Synthesis of UV-curable resin/ZnO composite films as pH buffering material

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Abstract: UV-curable Resin/ZnO composite film, which has advantages including UV-curable property and pH buffering ability, was prepared through incorporation of pre-made ZnO nanoparticles and UV-curable resin. The resins we used in this paper were R1 and R10. R1 was Bisphenol A epoxy diacrylate (EA) dissolved in propylene glycol monomethyl ether acetate (PGMEA), and R10 was synthesized by EA, pyromellitic dianhydride (PMDA) and 2-hydroxyethyl methacrylate (HEMA), and then followed by characterization using FTIR and GPC. The ZnO nanoparticles were prepared from Zinc acetate and Sodium hydroxide in 1-butanol by hydrothermal method. “Physical Adsorption” and “Mixture Coating” were two ways to prepare the Resin/ZnO composite film. Then, the pH buffering ability of the Resin/ZnO composite film was evaluated by soaking the film in the pH4 or pH10 solution, and the variation of pH value was recorded with time. The result shows that F10/ZnO composite film obtained from R10/ZnO by “Physical Adsorption” method could be a good buffering material to justify either pH4 or pH10 solution to pH7.4 in 5 min and F10/ZnO composite film by “Mixture Coating” method could be a long time pH buffering material.

Key words: UV-curable resin; ZnO; composite film; pH buffering

Introduction

UV-curable coating is an extremely interesting class of materials that has gained considerable attention in the past decade, due to the advantages of lower energy consumption, less environmental pollution and very rapid curing even at ambient temperature [1-3]. This kind of formulation consists of one or more photosensitive groups, C=C bonds for example, which can be polymerized under UV radiation. Among UV-curable resins, Bisphenol A epoxy acrylate has been widely used as coating, structure adhesives and advanced composite matrices because of its excellent chemical and solvent resistance, good thermal and adhesion properties, and versatility in cross-linking [4]. To satisfy needs to have pH buffering ability, carboxylic acid groups were introduced into UV-curable resin in the side chain of the resin. Nishikubo et al. [5] synthesized a hyper-branched polyimide containing both methacrylate and carboxylic acid groups at the chain ends through the reaction between carboxylic acid anhydrides, trisamines and the glycidyl methacrylate.

For high performance or other requirements, organic-inorganic hybrid materials may be a better choice. They offer the benefits: combining the properties of organic
polymers (toughness, processability) and inorganic solids (hardness, chemical resistance) [6, 7]. In addition, hybrid materials can also have excellent optical property, high mechanical stability [8], low water absorption and water vapor permeability [9].

Zinc oxide (ZnO) is a technologically important material. It is a semiconductor material with band-gap of 3.37eV and exciting binding energy of 60meV [10]. These properties make ZnO hybrid materials interesting for photonic application in the UV region [11]. The common ways to synthesize ZnO nanoparticles are Sol-gel Method [12], Homogeneous Precipitation [13], Chemical Vapor Deposition [14], and Hydrothermal Method [15].

In the previous research, ZnO were combined to poly(ethylene oxide), poly(methyl methacrylate), polyimide, poly(hydroxyethyl methacrylate), poly(ethylene glycol), Nylon-6 [16-19]. Moreover, one-dimensional nanostructures, such as nanorods, nanowires and nanotubes are believed to be potential components for further photoelectrical devices. Lu et al. [20] introduced pre-made ZnO nanoparticles into monomer mixtures of urethane-methacrylate oligomer and 2-hydroxyethyl methacrylate (HEMA) to prepare a UV-curable ZnO/polymer nanocomposite films.

ZnO is known to be an amphoteric substance that reacted with an acid or a base. In acidic medium, ZnO reacted with proton to form Zn$^{2+}$ and H$_2$O, while in a basic medium, ZnO reacted with hydroxide group to form [Zn(OH)$_4$]$^{2-}$. The reactions of ZnO in acid and in base medium are described in Reactions 1 and 2:

$$\text{ZnO} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \quad (1)$$

$$\text{ZnO} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow [\text{Zn(OH)}_4]^{2-} \quad (2)$$

In this study, we successfully introduced pre-made uniform and well-dispersed ZnO nanoparticles into UV-curable resin to prepare Resin/ZnO composite film which not only can be UV-curable, but also has pH-tuning ability. Two kinds of UV-curable resins, R9 and R10, were prepared and followed by characterizing the structure of resins by FTIR and GPC. ZnO nanoparticles were synthesized by Hydrothermal Method in the presence of NaOH. Consequently, Resin/ZnO composite films were prepared by two methods, “Physical Adsorption” and “Mixture Coating”. The pH buffering ability of Resin/ZnO composite films was evaluated.

**Results and discussion**

In this work, UV-curable resin, R9, was first prepared by the esterification between OH groups of EA and anhydride groups of PMDA at fixed molar ratio as shown in Fig. 1. Their structures were confirmed by FTIR and GPC analysis. As shown in Fig. 2, it could be seen in the spectrum of R9 that absorbance of hydroxyl group between 3200 and 3600 cm$^{-1}$ largely decreased and smoothed compared to EA originally. The reaction of PMDA and hydroxyl groups was the reason that the hydroxyl groups disappeared and the carboxylic acid groups appeared which exhibited a broad adsorption peak between 2500 and 3300 cm$^{-1}$. Meanwhile, the two adsorption peaks at 1780 and 1855 cm$^{-1}$ in R9 confirmed the formation of anhydride groups. Yet, small peak at 3500 cm$^{-1}$ is still observed indicating some unreacted hydroxyl groups in R9.

Fig. 3 shows the FTIR spectra of R9 and R10. It could be seen in the spectrum of R10 that the anhydride group at 1780 and 1855 cm$^{-1}$ disappeared compared to R9 due to the reaction of R9 and HEMA. This reaction produced more carboxylic acid groups which enlarged the peak between 2500 and 3300 cm$^{-1}$. 
Fig. 1. Synthesis and proposed structure of resin R9 and R10.

In addition, the GPC analysis is shown in Fig. 4 and Fig. 5. It could be seen that the original EA reactant (R1) has two peaks from Fig. 4, indicating that there are two different molecular weights in EA, n=0 and n=1 for repeating units respectively. The average n value calculated from the corresponding peak area in the spectrum is
about 0.3. The two peaks disappeared after the reaction with PMDA as the molar ratio of EA and PMDA was 1 : 2 , as seen in R9. Then, R9 reacted with HEMA at molar ratio 1:3, and a broad multi-peak with higher molecular weight was observed for the R10 product in Fig. 5.

**Fig. 2.** FTIR spectra of R1 and R9.

R9 and R10 are basically oligomers having molecular distribution, because they are synthesized from the compounds with functionality > 2. From GPC results, the
distribution curve of R10 shifts to higher MW region. Thus, the average MW of R10 increases as compared to R9.

Fig. 4. GPC curves of R1, PMDA and R9.

Fig. 5. GPC curves of R9, HEMA and R10.

The aim of this work was to obtain a UV-curable resin with pH buffering ability. In the experiment, the pH buffering ability was evaluated by soaking the resin films into a
testing solution with pH4 or pH10 at a weight ratio of 1:1000. The variation of pH was recorded at 5, 10 and 20 min.

Fig. 6(a) shows that the resin film, F1 was almost neutral and it did not provide pH buffering ability either in acid or in base solution. Therefore, a series of resins with carboxylic acid groups was further synthesized from R1 by adding PMDA and HEMA to obtain R9 and R10, respectively. The amounts of carboxylic acid groups in R9 and R10 can be theoretically determined by the structures shown in Fig. 1. When n is 0, for example, R9 has 2 and R10 has 4 carboxylic acid groups. When n is 1, R9 has 4 and R10 has 6 carboxylic acid groups. Consequently, R10 is more acidic than R1 and R9 to perform the better base buffering. Meanwhile, by means of base solution titration method, the acid value of R10 was determined and a piece of F10 film weighting 0.05 g had 2.25×10^{-4} mole of carboxylic acid groups approximately. However, From Fig. 6(b), F10 film could lower the pH significantly in the base solution.
but it is not working in the acid solution. Therefore, the resin film itself could not meet the requirement to be a pH buffering material in both acid and base solutions.

Fig. 7. TEM image of ZnO nanoparticles.

Fig. 8. SEM image of F10/ZnO composite film by “Physical Adsorption” method.

For this reason, ZnO was introduced to prepare composite films because ZnO was an amphoteric substance that reacted with an acid or a base. The TEM image of ZnO
nanoparticles synthesized by hydrothermal method with NaOH (Reaction 3) is shown in Fig. 7. It’s about 5-10 nm for each ZnO particle, well-dispersed in 1-butanol.

\[ \text{Zn(CH}_3\text{COO)}_2 + 2\text{NaOH} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{Na(CH}_3\text{COO)} \]  \hspace{1cm} (3)

Two methods, “Physical Adsorption” and “Mixture Coating” were used to prepare Resin/ZnO composite films. In the “Physical Adsorption” method, ZnO nanoparticles were deposited on the surface of the resin film and rinsed by 1-butanol. The pH buffering ability of F1/ZnO film was very poor in the base solution, as shown in Fig. 6(a). Although the F1/ZnO film could neutralize the acid solution, the pH value in the base solution remained nearly unchanged similar to F1 film. On the other hand, F10/ZnO composite film tuned pH4 or pH10 solution to pH7.4 quickly as seen in Fig. 6(b). The SEM image of F10/ZnO is shown in Fig. 8, in which ZnO nanoparticles were adsorbed on resin film F10 randomly. Consequently, by combining the functions of F10 and ZnO, F10/ZnO composite film by “Physical Adsorption” method presented a very good pH buffering ability.

Fig. 9. The pH tuning test of the composite films by “Mixture Coating” method (a) F1 and F1/ZnO film (b) F10 and F10/ZnO film.
The second method, “Mixture Coating”, was used to prepare a long time pH buffering composite film. Comparing to the “Physical Adsorption” method, ZnO was dispersed in various depth in the composite film. At the beginning of the buffering test, ZnO on the top surface exposed and functioned to the solution quickly. With time, the composite film in the water solution would swell and the ZnO nanoparticles inside would function and get exposed to the solution gradually and continually. The swelling phenomena let the film keep the buffering ability for a period of time. From Fig. 9(a) and 9(b), the pH buffering ability of F1/ZnO and F10/ZnO composite films was a little weaker in the first 20 minutes if compared with Fig. 6(a) and Fig. 6(b), but it would keep working continuously. Therefore, the “Mixture Coating” method was suitable for preparing a long time pH buffering composite film.

Conclusions
A new series of UV-curable resin with carboxylic acid groups were synthesized based on the reaction of the EA, PMDA and HEMA. The structure of resins, R1, R9 and R10 were confirmed by FTIR and GPC. Then, resin and ZnO were mixed to obtain composite films in order to provide a good pH buffering ability. F10/ZnO composite film by “Physical Adsorption” method could adjust pH4 or pH10 solution to pH7.4 in 5 min and the composite film by “Mixture Coating” method could retain the pH buffering ability for a longer time. Therefore, by controlling the number of carboxylic acid groups on the resin and changing the preparation method for the composite films, UV-curable composite films with different pH buffering ability could be prepared.

Experimental part

Materials
2-Hydroxyethyl methacrylate (HEMA, ACROS) and propylene glycol monomethyl ether acetate (PGMEA, Grand Chemical) were dried under vacuum prior to use. Bisphenol A epoxy diacrylate (EA) (Mw=512) was purchased from AGI Corporation to synthesize a series of Resin. Pyromellitic dianhydride (PMDA) was obtained from Acros. 2-Methyl-1,4-(methylthio)phenyl-2-morpholino-propan-2-one (I907) was used as a photo initiator received from Ciba. Zinc acetate, the material used for preparing ZnO was obtained from Sigma-Aldrich. 1-Butanol (HPLC, 99.5+) was purchased from Acros and used as a solvent during preparing ZnO solution. Sodium hydroxide (NaOH, SHIMAKYU) and hydrochloric acid (HCl, SHIMAKYU) were used in synthesizing ZnO and in preparing the acid and base solution.

Synthesis of Resins, R1 and R10
EA was dissolved in PGMEA at solid content 40% to prepare R1. EA and PMDA were mixed in PGMEA at molar ratio 1:2, and the solid content in PGMEA was also 40%. The reaction mixture was stirred by a magnetic stirring bar and kept at 100 °C for 12 h in a nitrogen atmosphere to synthesize a UV-curable resin, R9. R9 and HEMA at molar ratio 1:3 were further dissolved in PGMEA to synthesize a UV-curable resin containing COOH groups, R10. The solid content was 40% and the reaction condition was 100 °C for 12 h. The syntheses of R9 and R10 are shown in Fig. 1.
**Synthesis of ZnO**

In the preparation of ZnO nanoparticles, 9.9 g Zinc acetate and 3.6 g NaOH were separately dissolved in 135 ml and 90 ml 1-butanol, respectively. The NaOH/butanol solution was added drop by drop into the zinc acetate/butanol solution. The mixture was kept at 60 °C for 2 h, and ZnO nanoparticle dispersion solution was obtained.

**Preparation of film**

Resin films, F1 and F10, were prepared by dissolving 5% I907 in R1 and R10 solution respectively, and then spin coating onto a glass substrate at 300 rpm for 10 s. The films were then pre-baked at 50 °C for 5 min, dried at 50 °C for 1 h and subsequently exposed to UV light (Jiann Haur Machine co., JH1000-2) at wavelength 250~450 nm (1000 mJ/cm²) for curing. Finally, the resulting films, F1 and F10, were post-baked at 100°C for 1 hr. The film preparation is shown in Scheme 1.

**Scheme 1. Preparation of F1 and F10 films.**

Resin/ZnO composite film was prepared by two methods. The first method, called “Physical Adsorption”, was prepared by putting the film (F1 or F10) on the bottom of the suspension ZnO solution vessel for one hour. Then, the composite film was rinsed by 1-butanol and dried in the oven to obtain F1/ZnO and F10/ZnO composite films.

“Mixture Coating” was the second method to prepare Resin/ZnO composite film. To do this, 5 g of resin solution (R1 or R10 in PGMEA at 40 wt%) and 80 g of ZnO nanoparticle transparent dispersion solution were mixed under stirring to form a translucent solution due to the aggregation between the resin and ZnO. The Resin/ZnO composite translucent solution was centrifuged at 12000 rpm for 10 min, and the precipitate, which included resin and ZnO, was obtained and dried in vacuum at 50 °C for 24 h. Then, PGMEA was used to dissolve the dried Resin/ZnO mixture at solid content 40%. The preparation of Resin/ZnO composite films was the same as scheme 1: 5% I907 addition, spin coating at 300 rpm for 10 s, pre-baking at 50 °C for 5 min, drying at 50 °C for 1 h, UV curing (1000 mJ/cm²) and post-baking at 100 °C for 1 h. After all these steps, F1/ZnO and F10/ZnO composite films by “Mixture Coating” method were obtained.
Characterization

Functional groups in R1, R9 and R10 were characterized by Fourier transform infrared spectroscopy (FTIR, Digilab FTS4000) in the range of 4000-900 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). The resin solution was dropped on the KBr and dried in vacuum to form a resin film and a transmittance mode was used to obtain FTIR spectra. Molecular weights of resins and reaction compounds were determined by gel permeation chromatography (GPC) equipped with three columns (Waters 1000 Å, Phenomenex 50000 Å and 10\(^9\) Å), and a RI detector (Shodex RI-71) under the effluent of THF solvent at a flow of 1 ml/min and the reported molecular weight values were based on polystyrene standards. To observe the morphology of ZnO, Hitachi H-7100 Transmission Electron Microscope (TEM) was used. In addition, the morphology of Resin/ZnO composite film was recognized by using a JEOL JSM-6700F scanning electron microscope (SEM).

The pH tuning test was performed by pH meter (HORIBA F-51). HCl and NaOH were used to adjust the pH value of the testing solution. The pH buffering ability of the Resin/ZnO composite film was evaluated by soaking the film on the substrate into a testing solution with pH4 or pH10. 50 ml of the testing solution was used for 0.05 g film and the variation of pH value was recorded with time. The surface area (one side) of the film was about 9.88 cm\(^2\) in each experiment.

References