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Effect of coupling agents on thermal, flow, and adhesion properties of epoxy/silica compounds for capillary underfill applications

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ABSTRACT

In this study, the different silane coupling agents were added to epoxy/silica systems. The effects of the type of silane coupling agent in the epoxy/silica compounds on the thermal, flow and adhesion properties were investigated. The curing behavior was examined by differential scanning calorimetry (DSC), and the flow properties of the epoxy compounds were evaluated from penetration rate measurements. The adhesion strength as a mechanical property was determined by die shear strength testing. The silane coupling agent type had a significant effect on the thermal, flow and adhesion properties. The coefficients of thermal expansion (CTE) and adhesion of the DGEBF epoxy/SiO_2 systems could be enhanced by the addition of silane coupling agents. In addition, the penetration rate was increased by the addition of a coupling agent except for the CA-A coupling agent. This was interpreted in terms of the reactive functional groups and dispersion forces resulting in coupling agents on the interfaces between the DGEBF epoxy resin and silica.

1. Introduction

Thermosetting materials are very important materials that are used widely in electronic packaging owing to their excellent chemical and corrosion resistance, electric and physical properties, high adhesion, low shrinkage on curing, and good thermal stability [1–3]. Despite these advantages, thermosetting materials are the main source of damage for electronic packaging because they reduce control of the thermal properties, such as thermal dissipation and thermal expansion. The problem with these materials is that their heat control ability for electronic packaging is inferior, leading to a decrease in reliability. Therefore, thermosetting material/filler composites are often applied to overcome these problems [4–6].

Epoxy resins are used extensively as high performance materials in adhesives and encapsulants for electronic packaging [7–9]. The most widely studied and commercially used thermosetting epoxy resin composite for electronic packaging is an adhesive called "capillary underfill", which is a liquid encapsulant normally consisting of epoxy resins filled with fused silica (SiO2), that is applied between the chip and substrate to protect electronic devices [10]. Since capillary underfill is dispensed prior to a chip interconnection, control of the coefficient of thermal expansion (CTE) and flow behaviors is important for enhancing the reliability of electronic devices [11–14].

Capillary underfill is most generally used in the flip-chip assembly processes. On the other hand, this process has the limitation of a narrow gap and fine pitch with miniaturizing of the package [15]. Therefore, control of the flow behavior during the dispensing process is critical for achieving high reliability for flip-chip assembly processes [16]. Recently, the studies presented in these flip-chip assembly processes focused on understanding and modeling of the flow behavior [17,18]. The flow behavior is determined by two factors [19,20]. One is the homogeneous dispersion of fillers because the heterogeneous dispersion makes the flow of underfill difficult and the other is the interfacial shear strength between the underfill materials and substrates, which are affected by the shear rate, processing temperatures and flow geometry.

Considerable effort has been made to improve the interfacial properties to achieve packaging materials with good mechanical and flow properties. From this point of view, silane coupling agents are generally used to improve the dispersion forces and flow behavior at the interface separating the thermosetting resins, fillers and substrates [21]. On the other hand, there are few reports on the effects of silane coupling agents on the properties of the underfill material, such as the thermal and mechanical properties and flow behavior.

This study examined the effects of four typical silane coupling agents on the thermal and mechanical properties and flow behavior of underfill materials. Thermal properties were measured by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA). The adhesion of the underfill materials was measured from the shear strength using Dage 4000. In addition, the flow behavior was confirmed by measuring the penetration speed.

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2. Experimental

2.1. Materials

The epoxy resin used in this study was diglycidylether of bisphenol F (DGEBF supplied from Japan Epoxy Resins Co., Ltd.). The epoxide equivalent weight and density of the DGEBF were 170 g/eq. and 1.16 $g \cdot cm^{-3}$ at 25 °C, respectively. Novolak type phenol resin was used as a curing agent in this study. 2-Phenyl 4-methyl 5-hydroxymethyl imidazole (2PHZ) as a curing catalyst was purchased from Shikoku Chem. Corp. Japan. Four different coupling agents, 3-glycidoxypropyl trimethoxysilane (CA-G), 3-methacryloxypropyl trimethoxy silane (CA-M), 3-aminopropyl trimethoxysilane (CA-A) and 3-isocyanatepropyl triethoxysilane (CA-I), were purchased from Shin-Etsu Chemical Co. Fig. 1 shows the chemical structures of materials. The silica filler used had a mean particle diameter of approximately 3.3 μm.

2.2. Preparation of cured specimens

The epoxy resin, i.e., DGEBF was degassed in a vacuum oven at 100 °C for 1 h. The DGEBF resin was mixed fully with the Novolak type phenol resin and fillers, and stirred using a mechanical stirrer and degassed in a vacuum oven to eliminate air bubbles before adding the coupling agent and curing catalyst. Subsequently, the coupling agent and 2PHZ were mixed at room temperature. Table 1 lists the material and composition. The mixtures were then poured into a silicon rubber spacer mold, respectively. The curing condition was 150 °C for 1 h in a convection oven.

Table 1
Materials and compositions of the samples.

Epoxy	Phenol resin	Imidazole	Silca	Coupling agent	
Composition				Type	Composition
100	48	5	200	None	0
100	48	5	200	CA-G	1.4
100	48	5	200	CA-M	1.4
100	48	5	200	CA-A	1.4
100	48	5	200	CA-I	1.4

2.3. Thermal analyses

The curing behaviors was monitored by differential scanning calorimetry (model DSC 200, NETZSCH Instruments) between room temperature and 250 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

The CTE of the samples were measured by thermal mechanical analysis (TMA, TMA 202, NETZSCH Instruments). These samples had dimensions of 5×5×2 mm. The samples were mounted on the TMA

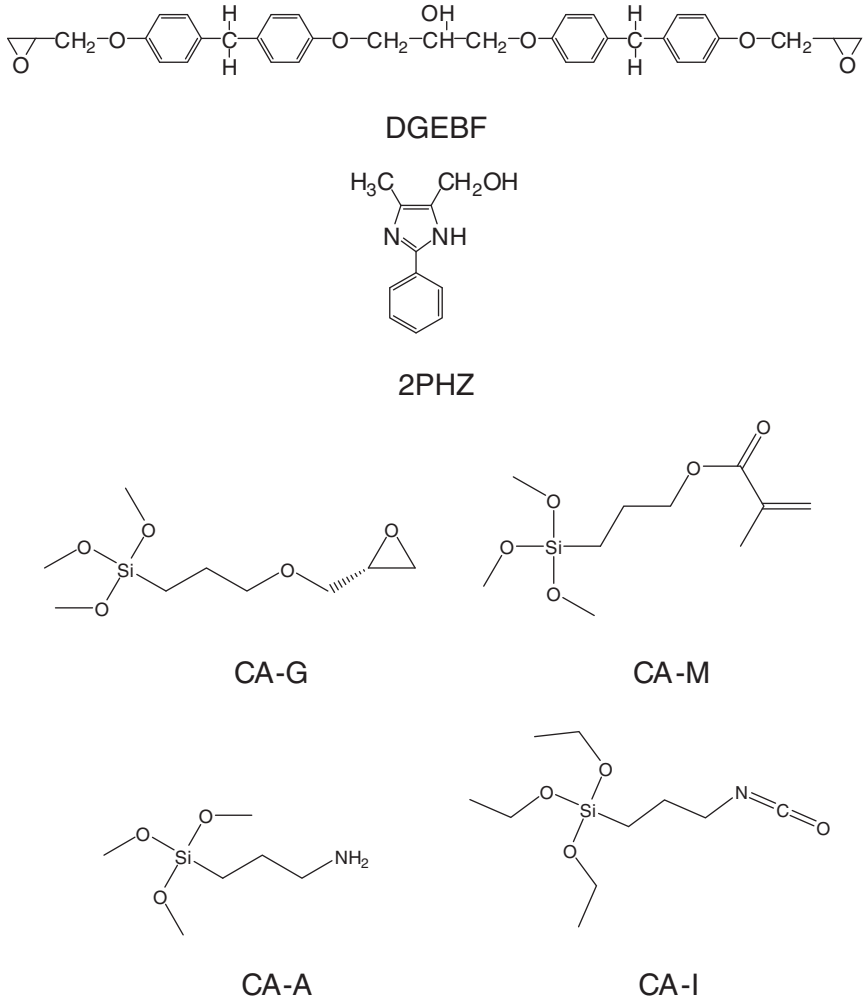

Fig. 1. Chemical structures of DGEBF, 2PHZ and coupling agents.