Promotion Effect of Bifunctional Five-Membered Cyclic Dithiocarbonate on Curing of One-Component Epoxy Resin by Imines as Latent Initiator

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ABSTRACT: This article deals with curing of a one-component epoxy resin containing a bifunctional five-membered cyclic dithiocarbonate **1** with an imine **2** as a latent initiator. When **1** was added to a mixture of epoxy resin and **2,** the curing rate and initial adhesive strength increased higher than that without **1.** It was supposed that the reaction of **1** and an amine released from **2** was much faster than the amine–epoxide reaction, and a thiol group formed by the reaction of **1** with the amine accelerated the amine–epoxide reaction. The adhesive strength of the one-component epoxy resin containing 10 mol % of **1** exhibited the highest value. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 961–964, 2004

Key words: adhesives; curing of polymers; addition polymerization

INTRODUCTION

The development of a one-component epoxy resin with an imine as a latent initiator is desirable for coatings, paintings, and adhesives, because it is stable under lower humidity conditions but can undergo curing by moisture at room temperature. This one-component epoxy resin curing system is composed of two steps: hydrolysis of the imine releasing an amine and the reaction of the amine with epoxide. On the other hand, a two-component system does not include the hydrolysis step. We have recently reported that diethyl ketone-based imines can hydrolyze much faster than imines industrially used.[1–3] We have more recently found that the presence of a monofunctional five-membered cyclic dithiocarbonate (MDTC) enhances the amine–epoxide reaction step.[4] MDTC by the reaction with an amine forms produces a thiourethane having a thiol group,[5,6] and the generated thiol group accelerates the epoxide–amine reaction. If we employ a bifunctional cyclic dithiocarbonate (BDTC) instead of a MDTC, a new latent system tolerant to bleeding out of low molecular weight compounds may be constructed. This work deals with the curing of a one-component epoxy resin containing BDTC **1** and adhesive properties of the cured resin.

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EXPERIMENTAL

Measurements

Curing times were measured with a Yasuda Seiki R.C.I. Drying Time Tester. Adhesive strengths and tensile strength were measured with a Shimadzu Autograph AG-50kNG.

Materials

BDTC **1** was synthesized from bisphenol A diglycidyl ether (Mitsubishi Gas Chemical Co., DER332) and carbon disulfide according to a previously reported method.[5] Imine **2** was synthesized by the reaction of diethyl ketone with 1,3-bis(aminomethyl)cyclohexane according to a previously reported method.[3] The structures of DER332, **1,** and **2** and are shown in Figure 1.

Formulation of one-component resin with 1, 2, and fillers

One-component epoxy resin was compounded as follows, DER332, **1,** and silica (RY200S) as a filler were mixed at 40°C under reduced pressure for 1 h by an Inoue Seisakusho PML-5L. After that, imine **2** was added to the mixture, and the resulting resin was further kneaded at room temperature for 1 h under N_2 atmosphere.

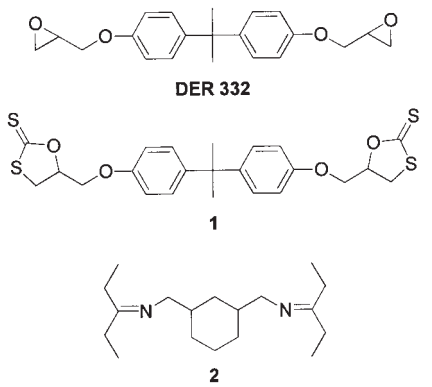


Figure 1 Structures of DER332, BDTC **1,** and imine **2.**

Evaluation of curing process

The curing rate was evaluated by the measurement of film set times. The one-component epoxy resin containing **1** and **2** was applied on a glass plate with 0.2 mm thickness and stored at 23°C and 50% RH for 1 day, and then the curing time was measured. The adhesive strength was evaluated by a compressive share test at 23°C. Wood was used as the adherent with the applied area of 25 × 25 mm^2 (Fig. 2). The applied adherents were stored at 23°C and 50% RH for 4 days, and then the adhesive strength was measured. Mechanical strength and elongation of a cured film was evaluated by a tensile test. The test pieces were made as follows. One-component epoxy resin was applied on a silicon film with 1.0 mm thickness and cured at 40°C and 90% RH for 3 days. The resin was removed from the film, and the reverse side was cured for 4 days under the same condition. After that, glass fiber-reinforced plastics was pasted on the test pieces with two-component epoxy resin (Fig. 3).

RESULTS AND DISCUSSION

Evaluation of curing process

We examined the curing time of a one-component epoxy resin, which is composed of a bisphenol A type epoxy resin (DER332), BDTC **1,** and imine **2** (Fig. 4). The curing rate increased as the concentration of **1** increased. BDTC produces a thiourethane compound

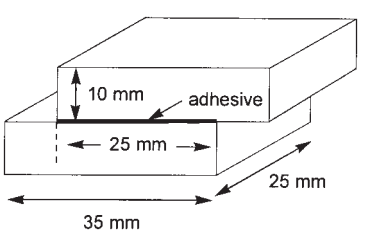


Figure 2 Schematic diagram of compressive share test.

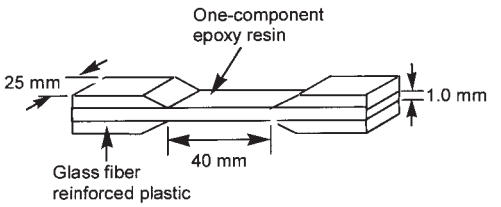


Figure 3 Schematic diagram of tensile strength test.

with a proton-donative thiol group by the reaction with an amine released from an imine.[7,8] The thiol group promotes the amine–epoxide reaction.[4] As described in the Introduction, we have reported in the promoter system using MDTC, the curing rate was retarded by end-capping of MDTC (Scheme 1), and therefore, the most efficient amount of MDTC was 10 mol %.[4] In the present BDTC-based system, the reaction of the amino and cyclic dithiocarbonate forms an amino- and cyclic dithiocarbonate-functionalized compound (**3** in Scheme 1), and the increase of curing rate was not retarded because BDTC served as a curable component (**4** in Scheme 2) as well as a promoter of the reaction.

Evaluation of adhesive properties

Adhesive properties were evaluated by a compressive share test (Fig. 5). In the early stage, the one-component epoxy resin containing **1** exhibited higher adhesive strength than that without **1** in every case. This result agrees with that of curing rate. In the final stage, the resin containing 10 mol % of **1** exhibited the highest adhesive strength. Suitable flexibility of cured adhesive is commonly more

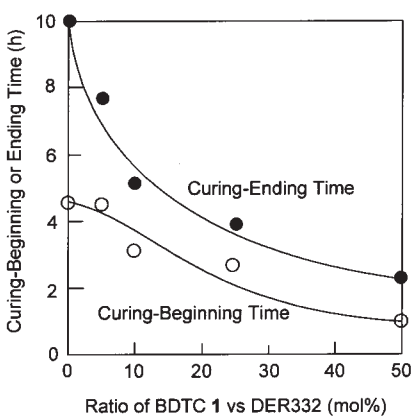
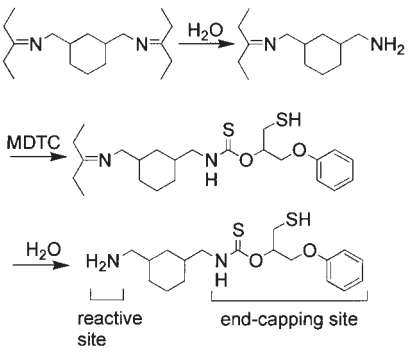


Figure 4 Curing beginning and ending time of one-component epoxy resin with BDTC **1** and imine **2** at 23°C. The curing beginning and ending time was estimated by a Yasuda Seiki R.C.I. Drying Time Tester. The one-component epoxy resin was a mixture of epoxy resin (DER332, 1 mol), BDTC **1** (0–0.5 mol), silica (RY200S, 15 g), and **2** (0.5–0.75 mol).



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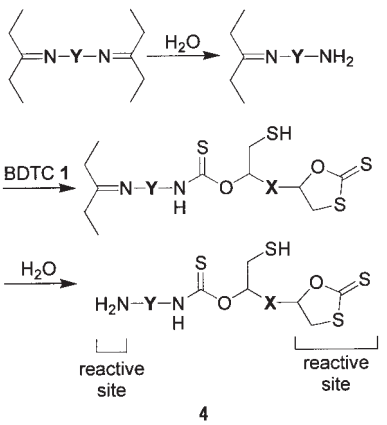
Scheme 1

effective for adhesive strength rather than the mechanical strength in this test. Mechanical strength and elongation of the cured film was measured by a tensile test to evaluate the flexibility (Figures 6 and 7). All the one-component epoxy resins containing **1** showed good properties, especially, 10 mol % of **1,** which showed the highest mechanical strength and elongation. One drawback of epoxy resin is brittleness. It can be improved by the addition of a plasticizer, but it lowers the curing rate. In the present study, it was confirmed that the brittleness could be improved, keeping a high curing rate by the addition of **1.** This result may be explained from the viewpoint of crosslinking density. In the absence of **1,** the bifunctional imine transforms into the corresponding bifunctional amine, which can react with two equivalents of epoxy group. While in the presence of **1,** the bifunctionality of the amine may decrease, because the amine partly reacts with **1.** As



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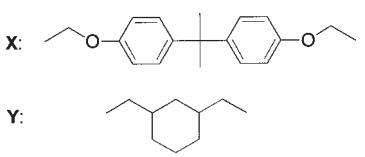

Scheme 2

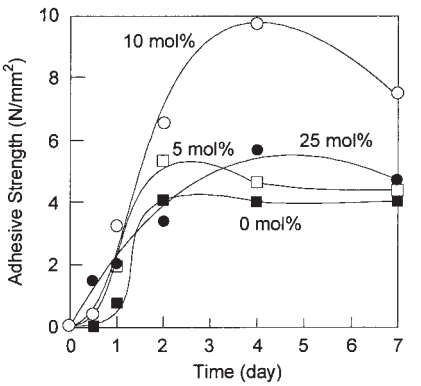

Figure 5 Adhesive strength of one-component epoxy resin with BDTC **1** and imine **2** at 23°C. The adhesive strength was estimated by a Shimadzu Autograph AG-50kNG. The one component epoxy resin was a mixture of epoxy resin (DER332, 1 mol), **1** (0–0.5 mol), silica (RY200S, 15 g), and **2** (0.5–0.75 mol).

a result, the crosslinking density may be lower compared to the former case. Therefore, the epoxy resin cured with **1** is more flexible than that without **1.** When 25 mol % of **1** was added in the epoxy resin, the elongation was lowered compared with that containing 10 mol % of **1,** presumably because the cohesive force of the former resin was lower due to the low crosslinking density. We can conclude that the addition of 10 mol % of **1** results in good balance between flexibility and cohesive force in this system.

CONCLUSION

We elucidated the curing of a one-component epoxy resin containing a bifunctional five-membered cyclic dithiocarbonate **1** with an imine **2** as a latent initiator and adhesive properties of the cured resin. The curing rate of the resin increased as the concentration of **1**

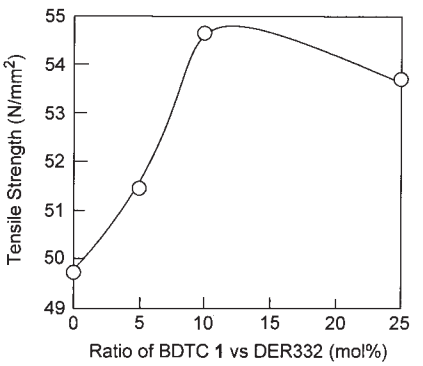

Figure 6 The tensile strength of one-component epoxy resin with BDTC **1** and imine **2** at 23°C. The tensile strength was estimated by a Shimadzu Autograph AG-50kNG. One-component epoxy resin was a mixture of epoxy resin (DER332, 1 mol), **1** (0–0.5 mol), silica (RY200S, 15 g), and **2** (0.5–0.75 mol).

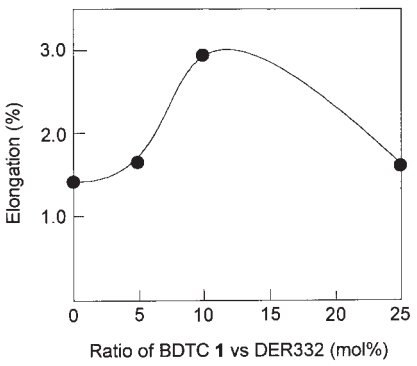

Figure 7 The elongation of one-component epoxy resin with BDTC **1** at 23°C. Condition: A mixture of epoxy resin (DER332, 1 mol), **1** (0–0.5 mol), silica (RY200S, 15 g), and **5** (0.5–0.75 mol) was cured for 7 days at 23°C, 50% RH. The elongation was estimated by a Shimadzu Autograph AG-50kNG. The one-component epoxy resin was a mixture of epoxy resin (DER332, 1 mol), **1** (0–0.5 mol), silica (RY200S, 15 g), and **2** (0.5–0.75 mol).

increased and one-component epoxy resin with 10 mol % of **1** showed the highest adhesive and mechanical strength.

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