

A study of conductive elastomer composites reinforced with sulfonic acid doped polyaniline coated titanium dioxide

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In the present study, we report on the fabrication of hybrid composites of conductive silicone elastomer with TiO₂/PANI-DBSA dispersion. The hybrid composites with conductive fillers, TiO₂/PANI-DBSA, were prepared via an in-situ polymerization method with various TiO₂ contents. The novel elastomer composites were prepared by dispersing TiO₂/PANI-DBSA at room temperature in vulcanized silicone elastomers. The morphological, structural and electrical properties of TiO₂/PANI-DBSA and their elastomer blends were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and electrical resistivity measurements. It was found that the electrical conductivity of the composite powder coated with about 20 wt.% PANI-DBSA was 46,000 (10⁴) times higher than that of bare TiO₂ powder. Also the electrical conductivity of the silicone elastomers composites of TiO₂/PANI-DBSA were changed from 10⁻¹⁴ S/cm to 0.295 S/cm (10 wt.% TiO₂/PANI-DBSA). The novel elastomer composite had a percolation threshold between 1-3 wt.% PANI-DBSA.

Key words: Polyaniline, Titania, Conductive elastomer, Percolation.

Introduction

Recently, the formation of electrically conducting elastic thermosetting composite materials such as antistatic and conductive adhesives containing metallic particles, fibers, flakes or other fillers like carbon black or metal oxides have received great interest. These materials have shown promising commercial viability in technological applications such as in rechargeable batteries, for conductive coatings or adhesives, for electromagnetic shielding (EMI), electrical and electrochemical devices and as gas separation membranes [1].

Polyaniline (PANI) is also a very important conducting additive and is also considered as a good candidate for the development of conducting blends because of its good conductivity, stability, easy synthesis from low-cost reagents [2]. The conductivities of PANI are transformed from insulating to conductive through doping, which is a redox process. PANI emerges in three different oxidation states: the fully oxidised, fully reduced and partially oxidised (emeraldine base, EB). PANI-EB can be returned to the conductive form through a non-redox reaction, known as protonation [3]. According to this process, EB is treated with a strong acid (H⁺A), e.g. dodecylbenzenesulphonic acid (DBSA) or camphorsulphonic acid (CSA), to give the conductive emeraldine salt (ES) [2-3]. Also, PANI from chemical oxidative polymerization is an insoluble and infusible polymer. Because of the stiffness of the backbone due to PANI's chain structure and strong intermolecular

interactions, melt processing is not possible due to decomposition at temperatures below the softening or melting point [4]. Although PANI is soluble only in N-methylpyrrolidone (NMP), selected amine, concentrated sulphuric acid and other strong acids, the PANI protonated with functionalized protonic acids, such as dodecylbenzene sulfonic acid (DBSA), PANI-DBSA has a high solubility or dispersibility in common organic solvents, allowing the preparation solution of cast or melt processable blends [2].

Among inorganic nanoparticles, TiO₂ has received particular attention due to its good stability, environmental friendliness and unique optical and electrical properties such as acting as a pigment, a charge carrier, being a photoelectric active center and optical cavity like a semiconductor [5]. A large number of studies have been devoted to preparation of TiO₂/PANI composites because of their well matched band gap for the charge transfer. TiO₂ is a typical n-type semiconductor while PANI is usually considered as p-type materials. These TiO₂/PANI composites have been applied to various applications with their photocatalytic activity and gas sensor for various materials [6].

The aim of the present study was to prepare elastomer composites reinforced with sulfonic acid doped PANI coated TiO₂ hybrid nanocomposites. The key issues for preparation of these elastomer is the good dispersibility of TiO₂/PANI composites in organic dispersants such as chloroform, toluene, hexane and the preparation of well-dispersed TiO₂ in the PANI matrix. The dispersion of TiO₂ nanoparticles is difficult with conventional methods due to the agglomeration caused by the high surface energy of the nanoparticles. This study was focused on the preparation of a highly conductive elastomer dispersed with TiO₂/PANI-DBSA particles.

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Materials and fabrication method

Materials

Reagent-grade aniline (ANI), ammonium persulfate (APS) and hydrochloric acid were purchased from Wako chemical Co. Ltd. in Japan. And dodecylbenzenesulfonic Acid (DBSA) was purchased from Tokyo Chemical Industry Co., Ltd. in Japan. The aerioxide TiO₂ P25 was purchased from Nippon Aerosil Co., Ltd. in Japan. Double distilled deionized water (D-water) was used to prepare the HCl solution for the polymerization. Aniline was distilled under reduced pressure, and stored under nitrogen in a refrigerator. The other reagents were used without further purification. The moisture-curing oxime type silicon resin (SHIN-ETSU Chemical Co., Ltd.) with a curing catalyst includes dibutyltin diacetate, dibutyltin dilaurate and a mixture of them.

Preparation of TiO₂/PANI hybrid composites

0.1 M of aniline monomer and different amounts of TiO₂ were added into a micellar solution with some dissolved DBSA in 190 ml of 1 M HCl aqueous solution. The solution was mixed and sonicated at 50 W for 5 minutes to make a homogeneous solution. Also it was maintained in a bath with magnetic stirring at 30 for 1 h because DBSA-anilinium composite could be extracted at low temperature. The 10 ml 1 M HCl aqueous solution including 0.04 M APS was added dropwise into the 190 ml micellar solution for approximately 20–30 minutes. After the induction period of about 30–40 minutes (including time of APS addition), the emulsion reaction mixtures turned into a bluish tint and the coloration became more pronounced as polymerization proceeded. Finally dark green colored PANI dispersions were obtained without any precipitation. The polymerization was carried out for 2 h at 30 under moderate stirring. After polymerization, 50 ml of methanol was poured into the emulsion to stop the polymerization. Then 100 ml hexane was poured into the vehicle and phase separation of TiO₂/PANI-DBSA into an organic phase occurred. To remove the unreacted DBSA, APS, and byproducts ((NH₄)₂SO₄ etc.), the solution was washed with methanol. To acquire the hexane dispersion of TiO₂/PANI-DBSA, the vehicles were separated in a funnel. PANI powders were collected on a filter and dried under a vacuum at 40 °C.

As a reference material, PANI-HCl was synthesized using the same process without DBSA and TiO₂. The resulting dark green solution was filtered and washed with methanol and acetone. The required PANI powders were collected on a filter and dried under a vacuum at 40 °C.

Elastic composite preparation

The silicone elastomer was added to the conducting polymer solution in different amounts in order to obtain the desired compositions. The mixed solutions were sonicated at 50 W applied power for 10 minutes. Solvent evaporation was done with a rotary evaporator under a vacuum at 30 °C. A viscous mix was then coated on a stainless substrate (SUS430, 20 mm × 50 mm × 0.5 mm) with 5 mm/s by a

micro dip coater MD-0408 (SDI Co. LTD., Japan). Samples were cured at 10 °C for 3 days. After curing, thin films about 100 μm in thickness were taken off the substrates. After curing films were sized into 5 mm × 5 mm for resistivity measurements.

Characterization

To probe the morphology, scanning electron microscopy (SEM, HITACHI S-5000 at an accelerating voltage of 5 kV) and transmission electron microscopy (HITACHI H-8100 at an accelerating voltage of 200 kV TEM) were used.

X-ray patterns of PANI were taken with Ni-filtered Cu-Kα radiation source ($\lambda = 0.151418$ nm) using a RINT2500 X-ray diffractometer (Rigaku Denki Co.). The diffractor was moved step by step ($\Delta 2\theta = 0.05^\circ$) from 5 to 80° at a speed of 1°/s and the X-ray power was 40 kV and 40 mA.

The thermal stability of PANI-DBSA was investigated by thermogravimetric (TGA) measurements, using a TG-DTA2000SA from BRUKER AXS. The sample was heated up to 900 °C at a rate 10 K minutes⁻¹ under an air atmosphere (40 ml/minutes).

To measure electrical conductivity of a 13-mm disk pellet of PANI powders, the conventional Van der Pauw method was employed (Resitest 8310, Toyo Technica, Japan).

Results and Discussions

a. Preparation of the TiO₂ coated with PANI-DBSA

The PANI-coated TiO₂ powder was pale green to dark green in appearance depending on the amount of TiO₂ added in the reaction mixture. Fig. 1 shows the SEM micrographs of TiO₂ composites. Fig. 1(a) shows the bare PANI doped with DBSA, which had nano-scaled rod-like fibers. With increasing TiO₂ content (Fig. 1(b)–(c)), the reduction of PANI like nano rod fibers was observed. Also the dispersed nature of TiO₂ was improved with an increase in the TiO₂ content. This suggests that the TiO₂ particles were coated with PANI, and the excess PANI formed a nano-rod like network. The average particle size determined from SEM was about 20–50 nm regardless of the quantity of the PANI formed during the polymerization reaction. Fig. 2 confirmed that the TiO₂ particles were coated with PANI.

Fig. 3 shows the WAXRD patterns for pure PANI-DBSA, pure PANI-HCl, TiO₂/PANI-DBSA composite and TiO₂. The PANI-DBSA exhibited the ES-I structure with a little crystallinity, generally it is known that class I materials are formed when the polymer is obtained from a protonated solution [7]. By Comparing the TiO₂/PANI-DBSA composite and TiO₂, it is clear that the diffraction patterns of the composites are identical to those of TiO₂ particles except for the peak around $2\theta = 10^\circ$ derived from PANI-DBSA. This confirmed that the PANI deposited on the surface of TiO₂ particles has no effect on the crystallization behavior of TiO₂ particles.

Fig. 4 shows the thermal stability of the TiO₂ composites.

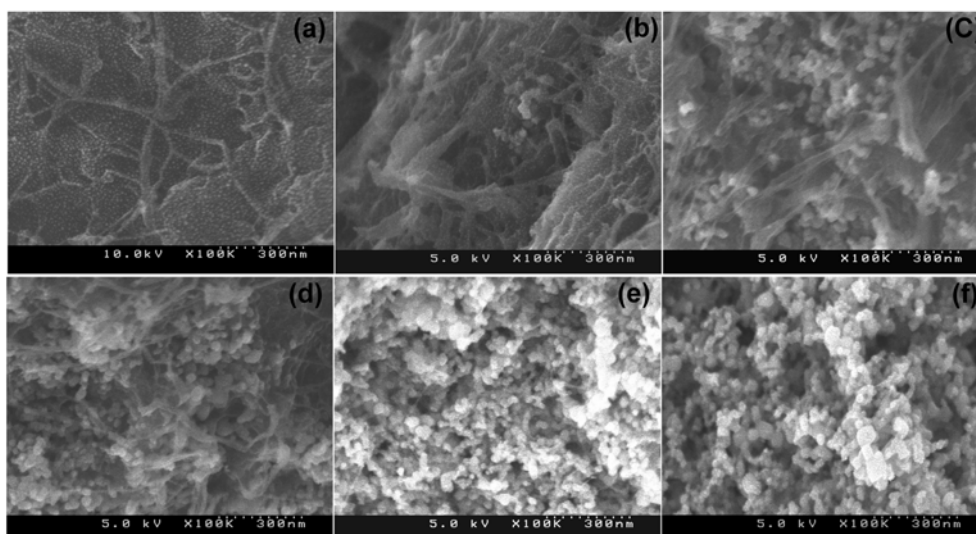


Fig. 1. SEM micrographs of TiO_2 /PANI-DBSA with (a) 0 g, (b) 0.1 g, (c) 0.5 g, (d) 1 g, (e) 3 g, (f) 5 g TiO_2 .

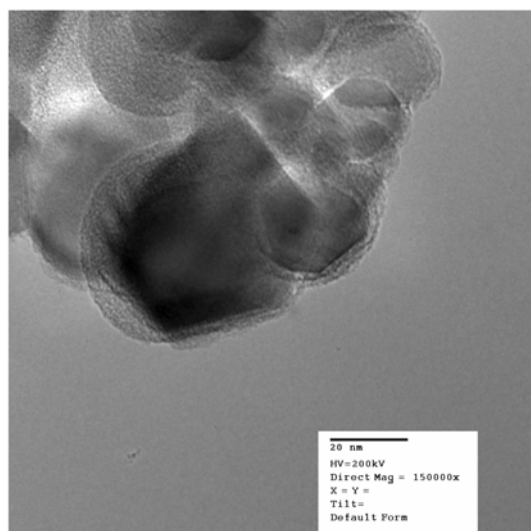


Fig. 2. TEM micrograph of TiO_2 /PANI-DBSA with 1 g TiO_2 .

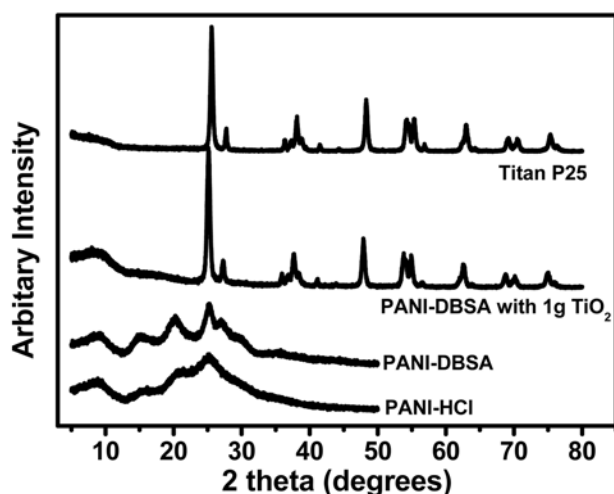


Fig. 3. X-ray diffraction patterns of PANI-HCl, PANI-DBSA, PANI-DBSA with 1 g TiO_2 , Titania P25.

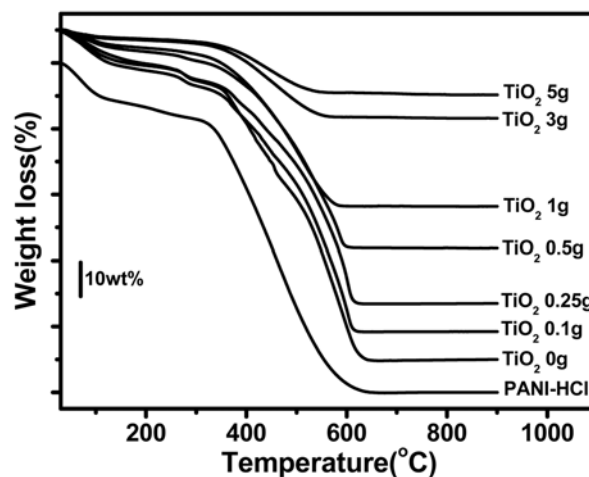


Fig. 4. TG thermograms of TiO_2 /PANI-DBSA composites with various TiO_2 contents.

It can be seen that there is a sharp weight loss observed at about 350 °C corresponding to the degradation of the PANI. The difference in sharp weight loss depends on the amount of the PANI present in the composite because the TiO_2 powder itself does not show any loss in weight in this temperature range of temperature. The composite synthesized in the DBSA solution without TiO_2 has a higher decomposition temperatures than those with no surfactant ones (PANI-HCl). This fact also supports the idea that the addition of the TiO_2 into the PANI during polymerization may cause less incorporation of DBSA molecules into the composite structure than DBSA only (PANI-DBSA) because DBSA acted not only as a dispersant for TiO_2 but also as doping agent.

The PANI portion in the composite was evaluated from these data by using the actual weight loss for the neat 100% PANI sample at the same temperature. The conductivities with various concentrations of PANI-DBSA in the composite are depicted in Fig. 5. This type of curve is typical in most

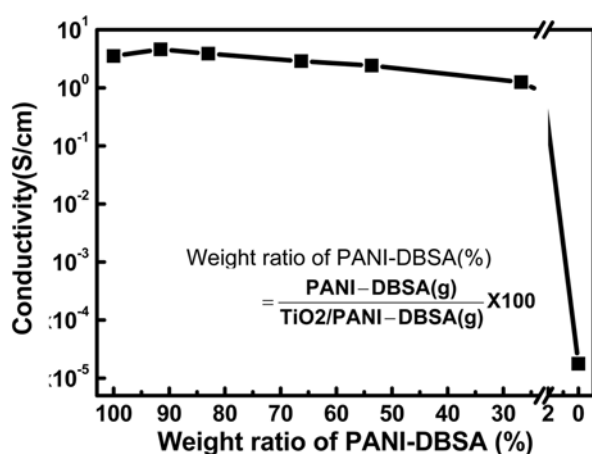


Fig. 5. The conductivities of $\text{TiO}_2/\text{PANI-DBSA}$ composite according to the amount of the TiO_2 .

reports of the composite for conductive materials [8]. The conductivity of the nanocomposite increased slightly with an increase in the TiO_2 content, and then decreased with excess TiO_2 content. Su and Kuramoto suggested that $\text{TiO}_2/\text{PANI-DBSA}$ induced a conformation change of the stiff PANI backbone due to the contacting TiO_2 . To verify this phenomenon, further studies are currently under way in our laboratory. The decrease in conductivity may be due to particle blockage of the conduction path by the TiO_2 nanoparticles embedded in the PANI matrix. An interesting feature of the present study is that the conductivity remained even at low concentrations of PANI-DBSA. This is because the material prepared consists of semi-conducting metal oxide particles covered with a conducting polymer.

b. Preparation of the elastomer composite including TiO_2 coated with PANI-DBSA

During the mixing procedure of the TiO_2 coated with PANI-DBSA solution with the silicone elastomer, the color of the blends remained green. This was the first positive evidence that the PANI-DBSA remained in its doped state because undoped PANI is purple. Fig. 6 shows the electrical conductivity versus PANI-DBSA weight content. As expected, the electrical conductivity of the blends increased as the concentration of the PANI-DBSA increased, from a value of 10^{-14} S/cm (corresponding to the neat silicon elastomer matrix) to 0.295 S/cm for 10 wt.% PANI-DBSA. The percolation threshold occurs at between 1 wt.% and 3 wt.% PANI-DBSA. For low concentrations of PANI-DBSA (less than 1 wt.%) the electrical conductivity of the blends remains at a low level. This might be due to the encapsulation of the dispersed $\text{TiO}_2/\text{PANI-DBSA}$ with the elastomer matrix. By increasing the $\text{TiO}_2/\text{PANI-DBSA}$ content, conductive pathways are allowed to be formed, leading to a steady rise of the conductivity values.

Conclusions

In this study we successfully fabricated conductive

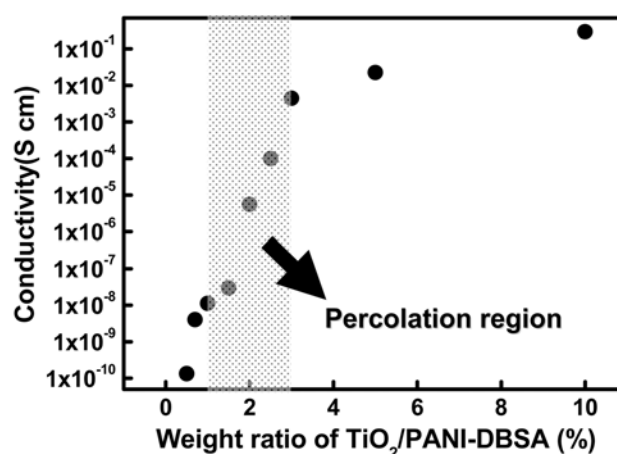


Fig. 6. Electrical conductivities of elastomer composites with various $\text{TiO}_2/\text{PANI-DBSA}$ contents.

silicone elastomer dispersed with $\text{TiO}_2/\text{PANI-DBSA}$ hybrid composites. As the conductive filler, $\text{TiO}_2/\text{PANI-DBSA}$ hybrid composites were prepared by chemical oxidative polymerization and their electrical conductivity slightly increased with an increase in the TiO_2 content and then decreased with further additions of TiO_2 . Also the electrical conductivity of the hybrid composite powder coated with about 20 wt.% PANI-DBSA was 46,000 times higher than that of bare TiO_2 . The novel elastomer-based composites were prepared to mix $\text{TiO}_2/\text{PANI-DBSA}$ dispersion in hexane with a silicone elastomer. This novel elastomer material had a percolation threshold between 1 wt.% and 3 wt.% of PANI-DBSA. For low concentrations of PANI-DBSA (less than 1 wt.%) the electrical conductivity of the blends remains at a low level due to the non-formation of conductive paths. By increasing the $\text{TiO}_2/\text{PANI-DBSA}$ content, conductive pathways are allowed to be formed, leading to a steady rise of the conductivity values. These conductive elastomer composites, which have excellent flexibility, can change their electrical resistance regularly in response to an external pressure, and thus these materials can be used as a sensitive element of a flexible force sensor [9].

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