Synthesis of a Bifunctional Base Amplifier Containing a Disulfide Bond and Its Application to Photoreactive Materials

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1. Introduction

Epoxy resins, one of thermoset resins, are used to fabricate rigid cured bulks in various kinds of industrial fields [1]. The cured materials are not dissolved toward any solvents, resulting in lack of their reworkability or recyclability. Epoxy polymers having degradable linkages such as tertiary alkyl ester [2], carbamate [3] and carbonate [4] have been reported, although they required relative high decomposition temperatures above 200°C. On the other hand, disulfide bond is known to be one of dynamic covalent bonds which would cause disulfide-disulfide exchange reactions under gentle heating [5]. Recently, Otsuka et al. proposed epoxy network polymers having disulfide bonds where thiol-disulfide exchange reactions were caused with monofunctional thiols in the presence of bases [6]. However, they applied thermal curing of the resins with aromatic diamine crosslinkers having low nucleophilicity.

In this communication, we have designed a carbamate of an aliphatic diamine having a disulfide bond, and proposed an anionic UV curing system consisting of a photobase generator (PBG, 1), carbamate 2 and bifunctional epoxy resin 3, as shown in Scheme 1. We examined whether 2 works as a base amplifier (BA) that generates a base molecule autocatalytically with a trigger base in a base proliferation reaction [7].

2. Experimental

Compound 2 was synthesized with cystamine dihydrochloride, 9-fluorenylmethyl chloroformate, and triethylamine with dichloromethane/water as solvents, and was obtained as a white solid in a 49% yield. The assignment was performed by 1H-NMR, FT-IR and high resolution MS. PBG 1

Scheme 1. Anionic UV curing materials containing disulfide bonds with PBG 1, BA 2 and bifunctional epoxy resin 3.

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and epoxy resin 3 that has a disulfide bond were also synthesized according to the literatures [6, 8]. Decomposition behavior in polystyrene (PS) films of 2 (20 wt%) was examined with heating at 160°C with/without hexamethylenediamine (18 mol%), monitored by FT-IR. Anionic UV curing of spin-coated films of 3 containing 1 (15 mol%) and 2 (20 mol% toward 3) was performed on glass substrates, by 365 nm light irradiation (50 mW cm⁻²) and postbaking with a releasing film at 160°C for 10-30 min.

3. Results and discussion

Compound 2 showed a thermal decomposition point at 175°C (measured by TG-DTA), and was dissolved into DMSO and HFIP (1,1,1,3,3,3-hexafluoro-2-propanol). THF, dioxane, and DMF dissolved 2 a little after ultrasonic treatment. Compound 2 was dispersed into a PST film, to examine the decomposition behaviors in a polymer matrix by FT-IR spectral measurements. As shown in Figure 1, the peak area assigned to carbonyl groups of 2 at 1710 cm⁻¹ decreased immediately with hexamethylenediamine. In contrast, the peak area did not change for 15 min before the subsequent nonlinear decomposition without diamines. This indicates that 2 is decomposed autocatalytically with primary amines, and that 2 is thermally stable in the absence of amines.

Anionic UV curing of 3 was then performed by using an HFIP solution including 1 and 2. Hardness of cured-films was evaluated by the pencil-scratch method based on JIS K5400 [9]. The hardness of pencil is arranged as follows: 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, 9H (hardest). In the cases of postbaking for 30 min, the pencil-hardness in a range from H to 2H was recorded, while the film was cured even without irradiation (Figure 2). By shorter postbaking, the value of 3B was observed after 5000 and 10000 mJ cm⁻² of irradiation without dark reactions. In this case, base proliferation reactions of 2 phototriggered by 1 would contribute to the curing reactions of 3.

In conclusion, these results mentioned above indicate that compound 2 works as a BA, as shown in Scheme 1 [7a]. In future, this UV curing system is expected to be used for a dismantlable photoadhesive material.

References and Notes

9. JIS K5400 defined by Japanese Industrial Standards is a simple method to test the scratch hardness of coatings. The pencil (in the range of 6B (softest) to 9H (hardest)) is moved scratching over the surface of the coating at a 45° angle with a constant pressure.