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Synthesis of a transparent hybrid layer photocatalyst having high rubbing resistance

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Abstract A transparent layer photocatalyst having high rubbing resistance was developed. A high temperature burning process cannot be applied to form transparence layer photocatalysts using a low heat-resistant plastic film. We were able to synthesize the transparence layer photocatalyst having high rubbing resistance by irradiation of the hybrid material consisted of urethane acrylic oligomer and titanium lactate using a high pressure mercury lamp. The layer formed through a hybrid reaction of photo-polymerization of urethane acrylic oligomer and the sol-gel reaction of titanium lactate at relatively low temperature. The layer showed high rubbing resistance and high transparency, and titanium include in it dispersed uniformly. Photocatalytic activity was confirmed by detection of radicals using electron spin resonance (ESR) and was also evaluated by measuring bleaching of methylene blue solution.

Introduction

Titanium dioxide (TiO_2) shows photocatalytic activity upon absorbing light [1, 2]. Since the photocatalytic properties of TiO_2 were established as being due to the Honda-Fujishima effect [3] early in the 1970s, many studies have been carried out. Various organic compounds were found to decompose by reaction with the photogenerated radicals at the surface of TiO_2. Therefore, this photocatalyst is used in many environmental applications such as pollution control, deodorization and antibacterial uses [3–5].

A transparent layer photocatalyst having high rubbing resistance on the flexible plastic films is expected for various applications in the buildings, furnitures and automobiles. Therefore, photocatalytic layers on the plastic films have been studied. But there have been no reports on photocatalytic layer having both transparency and surface hardness with high levels so far. As the plastic films do not have high heat-resistivity, the photocatalyst must be synthesized at low-temperature. In this paper, we propose a new method of low-temperature synthesis of a transparent layer photocatalyst having high rubbing resistance. The layer formed through a hybrid reaction of photo-polymerization of urethane acrylic oligomer and the sol-gel reaction of titanium lactate. The effects of composition of the raw hybrid materials on the surface hardness, microstructure, titanium distribution, and photocatalytic activities were investigated.

Experimental procedure

Synthesis of the photocatalytic layer

Organic titanium compounds (Matsumoto Chemical Industry, Orgatix) and urethane acrylic oligomer (GEN Maintenance Technology, WINUP ST3-A [6]) were used as raw materials. Poly (ethylene terephthalate) film was used as a substrate.

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Urethane acrylic oligomer and organic titanium compounds were mixed with solvents in a specific weight ratio as shown in Table 1 and 2. The mixture was coated on the poly (ethylene terephthalate) film and was dried at 100 °C for 30 s and was irradiated with a high pressure mercury lamp for 90 s. Irradiation intensity of the lamp was 0.25 W/cm^2 at 320–390 nm and the wavelength of center of the peak was 365 nm.

Characterization of the layer

Surface hardness of the layer synthesized by the above process was evaluated in accordance with JIS-K5600. Transparency of the layer at a wavelength of 400–800 nm was measured using a spectrophotometer (Jasco V-570). The microstructure of the layer was analyzed by scanning electron microscopy (SEM, Shimadzu SSX-550 and Hitachi S-4300, acceleration voltage: 15 kV and 10 kV respectively). The distribution of titanium was analyzed by energy-dispersive X-ray spectroscopy (EDS, Horiba EXMA-3770). The layer was also analyzed by Fourier-transform infrared ray spectroscopy (FT-IR, JASCO FT/IR-610).

Evaluation of photocatalytic activity of the layer

Radicals generated at the surface of photoaccelerated the layer synthesized by the above process was analyzed by ESR (JEOL JES-FE1XG X-band

Table 1 Chemical components and characteristics of hybrid layers

Chemical components of hybrid solutions	Weight ratio					
Urethane acrylic oligomer [WINUP ST3-A]	100	64	56	59	51	52
Tetra normal butyl titanate [Orgatix TA-25]		36				
Titanium acetyl acetonate [Orgatix TC-100]			40			
Titanium ethyl acetoacetate [Orgatix TC-750]				41		
Titanium lactate [Orgatix TC-310]					49	
Titanium triethanol aminato [Orgatix TC-400]						48
Toluene	100	100	100	100	100	100
Isopropyl alcohol					150	
Methyl ethyl ketone					150	
Characteristics						
Ti content of hybrid layers (%)	0.0	5.1	4.9	4.8	5.5	4.4
Surface hardness	2H	under 2B	not cured	not cured	2H	under 2B
Transperency [400-800 nm] (%)	82–90	4–30	–	–	81-91	69-88
Difference of absorbance at wavelength of 660 nm for methylene blue solutions under photoirradiation for 0–60 min [100 – Abs$_{60\ \mathrm{min}}$/Abs$_{0\ \mathrm{min}}$ × 100] (%)	1.3	–	–	–	0.0	–

Table 2 Chemical components and characteristics of photocatalytic layer synthesized by irradiation of hybrid material consisted of urethane acrylic oligomer and titanium lactate

Chemical components of hybrid solutions	Reference	Sample 1	Sample 2	Sample 3	Sample 4	Commercial product
	Weight ratio					
Urethane acrylic [WINUP ST3-A]	100	51	44	38	34	
Titanium lactate [Orgatix TC-310]		49	56	62	66	
Toluene	100					
Isopropyl alcohol		150	176	114	136	
Methyl ethyl ketone		300	352	266	210.8	
Characteristics						
Ti content of hybrid layers (%)	0.0	5.5	6.7	7.8	8.6	
Surface hardness	2H	2H	H	H	HB	under 2B
Transparency [400–800 nm] (%)	82–90	81–91	82–91	81–90	79–90	82–90
Difference of absorbance at wavelength of 660 nm for methylene blue solutions under photoirradiation for 0–60 min [100 – Abs$_{60\ \mathrm{min}}$/Abs$_{0\ \mathrm{min}}$ × 100] (%)	1.3	0.0	14.8	21.8	26.4	18.2

Spectrometer) using MgO:Mn^{2+} as a reference. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a spin-trap reagent to detect the radicals decayed rapidly [7–12]. A distilled water (800 mm^3) and DMPO (0.1744 g) were mixed. Then the portion of the solution (30 mm^3) and the hybrid layer coated on the poly (ethylene terephthalate) film (1 mm × 35 mm) were placed in a thin flat quartz cell (inner size 0.4 × 4.2 × 50 mm^3), which was set in an ESR apparatus for the measurements. A metal halide lamp (Ushio, US510) was used for photoexcitation of the specimen of the layer coated on the poly (ethylene terephthalate) film. The characteristics of the lamp are shown in Fig. 1 and the wavelength of center of the peak is 420 nm.

The photocatalytic activity of the layer synthesized by the above process was also evaluated by the methylene blue bleaching method [7, 13]. An aqueous solution of methylene blue (1500 mm^3, concentration: 10 ppm) was placed into a flat quartz cell (optical path length: 5 mm) and the absorbance at a wavelength of 660 nm was measured using a spectrophotometer (Jasco V-570). Then the hybrid layer coated on the poly (ethylene terephthalate) film (9 mm × 30 mm) was placed into a flat quartz cell. The cell was then irradiated with black light (27 W) for 60 min. The characteristics of the light are shown in Fig. 1 and the wavelength of center of the peak is 370 nm. After irradiation, the layer coated on the poly (ethylene terephthalate) film was removed from the cell, and the absorbance at a wavelength of 660 nm was measured again.

Results and discussion

Selection of organic titanium compound

Photocatalytic layers were synthesized by irradiation of hybrid material consisted of urethane acrylic oligomer and organic titanium compound using a high pressure mercury lamp. We used following five kinds of organic titanium compounds to mix with urethane acrylic oligomer: tetra normal butyl titanate, titanium acetyl acetonate, titanium ethyl acetoacetate, titanium lactate, and titanium triethanol aminato. The compounds mixed with solvents in specific weight ratios as shown in Table 1 were coated on the poly (ethylene terephthalate) films. The as-coated layers were dried and were irradiated using a high pressure mercury lamp. The layer synthesized by using urethane acrylic oligomer and titanium lactate was cured using a high pressure mercury lamp and only showed a high rubbing resistance. The layer also showed a high transparency. Then we selected titanium lactate for using as organic titanium compound to mix with urethane acrylic oligomer.

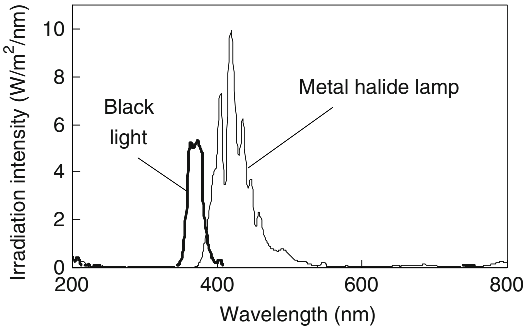


Fig. 1 Intensity of photoirradiation for lamps used in measurements for ESR and methylene blue bleaching

Mechanical properties of layers

Effects of the ratio of titanium lactate and urethane acrylic oligomer were investigated. In Table 2, Reference is the organic layer without titanium synthesized by irradiation of urethane acrylic oligomer using a high pressure mercury lamp. Table 2 also shows surface hardness and transparency of Sample 1–4 and Reference. Sample 4 (titanium content is 8.6%) doesn't show a high rubbing resistance and its surface hardness was identified as HB. On the other hand, Sample 1–3 and Reference showed a high rubbing resistance and a high transparency of about 80–90%. Surface hardness of Reference and Sample 1 were identified as 2H. Surface hardness of Sample 2 and 3 were identified as H. The surface hardness was found to be dependent of the ratio of urethane acrylic oligomer and titanium lactate. Sample 3 is considered to contain the maximum titanium content in the specimens showed a high rubbing resistance. The reproducibility was confirmed by repeating the characterization measurements. Surface hardness of hybrid layers were measured three times each and results were identical. Therefore, we think the hybrid layer has the reproducibility.

Microstructure and identification of the layer

Figures 2 and 3 show SEM images of Sample 3 (titanium content is 7.8%) and Reference, respectively. Sample 3 was uniform, and precipitation of the titanium compound was not observed. And the surface of Sample 3 was slightly rough compared with Reference. Figure 4 shows titanium mapping image of Sample 3 analyzed by SEM–EDS. In the titanium mapping image of Sample 3, titanium dose not segregate but dispersed uniformly. The quantity of titanium contained in the layer was about 8 wt%. It is almost identical with the chemical

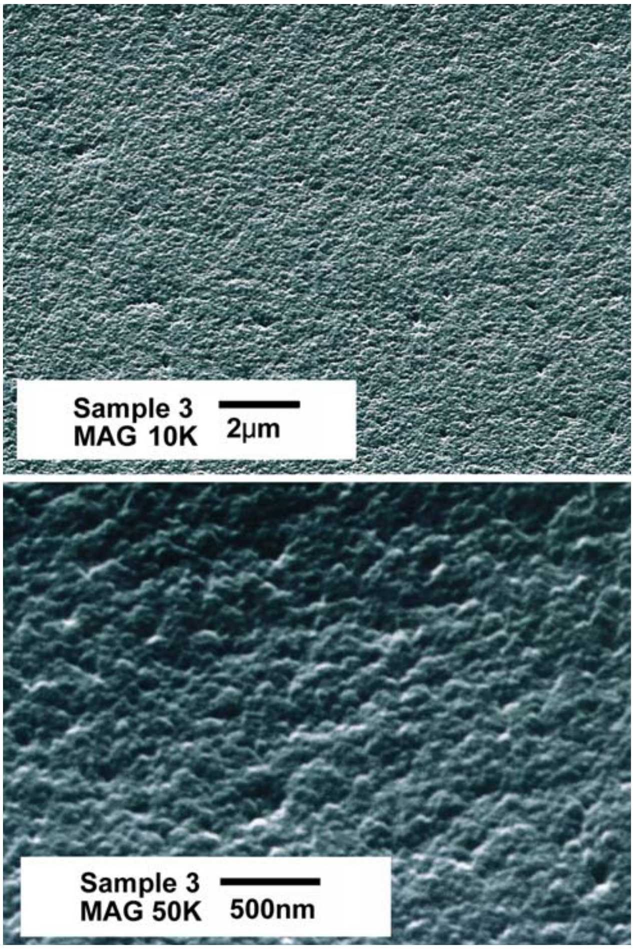


Fig. 2 SEM images of Sample 3

component of the raw mixture for coating. On the other hand, in the titanium mapping image of Reference, no titanium was observed.

The FT-IR spectra of Sample 3 and Reference were shown in Fig. 5. In the spectrum of Sample 3, absorption shoulders originating in Ti–O bonds were observed at 667 cm^{-1} and 617 cm^{-1}. On the other hand, in the spectrum of Reference, these shoulders were not observed. Based on the spectroscopic analysis, it is identified that the titanium detected in Fig. 4 was due to the metaloxane bond of Ti–O.

Evaluation of photocatalytic activity by methylene blue bleaching

Photocatalytic activities of Sample 1–4 and Reference for methylene blue bleaching were shown in Table 2 and Fig. 6 [7, 13]. The difference of absorbance (100 – $Abs_{60\ min}/Abs_{0\ min} \times 100$) at a wavelength of 660 nm for methylene blue solutions of Sample 3 with photoirradiation for 0–60 min was 21.8%. On the other hand, the value of Reference was 1.3%, and the value of the commercial product which declared the photocatalytic activity was 18.2%. Therefore, it was confirmed that Sample 3 had higher photocatalytic properties. The reproducibility was confirmed by repeating the characterization measurements. Methylene blue bleaching of hybrid layers were measured three times each and results were identical. Therefore, we think the hybrid layer has the reproducibility.

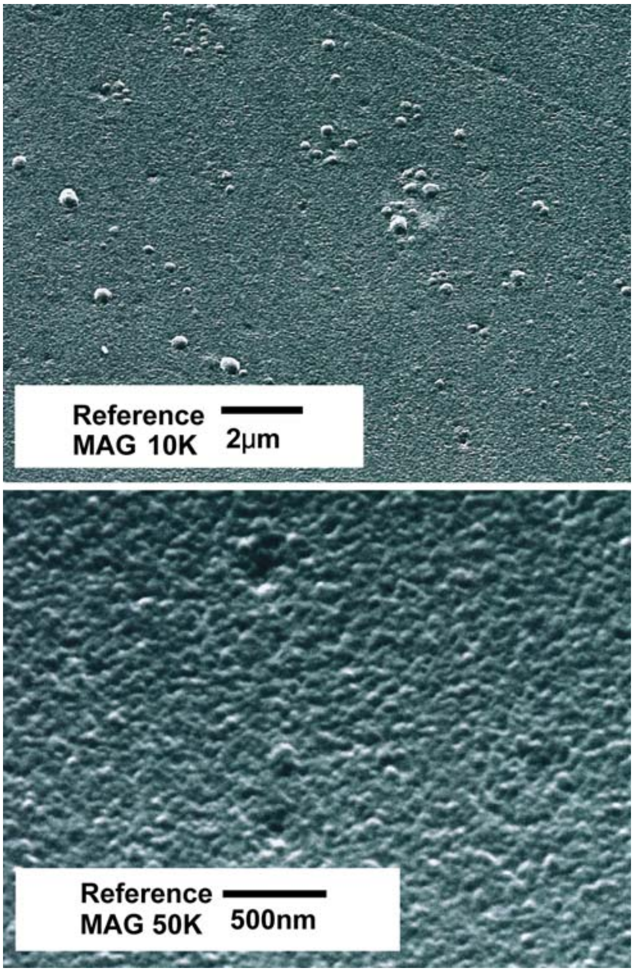


Fig. 3 SEM images of Reference (only organic layer)

Evaluation of photocatalytic activity by ESR measurements

In order to evaluate photocatalytic activity of the layer synthesized by irradiation of hybrid material consisted of urethane acrylic oligomer and titanium lactate, radicals generated at the surface of Sample 3 and Reference were analyzed by ESR. It has been explained the mechanism that TiO_2 show photoactivity in following Eq. (1)–(6) [7, 14, 15]. We focused our attention on OH· radicals on the surface of Sample 3

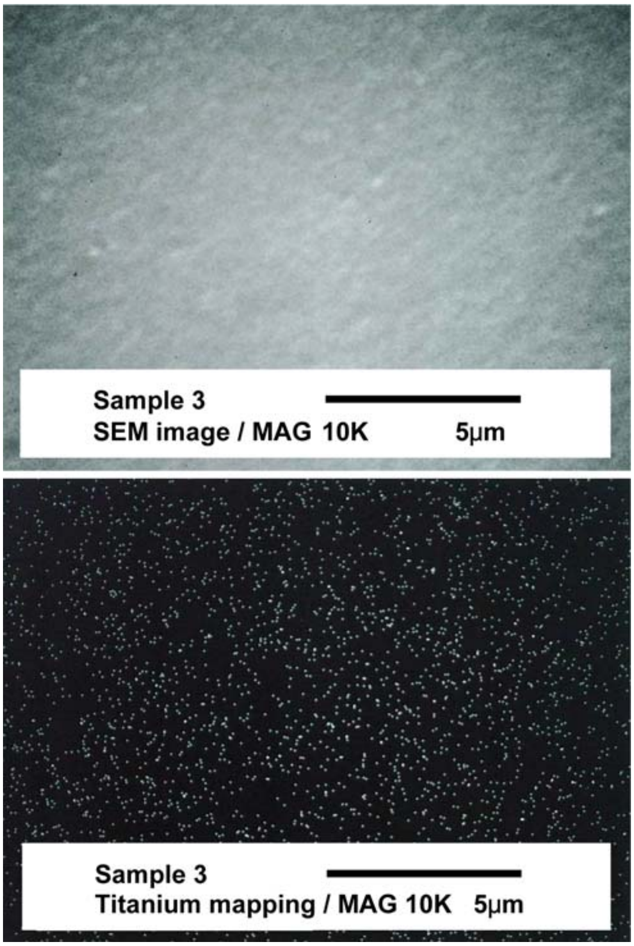


Fig. 4 SEM and titanium mapping images of Sample 3

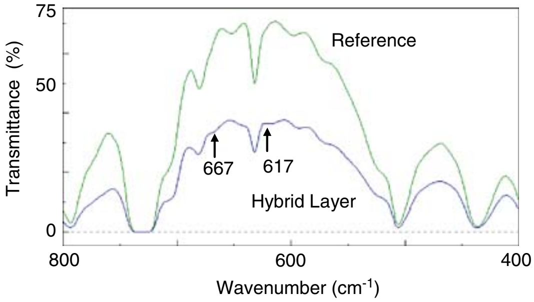


Fig. 5 IR spectra of Sample 3 and Reference (only organic layer)

generated by the reaction of a hole with water, described by Eq. (3). DMPO was used as a spin-trapping reagent to detect the OH· radicals by observing the stable ESR signals of DMPO–OH generated by chemical reaction (7).

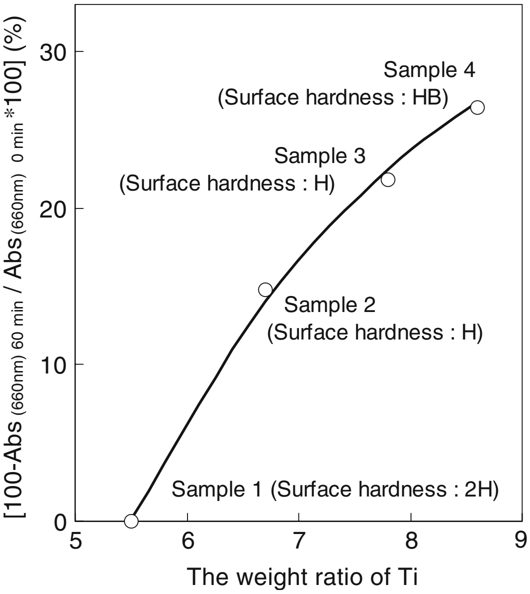


Fig. 6 Change of absorbance with weight ratio of Ti in hybrid layers. [100 – $\text{Abs}_{(660\ \text{nm})\ \ 60\ \text{min}}/\text{Abs}_{(660\ \text{nm})\ \ 0\ \text{min}} \times 100$]: The difference of absorbance at wavelength of 660 nm for methylene blue solutions with photoirradiation for 0–60 min

$$\mathrm{TiO_2} + hv \rightarrow e^- + h^+ \tag{1}$$

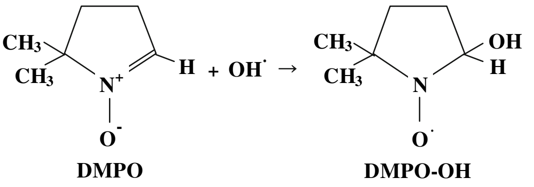
$$\mathrm{e^- + O_2 \rightarrow O_2^{-\cdot}} \tag{2}$$

$$\mathrm{h^+ + H_2O \rightarrow OH\cdot + H^+} \tag{3}$$

$$\mathrm{O_2^{-\cdot} + H^+ + e^- \rightarrow HO_2^-} \tag{4}$$

$$\mathrm{2O_2^{-\cdot} + H^+ \rightarrow HO_2^- + O_2} \tag{5}$$

$$\mathrm{OH\cdot + OH\cdot \rightarrow H_2O_2} \tag{6}$$



(7)

Figure 7 shows ESR spectra of Sample 3 in distilled water with DMPO (2 M) added as a spin-trapping reagent with photoirradiation. In the spectra of Sample 3 and Reference photoirradiated for 60 and 500 s, four signals ($g = 2.005(7)$, $a^{\mathrm{N}} = a^{\mathrm{H}} = 1.49$ mT) due to DMPO-OH were observed clearly near $H = 334.4$, 335.9, 337.4, and 338.9 mT [7–12]. These four signals due to DMPO–OH observed in the spectra of Reference were weaker than Sample 3. The intensity of the ESR signals of DMPO–OH is evaluated by comparison of $h{\cdot}\Delta H_{\mathrm{pp}}^2$, where h and ΔH_{pp} are the peak-to-peak

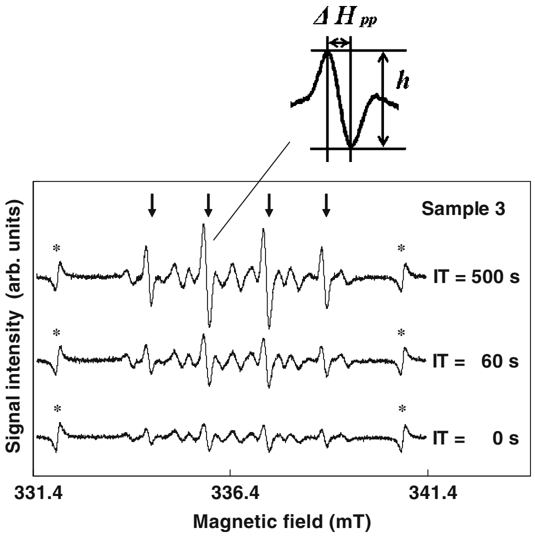


Fig. 7 ESR spectra of Sample 3 with DMPO (2.0 M). ↓: Signals of DMPO–OH. IT: Photoirradiation time. *h*: The peak-to-peak amplitude of the signal. ΔH_{pp}: The width of the signal

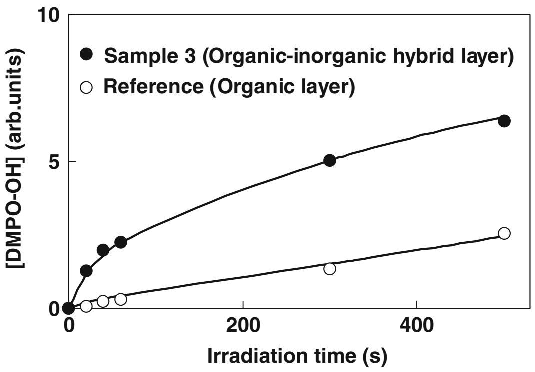


Fig. 8 Changes in amount of DMPO–OH for Sample 3 and Reference (only organic layer) with DMPO (2.0 M) during photoirradiation for 0–500 s

amplitude and width of the signal respectively with that of MgO:Mn^{2+} as a reference [16]. The net amount of DMPO–OH with respect to photoirradiation time was calculated from the difference in the intensity ratios of DMPO–OH to MgO:Mn^{2+} before and after irradiation, as shown in Eq. (8).

$$\begin{aligned}[\boldsymbol{DMPO-OH}]_{\mathrm{IT=0-500}} &= [I_{\boldsymbol{DMPO-OH}}/I_{\mathrm{MgO:Mn^{2+}}}]_{\mathrm{IT=0-500}} \\ &= [I_{\mathrm{DMPO-OH}}/I_{\mathrm{MgO:Mn^{2+}}}]_{\mathrm{IT=0}} \\ &(\text{where } I = h \cdot \Delta H_{\mathrm{pp}}^{2},\ \mathrm{IT}: \text{photoirradiation time})\end{aligned} \tag{8}$$

Figure 8 shows changes in amount of DMPO–OH for Sample 3 and Reference with DMPO (2 M) under photoirradiation. As for Sample 3, amount of photogenerated DMPO–OH increased with irradiation time. On the other hand, amount of photogenerated DMPO–OH for Reference was little. Then photocatalytic activity of Sample 3 was confirmed by detection of radicals using ESR.

Conclusion

A transparent layer photocatalyst having high rubbing resistance was synthesized on the poly (ethylene terephthalate) film by irradiation of the hybrid material consisted of urethane acrylic oligomer and titanium lactate using a high pressure mercury lamp. The layer formed via a hybrid reaction of photo-polymerization of urethane acrylic oligomer and the sol-gel reaction of titanium lactate proceeded at relatively low temperature as 100 °C with photoirradiation. The transparent layer showed a high surface hardness and homogeneous distribution of titanium. Photocatalytic activity of the layer was confirmed by detection of radicals using ESR and by measuring bleaching of methylene blue solution.

References

1. Bruner L, Kozak J, Z Elektrochem Angew Phys Chem 17 (1911) 354
2. Fujishima A, Honda K (1972) Nature 238:37
3. Fujishima A, Honda K (1971) Bull Chem Soc Jpn 44:1148
4. Hisanaga T, Harada K, Tanaka K (1990) J Photochem Photobiol A: Chem 54:113
5. Kato K, Tuzuki A, Taoda H, Torii Y, Kato T, Butsugan Y (1994) J Mater Sci 29:5911
6. Tominaga Y, Yamamura N (2002) United States Patent 6372340
7. Ichimura S, Ebisu H, Kato K (2005) Jpn J Appl Phys 44(7A):5164
8. Nosaka Y (2003) Photochemistry 34:14 [in Japanese]
9. Nosaka Y, Komori S, Yawata K, Hirakawa T, Nosaka AY (2003) Phys Chem Chem Phys 5:4731
10. Grela MA, Coronel MEJ, Colussi AJ (1996) J Phys Chem 100:16940
11. Horikoshi S, Hidaka H, Serpone N (2003) Chem Phys Lett 376:475
12. Hidaka H, Zhao J, Plzzetti E, Serpone N (1992) J Phys Chem 96:2226
13. Takami K, Nakasone T, Hashimoto K, Fujishima A (1998) Eng Mater 46(5):102 [in Japanese]
14. Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Chem Rev 95:69
15. Hirakawa T, Kominami H, Ohtani B, Nosaka Y (2001) J Phys Chem B 105:6993
16. Poole C (1983) In: Electron spin resonance, 2nd edn. John Wiley & Sons, New York, Chap. 12