Photoconductive properties of annealed TiO_2 dispersion composites

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It has been shown that the photoconductive characteristics of a dispersion composite of a photoconductive inorganic metal oxide, such as TiO_2, with a polymer are significantly enhanced by annealing. For the poly(methyl methacrylate) (PMMA) dispersion composite TiO_2–PMMA, the relative sensitivity is $10^1 \sim 10^2$ times higher than that of the unannealed sample. The space-charge limited current is observed in the dark current–voltage characteristics of the annealed TiO_2–PMMA. From the light intensity index of the annealed TiO_2–PMMA, it is found that the annealed sample has a large sensitizing effect.

(Keywords: dispersion composite; photoconductivity; titanium oxide; poly(methyl methacrylate))

INTRODUCTION

The remarkable progress of scientific technologies in recent years has made extremely high demands on materials. In particular, functional composite materials are being studied with keen interest because of the remarkable improvement and diversification of the material properties, and also of the active development of new materials having high functionality.

Among photoconductive dispersion composites, titanium oxide dispersion composites have been developed as electrophotographic sensitive materials using metal oxide[1], metal ion[2] doped TiO_2 or dye absorbed[3] TiO_2 to improve the sensitive layers in the TiO_2–polymer dispersion composites. It is well known that their photoconductive properties vary greatly depending on the nature and volume of the polymer used as the binding material[4,5]. Previously, we have found that the relative sensitivity is increased by annealing the conventional dispersion composites[6]. In this report, the effect of annealing on the photoconductive properties of TiO_2 dispersed in poly(methyl methacrylate) (PMMA) are investigated.

EXPERIMENTAL

Materials

Titanium dioxide powders from Sakai Chemical Co. Ltd. (TK-1C; rutile type; Φ 0.3 μm; BET surface 9.0 $m^2 g^{-1}$) were used. Methyl methacrylate (MMA) was distilled in vacuum before the polymerization. The initiator 2,2′-azobis-2-amidinopropane dihydrochloride (AIBA·2HCl) was of commercial grade (Waco Pure Chemical Industries Co. Ltd) and was used without further purification.

Preparation of the polymer and TiO_2 dispersion composite

The emulsion polymerization of MMA was carried out at 60°C for 3 h using a four-necked flask connected to a stirring apparatus, condenser, and an N_2 introduction pipe. The experimental conditions were as follows: monomer 0.5 mol l^{-1}; initiator 5 mmol l^{-1}; H_2O 600 ml. After the reaction, the unreacted monomer was separated with diethylether. Then the polymer (T_g = 105°C; M_v = 66000) was dried under vacuum at 40°C for 48 h.

For the TiO_2 dispersion composite, the polymers were dissolved in acetone and the TiO_2 was dispersed into the polymer solution. The solvent was then evaporated off with sufficient stirring in vacuum. The determination of the dispersion ratio, D_r of the composite was calculated by the following equation using thermobalance differential thermal analysis (TG-DTA, model 2000, Mac Science Co. Ltd).

$$D_r = W_p / W_{dp} \times 100 \text{ (wt\%)}$$

where W_p = weight of polymer in the dispersion composite and W_{dp} = weight of TiO_2.

Preparation and measurement of photoconductive properties

After adding a certain volume of a mixed solvent (1:1) of toluene and tetrahydrofuran to the dispersion composite, it was dispersed adequately using an agate mortar. The sample was applied onto the glass substrates with a bar corder to a thickness of $\sim$50 μm, and dried in vacuum at 40°C for 24 h. Then, a pair of comb-shaped silver–indium electrodes (electrode distance $\sim$0.37 mm; effective length 10.8 mm) was vacuum-deposited to provide samples for measurement.

A schematic diagram of the measuring instrument is shown in *Figure 1*. The sample was placed in a black box which was electrically shielded. An applied voltage of 10 V d.c. was used except for the voltage–current characteristics (2–150 V), and a halogen lamp (100 V/300 W) was used as the light source. The dark and photocurrent were measured by the use of an electrometer (TR-8652; Advantest Co. Ltd). The sample was irradiated with light in the basic absorption region through an interference filter of 425 nm (IF-S; Vacuum Optics Corp. of Japan). The light intensity was varied using a neutral density filter (ND filter; Vacuum Optics Corp. of Japan).

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RESULTS AND DISCUSSION

Effect of annealing on photoconductive properties

Table 1 shows the photoconductivities of TiO_2, TiO_2 dispersed in PMMA (TiO_2–PMMA) and their annealed sample. Here, the relative sensitivity is represented as photocurrent (I_p) divided by the dark current (I_d). In comparison with TiO_2, I_d, I_p and the relative sensitivity of TiO_2–PMMA is increased; the relative sensitivity is strongly increased by annealing.

The relationship between the relative sensitivity and the annealing temperature is shown in *Figure 2*. *Figure 2* shows that the relative sensitivity of TiO_2–PMMA is a maximum at 120°C. The relationship between the relative sensitivity and the annealing time at 120°C is shown in *Figure 3*. The relative sensitivity is a maximum at 3 h and is relatively high after 3 h, though it decreases slightly with increase in annealing time.

Recently, many analyses of the surface and interface have been carried out using techniques such as Fourier transform infra-red spectroscopy and X-ray photoelectron spectroscopy. For example, the filler–matrix interface of PMMA reinforced with Kevlar fibres was analysed to clarify the interaction between the carbonyl groups of PMMA and the amide groups of Kevlar and to describe the interfacial structure. It was found that the interfacial structure depends greatly on the tacticity of the matrix and that many carbonyl groups of PMMA exist on the fibre interface in the case of atactic and syndiotactic PMMA[7,8]. Since the chemical structure of the bulk matrix polymer can be different from that of the interfacial matrix polymer, depending on the polarity of the fillers in the composite material, it is natural to assume that the polarity affects the properties of the composite. Further, the hydroxyl group has been observed on the surface of rutile TiO_2 from infra-red studies[9,10]. Therefore, it is suggested that a special molecular aggregation of PMMA on TiO_2 is formed on annealing. As to a possible reason for the increased photoconductivity properties of the annealed TiO_2–PMMA, it is suggested that the interfacial interaction between TiO_2 and PMMA is enhanced and at such interfaces electron depletion occurs or an electron-enriched layer is formed.

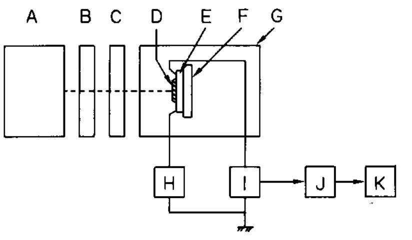

Figure 1 Schematic diagram of the measuring instrument: (A) light source; (B) IF-S filter; (C) ND filter; (D) sample; (E) glass; (F) insulator; (G) black box; (H) direct current power source; (I) electrometer; (J) analogue/digital, digital/analogue converter; (K) microcomputer

Dark current–voltage characteristics of the TiO_2 dispersion composites

The dark current– voltage characteristics of the TiO_2 dispersion composites are shown in *Figure 4*. The TiO_2 and TiO_2–PMMA are characterized by obeying Ohm's law ($J \propto V^n$; where $n \simeq 1$, J is the current density and V is the applied voltage) in the voltage range of 2–150 V. Meanwhile, the annealed TiO_2–PMMA is characterized by obeying Ohm's law in the voltage range of 2–30 V and shows an exponential dependence on the voltage at an applied voltage of >30 V. The dark current–voltage characteristics are similar to those obtained by Cardon[11]. The exponential dependence of the dark current suggests a space-charge limited current. It is well known that the phenomena include field emission from electrodes, traps

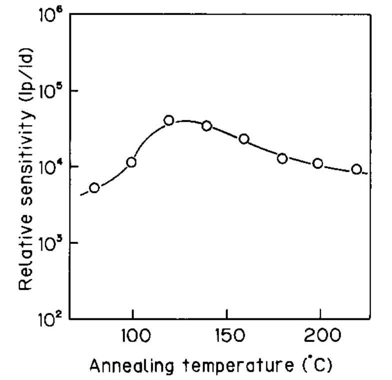

Figure 2 Relationship between relative sensitivity and annealing temperature for 1 h on TiO_2–PMMA (D_r = 4.04 wt%)

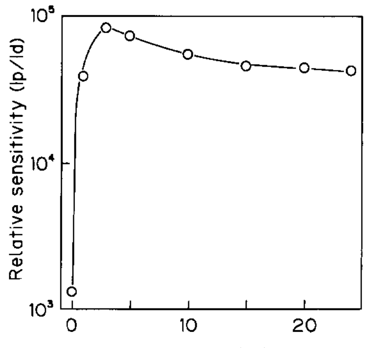

Figure 3 Relationship between relative sensitivity and annealing time at 120°C on TiO_2–PMMA (D_r = 4.04 wt%)

Table 1 Photoconductivity of TiO_2 and the TiO_2–PMMA dispersion composite

	Dispersion ratio (wt%)	Annealing conditions	Dark current, I_d (A)	Photocurrent, I_p (A)	Relative sensitivity (I_p/I_d)
TiO_2	—	—	5.64×10^{-12}	1.33×10^{-9}	2.36×10^{2}
TiO_2–PMMA	4.04	—	1.05×10^{-11}	1.33×10^{-8}	1.27×10^{3}
		120°C, 1 h	1.65×10^{-11}	6.36×10^{-7}	3.86×10^{4}
		120°C, 3 h	1.38×10^{-11}	1.14×10^{-6}	8.26×10^{4}

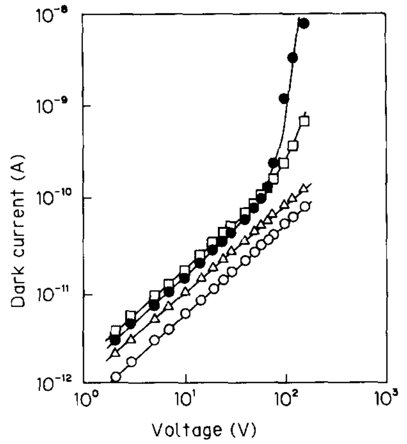

Figure 4 Dark current–voltage characteristics on TiO_2 (○), TiO_2–PMMA (D_r = 4.04 wt%) (△) and annealed TiO_2–PMMA at 120°C for 1 h (□) and 3 h (●)

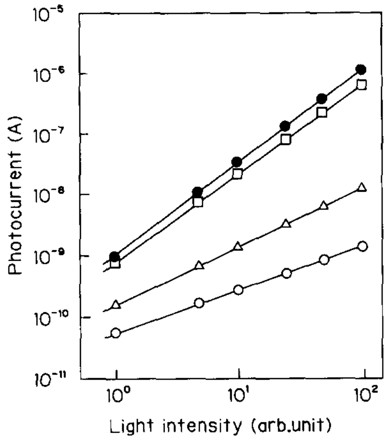

Figure 5 Relationship between photocurrent and light intensity on TiO_2 (○), TiO_2–PMMA (D_r = 4.04 wt%) (△) and annealed TiO_2–PMMA at 120°C for 1 h (□) and 3 h (●)

or the valence band, collision ionization of trapped or valence electrons, poor contact, barriers, and heating effects. Although the effects in annealed TiO_2–PMMA are not completely understood it is reasonable to assume that they are due to the migration of O vacancies under the influence of the applied voltage to the negative electrode and heating effects. The order of the exponential dependence is: TiO_2–PMMA < TiO_2–PMMA (annealed at 120°C for 1 h) < TiO_2–PMMA (annealed at 120°C for 3 h). Since the order is the same as that for the values of relative sensitivity, the exponential dependence seems to largely depend upon the total trapped electron density in the sample. It is considered, therefore, that the photosensitizing effect is increased to increase the trapped electron density by annealing.

Photocurrent dependence on light intensity

Figure 5 shows the relationship between photocurrent and light intensity. In general, a photocurrent is observed as a result of generating electron-hole pairs on light irradiation, and the pseudo-Fermi level is heightened with increasing light intensity:

$$I_p \propto L^n$$

where I_p is the photocurrent, L is the light intensity and n is a constant. For both TiO_2 and TiO_2–PMMA, n is <1 and for the annealed TiO_2–PMMA, n is >1 and a super linearity is observed. These phenomena are due to the existence of hole traps[12]. Also, the increase in photoconductivity may be interpreted by the above mechanism.

Figure 6 shows the temperature dependence of the photocurrent–light intensity characteristics for annealed TiO_2–PMMA. For the measurement temperatures, the dependences of the photocurrent on the light intensity are shifted in parallel to each other.

The rise characteristics in a super-linear region of the annealed TiO_2–PMMA are shown in *Figure 7*. It is assumed that the photocurrent decays rapidly because the hole demarcation level is further away from the filled zone with increase in temperature[13].

Figures 8 and *9* show the rise and decay characteristics of the photocurrent. The results of the rise characteristics of the photocurrent in air appear as overshoots. Meanwhile under vacuum, the overshoots disappear and the slowly rising and decay characteristics are observed. Accordingly, it is possible that the photocurrent is largely affected by the release of oxygen and photoreduction processes on the surfaces.

Wavelength dependence of the photocurrent

Figure 10 shows the relationship between photocurrent

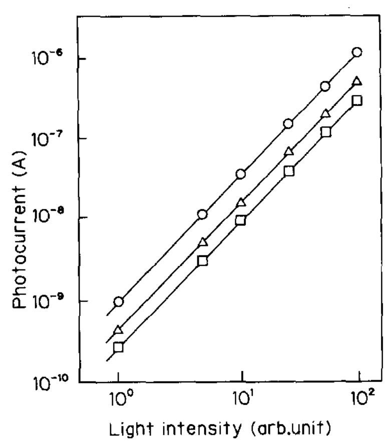

Figure 6 Temperature dependence of the photocurrent–light intensity characteristics on annealed TiO_2–PMMA (D_r = 4.04 wt%) at 120°C for 3 h. Temperature: (○) 30°C; (△) 45°C; (□) 60°C

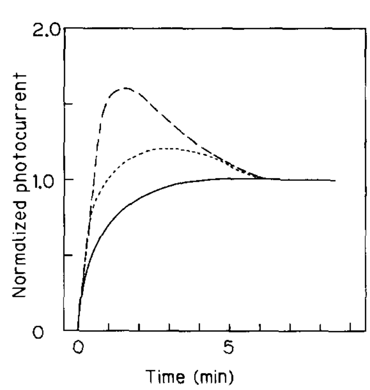

Figure 7 Temperature dependence of the rise characteristics of the photocurrent on annealed TiO_2–PMMA (D_r = 4.04 wt%) at 120°C for 3 h. Temperature: (——) 30°C; (– – –) 45°C; (------) 60°C

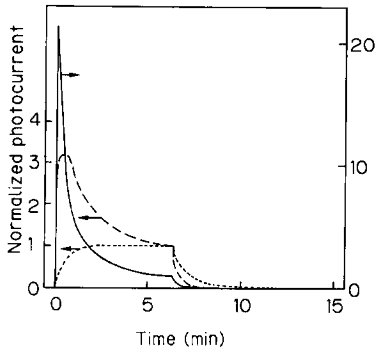

Figure 8 Rise and decay characteristics of the photocurrent in air on TiO_2 (——), TiO_2–PMMA (D_r = 4.04 wt%) (– – –) and annealed TiO_2–PMMA at 120°C for 3 h (------)

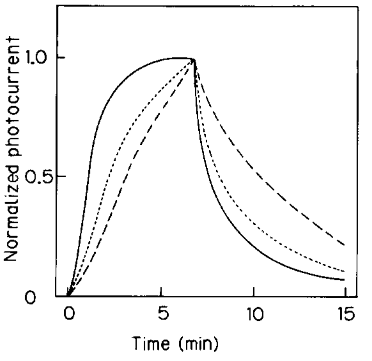

Figure 9 Rise and decay characteristics of the photocurrent in vacuum on TiO_2 (——), TiO_2–PMMA (D_r = 4.04 wt%) (– – –) and annealed TiO_2–PMMA at 120°C for 3 h (------)

and wavelength. The peaks of the photocurrent are near 400 nm and the photocurrent decreases at longer wavelengths. The width of the forbidden zone of TiO_2 is ~3.01 eV (at 413 nm) and the peaks of the photocurrent of all the samples shift to 2.88 eV at a slightly longer wavelength. It is known that the excitation wavelength of TiO_2 generally shifts to the shorter wavelength side than that of the single crystal[14]. It is considered, therefore, that the annealed TiO_2–PMMA has a sensitizing effect on the improvement of the intrinsic absorption peak of TiO_2.

CONCLUSIONS

The relative sensitivity of TiO_2–PMMA is greatly increased by annealing at 120°C for 3 h. Although the cause is not completely clear, it is considered that the interfacial interaction between TiO_2 and PMMA is enhanced, a special molecular aggregation of PMMA on

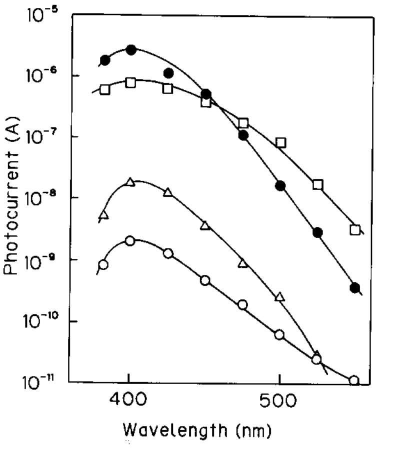

Figure 10 Relationship between photocurrent and wavelength on TiO_2 (○), TiO_2–PMMA (D_r = 4.04 wt%) (△) and annealed TiO_2–PMMA at 120°C for 1 h (□) and 3 h (●)

TiO_2 is formed, and at such interfaces, an electron depletion occurs or an electron-enriched layer is formed. The space-charge limited current is observed in the dark current–voltage characteristics of the annealed TiO_2–PMMA. From the light intensity index of the annealed TiO_2–PMMA, it is found that the annealed sample has a large sensitizing effect. It is considered from the rise and decay characteristics that the photocurrent is caused by photochemical processes such as the elimination of oxygen from the surface and reduction by light.

A detailed discussion of the molecular aggregation of PMMA on the TiO_2 surface and the photosensitive mechanism will be reported elsewhere.

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