Novel Moisture-Curable Epoxy Resins and Their Characterization

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ABSTRACT: The shelf-life stability and curability of a moisture-curable epoxy resin system were evaluated with ketimines, which were used as moisture-latent hardeners and were derived from different kinds of ketones as protective groups. Both the shelf-life stability and curability of the compounds were mainly influenced by the steric hindrance of the ketimines. The theoretical results calculated by MOPAC showed good agreement with the experimental results. Methyl i-propyl ketone and methyl t-butyl ketone, having a narrow space (<4.2 Å) around ketimine N and a wide space (>3.7 Å) around ketimine C, were demonstrated to be the optimum ketones for the ketimines. The lap shear strength, with respect to the adhesive properties of the ketimines, was higher with a large-volume ketone than with a small-volume ketone as the protective group. This was due to the higher reaction conversion of the epoxide for the system. In addition, the large plasticizing effect of the large ketone volume could lead to a large relaxation of the stress generated at the bonding interface. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 91–95, 2003

Key words: epoxy; ketimine; moisture-curing; one-part; shelf-life

INTRODUCTION

Epoxy resins are widely used as adhesives and coating compounds in industry. Most of them that are used outside, such as those used in civil engineering, have a two-part form at room temperature. Various attempts have been made to develop a one-part form with moisture-latent hardeners such as ketimines (Fig. 1).[1,2] However, no such compound has yet been developed that exhibits a good balance between shelf-life stability and curability. The problem is the basicity of the ketimines, even though their amino groups are protected by ketones. Therefore, mixtures of ketimine compounds and epoxy resins suffer from gelation during storage (Fig. 2). It has been hypothesized that the steric repulsion of a ketimine from the epoxide can suppress the reaction between the ketimine group and epoxide and result in a stable state during storage. In this study, six kinds of ketimines, causing different steric hindrance effects, were evaluated as latent hardeners.

The ketones that formed after the hydrolysis of the ketimines remained inside after curing and influenced the properties. However, there have been no reported studies about them. Therefore, the adhesive properties of the one-part epoxy curing system were also studied.

EXPERIMENTAL

Preparation of the ketimines

In this study, acetone (ACE), methyl ethyl ketone (MEK), methyl i-butyl ketone (MIBK), methyl i-propyl ketone (MIPK), methyl t-butyl ketone (MTBK), and diisopropyl ketone (DIPK) were used as protective groups of the ketimines. The ketimines were prepared by the dehydration reaction between 1,3-bis(aminomethyl)cyclohexane (1,3-BAC) and two equivalent weights of each ketone in toluene (Fig. 3). The reactions were finished after the theoretical amount of water formed. The structures were confirmed by ^{1}H-NMR measurements after the removal of excess ketones and toluene.

Curing of the epoxy resins

A stoichiometric mixture of the epoxy resins [diglycidyl ether of bisphenol A (DGEBA); weight per epoxide equivalent (WPE) = 190; Epicote 828, Japan Epoxy Resins Co., Ltd., Tokyo, Japan], the ketimines, and H_2O were cured in a closed vessel at 25°C for 2 weeks.

Measurements

Shelf-life stability and curability with the model compound

An equivalent mixture of glycidyl phenyl ether (GPE) as a model compound of the epoxy resins and each
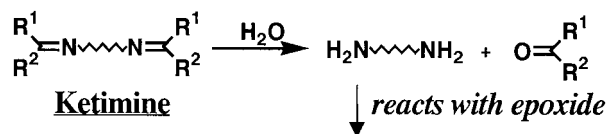
Figure 1 Moisture curing system with ketimine.

Figure 2 Reaction of ketimine during storage.

ketimine was stored in a glass bottle with N_2 gas at 25°C. After 30 days, the reaction conversions of the epoxide were measured for an evaluation of their shelf-life stability. Similarly, GPE, ketimines, and H_2O were stoichiometrically mixed, and this was followed by storage for 48 h at 25°C for an evaluation of their curability. The reaction conversion of the epoxide was calculated from the ^{1}H-NMR peak intensity ratio between the α-methylene and GPE benzene ring.

Reaction conversions of the epoxide in the DGEBA/ketimine system

The reaction conversions of the epoxide were measured by Fourier transform infrared spectroscopy (Spectrum 2000, PerkinElmer Japan Co., Ltd., Yokohama, Japan). They were calculated from the changes in the magnitude of the absorption peak at 910 cm^{-1}
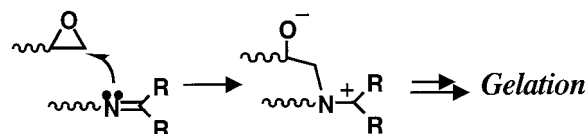
(epoxy group), with the peak at 1580 cm^{-1} (benzene ring) used as an internal standard.

Lap shear strength

The lap shear strengths of the adhesive joints were measured with an Instron-type tensile machine (Autograph AGS-2000E, Shimazu Co., Ltd., Kyoto, Japan) at a crosshead speed of 50 mm min^{-1} at room temperature.

RESULTS AND DISCUSSION

Relationship between the shelf-life stability and the curability

Figure 4 shows the relationship between the shelf-life stability and curability when the protective group of
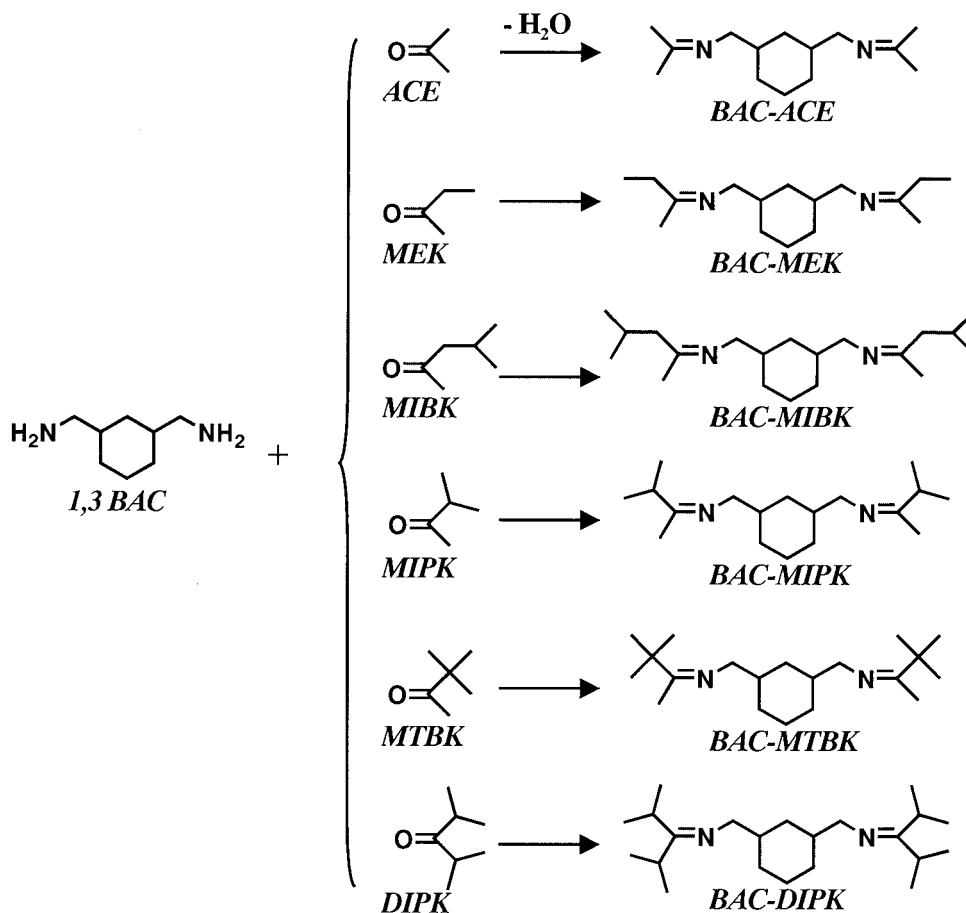

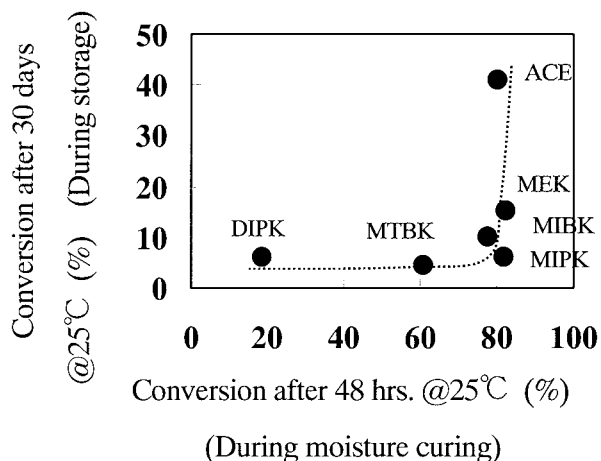**Figure 3** Ketimines and their starting materials.

Figure 4 Relationship of the epoxy conversion during storage and moisture curing for GPE/ketimine.

Figure 6 Reaction moieties of ketimines during storage and moisture curing.

the amines was changed in a stoichiometric mixture of GPE and ketimine. The ordinate represents the reaction conversion of the epoxide at 25°C after 30 days, which is related to the shelf-life stability. The abscissa represents the reaction conversion of the epoxide with a stoichiometric mixture of water at 25°C after 2 days, which is related to the moisture curability. Therefore, a lower level of the ordinate and a higher level of the abscissa should show a good balance between the shelf-life stability and curability of these curing systems.

As shown in Figure 4, the reaction conversions during both storage and moisture curing were high with the ACE protective group of the ketimine, whereas those for DIPK were low. The MIPK protective group of the ketimine was proven to give a well-balanced composition with good shelf-life stability and curability.

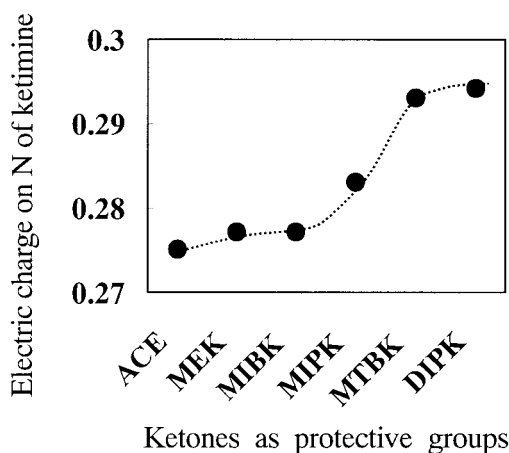These experimental results could be demonstrated by theoretical results with MOPAC calculations. The electric charge on N of the ketimines increased with increasing alkyl group sizes of the ketones, as shown in Figure 5. In general, the reactivity between the epoxide and ketimine during storage should increase with the increasing electric charge of N. However, the experimental results (Fig. 4) showed the opposite effect. Therefore, this would indicate that these reactions should be governed by steric hindrance rather than electric effects. Next, the spaces around N of the ketimine groups were calculated for an estimation of their steric hindrance effect. The shelf-life stability may depend on the reactivity between the nitrogen atom of the ketimine and epoxide, and the moisture curability depends on the reactivity between the carbon atom of the ketimine and H_2O (Fig. 6). Figure 7 shows a three-dimensional (3D) model of the ketimine that was prepared from n-propyl amine and MIPK as a model ketimine compound. The shelf-life stability and curability are influenced by the H—H distances A and B, respectively. The H—H distance A represents the space around ketimine N, which approaches the epoxide during storage. H_2O molecules approach ketimine C through distance B to hydrolyze them upon moisture curing. An approach of H_2O to the ketimine group from the other direction would be difficult because of the large steric hindrance or electrical repulsion between the H_2O molecule's O and ketimine N. The relationships between the H—H distances A and B of the ketimines are shown in Figure 8. For MIPK or MTBK, the narrow space (H—H distance A < 4.2 Å) makes it difficult for ketimine N to react with the epoxide during storage, and the wide space (H—H distance B > 3.7 Å) makes it easy for H_2O and ketimine C to react during moisture curing. These results imply that moisture-curable epoxy resins can be
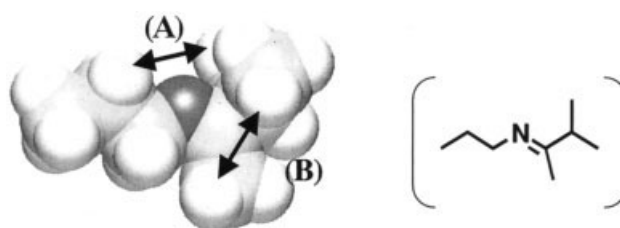

Figure 5 Electric charge on N for each ketimine.

Figure 7 3D model of ketimine (n-propylamine/MIPK).
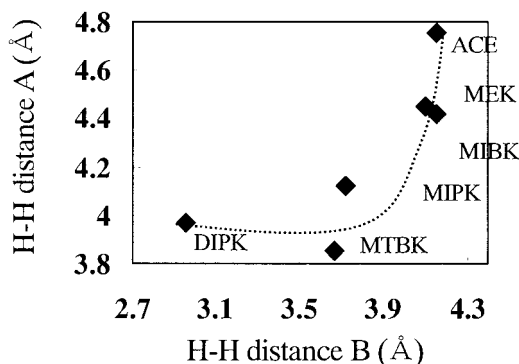
Figure 8 Relationship between H—H distances A and B.

Figure 10 Lap shear strength of the DGEBA/ketimine/ H₂O system at 25°C: (▲) 1,3-BAC, (○) BAC-ACE, (●) BAC-MEK, (◇) BAC-MIPK, and (■) BAC-MIBK.

achieved with a good balance between the shelf-life stability and curability with ketimines that are derived from MIPK or MTBK. In addition, these theoretical studies focused on the relationship between the H—H distances A and B of the ketimines, which showed good agreement with the experimental measurements.

Reaction conversion of the epoxide in the DGEBA/ketimine system

Four kinds of ketimine compounds protected with ACE, MEK, MIPK, and MIBK, which were soluble in the epoxy resin, were used to evaluate the generalities of the ketimines. Higher reaction conversions of the epoxide with ketimines were observed with a large-volume ketone after 8 days, as shown in Figure 9; this is different from the results for GPE in Figure 4. These results may be caused by the increase in the glass-transition temperature (T_g) of the cured epoxy resins with the curing time. When T_g of cured resins exceeds the ambient temperature, the cured resins become glassy solids. The speed of the chemical reaction in the glassy solids is controlled by the diffusion rate of the functional groups and so is very low in comparison
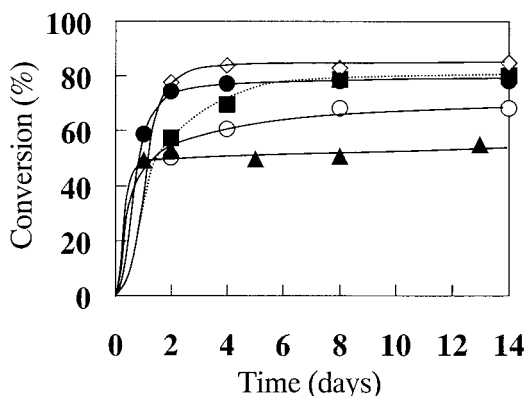
with that of rubbery and liquid compounds. The ketimine protected with a larger ketone forms larger ketone volumes after hydrolysis, and this accelerates the diffusion rate of the ketimine because of the large plasticizing effect from the large ketone volume. Therefore, the end of the chemical conversion of the epoxide is higher in the systems cured with the ketimine protected with a large ketone. In other words, ketones have important roles that affect their reactions as well as the protective groups of the amine.

Adhesive properties

The lap shear strength of the epoxy adhesives cured with four kinds of ketimine compounds are shown in Figure 10. The lap shear strength of the resin cured for 2 days is higher with a ketimine protected with a smaller volume ketone (ACE). This is attributed to the difference in the hydrolysis rates. However, the lap shear strength after 14 days increased with an increase in the ketone volume of the ketimine. This is due to the high epoxy conversion of the system cured with the ketimine protected by a large-volume ketone. In addition, the large plasticizing effect of the large ketone might lead to high adhesive properties because of the large relaxation of the stress generated at the bonding interface. These phenomena could be explained by the fact that the lowest strength is observed with 1,3-BAC, which does not have any protective groups. The higher chemical conversions of the epoxide with ketimines would result in higher strengths and higher plasticizing effects with MIPK or MIBK in these systems.

Figure 9 Chemical conversion of the epoxide in the DGEBA/ketimine/H₂O system at 25°C: (▲) 1,3-BAC, (○) BAC-ACE, (●) BAC-MEK, (◇) BAC-MIPK, and (■) BAC-MIBK.
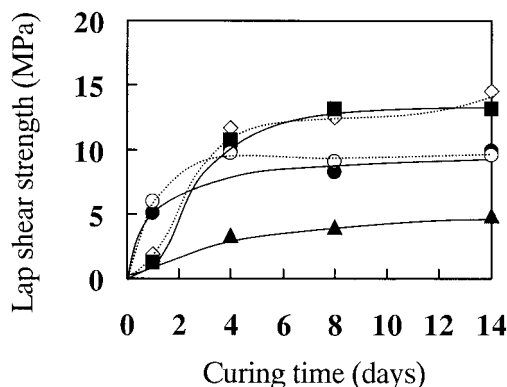
CONCLUSIONS

Several ketimine compounds were investigated as moisture-latent hardeners of an epoxy resin composition, particularly as protecting groups with ketones. The reaction conversion of the epoxide with a keti-

mine protected by a small steric hindrance ketone (ACE) was high during storage, whereas the ketimine protected by a large one (DIPK) was low. Compositions with a good balance between the shelf-life stability and curability were obtained with MIPK or MTBK as the protecting group. These experimental results are strongly supported by theoretical results from MOPAC calculations. A space of less than 4.2 Å around the N of the ketimine makes it difficult for a reaction to occur with the epoxide during storage, but a wider space of more than 3.7 Å around the C of the ketimine makes a reaction with H_2O easy. The higher lap shear strength of the cured resin was confirmed with the ketimine derived from the larger volume ketone, and this was attributed to both the higher plasticizing effects and the reaction conversions of the epoxide due to their large ketone volume. Therefore, protective ketone groups of the ketimines strongly influence their adhesive properties and their balance between shelf-life stability and curability. These results should be very useful for one-part epoxy resin systems, which are curable at room temperature, in industry as adhesives or paints.

References

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