PHOTOCATALYSIS AND INFLUENCE ON THE RESIN OF Ti(IV) DOPED HYDROXYAPATITE

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Abstract Photocatalytic apatite (PCAP) particles doped with Ti(IV) ions were synthesized by a coprecipitation method. Adsorption and decomposition of methylene blue were examined by spectrophotometry. Under dark conditions, PCAP showed higher adsorption of methylene blue than TiO₂ did. The particles were irradiated with black light after reaching adsorption equilibrium, and absorbance was decreased by the photocatalyst reaction of the PCAP as well as by the TiO₂. Decrease in absorbance of PCAP was larger than in TiO₂, and consequently the decomposition of methylene blue was seen to be much more effective by PCAP. Further, the photocatalysts were kneaded separately into resin, effects of photocatalysis by both PCAP and TiO₂ were observed in the resin, and influence on the resin was examined. Chalking occurred on the surface of the resin with TiO₂, but was not observed on the resin with PCAP, and it was determined that PCAP had little overall influence on the resin.

INTRODUCTION

Recently, TiO₂, which has photocatalytic properties, has been applied in various areas such as anti-bacterial agents, deodorizers, environmental-cleaning agents, and so on.¹ However, TiO₂ itself does not have active power to adsorb organic materials. To solve this problem, a compound of this photocatalyst and an absorbent was examined. It is well known that apatite has excellent adsorption power for proteins and lipids.² Wakamura et al. had previously investigated a method to give photocatalytic properties to apatite, and PCAP for which some of the Ca ions in crystallized apatite were replaced with Ti was synthesized by a coprecipitation method they described.³ Research into uses of PCAP as anti-bacterial agent, environmental-cleaning agent, dental material, etc., is now advanced.⁴,⁵ In this study, we examined absorbance of this photocatalyst and effects on resin.
EXPERIMENTAL

PCAP, synthesized based on the methods of Wakamura et al., 0.09mol Ca(NO₃)₂, and 0.01mol Ti(SO₄)₂ were dissolved in 1dm³ distilled water. 0.06mol H₃PO₄ was added to the solutions and the pH was adjusted to 9 with NH₄OH solution. The resulting suspension was aged at 100°C for 6h. The resulting precipitates were filtered off, washed with distilled water, and finally dried in an air oven at 150°C for 10h. Photocatalyst-grade Anatase type TiO₂ was used. The particle size and crystal shape of the photocatalysts were evaluated by transmission electron microscope (TEM). Specific surface areas of photocatalysts were evaluated by the BET method. X-ray diffraction (XRD) patterns were analyzed by a powder X-ray diffractometer. The characteristics of photocatalysts used in this study are summarized in Table 1.

Photocatalysts (1g) were added into separate 13.3µmol/L methylene blue aqueous solutions (100 cm³), and the suspensions were stirred for 30 to 120 min. For the first 60 minutes, the solutions were stirred under dark conditions, and for 60 minutes afterwards they were stirred while irradiating with ultraviolet rays (1mW/cm²). The suspensions were then filtered, and the absorbance of the filtrates were measured at 668 nm spectrophotometrically.

Photocatalysts (500g) were mixed separately with polypropylene(4.5kg) with an extrusion molding machine for chalk (BT30-S-30L, PLABO Co., Ltd.), and a master batch was made. Test pieces were made from this master batch with an injection molding machine (FS120S 18ASE, Nissei Plastic Industrial Co., Ltd.). This test piece was placed in 10mmol/L methylene blue solution, and heated for 24 hours at 90°C. The test pieces changed color to purple. These purple test pieces were used for the bleaching examination. Half of the colored test pieces were shaded with aluminum foil, they were irradiated with ultraviolet rays (5mW/cm²) for 24 hours, and bleaching was observed. Moreover, the test piece that was not colored was irradiated with ultraviolet rays (5mW/cm²) for 100 hours, and the status of the surface was observed with an electron probe microanalyzer (EPMA).

Table 1 Characteristics of photocatalysts

<table>
<thead>
<tr>
<th></th>
<th>Crystal form</th>
<th>Particle size (nm)</th>
<th>Specific surface area (m²/g)</th>
<th>XRD Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCAP</td>
<td>pillar-shaped</td>
<td>50</td>
<td>49.70</td>
<td>Hydroxyapatite (ICDD 9-432)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>spherical</td>
<td>20</td>
<td>281.78</td>
<td>Anatase (ICDD 21-1272)</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Adsorption and decomposition of methylene blue

Fig. 1 shows the result of measuring the absorbance of methylene blue solution. PCAP adsorbed methylene blue under dark conditions. On the other hand, methylene blue was hardly adsorbed by TiO₂. The test pieces were irradiated under black light after reaching adsorption equilibrium, and absorbance had decreased by the photocatalyst reaction on the PCAP as well as by TiO₂. Decreasing of absorbance by PCAP was larger than TiO₂. It is suspected that the decomposition of methylene blue was much more effective by the adsorption action of PCAP.

Photocatalysis and influence on the resin

Fig. 2 shows the result of the examination of resin bleaching. Methylene blue bleached both the resin with PCAP and the resin with TiO₂. As a result, the photocatalyst kneaded into the resin was also confirmed to show the photocatalytic effect. Fig. 3 shows the SEM photograph on the surface of the resin after ultraviolet irradiation. The resin with TiO₂ was decomposed, and chalking was seen. On the other hand, chalking was hardly seen on the surface of the resin with PCAP.

![Graph showing absorbance over irradiation time](image)

**Fig. 1 Adsorption and Decomposition of methylene blue**

![SEM photographs of resins](image)

**Fig. 2 Decomposition of methylene blue in resin**
CONCLUSIONS

Photocatalytic apatite (PCAP) particles doped with Ti(IV) ions were synthesized by a coprecipitation method, and photocatalysis and its influence on the resin was examined. In a bleaching examination of methylene blue, an absorbance decrease was seen for PCAP under dark conditions. PCAP decomposed methylene blue by the adsorption action more efficiently than TiO$_2$ under black light irradiation. Moreover, the PCAP kneaded into the resin confirmed the photocatalytic effect, and chalking was not seen in the resin sample with PCAP after ultraviolet irradiation. Applications of PCAP in resin are expected.

REFERENCES

1) A. Fujishima and K. Honda, Nature, 238, 5358 (1972)