

Thermally Curable Adhesive Tapes with Complex Catalyst System for Fabricating Semiconductor Packages

Naoya Saiki, Emi Nakajima, Hironori Shizuhata, Hideo Seno, Kazuyoshi Ebe

R & D Division, LINTEC Corporation, Japan

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ABSTRACT: Thermal curing of adhesive films was investigated to facilitate the fabrication of a reliable bonding for semiconductors. The formulated adhesive films contained acrylic polymer, epoxy resins, phenol resin, and an imidazole derivative that was the catalyst for curing the epoxy resins with phenol resin. The solubility, thermally latent characteristics, mechanical and adhesive properties of 2-methylimidazole/boron trifluoride (2MZ/BF₃), and 2MZ/aluminum trisacetylacetonate (AlAC) were investigated. It was found that 2MZ/BF₃ and 2MZ/AlAC had excellent solubility in adhesive materials and they had excellent latent characteristics as thermal curing catalysts

for epoxy resins, whereas conventional catalysts (2MZ and 2-phenyl-4, 5-dihydroxymethylimidazole (2PHZ)) could not achieve both excellent solubility and thermally latent characteristics. The mechanical and adhesive properties of the post-thermal-cured adhesive film that contained 2MZ/BF₃ or 2MZ/AlAC were comparable to those of the post-thermal-cured adhesive films that contained conventional catalysts. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 298–303, 2009

Key words: adhesion; irradiation; modulus; monomers; thermosets

INTRODUCTION

Paste adhesives made of epoxy resins are now widely used to bond silicon chips and substrates in chip-scale packaging systems for integrated circuits (ICs).^{1,2} However, it has been pointed out that paste adhesives have such problems as the paste sticking out and uneven bonding because the paste adhesives are easily deformed by bonding pressure. In addition, most conventional paste adhesives must be kept in a freezing chamber because the paste adhesives are not stable at ambient temperature.

To solve these issues, an adhesive film consisting of epoxy resins and acrylic copolymers was developed.³ The film formation of the adhesive film gives it a uniform thickness, and makes it less deformable than paste adhesives. In addition, an insoluble imidazole compound as a thermally latent curing agent gave the adhesive film excellent stability at ambient temperature.

Because of the excellent mechanical properties that they produce in the cured resin, imidazole compounds are widely used as catalysts for curing epoxy resins by various curing agents, e.g., dicyandiamide and phenol resins.⁴

In general, imidazole compounds as thermally latent catalysts are insoluble in organic solvents and

in materials included in the adhesive films. The insolubility gives them thermally latent characteristics and makes them suitable for use in one-pot compositions.

Conversely, soluble curing catalysts in adhesive materials are highly desirable because heterogeneous dispersions are liable to settle out or agglomerate on storage. It is also useful to be able to form a solution containing the other adhesive materials and the curing catalysts for the stable manufacture of adhesive films. In addition, soluble curing catalysts enable the adhesive films to change their thickness freely, whereas insoluble catalysts prevent adhesive films from being thinner than the particle size of the catalyst. To achieve both solubility and stability for the advantages above, some imidazole complexes have been reported. Barton et al.^{5,6} found that the copper (II) complex of 2-methyl-4-methylimidazole was stable at ambient temperature and soluble in epoxy resins.

However, the investigation of various properties of film-shaped adhesive materials containing soluble metal complex imidazole catalysts was inadequate.

In this study, the feasibility of using 2-methylimidazole/trifluoroborane (2MZ/BF₃) and 2MZ/aluminum trisacetylacetonate (AlAC) as thermally curable catalysts for adhesive films was examined. The notable difference of these catalysts after dissociation, that free BF₃ is a gas but AlAC is a solid, was taken into consideration for this investigation. Not only the solubility and stability of the complexes as

Correspondence to: N. Saiki (n-saiki@post.lintec.co.jp).

TABLE I
Applied Thermal Curing Catalysts

Catalyst	Abbreviation
2-Methylimidazole	2MZ
2-Phenyl-4,5-dihydroxymethylimidazole	2PHZ
2-Methylimidazole/boron trifluoride (1/1 mol)	2MZ/BF3(1/1)
2-Methylimidazole/aluminum trisacetylacetonate (3 mol/1 mol)	2MZ/AlAC (3/1)
2-Methylimidazole/aluminum trisacetylacetonate (6 mol/1 mol)	2MZ/AlAC (6/1)
2-Methylimidazole/aluminum trisacetylacetonate (12 mol/1 mol)	2MZ/AlAC (12/1)

catalysts but also the mechanical and adhesive properties of the adhesive films were investigated.

EXPERIMENTAL

Materials

The acrylic copolymer used in this study was tailor made and consisted of methyl acrylate (96 mol%) and 2-hydroxyethyl acrylate (4 mol%) (M_w : 8.0×10^5 measured by GPC calibrated with standard polystyrene).

The epoxy resins were bisphenol A diglycidyl ether (32 wt %, Epikote828, Japan Epoxy Resins) and α -2,3-epoxypropoxyphenyl- ω -hydro poly {2-(2,3-epoxypropoxy) benzylidene-2,3-epoxypropoxyphenylene} (35 wt %, EPPN-502H, Nihon Kayaku), including *o*-cresol novolak phenol resin as a thermally curing agent (33 wt %, BRG-556, Showa Highpolymer).

2-Methylimidazole (Shikoku Chemicals), 2-phenyl-4,5-dihydroxymethylimidazole (maximum diameter: 0.020 mm, Shikoku Chemicals), 2-methylimidazole/boron trifluoride (Stella Chemifa) and aluminum trisacetylacetonate (Kawaken Fine Chemicals) were prepared for thermally curing catalysts, as shown in Table I.

The standard adhesive formulation contained 40 wt % of the above-mentioned acrylic copolymer and

60 wt % of epoxy resins, which includes the thermally curing catalysts. The thermally curing catalysts were added from 1 to 3 mol % of glycidyl ether.

The adhesive film was prepared using the following procedure. All materials were dissolved or dispersed in butanone to produce 30 wt % at room temperature. The solution was coated on a polyolefin film to a thickness of 0.025 mm after air drying at 100°C for 1 min to vaporize the butanone.

In this report, these formulated adhesives will be named after the thermally curing catalyst being used, e.g., "the 2MZ adhesive."

The chemical structures of epoxy resins, phenol resin, raw materials of thermal curing catalysts are shown in Figure 1.

Curing and measurement

The solubility was evaluated in water, methanol, ethanol, isopropanol, butanone, and toluene. A total of 0.1 g of each catalyst was added to 10 g of each solvent. The solution was observed after stirring for 1 h at 23°C.

Differential scanning calorimetry (DSC) thermograms were recorded with DSC Q2000 (TA Instruments) with a heating rate of 10°C/min under a nitrogen gas flow of 50 mL/min.

Thermal curing was performed at 175°C for 60 min in an oven. The elastic modulus of the post-thermal-curing adhesives was measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments), at a frequency of 11 Hz and a heating rate of 3°C/min. The post-thermal-curing shear strengths were measured with a bond tester (series 4000, Dage F. E.) on a 2 mm \times 2 mm chip at a releasing speed of 12 mm/min, where a copper (JIS H3100 C1100P) plate was used as the adherend.

Performance tests at the manufacturing procedure

The adhesive film of 0.010 mm was prepared by the same procedure above. The adhesive film was

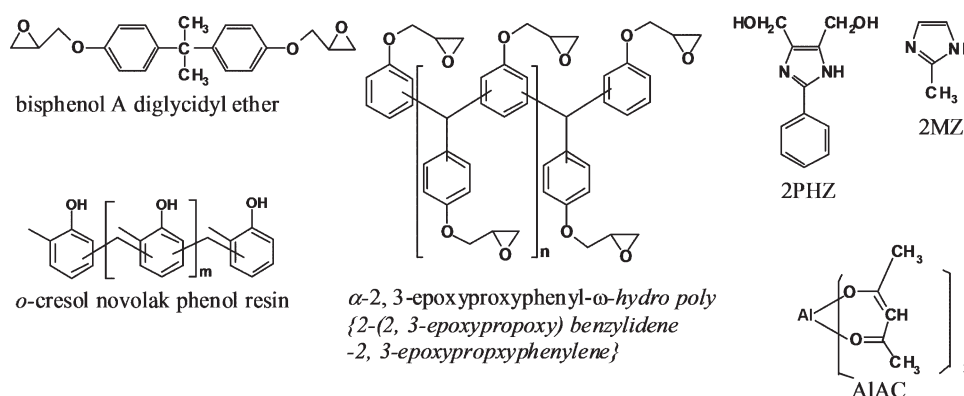


Figure 1 Chemical structures of epoxy resins, phenol resin, raw materials of thermal curing catalysts.

TABLE II
Solubility of Thermal Curing Catalysts^a

Catalyst	H ₂ O	Methanol	Ethanol	Isopropanol	Butanon	Toluene	Adhesive material/Butanone ^b
2MZ	Soluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Soluble
2PHZ	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
2MZ/BF ₃ (1/1)	Soluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Soluble
2MZ/AlAC (3/1)	Insoluble	Soluble	Soluble	Soluble	Soluble	Insoluble	Soluble

^a 1 wt% solution.

^b 40 wt% of the adhesive material was previously dissolved in Butanone.

laminated on backside of a silicon wafer (6-inch diameter, 0.2-mm thickness). The wafer was diced into each chip (8 mm × 8 mm) with a dicing machine (DFD651, Disco). The chip was bonded on a 2-layered-build-up substrate composed of glass cloth and epoxy resin with a bonding machine (BESTEM D02, Canon machinery) at 150°C for 1 s. Finally, the substrate with silicon chip was molded with a molding machine (G-cube manual press, APIC Yamada) at 175°C for 5 h. The manufactured package was square 12 mm on a side and the total thickness was 1.2 mm.

RESULTS AND DISCUSSION

Adhesives containing boron trifluoride/2-methylimidazole as a thermally curing catalyst

First, the solubility of 2MZ/BF₃ (1/1) was investigated in comparison with 2MZ and 2PHZ (Table II). 2MZ/BF₃ (1/1) as well as 2MZ were soluble in high-polarity solvents: water, methanol, ethanol, isopropanol, butanone, and adhesive material/butanone solution. In butanone, however, it was found that more than 50 wt % of 2MZ/BF₃ (1/1) was soluble, whereas only about 10 wt % of 2MZ was soluble. It is thought that the polar covalent bonds of BF₃ increase the solubility of 2MZ. This indicates that 2MZ/BF₃ (1/1) has a better solubility than 2MZ. 2PHZ was insoluble in all solvents.

The thermal curing reactions of the 2MZ, 2PHZ, 2MZ/BF₃ (1/1) adhesives were monitored with DSC (Fig. 2). Each adhesive contained 1 mol % of the total glycidyl ether as thermal curing catalyst. An exothermic peak for the 2MZ adhesive was observed at 165°C, which is lower than that of 2PHZ at 174°C. This difference is thought to be due to the difference in solubility, 2MZ being soluble in the adhesive, whereas 2PHZ is insoluble in the adhesive. Despite being soluble in adhesive materials, 2MZ/BF₃ showed an exothermic peak at 207°C, which is considerably higher than that of 2MZ and 2PHZ. This result indicates that the complex of 2MZ and BF₃ exhibits excellent thermally latent characteristics for initiating thermal curing of epoxy resins.

The influence of the amount of thermal curing catalyst (1–3 mol% of total glycidyl ether) in the adhesives was also investigated (Fig. 3). As the amount of 2MZ increases, the exothermic peaks of the 2MZ adhesives move to lower values. The reason seems to be that the increase in 2MZ caused the initiating points for thermal curing to rise. On the other hand, the exothermic peaks of 2MZ/BF₃ (1/1) adhesives did not decrease on increasing the amount of 2MZ/BF₃. The thermal curing of 2MZ/BF₃ adhesives was initiated by dissociation of the complex. Hence, this result indicates that the dissociation temperature was fixed regardless of the concentration of 2MZ/BF₃. From this result, it was found that the complex of 2MZ and BF₃ shows excellent thermal latent characteristics regardless of the concentration.

Figure 4 gives the result of dynamic mechanical analysis of postcured 2MZ and 2MZ/BF₃ (1/1) adhesives. The content of each thermal curing catalyst is 1 mol % of the total glycidyl ether. There was no difference between postcured 2MZ adhesive and postcured 2MZ/BF₃ (1/1) adhesive. To investigate how the thermal curing catalyst affects the postcured adhesion, the shear strength was also investigated, as shown in Figure 5. Again, there was no difference

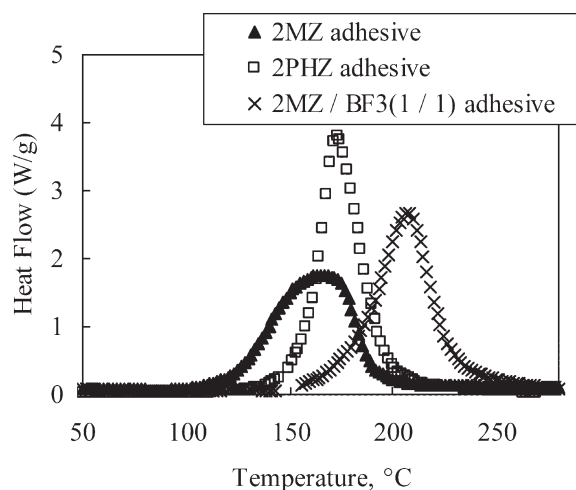


Figure 2 DSC heating scan thermograms of 2MZ, 2PHZ, 2MZ/BF₃ (1/1) adhesives. *The content of each thermal curing catalyst was 1 mol % of total glycidyl ether.

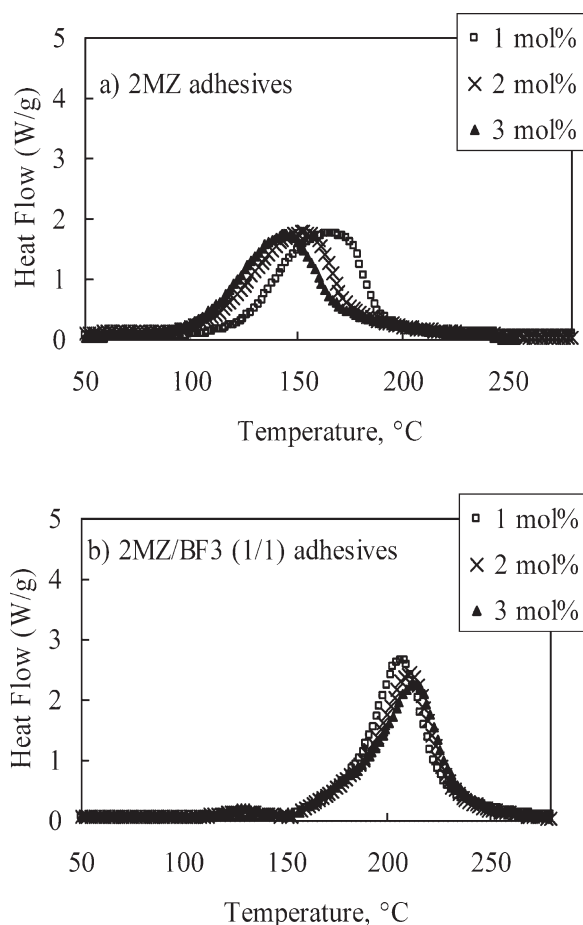


Figure 3 DSC heating scan thermograms of (a) 2MZ adhesives and (b) 2MZ/BF3 (1/1) adhesives. *The content of each thermal curing catalyst was 1–3 mol% of total glycidyl ether.

between postcured 2MZ adhesive and postcured 2MZ/BF3 (1/1) adhesive. As a reference, the shear strength of 2PHZ adhesive was also shown in Figure

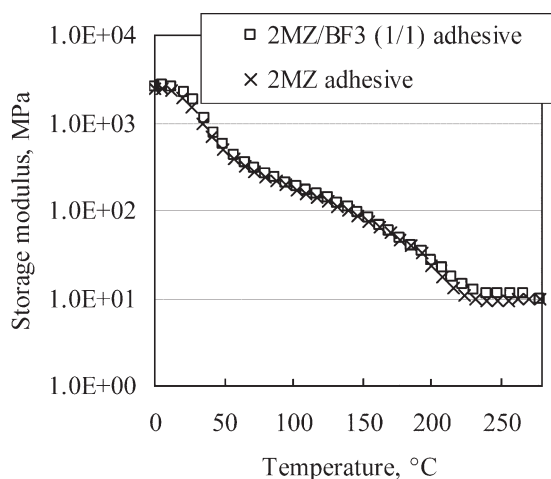


Figure 4 Storage modulus of 2MZ and 2MZ/BF3 (1/1) adhesives. *The content of each thermal curing catalyst was 1 mol % of total glycidyl ether.

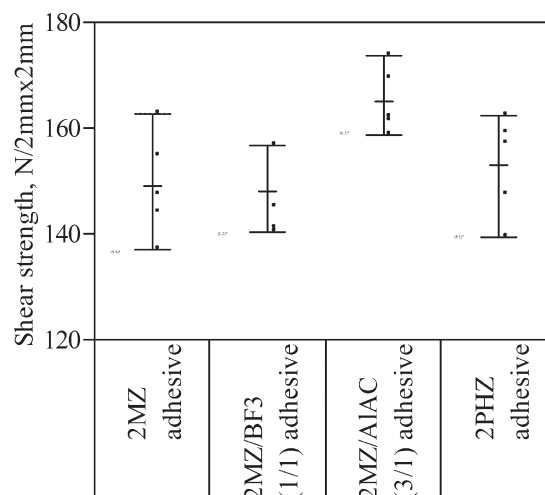


Figure 5 Shear strength of post-2MZ, 2MZ/BF3 (1/1), and 2MZ/AIAC (3/1) ADHESIVES. *The content of each thermal curing catalyst was 1 mol % of total glycidyl ether, thermal curing condition: 175°C for 1 h under air. *(): Standard deviation.

5. The shear strength of 2PHZ adhesive was almost same as that of 2MZ adhesive and 2MZ/BF3 (1/1) adhesive.

The gas state of free BF3 means that BF3 is evaporated after dissociation from 2MZ by the thermal curing reaction. Therefore, the composition of 2MZ adhesive is thought to be the same as for 2MZ/BF3 (1/1) adhesive after thermal curing. It is assumed that the similarity in the composition after thermal curing caused the identical mechanical properties and adhesion of 2MZ/BF3 (1/1) adhesive and 2MZ adhesive.

From these results, it was found that 2MZ/BF3 adhesive shows excellent latent characteristics regardless of the soluble thermal curing catalyst. In addition, the composition did not impair the mechanical and adhesive properties compared with 2MZ adhesive.

Adhesives containing aluminum trisacetylacetonate/2-methylimidazole as a thermally curing catalyst

The solubility of 2MZ and 2MZ/AIAC (3/1) was investigated (Table II). A difference in solubility was found only in the case of water. 2MZ was soluble but 2MZ/AIAC (3/1) was insoluble in water. The reason seems to be due to the hydrophobicity of AIAC.

The curing reactions of the 2MZ, 2MZ/AIAC (3/1), 2MZ/AIAC (6/1), 2MZ/AIAC (12/1) adhesives were monitored with DSC (Fig. 6). The content of each thermal curing catalyst was 1 mol % of total glycidyl ether. An exothermic peak for 2MZ/AIAC (3/1) adhesive was observed at 175°C, which is higher than that of 2MZ at 165°C, although this

temperature was lower than that of 2MZ/BF₃ adhesive. This means that 2MZ/AlAC (3/1) shows better thermal latent characteristics than 2MZ. The ratio of 2MZ and AlAC was also investigated. As the content of AlAC decreases, the exothermic peaks of 2MZ/AlAC adhesives move to lower values. The exothermic peaks of 2MZ/AlAC (6/1) adhesive and 2MZ/AlAC (12/1) adhesive were 170°C and 167°C, respectively, which were almost the same as that of 2MZ adhesive at 165°C.

One AlAC molecule can be bound to three imidazole molecules by coordinate covalent bonds because of its chemical structure (Fig. 1). This means that 2MZ is equivalent to AlAC in 2MZ/AlAC (3/1) adhesive. Therefore, free 2MZ must exist in 2MZ/AlAC (6/1) and 2MZ/AlAC (12/1) adhesives. The free 2MZ seems to lower the thermal curing temperature.

Figure 7 gives the dynamic mechanical properties of postcured 2MZ and 2MZ/AlAC (3/1) adhesives. It was observed that the storage modulus of 2MZ/AlAC (3/1) adhesive was higher than that of 2MZ adhesive below 175°C. AlAC was left in the adhesive material after dissociation on thermal curing, which was different from the case of 2MZ/BF₃. Metal chelates like AlAC are widely used as crosslinking agents for acrylic copolymers in pressure-sensitive adhesives to obtain cohesive strength.⁷⁻⁹ Therefore, it is assumed that free AlAC coordinates to acrylic copolymer and increases the storage modulus.

To investigate how the thermal curing catalyst affects the postcured adhesion, the shear strength was investigated, as shown in Figure 5. The shear strength of 2MZ/AlAC (3/1) adhesive was higher than that of 2MZ. The reason is the same as for the dynamic mechanical properties.

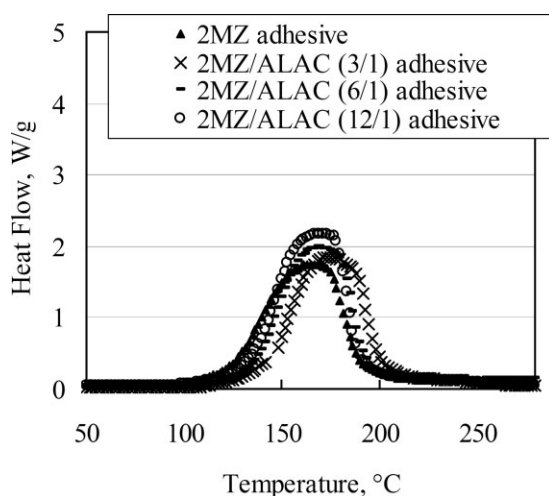


Figure 6 DSC heating scan thermograms of 2MZ, 2MZ/AlAC (3/1), 2MZ/AlAC (6/1), and 2MZ/AlAC (12/1) adhesives. *The content of each thermal curing catalyst was 1 mol % of total glycidyl ether.

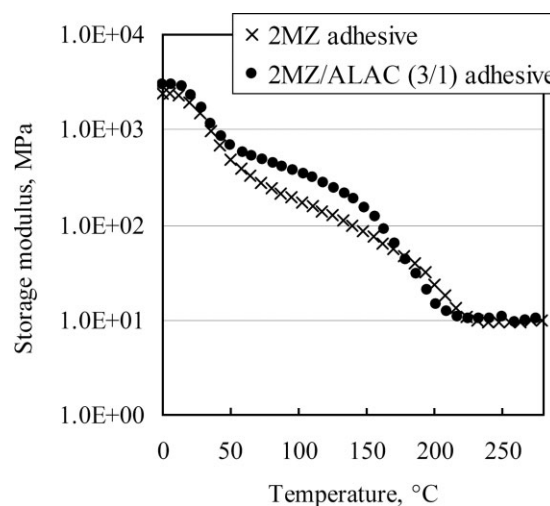


Figure 7 Storage modulus of 2MZ and 2MZ/AlAC (3/1) adhesives. *The content of each thermal curing catalyst was 1 mol % of total glycidyl ether.

From these results, it was found that 2MZ/AlAC (3/1) adhesive shows good latent characteristics regardless of the soluble thermal curing catalyst. In addition, the storage modulus and adhesion were higher than those of 2MZ adhesive, which were different results from those of 2MZ/BF₃ adhesive.

Performance tests at the manufacturing procedure

From the above evaluation, 2MZ/BF₃ adhesive and 2MZ/AlAC (3/1) adhesive showed excellent latent characteristics and solubility. To demonstrate the properties of the actual products, the performances of the tapes were examined. First, a solution of those adhesives was coated to 0.010-mm thickness after drying, which was a difficult thickness to obtain if 2PHZ was used because of its insolubility. Then, the adhesive films were kept for a month at 23°C under 50% RH ambient. After that, the adhesive films were applied to the actual IC package. The IC package was successfully produced, whereas the IC package using 2MZ adhesive had defects in the process. It is thought that 2MZ is cured gradually under storage condition and causes the defects.

CONCLUSION

In this work, the solubility, thermally latent characteristics, mechanical properties, and adhesion of 2MZ/BF₃ and 2MZ/AlAC adhesives were investigated in comparison with 2MZ.

2MZ/BF₃ and 2MZ/AlAC showed excellent solubility in various solvents, although 2MZ/AlAC was not soluble in water due to the hydrophobicity of AlAC. Both 2MZ/BF₃ and 2MZ/AlAC were stable in adhesives and cured at higher temperature than

2MZ. It was found that the storage modulus and shear strength of post-thermal-cured 2MZ/BF₃ adhesive were the same as those of 2MZ adhesive, whereas the storage modulus and shear strength of 2MZ/AlAC adhesive were higher than those of 2MZ adhesive.

As a result, both 2MZ/BF₃ and 2MZ/AlAC showed excellent thermally latent characteristics in addition to excellent solubility in organic solvents and adhesive materials.

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