

# TiO<sub>2</sub> nano-particle-dispersed polyimide composite optical waveguide materials through reverse micelles

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Optically transparent polyimide:titanium dioxide (TiO<sub>2</sub>) composite waveguide materials were prepared by the dispersion of nano-sized TiO<sub>2</sub> particles into polyimide. The particles were produced through reverse micelles using the sol-gel method, and were dispersed into the fluorinated polyimide solution. The solution was coated on a glass substrate, and a polyimide:TiO<sub>2</sub> composite waveguide (4 wt% TiO<sub>2</sub> concentration) was successfully produced after the heat treatment. Because the particle size was very small, no noticeable scattering loss was observed in the resultant slab waveguide. The measured optical propagation loss at 633 nm was 1.4 dB cm<sup>-1</sup>. It is equivalent to that of the pure polyimide, and the refractive index was increased from 1.550 to 1.560 by the incorporation.

## 1. Introduction

Composite materials consisting of sol-gel processed inorganic materials and polymers are useful for the fabrication of optical waveguides, because they have improved thermal and mechanical properties over equivalent pure polymers. Furthermore, they provide the freedom of manipulation of the refractive index [1–5]. The improved mechanical stability is an especially favourable characteristic for the fabrication of a channel waveguide, because the hard materials easily provide a better edge-polishing capability, resulting in lower coupling losses.

Polyimide is one of the most intriguing materials for optical waveguide applications, because it has outstanding thermal stability, high mechanical strength, and low thermal expansion coefficient due to its rigid molecular structure. The amorphous structure of polyimide also provides a low scattering loss; however, at short wavelengths such as 633 nm, conventional polyimides possess high absorption loss due to the charge-transfer structure originated in its aromatic system. Extended efforts have been made to achieve lower absorption loss by introducing bulky fluorine into the molecular structure to hinder the charge transfer by twisting the aromatic plane [6–8]. Therefore, polyimide is an ideal polymer for composite materials for optical applications.

The polyimide composite materials with inorganic molecules such as silicon dioxide and/or titanium dioxide have also been studied by many researchers to improve the mechanical strength of the polymer by forming three-dimensional networks of inorganic sub-

stances [9–14]. The use of the sol-gel method to incorporate polyimide and inorganic materials can be categorized into three approaches: (1) ORMOSIL (organically modified silane) [9, 10], (2) the site isolation concept [11, 12], and (3) the use of a coupling agent [13, 14]. ORMOSIL is a class of molecules possessing two functional groups: one functional group reacts with polyimide monomers and the other reacts with sol-gel precursors, resulting in the formation of a chemical bond between the polyimide backbone and the sol-gel network. The site isolation concept uses polyamic acid, the precursor of polyimide. The carbonyl group of the polyamic acid reacts with the alkoxy group of the sol-gel precursor, forming a bond between the polyimide and the sol-gel material. The use of coupling agents also produces a bond between the polyimide and the sol-gel materials. To achieve polyimide:inorganic composite materials, these approaches were necessary because a simple mixing of polyimide solution and the sol-gel precursor results in phase separation, and the resultant composite materials have large domains which become scattering centres. The present work suggests a new class of polyimide composite materials for optical waveguide applications.

Ultrafine particles have received a great deal of attention because of the novel properties they exhibit which greatly differ from the bulk properties [15]. These include quantum size effect on photochemistry [16], non-linear optical properties of semiconductors [17], and metallic nanoclusters [18]. Various chemical methods have been proposed for the synthesis of

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these particles. Because the particles are prone to aggregate into larger particles, it is necessary to prevent uncontrolled aggregation during the course of preparation. To be able to make these nanostructures, reverse micelles are good candidates [19].

Reverse micelles are spheroidal aggregates formed by the dispersion of a surfactant in an organic solvent [20]. They can be formed both in the presence and absence of water. The presence of water is, however, necessary to form large surfactant aggregates. Water can be readily solubilized in the polar core, forming a "water pool" defined by  $W_0$ , the water-surfactant molar ratio ( $W_0 = [\text{H}_2\text{O}]/[\text{S}]$ ). The aggregates containing a small amount of water (below  $W_0 = 15$ ) are usually called reverse micelles, whereas droplets containing a large amount of water molecules (above  $W_0 = 15$ ) are called microemulsions [21]. Therefore, reverse micelles consist of nanometre-sized water cores which are dispersed in an apolar solvent. Sodium *bis*(2-ethyl hexyl) sulphosuccinate (AOT) is the most common surfactant used to form reverse micelles [22]. These three component systems, hydrocarbon/AOT/ water present enormous advantages. They form spheroidal and monodispersed aggregates where hydrophilic components can be readily solubilized in the polar core. When using iso-octane as a continuous medium, the water pool radius,  $R_w$  is found to be linearly dependent on the water content ( $R_w(\text{\AA}) = 1.5W$ ) [22] which in turn is related to the size of the particles. As a result, particles of various sizes can be synthesized by varying the size of the water pool which serves as a microreactor for carrying out various reactions. Therefore, this approach provides several advantages over conventional methods for the synthesis of fine particles. In conventional methods, chemical reaction in a bulk aqueous medium leads to nucleation and subsequent growth of precipitated particles in an uncontrolled manner. This, as a result, leads to the formation of large particles having a wide distribution of particle sizes. These problems can be overcome using reverse micelle as a reaction medium. In this case, the aqueous pools of reverse micelles are utilized which serve as a small micro- or even nano-reactor in which reaction can be carried out.

The reverse micelle and microemulsion techniques have a further (potential) advantage which is yet to be investigated. That is, depending on the location within the phase diagram, the microemulsion may assume a variety of structures: spherical, cylindrical, lamellar, etc. Thus besides the size, one can even control the morphology of the particles.

In the present work, the synthesis of  $\text{TiO}_2$  particles was done by carrying out the hydrolysis of titanium isopropoxide (TIP) in an AOT/isooctane reverse micellar system. TIP was dissolved in the bulk oil continuous medium (isooctane) and water required for the hydrolysis was provided by the aqueous pools of reverse micelles. When the solution containing TIP was mixed with the reverse micellar solution containing water in the reverse micelles, TIP slowly diffuses into the reverse micelles and hydrolysis and polycondensation reactions take place in the reverse micellar microreactor, resulting in the formation of  $\text{TiO}_2$  par-

ticles. The  $\text{TiO}_2$  particles were extracted from the solution, and dispersed into a fluorinated polyimide solution. The solution was then coated on a glass plate, and a polyimide: $\text{TiO}_2$  composite optical waveguide film was formed after a heat treatment. This approach differs from the above-mentioned three approaches to realize polyimide composite materials in that it is solid-state impregnation using pre-prepared nano-sized particles, but the resultant materials still possess optical quality.

## 2. Experimental procedure

The reagents used in this work: sodium *bis*(2-ethyl hexyl) sulphosuccinate (AOT), titanium iso-propoxide (TIP), isopropanol, isooctane (2,2,4 trimethyl pentane), and *N*-methyl pyrrolidinone (NMP) were obtained from Aldrich and used without further purification. The polyimide we used was a fully fluorinated polyimide obtained from Amoco Chemical Co. (Ultradel 9020D), which had the solid concentration of 8.7 wt % in gamma-butyrolactone solvent system.

The reverse micellar solution was prepared by dissolving AOT in isooctane (0.1 M) and the resulting solution was filtered using a Teflon membrane filter (0.2  $\mu\text{m}$  pore size, Spartan-T). This was followed by the addition of the required amount of prefiltered distilled water. The water-surfactant ratio,  $W_0$ , was varied in the range 1–8. TIP was diluted with isopropanol to be 13 wt %, and the hydrolysis of TIP was carried out in a conical flask (100 ml) at room temperature. The reaction was initiated by the injection of the TIP solution (200  $\mu\text{l}$ ) into the reverse micellar solution (30 ml) with mild stirring on a magnetic stirrer. The formation of  $\text{TiO}_2$  particles within the reverse micelles was characterized through UV-visible absorption spectra recorded on a Shimadzu UV-VIS-NIR spectrophotometer (Model UV 3101 PC) with a quartz cuvette possessing an optical path length of 1 cm. The  $\text{TiO}_2$  particles were then extracted from the reverse micellar solution by the addition of a known volume of NMP (4 ml). Immediate phase separation occurred and the particles were extracted in the lower NMP phase. To this NMP solution containing  $\text{TiO}_2$  particles, the polyimide solution was added under stirring, and a uniform, clear, viscous solution was obtained.

Corning micro-slide glass plates (number 2947) were used as the substrates. The substrates were cleaned with acetone and dried with blowing air after rinsing with ethanol. The adhesion promoter obtained from Amoco Chemical Co. (Ultradel A600) was spin-coated on the surface of the substrate at 3000 r.p.m. for 20 s, and baked at 150 °C for 10 min to provide better adhesion between the substrate and the film.

To fabricate optical waveguides, the  $\text{TiO}_2$  particle-containing polyimide solution was cast on the substrate with Teflon tapes (thickness  $\sim 100 \mu\text{m}$ ) as the spacer between the substrate and the casting blade. The film was immediately baked on a 100 °C hot plate for 10 min, otherwise the film became opaque due to moisture intake from the air. The film was then baked at 200 °C for 30 min, followed by heat treatment of

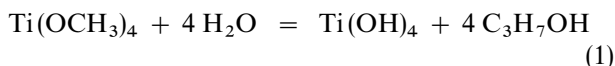
300 °C for 30 min in a nitrogen atmosphere with the increasing temperature rate of 6.67 °C min<sup>-1</sup>.

Refractive index and film thickness were calculated from coupling angles measured by the prism coupling technique [23] using a TiO<sub>2</sub> rutile prism and a He–Ne laser (Melles Griot, wavelength 632.8 nm, output lower 3 mW). Optical propagation loss was measured by observing the optical intensity decay of the streak line with a CCD camera (Electrim Corp., Computer camera EDC-1000). The intensity decay in each pixel of the CCD camera was digitized and plotted (in dB) with respect to the propagation distance (cm). The slope is the optical propagation loss (dB cm<sup>-1</sup>). All measurements in the present work were proceeded in the TE mode .

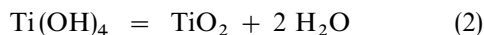
Thermal properties of the materials were evaluated with a thermogravimetric analyser (TGA, Shimadzu TGA-50) with the temperature ramping rate of 10 °C min<sup>-1</sup> up to 500 °C and a flow of nitrogen gas.

### 3. Results and discussion

The formation of metal oxide particles by hydrolysis of metal alkoxide involves a hydrolysis stage, a nucleation stage, and a particle growth stage. The first stage is the hydrolysis of the metal alkoxides and the formation of hydrolysed species. In the case of TIP, the overall hydrolysis reaction is described as



Titanium dioxide is then formed by the polycondensation of the hydrolysed species



In the nucleation stage, the nuclei are formed from the hydrolysed molecules. Because small particles have high solubility, a certain number of hydrolysed molecules in the oversaturated solution are required in order to form stable nuclei which grow to larger particles. In the growth stage, larger particles are formed by particle growth, aggregation and Ostwald ripening. Particle growth, however, is the principal process and this occurs by the addition of hydrolysed molecules while aggregation is the result of Brownian motion and coagulation of particles.

Fig. 1 shows the UV–visible absorption spectra obtained from the hydrolysis of TIP in various reverse micellar systems ( $W_0 = 1–8$ ). In all the spectra, the peak around 300 nm suggested that TiO<sub>2</sub> particle formation had taken place in all cases [24]. The absorption became stronger with time, and was saturated in 60 min. The spectra in Fig. 1 were collected after the saturation. It is also observed in Fig. 1 that the peak height varies depending on droplet size,  $W_0$ ; the peak height increased until  $W_0 = 5$ , then decreased. This is because at larger droplet size, the particle size being large, the density of the particle in the solution becomes low; therefore, the absorption peak decreases. In addition, when the particle size is large, scattering of light takes place at the surface of the particles; as a result, light cannot penetrate TiO<sub>2</sub> particles.

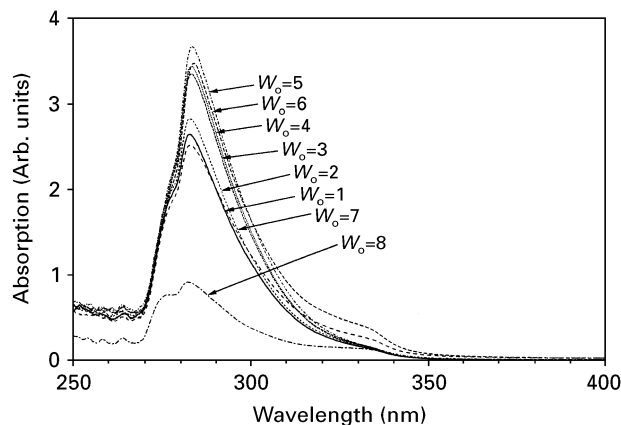


Figure 1 UV–visible spectra of reverse micellar solutions prepared with different water to surfactant ratios,  $W_0$ .

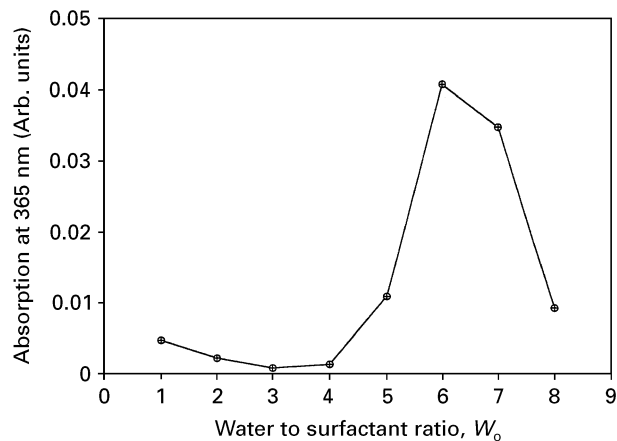


Figure 2 The absorption values at the wavelength of 365 nm obtained from Fig. 1 as a function of  $W_0$ . This wavelength is far from the absorption wavelengths; therefore, the value represents scattering loss from the solution.

Fig. 2 shows the absorption values at the wavelength of 365 nm obtained from Fig. 1 as a function of  $W_0$ . This wavelength is off the absorption wavelengths; therefore, the value represents scattering loss of the solution. In Fig. 2, it is observed that at smaller droplet sizes ( $W_0 < 4$ ), the size of particles being small, the scattering obtained due to the size is considerably low. With increasing water pool size ( $W_0 > 5$ ), various factors such as Brownian motion, interparticle diffusion, aggregation, come into force, thereby causing growth/increase of particle size and hence lead to scattering. However, when  $W_0$  is over 7, the absorption eventually decreases because of low TiO<sub>2</sub> particle density in the solution. Therefore, TiO<sub>2</sub> particles produced with  $W_0 = 2–4$  are suitable for the impregnation into the polyimide system.

Another interesting observation from Fig. 1 is the shift of the absorption peak position. In Fig. 3, the peak positions obtained in Fig. 1 were plotted with respect to  $W_0$ . It was observed that with decrease in the size of TiO<sub>2</sub> particles, the absorption peak shifts to shorter wavelengths (blue shift) [25]. However, above  $W_0 = 7$ , the position shifted back to a shorter wavelength due to increased scattering loss contribution at shorter wavelengths. This result indicates that

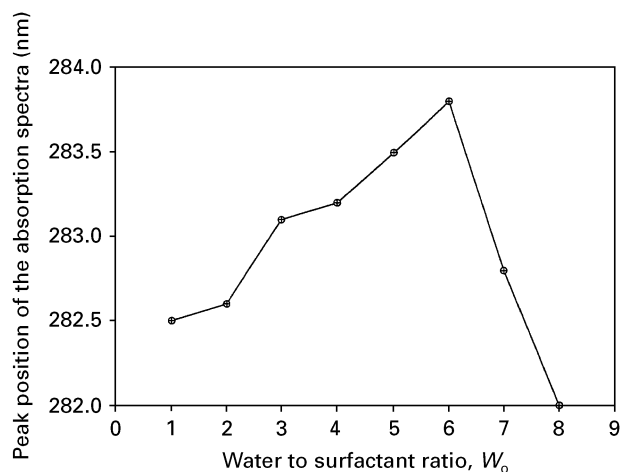


Figure 3 Change of peak position in the absorption spectra in Fig. 1 as a function of  $W_0$ .

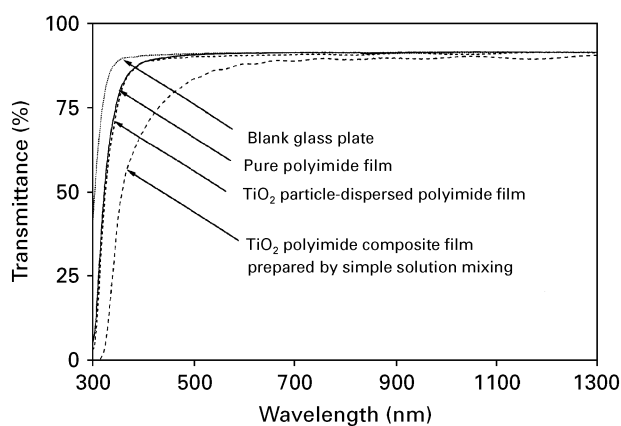


Figure 4 Transmission spectra of various polyimide-processed films.

the  $\text{TiO}_2$  particle size can be controlled by changing  $W_0$ ; the smaller the  $W_0$ , the smaller is the  $\text{TiO}_2$  particle size.

We chose the droplet size of  $W_0 = 2$  to produce  $\text{TiO}_2$  particle-dispersed polyimide films. The resultant film possessed a  $\text{TiO}_2$  concentration of 4 wt %. This value was calculated from the doses of TIP and polyimide. We also tried to fabricate composite films with higher  $\text{TiO}_2$  concentrations; however, concentrations higher than 4 wt % resulted in high scattering losses in the optical waveguides due to the aggregation of the  $\text{TiO}_2$  particles. The  $\text{TiO}_2$ :polyimide composite film with the  $\text{TiO}_2$  concentration of 4 wt % was used for further investigation in the present work.

The UV-visible transmission spectra of the  $\text{TiO}_2$  particle-dispersed polyimide film, along with those of a pure polyimide film, and a blank glass slide, are shown in Fig. 4. These results suggest that the impregnation of  $\text{TiO}_2$  particles does not show any significant absorption increase due to the discoloration of the material. For comparison, we also prepared a film by simple mixing of TIP/2-propanol solution with the polyimide solution, followed by film casting and heat treatment. This process produced a yellow film due to the discoloration of the system, and the film had a strong absorption at shorter wavelengths. The spectrum of this film is also shown in Fig. 4. This discoloration must originate from the absorption of

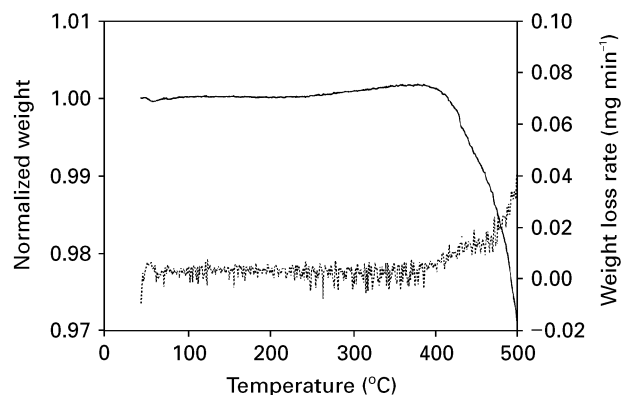


Figure 5 The TGA curve of the  $\text{TiO}_2$  dispersed polyimide (4 wt %).

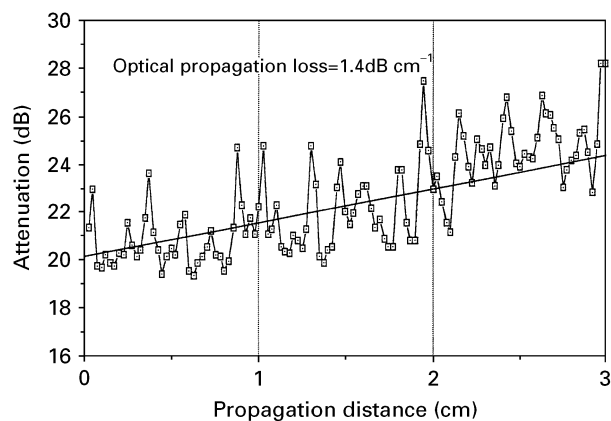


Figure 6 Results of the measurement of the optical intensity decay along the streak line in the  $\text{TiO}_2$  particle-dispersed polyimide waveguide.

a titanium complex produced by the reaction of TIP and polyimide or the impurity of polyimide in the solution state. The advantage of our approach is that it avoids the formation of this titanium complex, and therefore, yields a more transparent film.

The thermal stability of the  $\text{TiO}_2$ -dispersed (4 wt %) polyimide was evaluated using the TGA technique. A sample for the TGA study was prepared by the same procedure as the film preparation described above. The result is shown in Fig. 5, and it is identical to that of the pure polyimide. It yields a 1% weight loss in nitrogen at  $461^\circ\text{C}$ , which is almost the same as is provided in the technical data sheet of Ultradel from Amoco Chemical Co. ( $475^\circ\text{C}$ ). This suggests that impregnation of the  $\text{TiO}_2$  particles produces no change of the thermal characteristics of the polyimide host.

The  $\text{TiO}_2$  particle-dispersed film was evaluated as an optical waveguide, and the measured optical propagation loss curve is shown in Fig. 6. The optical propagation loss was calculated to be  $1.41\text{ dB cm}^{-1}$  from the slope. This number is the same as that of pure polyimide. This suggests that the particle size of  $\text{TiO}_2$  is small enough to avoid scattering loss, and no absorption loss is created by the dispersion of  $\text{TiO}_2$  particles. This is because  $\text{TiO}_2$  is dispersed in the solid state in the present approach; therefore, the formation of various kinds of absorbent species, such as a titanium complex, is avoided, which is a common

problem in solution state impregnation. The optical propagation loss of the above-mentioned sample which was prepared by the simple mixing of TIP solution and polyimide solution, was also measured; however, no visible streak line was observed because of a high absorption loss due to a long absorption tail. The propagation loss of this sample was estimated to be over  $20 \text{ dB cm}^{-1}$  at 633 nm.

The refractive index of the  $\text{TiO}_2$  particle-dispersed polyimide film was also calculated from the prism coupling angles, and was 1.560, which is 0.010 higher than that of pure polyimide (1.550). The refractive index of amorphous  $\text{TiO}_2$  is around 2.2, therefore the expected refractive index of 4 wt %  $\text{TiO}_2$  in polyimide should be 1.576, which is higher than that measured. This may be due to a portion of  $\text{TiO}_2$  particles having been lost during the process, which leads to the real concentration being lower than 4 wt %.

In conclusion, we have demonstrated a new approach to prepare a polyimide:inorganic composite material for optical waveguide applications. This approach is a unique solid-state impregnation using pre-prepared nano-sized particles in reverse micellar micro-reactors, and has a potential to impregnate different kinds of active inorganic materials into a polymer matrix to add functions, without the loss of optical quality.

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