



Short communication

Anionic UV curing of epoxy resins containing dispersed scaly silica modified with base-amplifying groups

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ABSTRACT

A cured organic-inorganic composite material where scaly silica (SS) was well-dispersed has been successfully fabricated with a tetrafunctional epoxy resin and chemically-modified SS through an effective anionic UV-curing system using base proliferation reactions. SS chemically-modified with base-amplifying groups (1.4 wt% toward SS) was prepared, and anionic UV curing of an epoxy resin containing 100 wt% of chemically-modified SS was achieved after 5000 mJ/cm² of light irradiation at a wavelength of 365 nm and subsequent heating at 160 °C for 30 min. It was found by scanning electron microscopic study that the chemically-modified SS was well dispersed in the UV-cured film, and that unmodified SS was found to be aggregated.

1. Introduction

UV-cured materials are widely used to protect the surfaces of various kinds of industrial products [1]. UV-curing systems are classified into radical, cationic and anionic. In a conventional radical UV-curing system, polymerization reactions triggered by photoradical initiators proceed quickly, although volume shrinkage and inhibition by oxygen during the reactions are serious problems not to be ignored [2,3]. A cationic UV-curing system with photoacid generators overcomes such problems; however, the erosion of metallic substrates by the photo-generated acids is of concern. Comparing these two curing systems, an anionic UV-curing system would circumvent all the above-mentioned problems, whereas photobase generators (PBGs) have low quantum yields in general [4]. Recently, this situation has been markedly improved, resulting in base-reactive materials having high photosensitivity [5]. Furthermore, our group has proposed the incorporation of base proliferation reactions [6a] of base amplifiers into anionic UV-curing systems, to increase the apparent quantum yields of PBGs. A base amplifier is defined as a compound that can increase the concentration of base molecules secondarily, by its autocatalytic decomposition reaction triggered by a small amount of base. Various kinds of base amplifiers have been designed and reported [6]. For example, epoxy polymers are one of the common base-reactive materials that have been insolubilized more efficiently by using base amplifiers with PBGs than by using PBGs only [7].

Photo-triggered base proliferation reactions are applied to UV

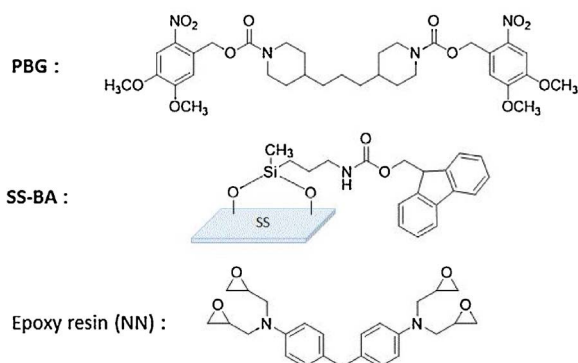
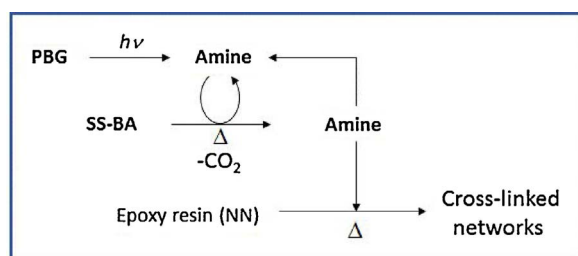
curing of organic-inorganic compositions, because the base proliferation reaction itself does not require UV irradiation and proceeds even in the dark under inorganic components. In recent years, organic-inorganic composite materials, where inorganic compositions are combined with organic polymer networks to improve the physical properties of resulting cured materials, have become attractive [8–16]. Our group has reported the fabrication of anionic UV-cured epoxy films containing silica particles with a high filling rate without any aggregation, by using base-amplifying silica particles [17]. The resulting organic-inorganic composite material showed high mechanical strength and transparency.

Silica, a typical inorganic component, has low toxicity and high general versatility, and it can be manufactured in various shapes [18]. It is generally known that a high aspect ratio of the inorganic components contributes to a high mechanical strength of the composite material [19]. In this communication, scaly silica (SS) chemically modified with base-amplifying groups (SS-BA) was prepared and mixed with an epoxy resin. As shown in Scheme 1, SS-BA having organic modifying groups was dispersed in a tetra-functional epoxy resin, 4,4'-methylenebis(*N,N*-diglycidylaniline) (NN). In a composite material, it is important to ensure compatibility between the organic and inorganic components, for the dispersion of the latter component. A trigger amount of diamines was photo-generated from PBG [17], and then the base-amplifying groups of SS-BA decomposed autocatalytically into primary amino groups. The chosen base amplifier was 9-fluorenylmethyl carbamate, where an amine is generated via an abstraction reaction of the methane proton by a base [4a,c,20]. The epoxy groups of

Abbreviations: PBG, photobase generator; SS, scaly silica; THF, tetrahydrofuran; TGA, thermogravimetric analysis

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Scheme 1. Anionic UV curing of an epoxy resin, NN, with a PBG and SS-BA (a hypothetical structure).

NN react with these amino groups to form rigid cross-linked networks that immobilize the SS both physically and chemically.

2. Material and methods

2.1. Materials

3-Aminopropyl-diethoxymethylsilane and 9-fluorenylmethyl chloroformate were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). SS (SUNLOVELY) was supplied by AGC Si-Tech Co., Ltd. (Fukuoka, Japan). NN was purchased from Sigma-Aldrich Japan (Tokyo, Japan). All chemicals and reagents were used without further purification.

2.2. Physical measurements

^1H NMR measurements were performed using a JNM-ECO300 FT NMR (JEOL) system. For the FT-IR measurements a Jasco FT/IR-6100 spectrometer was used. TG-DTA measurements were performed using a Mac Science TG-DTA2000 thermal analyser. Photoirradiation with light at 365 nm wavelength was conducted using a 15 LHPUV365 LED lamp (Iwasaki Electric Co. Ltd.). The pencil-hardness tests of the UV-cured films were performed using a No. 533-M Electric System Pencil Scratch Hardness Tester (Yasuda Seiki Seisakusho). The SEM was model S-3000N (Hitachi High-Technologies Corporation).

2.3. Synthesis of Silane-BA

Silane-BA was synthesized in one reaction step [17]. To a solution of 9-fluorenylmethyl chloroformate (2.0 g, 11 mmol) in dry tetrahydrofuran (THF, 30 mL) were slowly added (3-aminopropyl)methyldiethoxysilane (1.8 g, 9.4 mmol) and triethylamine (1.2 g, 11 mmol) in dry tetrahydrofuran (THF, 30 mL) at 0 °C. The mixture was stirred at room temperature for 1.5 h. After removing the solvent, the crude product was purified by TEOS column chromatography with hexane/ethyl acetate (3/1, v/v) to give the product with 95% yield as a white solid (3.9 g). ^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.13 (3H, s, $-\text{Si}-\text{CH}_3$), 0.62 (2H, t, $J = 7.2$ Hz, $-\text{Si}-\text{CH}_2-$), 1.21 (6H, t, $J = 6.9$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_3$), 1.61 (2H, quin, $J = 6.9$ Hz, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), 3.18

(2H, q, $J = 6.9$ Hz, $-\text{CH}_2-\text{NH}-$), 3.76 (4H, q, $J = 6.9$ Hz, $-\text{O}-\text{CH}_2-\text{CH}_3$), 4.21 (1H, t, $J = 7.2$ Hz, $> \text{CH}-$), 4.41 (2H, d, $J = 7.2$ Hz, $-\text{COO}-\text{CH}_2-$), 5.11 (1H, t, $J = 7.2$ Hz, $-\text{NH}-$), 7.31 (2H, d, $J = 7.2$ Hz, Ar-H), 7.40 (2H, t, $J = 7.2$ Hz, Ar-H), 7.60 (2H, d, $J = 7.2$ Hz, Ar-H), 7.76 (2H, d, $J = 7.2$ Hz, Ar-H). m.p.: 43.3 °C, T_d : 139.0 °C.

2.4. Preparation of SS-BA

SS-BA was prepared in one reaction step. To SS (3.0 g) in dry toluene (30 mL) were added **Silane-BA** (0.30 g, 0.73 mmol) and 6 M of HCl aqueous solution (0.05 g), and the mixture was refluxed for 5 h. The white precipitate was separated and washed three times by centrifugation with methanol. The resulting precipitate was dried in vacuo at 80 °C for 3 h to give **SS-BA** (2.9 g).

2.5. FT-IR spectral measurements of composite films during anionic UV curing

A solution of NN (0.15 g) and 12 mol% of **PBG** (toward resin, 0.015 g) dispersing 100 wt% of **SS-BA** (toward resin) was prepared with THF (0.45 g). The organic-inorganic composite NN films were prepared on an Si wafer by an applicator (5 mil), and were prebaked at 80 °C for 2 min. Samples were exposed with 0 or 5000 mJ/cm^2 to light at 365 nm wavelength, and subsequently baked at 160 °C for FT-IR measurements.

2.6. Evaluation of the cured films after anionic UV curing

A THF solution of NN and 12 mol% of **PBG** (toward resin) dispersing 100 wt% of **SS-BA** (toward resin) was prepared as mentioned above. The NN films were prepared on a Si wafer by an applicator (5 mil), and were prebaked at 80 °C for 2 min. As a control, NN films consisting of the same amounts of **PBG**, unmodified SS, and **Silane-BA** were also prepared. Samples were exposed 0–5000 mJ/cm^2 of light at 365 nm, and subsequently baked at 120–160 °C for 30 min, to evaluate pencil hardness of the samples.

3. Results and discussion

First, a silane-coupling reagent having a base-amplifying group (**Silane-BA**) was synthesized in one reaction step with 95% yield. **SS-BA** was then prepared with SS and **Silane-BA** that were refluxed in dry toluene. The chemical modification of SS was confirmed by thermogravimetric analysis (TGA) and Fourier transform infrared (FT-IR) spectroscopy. Considering that the decomposition point of 9-fluorenylmethyl carbamates is around 200 °C, it is estimated from results of the TG measurement that 1.4 wt% of base-amplifying units are used for modification of the surface of SS (Fig. 1). In the FT-IR spectrum of **SS-BA**, the peaks at 1533 and 2990 cm^{-1} assigned to C–H bonds and a

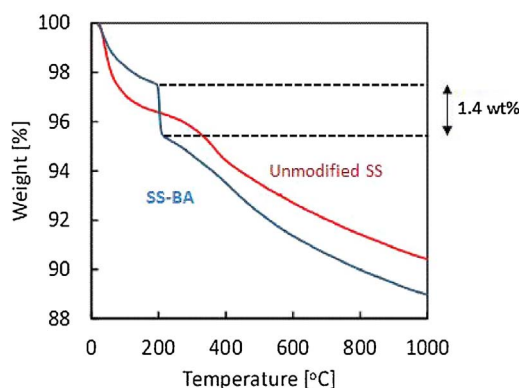


Fig. 1. TGA curves of unmodified SS and **SS-BA**.

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