Cysteine-derived Cross-linker for Anionic UV Curing of Epoxy Resins

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Keywords: cysteine, cross-linker, anionic UV curing, epoxy resin, thiol, amine

1. Introduction

Epoxy resins are one of famous thermosetting resins, and they have been used to fabricate many industrial materials such as electronic parts, adhesives and coating films [1]. Network polymers in their cured materials are formed with cross-linkers or hardeners. Alcohols, phenols, carboxylic acids, acid anhydrides, and amines have been examined as hardners [2]. Recently, our group has developed an epoxy resin curing system with a tetrafunctional thiol and photobase generator providing a strong organic base [3]. In this communication, we have focused a unique chemical structure of L-cysteine (Cys) which has thiol and primary amino groups. Both functional groups can be used to form cross-linked networks with epoxy resins, and we examined roles of these functional groups in a UV-triggered anionic curing reaction of an epoxy resin (Scheme 1). Thiol group of Cys-derived cross-linker **1** is protected by a photolytic protecting group decomposing via an intramolecular cyclization reaction [4, 5]. On the other hand, amino

group of **1** is protected by 9-fluorenylmethyloxycarbonyl (Fmoc) group that is decomposed by basic species [6]. Another functional group, carboxyl group, is used for adjustment of solubility of the derivative.

2. Method

Cys-derived cross-linker **1** was synthesized from Fmoc-Cys(Trt)-OH (an available compound for solid phase peptide synthesis, Trt: trityl) in a 46% total yield via four reaction steps. Identification was performed by ¹H NMR, ¹³C NMR, FT-IR, and high resolution MS. Decomposition behaviors of **1** were investigated in a poly(tetramethylene ether glycol) (PTMG) film with 365 nm light irradiation or heating at 120°C in the presence of 2-methyl-1,5-diaminopentane, monitored by FT-IR. Anionic UV curing of a tetrafunctional epoxy resin (NN) was performed by 365 nm light irradiation and postbaking at 120°C for 30 min. Preliminary adhesion test was performed at room temperature with stainless substrates at a shear speed of 50 mm/min.

Scheme 1. Anionic UV curing system of a tetrafunctional epoxy resin (NN) containing Cys-derived cross-linker **1** and PBG **2**.

Figure 1. Decomposition behaviors of **1**, monitored by FT-IR. (a) Generation of a coumarin analogue by-product (1723 cm^{-1}) during 365 nm light irradiation. (b) Consumption of Fmoc groups of **1** (1658 cm^{-1}) with 0 (circle, open) or 8.4 mol% (triangle, close) of diamine during heating at 120°C .

3. Results and Discussion

Cys-derived cross-linker **1** was well dissolved toward common organic solvents such as alcohols, acetone, THF, dichloromethane and ethyl acetate. A PTMG film containing **1** was prepared, and 365 nm light was irradiated to monitor the intensity of a peak at 1723 cm^{-1} assigned to carbonyl group of the coumarin analogue by-product (Figure 1a). Increase and saturation of the intensity indicated that the protecting group of thiol group of **1** is quantitatively photodecomposed. On the other hand, liberating amino group of **1** was confirmed by monitoring peak intensity of the carbonyl group of Fmoc moiety at 1658 cm^{-1} (Figure 1b). The peak intensity was decreased during heating at 120°C in the presence of 8.4 mol% of diamine (toward **1**), while the intensity did not change after heating for 90 min without diamine.

An anionic UV curing was then performed with **1**, PBG **2** [7] and NN as shown in Scheme 1, to examine the curing ability of **1**. Hardness of cured-films was evaluated by the pencil-scratch method based on JIS K5400 [8]. 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). Results are shown in Figure 2. Without UV irradiation, films were not cured, and the hardness value was below 6B. Increasing irradiation energy made the resulting cured films hard, and the maximum value of 2B was recorded with 10000 mJ cm^{-2} of irradiation. On the other hand, in the case without PBG **2** (1/NN in the Figure), the value of 6B was obtained after 10000 mJ cm^{-2} of irradiation, indicating that amino groups of **1** contribute mainly to the curing. Nevertheless, thiol groups of **1** also contribute a little, because films were not cured at all in the case without **1** (2/NN in the Figure). Finally, a preliminary adhesion test was performed under these conditions (10000 mJ cm^{-2} of

Figure 2. Pencil-hardness of cured NN films containing 11 mol% of **1** and/or 1.1 mol% of **2** (toward epoxy groups of NN) after 0–10000 mJ cm^{-2} of 365 nm light irradiation and postbaking at 120°C for 30 min.

365 nm light irradiation, subsequent heating at 120°C for 30 min). A clear difference of shear strength was observed between samples of 1/2/NN (1.7 MPa) and 1/NN (0.9 MPa), indicating again contribution of amino groups of **1**.

In summary, we have designed a heterobifunctional cross-linker by using Cys as a starting compound, and evaluated its curing ability in an anionic UV curing system of epoxy resins. Further application of this type of cross-linker is under investigation.

References and Notes

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7. PBG **2** was synthesized according to the literature [5b].
8. 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.