders, nanospheres, and nanohollow spheres. Among these, Y_2O_3 hollow microspheres with controllable size and morphology can reduce the consumption of expensive rare earth materials and lower the cost of phosphor materials. Methods for synthesizing Y_2O_3 hollow microspheres include one-step hydrothermal methods, polystyrene (PS) template methods, carbon sphere template methods, and melamine-formaldehyde (MF) resin template methods.

Noise pollution seriously affects quality of life. Current noise monitoring primarily focuses on medium and high-frequency noise from industrial production and transportation, while low-frequency noise (<250 Hz) has not received sufficient attention. Low-frequency noise can directly reach the human ear bone and is extremely harmful. Compared with medium and high-frequency sound waves, low-frequency sound waves decay slowly in air, have long wavelengths, easily bypass obstacles, and possess strong penetration ability. Traditional sound-absorbing materials currently in use exhibit poor absorption of low-frequency sound waves. Therefore, developing lightweight low-frequency sound-absorbing materials is of significant practical importance. The sound-absorbing performance of viscoelastic rubber materials depends on both the rubber matrix and fillers. Studies by White and Yu Ligang have shown that the introduction of hollow materials can improve the mechanical damping of viscoelastic composites and attenuate low-frequency sound waves. In addition to adding fillers, foaming, or changing the structure of rubber sound-absorbing components, the sound-absorbing performance of rubber can also be enhanced by combining it with optical, electrical, or magnetic effects.

In this work, monodisperse PMMA microspheres synthesized by dispersion polymerization were used as templates. Y_2O_3 hollow spheres were prepared by urea-based homogeneous precipitation and high-temperature calcination. Y_2O_3/butyl rubber composites were then fabricated using both Y_2O_3 hollow microspheres and powders as fillers to investigate the effect of the hollow structure on low-frequency damping performance.

Experimental Methods

Materials

Polyvinylpyrrolidone (PVP) K-30, methyl methacrylate (MMA), urea, yttrium nitrate hexahydrate, azobisisobutyronitrile (AIBN), methanol, and anhydrous ethanol were all analytical grade. Deionized water was laboratory-prepared.

Preparation of PMMA Microspheres

Monodisperse PMMA microspheres were prepared by dispersion polymerization. In a 250 ml three-neck flask, a certain amount of refined MMA monomer, dispersant PVP, initiator AIBN, and dispersion medium (deionized water and methanol) were added. The mixture was stirred at 3000 r/min for pre-dispersion for 0.5 h, then slowly heated to 75°C. After 1 h of constant temperature reaction, a prepared mixture (0.25 g monomer, 1.625 g methanol, and 0.825 g deionized water) was added dropwise. After the addition was complete, the reaction continued at constant temperature for 4 h, then cooled and collected.

Preparation of Y_2O_3 Hollow Microspheres

Five milliliters of the prepared PMMA emulsion were washed with methanol and deionized water. Then, 0.1 g of PMMA microspheres and 0.5 g of PVP were added to 20 ml of deionized water and ultrasonically dispersed for 20 min. A freshly prepared 1 mmol yttrium nitrate hexahydrate solution was added, followed by ultrasonic dispersion to obtain a homogeneous suspension. The suspension was transferred to a three-neck flask, heated to 85°C under stirring at 3000 r/min, and 30 ml of 25% urea aqueous solution was added uniformly. After reacting at 85°C for 5 h, the product was filtered, washed with deionized water and anhydrous ethanol, and dried in a vacuum oven at 50°C for 12 h to obtain PMMA/$Y(OH)CO_3$ composite microspheres. The dried composite microsphere powder was calcined in a muffle furnace at 900°C for 4 h to obtain Y_2O_3 hollow spheres.

Preparation of Y_2O_3/Rubber Composites

Y_2O_3 hollow spheres (100 parts by weight) and coupling agent (1-5 parts) were placed in a high-speed mixer and stirred at 1200-1500 r/min for 10-30 min to obtain pretreated hollow spheres. Butyl rubber was plasticized on a two-roll mill for 3 min, then pretreated Y_2O_3 hollow spheres, zinc oxide, stearic acid, sulfur, softener, and benzothiazole disulfide were added sequentially. The mixture was milled for 15 min to obtain a uniformly dispersed compound. The compound was vulcanized at 140°C for 30 min to obtain the Y_2O_3/rubber composite.

Characterization

FT-IR spectra of the monodisperse microsphere samples were recorded using a Magna-IR750 Fourier transform infrared analyzer. The morphology and particle size of the precursor PMMA/$Y(OH)CO_3$ composite microspheres and Y_2O_3 hollow sphere samples were characterized using a JSM-5510LV scanning electron microscope (SEM) and a Hitachi H600-2 transmission electron microscope (TEM). Thermogravimetric (TG) curves were measured using a KRATOS SAM-PTR-2 thermobalance and CR-T high-temperature differential thermal analyzer. The crystal structure of samples calcined at different temperatures was determined using a D/MAX-III X-ray diffractometer (XRD). The damping properties of the samples were tested using a DMA27 viscoelastic spectrometer in double cantilever beam mode to determine the loss factor (tanδ).

Results and Discussion

2.1 Morphology and Structure Analysis

[Figure 1: see original paper] shows SEM images of PMMA microsphere templates, PMMA/$Y(OH)CO_3$ composite microspheres, Y_2O_3 hollow spheres, and a TEM image of Y_2O_3 hollow spheres. As shown in [Figure 1: see original paper]a, the PMMA microspheres prepared by dispersion polymerization were

relatively uniform in size with a diameter of approximately 0.9 µm and good monodispersity. The PMMA/$Y(OH)CO_3$ composite microspheres in [Figure 1: see original paper]b inherited the spherical morphology and good monodispersity of the template microspheres. During the self-assembly and homogeneous precipitation process, the PMMA microsphere surface was coated with relatively loose precursor particles, increasing the particle size to 1.2 µm. [Figure 1: see original paper]c shows that the Y_2O_3 hollow spheres had a diameter of approximately 1 µm, representing a certain degree of shrinkage compared to the PMMA/$Y(OH)CO_3$ composite microspheres. This shrinkage occurred because the nano-sized Y_2O_3 in the shell layer crystallized during high-temperature calcination, forming nanoparticles that accumulated on the template surface, and the shrinkage during calcination made the arrangement more compact, reducing the particle size. The TEM image in [Figure 1: see original paper]d reveals the hollow structure of the Y_2O_3 spheres, with a lighter center and a darker outer ring after removal of the PMMA template. The outer layer of the Y_2O_3 hollow spheres was formed by the close packing of dense Y_2O_3 nanoparticles, with a particle size of approximately 1 µm and a shell thickness of about 80 nm, which is consistent with the SEM analysis results.

2.2 FT-IR Analysis

[Figure 2: see original paper] presents FT-IR spectra of PMMA microspheres, PMMA/$Y(OH)CO_3$ composite microspheres, and Y_2O_3 hollow spheres. In [Figure 2: see original paper]a, the peaks at 2992 cm^{-1} and 2951 cm^{-1} correspond to the stretching vibrations of methyl and methylene groups, respectively. The peak at 1730 cm^{-1} represents the characteristic C=O stretching vibration in PMMA microspheres. The peaks at 1446 cm^{-1} and 1487 cm^{-1} are characteristic of methylene bending vibrations, while the range of 1148-1270 cm^{-1} corresponds to C-O-C stretching vibrations. [Figure 2: see original paper]b shows that the characteristic peaks of PMMA microspheres still existed but were significantly weakened, indicating that $Y(OH)CO_3$ formed by yttrium nitrate hydrolysis was well-coated on the PMMA microsphere surface. In [Figure 2: see original paper]c, all characteristic peaks related to PMMA microspheres disappeared, indicating that the PMMA template had been completely removed. The peak at 584 cm^{-1} corresponds to the Y-O characteristic peak, which is consistent with the standard Y_2O_3 spectrum, confirming that Y_2O_3 was obtained after calcination at 900°C.

2.3 TG Curve Analysis

[Figure 3: see original paper] shows TG curves for PMMA microspheres (curve a), PMMA/$Y(OH)CO_3$ composite microspheres (curve b), and Y_2O_3 hollow spheres (curve c). For the PMMA microspheres, weight loss below 320°C was mainly due to evaporation of residual solvents and physically adsorbed water, while weight loss in the 320-500°C range resulted from combustion and decomposition of PMMA microspheres. Almost no residue remained above 500°C,

indicating complete decomposition of PMMA microspheres at 500°C. For the PMMA/$Y(OH)CO_3$ composite microspheres, three weight loss regions were observed: below 350°C, 350-550°C, and 550-800°C. The region below 350°C corresponded to evaporation of physically adsorbed water, the 350-550°C region to decomposition of PMMA microspheres, and the 550-800°C region to chemical decomposition of $Y(OH)CO_3$, releasing water and carbon dioxide. The Y_2O_3 hollow spheres showed almost no weight loss, indicating that the PMMA microspheres had been completely removed from the $Y(OH)CO_3$/PMMA composite microspheres during high-temperature calcination, and no organic substances remained in the Y_2O_3 hollow spheres, confirming their successful preparation.

2.4 XRD Analysis

[Figure 4: see original paper] shows XRD patterns of PMMA/$Y(OH)CO_3$ composite microspheres calcined at 500°C, 700°C, and 900°C for 4 h. As shown in [Figure 4: see original paper], the sample calcined at 500°C exhibited indistinct peaks, indicating an amorphous structure ([Figure 4: see original paper]a). The sample calcined at 700°C showed obvious diffraction peaks corresponding to Y_2O_3, but the peaks were not well-defined, indicating that Y_2O_3 had begun to crystallize but the process was incomplete ([Figure 4: see original paper]b). [Figure 4: see original paper]c shows that after calcination at 900°C, distinct diffraction peaks appeared at 2 = 29.17°, 33.79°, 48.54°, and 57.62°, which correspond to the (222), (400), (440), and (622) planes of Y_2O_3, respectively, according to the standard Y_2O_3 diffraction card (JCPDS 25-1200). This indicates that the Y_2O_3 hollow microspheres obtained after calcination at 900°C had a complete crystal structure and pure cubic phase.

2.5 XPS Analysis

[Figure 5: see original paper] shows the XPS wide-scan spectrum and Y 3d scan spectrum of Y_2O_3 hollow microspheres. As shown in [Figure 5: see original paper]a, only Y 3d, O 1s, and C 1s peaks were observed in the wide-scan XPS spectrum, with no impurity peaks. The C 1s peak originated from contaminant carbon used for calibrating the electron binding energy, confirming that the product contained only yttrium and oxygen elements. [Figure 5: see original paper]b presents the Y 3d spectrum of Y_2O_3 hollow spheres, where the characteristic peak at 157.78 eV indicates that yttrium primarily exists in the +3 oxidation state. The oxygen characteristic peak at 530.1 eV in [Figure 5: see original paper]a indicates that the oxygen in the sample is O^{2-} rather than adsorbed oxygen, further confirming that the composition of the obtained hollow spheres is Y_2O_3.

2.6 Low-Frequency Damping Properties of Y_2O_3 Hollow Sphere/Butyl Rubber Composites

Rubber materials with high internal friction and good damping properties, such as butyl rubber, nitrile rubber, and polyurethane rubber, are suitable for sound-

absorbing applications. The damping performance of materials is generally characterized by internal friction (tanδ). [Figure 6: see original paper] shows the internal friction (tanδ) of butyl rubber composites filled with 30 parts of Y_2O_3 powder and Y_2O_3 hollow spheres at different temperatures. As shown in [Figure 6: see original paper], the addition of Y_2O_3 filler improved the damping properties of butyl rubber, and the composites with Y_2O_3 hollow spheres exhibited better damping performance than those with Y_2O_3 powder. This is because the addition of various inorganic or organic fillers containing bubble-like structures, such as cork powder, metal powder, vermiculite powder, and hollow glass microspheres, can form uniformly stable cavity structures in rubber, effectively increasing internal friction and improving the mechanical damping of viscoelastic composites.

[Figure 7: see original paper] shows the damping properties of butyl rubber composites filled with 30 parts of Y_2O_3 powder and Y_2O_3 hollow spheres at room temperature (25°C) over a frequency range of 0-100 Hz. [Figure 7: see original paper] indicates that compared with Y_2O_3 powder, the addition of Y_2O_3 hollow spheres significantly improved the damping properties of butyl rubber. The composites exhibited multiple damping peaks in the 0-100 Hz range, with larger loss factors at frequencies near 8, 18, 28, 50, 65, and 90 Hz, making them suitable for vibration and noise reduction in different low-frequency environments.

Conclusion

Using monodisperse PMMA microspheres with a diameter of 0.9 m as templates, PMMA/$Y(OH)CO_3$ core-shell composite microspheres were prepared by homogeneous precipitation. After high-temperature calcination to remove the templates, Y_2O_3 hollow microspheres were successfully obtained. The hollow spheres had a diameter of approximately 1 m and a shell thickness of about 80 nm, with a cubic crystal system and chemical composition of Y_2O_3. Compared with the addition of Y_2O_3 powder, the addition of Y_2O_3 hollow spheres significantly improved the damping properties of butyl rubber. The composites exhibited multiple damping peaks in the 0-100 Hz range, with larger loss factors at frequencies near 8, 18, 28, 50, 65, and 90 Hz.

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Note: Figure translations are in progress. See original paper for figures.