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Prevention of photocatalytic deterioration of resins using TiO_2 pillared fluoromica

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ABSTRACT

The TiO_2 pillared fluoromica powder was kneaded with polylactic acid resin. The composite showed high photocatalytic activity for degradation of acetaldehyde and toluene gas, especially at the range of 1–3 wt.% pillared mica powder, and this photocatalytic activity was higher than that of resins containing even higher amounts of commercial TiO_2 (P-25, Degussa). The composite test pieces of pillared mica showed smaller photocatalytic deterioration than the samples with P-25 powder in out-door weathering tests. Thus, the TiO_2 pillared clay resin composite shows excellent prevention of photocatalytic deterioration and high photocatalytic activity in comparison with P-25.

1. Introduction

TiO_2 has photoinduced strong oxidizing power and has been used practically as photocatalyst material (Linsebigler et al., 1995; Fujishima et al., 2000). TiO_2 is found in wide application in various fields, for example, self-cleaning material (Wang et al., 1997; Fujishima et al., 2000), antibacterial material (Kikuchi et al., 1997), air purification (Ibusuki and Takeuchi, 1994) and water purification (Pruden and Ollis, 1983; Mathews, 1984; Legrini et al., 1993; Hoffman et al., 1995). However, the use of TiO_2 is limited in the case of composites with organic materials, such as plastics, organic paint, textile and paper. The organic materials in the composite are decomposed and deteriorated by the oxidizing power of TiO_2, with the consequence that the composite becomes friable or that chalking occurs on the surface of the composite. Even TiO_2 particles coated partially with apatite or silica (Nonami et al., 2004) showed insufficient prevention effects for photocatalytic deterioration.

TiO_2 pillared clay has a meso-porous structure due to its nano-sized TiO_2 particles which are located as pillars between the silicate layers (Sterte, 1986; Yamanaka et al., 1987; Bernier et al., 1991; Khalfallah Boudali et al., 1994; Yamanaka and Makita, 1995; Kitayama et al., 1998; Ding et al., 1999; Ooka et al., 1999; Kaneko et al., 2001a; Vicente et al., 2001a,b; Mogyorósi et al., 2003; Kun et al., 2006). It shows high adsorption ability due to its large specific surface area, and this adsorption property accelerates photocatalytic reactions (Yoneyama et al., 1989; Yoshida et al., 1999; Ooka et al., 1999, 2003, 2004a,b; Kaneko et al., 2001b; Shimizu et al., 2002; Murayama et al., 2002; Kun et al., 2006). Therefore, it has attracted much attention as a new type of photocatalyst. Fig. 1 shows the schematic model of aggregated particles of the TiO_2 pillared clay, which was proposed in our previous work (Ooka et al., 1999). In the pillared clays, most of TiO_2 is intercalated in the clay layer and only minor part of TiO_2 seems to be exposed on the exterior of the aggregated particle. Thus, it is expected that the TiO_2 pillared clay shows a high prevention effect for photocatalytic deterioration in the composites with organic materials.

In this research, we evaluated the photocatalytic activity of the TiO_2 pillared clay blended with a resin and the extent of photocatalytic deterioration of the blended resin under light irradiation.

2. Experimental procedures

2.1. Preparation and characterization of the TiO_2 pillared clay

TiO_2 pillared clay was prepared as described previously (Ooka et al., 2003, 2004a,b). Titanium tetra-*iso*-propoxide was added to stirred acetic acid solution of 80 wt.%. The molar ratio of acetic acid to the alkoxide was 24. The resulting white slurry was stirred at room temperature to give a clear TiO_2 sol. Synthetic expandable fluoromica (Somasif ME-100, COOP Chemical Co, Ltd., Tateyama et al., 1992 and 1996) was used and its cation exchange capacity (CEC) was 0.7 meq/g. The TiO_2 sol was mixed with 1 wt.% aqueous dispersion of the fluoromica. The mixed suspension was stirred for 3 h at room temperature. The product was centrifuged and washed with water several times for removing excess TiO_2 sol. The wet product of the washed TiO_2 pillared mica was powdered by freeze-drying and grinding.

The dried powder of the TiO_2 pillared mica was characterized by X-ray diffraction (XRD), X-ray fluorescence and nitrogen adsorption.

The XRD patterns were recorded on a diffractometer using Cu Kα radiation (Rigaku Corporation, RINT-2500V). The crystal size of TiO_2 pillars was calculated from the integral width of the anatase (101) reflection (2θ=25.3°) using the Scherrer equation. The anatase (101) reflection was separated from background and a neighboring reflection using the pattern decomposition method (Young et al., 1982); 0.162° of the instrumental width at 2θ=25.3° was used from the calibration curve obtained from the measurements of silicon powder (Standard reference material, NIST).

TiO_2 content of the TiO_2 pillared mica powder was determined by the elemental analysis using X-ray fluorescence method (Rigaku Industrial Corporation, RIX-2000, glass bead method).

Nitrogen adsorption–desorption isotherms of the TiO_2 pillared mica degassed at 393 K, were obtained at 77 K (Quantachrome Corporation, Autosorb-1). The specific BET

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surface area, the total pore volume, the average pore diameter and the pore size distribution curve were calculated from the adsorption isotherm. The average pore diameter was obtained using the cylindrical pore model. The pore size distribution curve was calculated by the BJH method.

2.2. Preparation of the resin test pieces

The TiO_2 pillared mica was mixed with polylactic acid resin (Unitika Ltd., Terramac TE4000) and kneaded at 448 K, and molded into a piece of dumbbell form (area of one side: ca. 4 cm^2, Fig. 2). The content of TiO_2 pillared mica was varied from 0.2 to 10 wt.%. Commercial TiO_2: P-25 (Degussa) was employed as a reference.

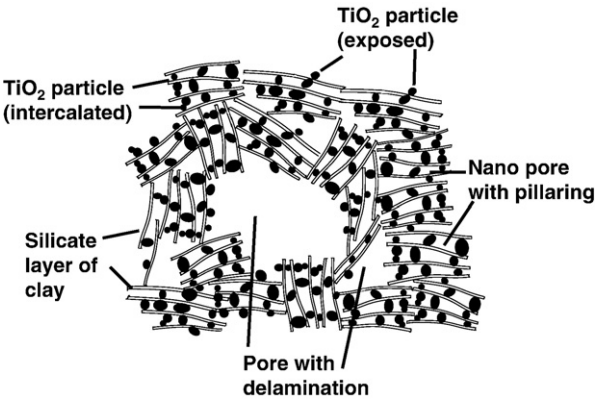

Fig. 1. Schematic model of aggregated particles of TiO_2 pillared clay (Ooka et al., 1999).

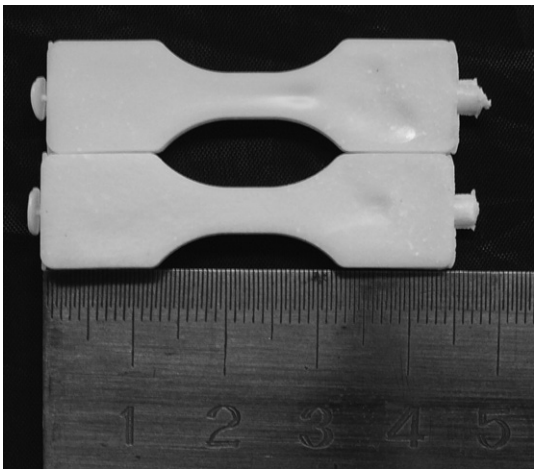

Fig. 2. The test pieces for out-door weathering tests and photocatalytic activity experiments.

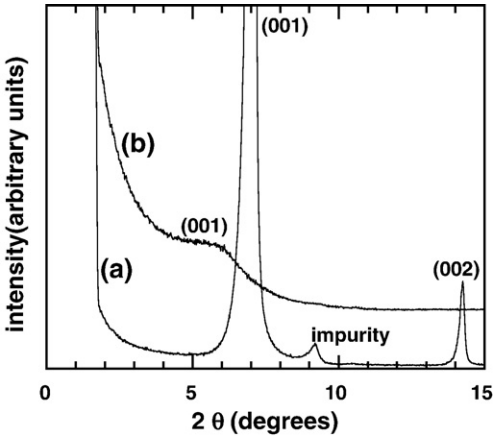

Fig. 3. XRD patterns in small angle range of the raw mica (a) and the TiO_2 pillared mica (b).

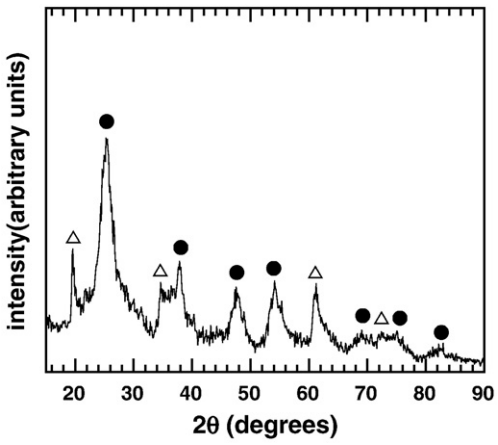

Fig. 4. XRD pattern in wide-angle range of the TiO_2 pillared mica. Closed circles: anatase, open triangles: raw mica.

2.3. Photocatalytic degradation experiments

The test pieces were irradiated by a UV black light (UV wave-length of the maximum intensity: 365 nm, UV illumination at the surface of the test piece: 1.0 mW/cm^2) for 24 h in the air for cleaning up the photocatalyst surface. Two test pieces were put in a gas sampling bag made of polyvinyl fluoride (Tedlar) film having 5 dm^3 capacity, then the bag was sealed. Acetaldehyde or toluene gas of 3 dm^3 was introduced into the bag through a valve. The concentration of acetaldehyde and toluene gas was adjusted to ca. 40 and 50 ppm, respectively, with the air that contained 20–30% relative humidity. The bag was set in the dark at room temperature. A part of the gas was extracted with a syringe through the valve for measuring the acetaldehyde or toluene concentration. The changes of the concentration were measured by a gas chromatograph (Shimadzu Corporation, GC-2010 with a fused silica capillary column, J & W Scientific, DB-1). After the adsorption equilibrium was achieved in the dark, the concentration of acetaldehyde or toluene was determined and UV irradiation was carried out at room temperature by the UV black light (the same condition as above). The concentration was monitored during the irradiation. In the preliminary test, the degradation fitted the first order rate expression. The photocatalytic activity in the initial stage of the degradation was indicated with the reaction rate constant (pseudo-first-order).

2.4. Out-door weathering tests

The test piece containing 5 wt.% photocatalyst, either P-25 or the TiO_2 pillared mica, was exposed to the sunlight and the rain for 1 month of August, 2004 in Nagoya. The surface morphology after exposure was evaluated by visual inspection and by a scanning electron microscope (SEM; JEOL Ltd., JSM-6300F).

3. Results and discussion

3.1. Structure of the TiO_2 pillared clay

The raw mica showed a (001) reflection at around $2\theta=7°$ and a (002) reflection at around $2\theta=14°$ (Fig. 3a). The reflection at around $2\theta=9°$ is due to the impurity of nonexpandable material included in the raw mica (Tateyama et al., 1992 and 1996). The TiO_2 pillared mica showed a very weak and broad (001) reflection at around $2\theta=5°$ and small angle scattering at around $2\theta=2$–$5°$ (Fig. 3b). These results indicate that the interlayer space of the pillared mica was expanded by TiO_2 pillars and the structure was delaminated and disordered (Pinnavaia et al., 1984; Occeli, 1988). The aggregation of delaminated

Table 1
Characterization of the TiO_2 pillared mica

Crystal size of TiO_2[a] (Å)	Average pore diameter[b] (Å)	Total pore volume[b] (cm^3/g)	Specific BET surface area[b] (m^2/g)	TiO_2 content[c] (wt.%)
34	36	0.300	329	32

[a] Calculated from the (101) reflection of anatase using Scherrer equation.
[b] Determined from nitrogen adsorption isotherm.
[c] Determined by elemental analysis using X-ray fluorescence.