Fabrication and characterization of Eco-Friendly Heat Insulating Materials using inorganic Nanofillers such as Titanate Nanotubes and Layered Double Hydroxides

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ABSTRACT

In this work, we have synthesized Titanate nanotube(TiNT) and Layered Double Hydroxide(LDH) nanoparticles and studied about their applicable properties as inorganic filler due to their high porous structure, and then the obtained nanoparticles were dispersed in exfoliated vermiculites, in order to apply this technology to the fabrication process of vermiculite-TiNT/LDH filler composites for heat inulating materials. The changes in thermal conductivity of heat insulating composites was compared according to the type and amount of inorganic filler. The thermal conductivities were confirmed to be reduced in proportion with the amount of inorganic nanofillers, which led to more effective heat insulating properties. Especially, the trends were observed more obviouly in TiNT with more porous structure.

Keywords: heat insulating material, nanofiller

1 INTRODUCTION

Recently, as the environmental pollution and safety facilities such as fire protection comes to important issue in world wide, the development of environment-friendly materials capable of replacing the established ones have received a great attention. In the field of construction, much attention have also been paid for the fbrication of various inorganic filler materials as eco-friendly and non-flammable ones due to their heat resistant and flame retardant properties in order to replace glass fibers. Especially, it is very important to how to control the size and structure of inorganic nano fillers, which plays a critical role in heat insulating applications.

In this work, we have synthesized Titanate nanotube(TiNT) and Layered Double Hydroxide(LDH) nanoparticles and studied about their applicable properties as inorganic filler due to their high porous structure. The synthetic parameters affecting the particle size and morphology have been investigated on the basis of crystal growth mechanism. In addition, we would intend to apply this technology, in more industrial point of view, to the fabrication process of vermiculite-TiNT/LDH filler composites, where nano-sized TiNT and LDHs were dispersed in exfoliated vermiculites.

Titanate nanotube and LDH nanoparticles have been prepared by hydrothermal method.[1,2] In order to control the size and morphology of both fillers, various synthetic conditions are systematically studied. The well-dispersed TiNT/LDH-vermiculite composites were obtained by wet-chemical mixing method considering surface charges of two components. The changes in thermal conductivity of heat insulating composites was compared according to the type and amount of inorganic filler. The thermal conductivities were confirmed to be reduced in proportion with the amount of inorganic nanofillers, which led to more effective heat insulating properties. Especially, the trends were observed more obviouly in TiNT with more porous structure. These results were discussed upon the basis of the morphology and surface area of nano fillers.

2 EXPERIMENTAL

The LDH nanoparticles were directly synthesized by hydrothermal method using the hydrolysis reaction of the mixed aqueous solutions of magnesium nitrate, aluminum nitrate and sodium bicarbonate at pH 10~11 by dropwise addition of an aqueous sodium hydroxide solutionwith vigorous stirring under atmosphere. After the suspensions were aged for 4 hours, the products were separated and washed with distilled water and dried at vacuum oven.[1]

Layered titante nanotube was synthesized by recrystallization reaction of P25. P25 was added into 10M NaOH solution and the mixture was refluxed at 150 ˚C for 48 hr. And then the precipitates were washed with distilled water more than three times and dried by freeze drying. Obtained layered titanate nanotubes are denoted as TiNT.

In order to prepare the well-dispersed inorganic heat insulating composites (TiNT/LDH-vermiculite composites), vermiculate was firstly dispersed in distilled water and then chemically exfoliated by addition of H_2O_2 solution for 24 hour. Vermiculite-TiNT/LDH filler composites for heat inulating materials were obtained by wet-chemical mixing method considering surface charges of two components, where the obtained H_2O_2-treated vermiculate and TiNT/LDH nanoparticles were mixed for 24 hours with vigorously strirred,

The transmission electron micrographs were obtained by using the high resolution transmission electron microscope (HR-TEM, JEM-2200FS). X-ray diffraction (XRD) patterns were obtained with an X-ray diffractometer (Rigaku D/MAX-2500, 18 kV) using Cu-K_{a1} radiation. Zeta potentials were measured using an electrophretic light scattering spectrophotometer (Zetasizer, Malvern) The Brunauer-Emmett-Teller (BET) surface areas were determined from nitrogen adsorption-desorption isotherms at 77K (ASAP 2020 Micromeritics). The thermal characteristics such as thermal conductivity and diffusivity were measured by using the laser flash apparatus(NETZCN 478).

3 RESULTS AND DISCUSSION

The chemical analysis results for all the samples indicate the Mg/Al ratio is 2:1. According to the X-ray diffraction patterns as shown in Figure. 1, all the hydrothermally treated samples are well crystallized and exhibit sharp and symmetric peaks at low 2θ angles in the one hand, but broad and asymmetric ones at higher 2 θ angles, which are characteristic of clay minerals with a layered structure [3]. The hexagonal cell parameters are determined to be a_0 = 3.050(3) A ° , and c_0 = 22.800(2) A °, which are in good agreement with those of well known hydrotalcite LDH [1]. Generally, the sharpness and intensity of XRD peak is considered to be proportional to the crystallinity. Some references are describing the relationship between crystallinity and peak intensity or sharpness [4,5]. A closer examination of Figure. 1 reveals that the peak sharpness and intensity increase as the hydrothermal treatment is prolonged and the temperature are raised, indicating an improved crystallinity

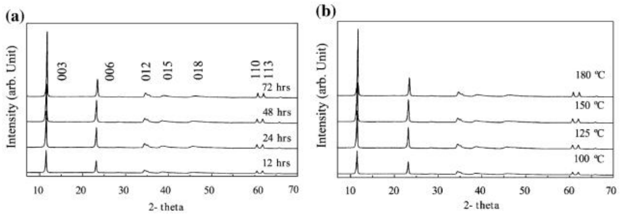


Fig. 1. X-ray diffraction patterns for LDH synthesized hydrothermally at (a) the aging time, 12, 24, 48, and 72 h; (b) the reaction temperature, 100, 125, 150, and 180 °C.

Figure 2 shows the TEM or HR-TEM images for TiNT synthesized by hydrothermally treated P25 for 1 hr. The TEM image of the original P25 confirms the 20 ~ 30 nm size range of the primary particles. At a hydrothermal treatment for 1 hr, the spherical types of particles are converted to the several hundred sizes of sheets. After hydrothermal treatment for 24 hr, nanotubes are formed as shown in Figure 2 (c). It was estimated that the nanotubes were about 10 ~ 20 nm in diameter and several hundred nanometers in length.

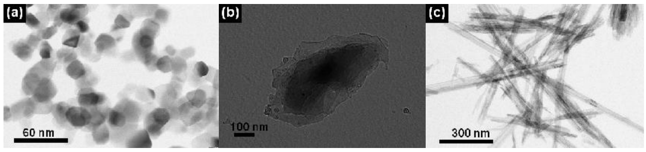


Figure 2. TEM images of (a) P25, (b) Hydrothermally treated P25 for 1 hr, and (c) TiNT.

Figure 3 shows the XRD patterns of the P25, TiNT, and TiNT-AT. The P25 is composed with anatase and rutile mixture phase. The XRD pattern of TiNT is similar to that the layered titanate such as $H_2Ti_3O_7{\cdot}xH_2O$ [6, 7] and $H_2Ti_2O_5{\cdot}H_2O$ [22]. The 2θ values were obtained for 9.6, 24.2, 28.3, and 48.2, which correspond to the (200), (110), (310), and (020), respectively. The diffraction peaks are broader, indicating a poor crytallinity of TiNT.

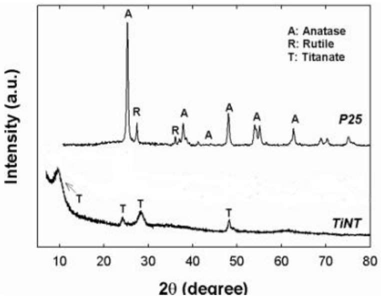
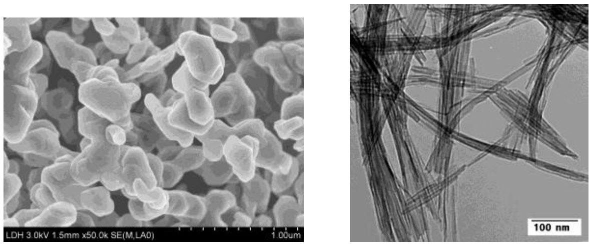


Figure 3. XRD patterns of P25, and TiNT.

Figure 4. shows the morphology of LDH and TiNT. These porous nanostructured materials were expected to play an effective role on heat insulating property as filler. In this point of view, expanded vermiculites and H_2O_2 treated exfoliated vermiculite as inorganic heat insulating material were mixed with these nano fillers to composites by wet chemical mixing. Figure 5 shows the variation of zeta potentials of suspended vermiculite, TiNT, and LDH particles in water as a function of pH. During the wet chemical mixing of TiNT and vermiculites, pH condition remained to be 3.5 for electrostatic interaction between vermiculite and nanofillers.

Relative surface areas and pore volumes of vermiculite



(a) (b)

Figure 4. The morphology of (a) Layered Double Hydroxides (b) Layered Titanate Nanotubes.

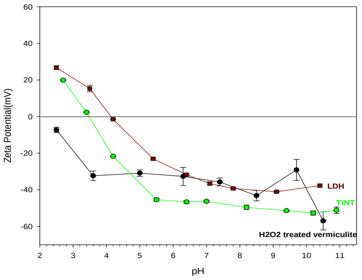


Figure 5. Zeta potentials of vermiculate, LDH and TiNT in aqueous suspensions as a function of pH.

and vermiculite-nano filler composites are listed in Table 1. Relative surface area and pore volume of all the composites were larger than ones of vermiculite alone. In addition, as the amount of nano filler added are increased, relative surface area and pore volume become larger for both LDH and TiNT. It is also notable that they were remarkably inreased in the composites loaded with TiNT, which have open open frame structure of tubular type. Such a porous property were expected to improve the heat insulating property.

Table 1. Relatvie surface areas and pore volumes of H_2O_2 treated vermiculite, its LDH (5wt% and 10wt%) composites and TiNT (5wt % and 10wt%) ones.

	Vermiculite	Vermiculite-LDH 5%	Vermiculite-LDH 10%	Vermiculite-TiNT 5%	Vermiculite-TiNT 10%
Relative Surface Area (m^2/g)	4.7	9.9	11.1	34.7	50.1
Cumulative Pore Volume (cm^3/g)	0.012	0.037	0.038	0.104	0.188

The investigation on thermal properties for these composites, expanded vermiculite and H_2O_2 treated exfoliated vermiculite were carried out by using laser flash apparatus. Firstly, thermal properties of heat expanded vermiculte and its nano filler 10wt % loaded composites were compared in Table 2. All nano filler composites showed lower thermal conductivity than expanded vermiculite. In comparion between nanofiller composites, thermal conductivity of TiNT loaded composite was lower than that of LDH loaed composite. It is found that such results are in very good agreement with expectation from the surface area and pore volume. On the other hand, we also choose exfoliated vermiculite as insulating base material in order to improve the porosity and make the dispersion of nano fillers easy. Exfoliated vermiculte was obtained through the chemical treatment by using H_2O_2. There are listed thermal properties in Table 3 and 4 for LDH composites and TiNT composites, respectively.

Compared with expanded vermiculite, H_2O_2 treated exfoliated vermiculite and its nanofiller composites show remarkably lower thermal conductivities. Trend of thermal conductivity according to the type and amount of nanofiller is also in a good agreement with previous expectation from surface properties. It is als found that TiNT 10% loaded composites shows a prominent reduction of thermal conductivity.

In conclusion, The thermal conductivities were confirmed to be reduced in proportion with the amount of inorganic nanofillers, which led to more effective heat insulating properties. Especially, the trends were observed more obvioulу in TiNT with more porous structure.

Table 2. Thermal properties of expanded vermiculite and vermiculite-nanofiller composites.

	Temp. (℃)	Diffusivity (mm^2/s)	Conductivity (W/m*K)
Heat Expanded Vermiculite	25.3	0.166	0.360
	300.1	0.148	0.400
	600.1	0.142	0.449
Expanded Vermiculite +LDH10%	25	0.114	0.347
	299.9	0.099	0.351
	600	0.101	0.381
Expanded Vermiculite +TiNT10%	24.6	0.106	0.275
	300.3	0.091	0.300
	600.7	0.093	0.350

Table 3. Thermal properties of H_2O_2 treated exfoliated vermiculite and its LDH loaded composites.

	Temp. (℃)	Diffusivity (mm2/s)	Conductivity (W/m*K)
H_2O_2 treated Vermiculite	25.2	0.106	0.248
	600.2	0.092	0.308
LDH-5% composite	25.2	0.077	0.244
	600.6	0.071	0.283
LDH-10% composite	25.2	0.08	0.213
	599.9	0.08	0.289

Table 4. Thermal properties of H_2O_2 treated exfoliated vermiculite and its TiNT loaded composites.

	Temp. (℃)	Diffusivity (mm2/s)	Conductivity (W/m*K)
H_2O_2 treated vermiculite	25.2	0.106	0.248
	299.8	0.097	0.298
	600.2	0.092	0.308
TiNT 5% composite	25.4	0.092	0.235
	299.9	0.079	0.251
	600.1	0.084	0.286
TiNT 10% composite	25.2	0.049	0.133
	300.3	0.041	0.133
	600.7	0.041	0.142

4 ACKNOWLEDGMENT

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