

# UV/Heat Dual-Curable Adhesive Tapes for Fabricating Stacked Packages of Semiconductors

Naoya Saiki, Osamu Yamazaki, Kazuyoshi Ebe

Technology Administration, R & D Division, LINTEC Corporation, Japan

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**ABSTRACT:** To facilitate the fabrication of a reliable stacked package for a semiconductor, UV/heat dual curing of adhesives was investigated. The formulated adhesives contained acrylic monomer and epoxy resins. First, UV curing was conducted on the acrylic monomer, followed by heat curing. It was found that UV-curable acrylic monomers affected the adhesive's properties, e.g., adhesion, water absorption, and viscoelasticity. As the acrylic monomer, neopentylglycol diacrylate (NPGDA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol hexaacrylate (DPHA), and tricyclodecanedi-

methanol acrylate (TCDDA) were used to investigate the effect of functional group numbers and structure. As a result, an acrylic monomer that has two functional groups with a rigid moiety (TCDDA) showed acceptable properties as adhesives for the fabrication, and thus a UV/heat-curing adhesive has been successfully developed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1178–1183, 2008

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

## INTRODUCTION

There has been an increasing market demand for electronic appliances to be more compact and to perform well these days. This market demand inevitably promoted the development of chip-scale packaging systems for integrated circuits (IC).<sup>1,2</sup> A typical packaging system uses pressure-sensitive adhesive (PSA) tape to cut a wafer to chips, then bonds very thin IC chips on the substrate by injecting a paste adhesive with a dispenser [Fig. 1(b)].<sup>3</sup>

The internal stress of epoxy resins, however, which have been widely used as the paste adhesives for their excellent heat, moisture, solvent, and chemical resistance, causes defects in the packages because thinner IC chips means that they are more vulnerable. In addition, this technique has been pointed out to have such problems as stick-out and rolling-up of the paste and uneven bonding because the paste adhesives are easily deformed by bonding pressure.

To decrease this internal stress, acrylic resins are generally used as dispersed particles<sup>4–9</sup> or as interpenetrating polymer networks (IPN).<sup>10,11</sup>

Because the PSA is in the form of a film, its thickness is uniform and it is less deformable than in the case of paste adhesives. These properties of PSA tape can prevent the aforementioned problems of the paste. Ebe et al. noted that UV-curable PSA tapes, which are made of acrylic copolymers and UV-curable acrylic

monomers, showed excellent performance when cutting a wafer into IC chips for a dicing tape.<sup>12–16</sup>

Thus, the development of the aforementioned tape led us to convert the PSA layer material to a film adhesive, as an alternative material for paste adhesives, that solves the aforementioned issues. Specifically, the film adhesives are composed of acrylic copolymer, UV-curable acrylic resin, and epoxy resins. In this process, the film adhesive changes its condition stepwise by UV irradiation and heating.

The novel film adhesives are used in the IC packaging process as follows [Fig. 1(a)]:

1. Lamination of a PSA tape onto a silicone wafer
2. UV irradiation through the backside of the tape
3. Dicing into chips
4. Picking up of IC chips with film adhesive from the face material of the PSA
5. Die bonding with a substrate by heat curing (followed by the stacking process)

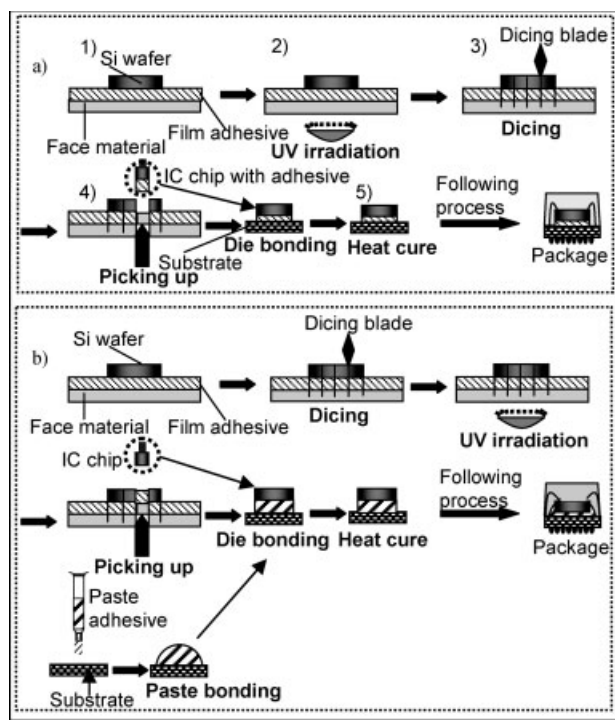
This article reports how the number of functional groups and the main chemical structure of UV-curable acrylic monomers influence the storage modulus, the adhesive strength of each process, and the water absorption and reliability of the final products.

## EXPERIMENTAL

### Materials

The acrylic copolymer used in this study was tailor-made and composed of butyl acrylate (66 mol %),

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



**Figure 1** Schematic cross section diagram for dual-curable adhesive tapes (Above: proposed process, below: conventional process).

2-hydroxyethyl acrylate (17 mol %), and glycidyl methacrylate (17 mol %,  $M_w$ :  $6.5 \times 10^5$  measured by GPC calibrated with standard polystyrene).

The multifunctional acrylic monomers shown in Table I include a photoinitiator (1-hydroxycyclohexylphenyl ketone, Chiba Specialty Chemicals (Tokyo, Japan), Irgacure 184, 4 wt % of monomer). Every monomer was from Nihon Kayaku Co. (Tokyo, Japan).

The epoxy resins were bisphenol A diglycidyl ether (Epikote828 (30 wt %), Epikote1055 (30 wt %), Japan Epoxy Resins Co., Tokyo, Japan) and *o*-cresol novolak epoxy resin (EOCN104S (8 wt %), Nihon Kayaku Co.), including a heat-curing agent (dicyanodiamide (1 wt %), Asahi Denka Co., Tokyo, Japan) and (imidazole (1 wt %), Shikoku Chemicals Co., Kagawa, Japan).

The standard adhesive formulation contained 20 wt % of the above mentioned acrylic copolymer, 70 wt % of epoxy resins including a heat-curing agent, and 10 wt % of DPHA. In cases when other acrylic monomers were used, the amount was adjusted to be the same as the vinyl group content of the DPHA (Table I).

The adhesive film was prepared using the following procedure. All materials were dissolved in methyl ethyl ketone to produce 50 wt % at room temperature. The solution was coated on a polyolefin film to a thickness of  $20 \pm 2 \mu\text{m}$  after air-drying at  $100^\circ\text{C}$  for 1 min to vaporize the solvent.

These formulated adhesives will hereafter be named after the acrylic monomer being used, e.g., "the DPHA adhesive."

### Curing and measurement

UV irradiation was conducted with a dose of  $155 \text{ mJ}/\text{cm}^2$  at an exposure rate of  $340 \text{ mW}/\text{cm}^2$  with a UV irradiator (RAD2000 m/8, LINTEC Corporation) equipped with a high-pressure mercury-vapor lamp and a constant illumination controlling system.

Heat curing was carried out at  $160^\circ\text{C}$  for 60 min in a heating oven.

The elastic modulus of the UV-cured adhesives was measured with a dynamic analyzer RDA II (manufactured by Rheometric Scientific F.E.) at a frequency of 1 Hz and the elastic modulus of the dual-cured adhesives with a dynamic mechanical analyzer, RHEOVIBRON DDV-II-EP (A&D F.E.), at a frequency of 11 Hz and a heating rate of  $3^\circ\text{C}/\text{min}$ . The post-UV curing adhesive strength was measured according to JIS Z 0237. The post-heat-curing adhesive strengths were measured with a tensile testing machine (A&D F.E., Tokyo, Japan) on a  $10 \text{ mm} \times 10 \text{ mm}$  sized chip at a releasing speed of 50 mm/min, where a copper (JIS H3100 C1100P) plate was used as the adherend. Water absorption was measured by the weight change of the sample under  $85^\circ\text{C}$ , 85% RH conditions. A performance test using the actual manufacturing procedure was conducted using the standard process parameters and dicing machine DFD651 (DISCO F.E.), die bonder 7200B (WEST-BOND F.E.), molding press G-CUBE (APICYA-MADA F.E.), and an IR reflow (SAGAMI RIKO F.E., Tokyo, Japan).

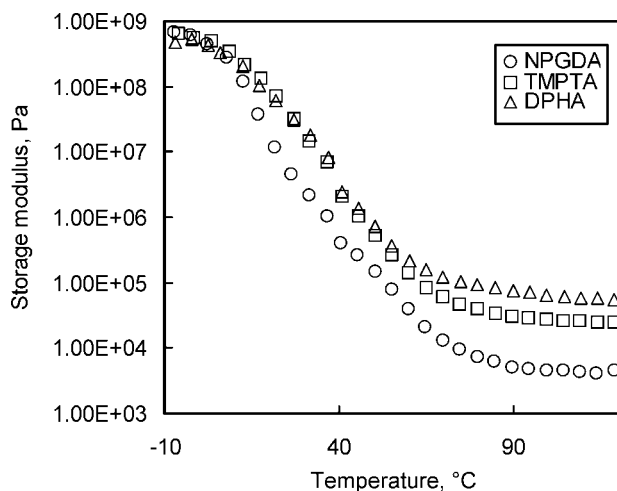
## RESULTS AND DISCUSSION

### The influence of the number of UV-curable functional groups

A higher storage modulus was expected to be more suitable for supporting the wafer during the dicing

**TABLE I**  
Applied UV-Curable Monomer

Monomer	Abbreviation	Functional group	Product name
Neopentylglycol diacrylate	NPGDA	2	Kayarad NPGDA
Trimethylolpropane triacrylate	TMPTA	3	Kayarad TMPTA
Dipentaerythritol hexaacrylate	DPHA	6	Kayarad DPHA
Tricyclodecane dimethanol acrylate	TCDDA	2	Kayarad R-684

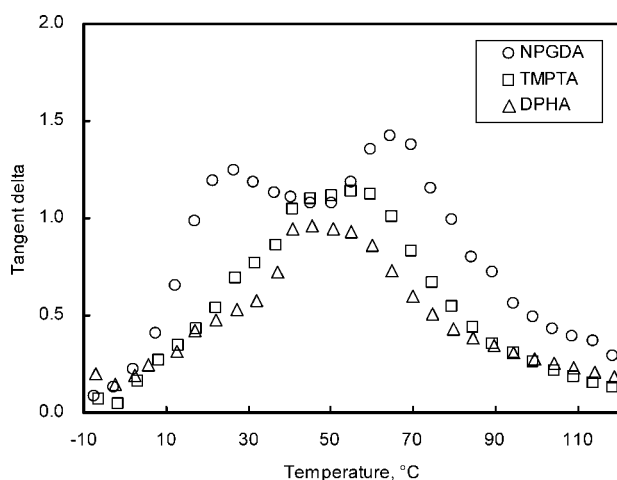


**Figure 2** Thermogram of UV-cured adhesives.

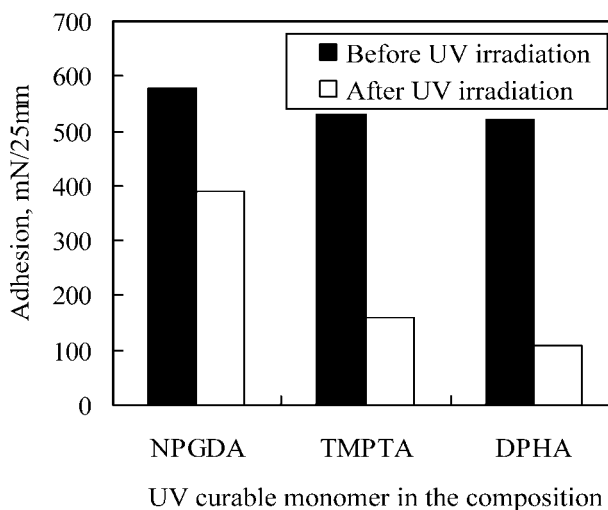
and picking up of the diced chips, together with the adhesive layer from the face material.<sup>16</sup> To investigate the effect of the number of functionalities on the storage modulus, the adhesive compositions containing NPGDA and TMPTA, or DPHA, were investigated.

The thermograms of the storage modulus post-UV curing and heat curing (dual-curing) are shown in Figures 2 and 3, respectively. Figure 2 clearly shows that the storage modulus increases as the acryloyl groups in the monomer molecule do. Figure 3 shows that the tangent delta of the NPGDA adhesive has two peaks. One is assumed to result from the acrylic copolymer and the other from the epoxy resins. Meyer et al. noted that two tangent delta peaks mean that the two components move separately, and this causes lack of adhesion.<sup>17,18</sup> Other adhesives only have a single peak each.

It is necessary for the adhesive layer to be picked up easily with a chip after dicing. Therefore, lower adhesion between the post-UV-curing adhesive layer



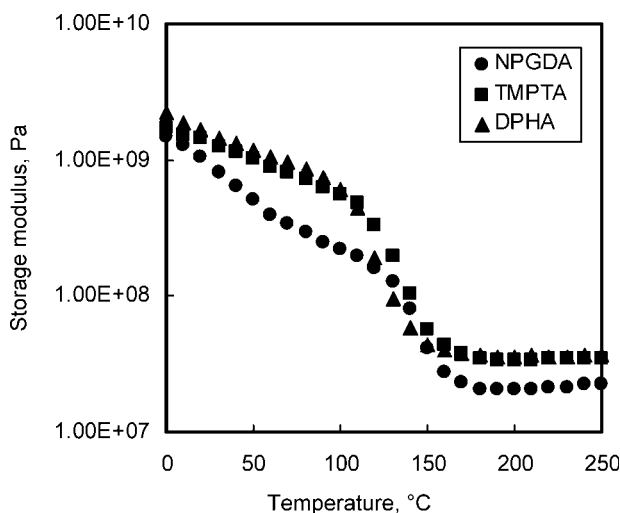
**Figure 3** Tangent delta of UV-cured adhesives.



**Figure 4** The effect of functionality on the decrease of post-UV adhesion between adhesive layer and face material.

and the polyolefin film is more suitable for this process. To investigate how the functionality of the UV-curable monomers affects the adhesion, the peel strength between an adhesive film and a polyolefin film was investigated as shown in Figure 4. The peel strength of each adhesive film shows almost the same value as for pre-UV irradiation. On the other hand, the peel strength of TMPTA and DPHA adhesives decreases drastically upon UV irradiation, while one of the NPGDA adhesives shows only a slight decrease.

Figure 5 shows that post-heat-curing adhesives show effects on the storage modulus similar to the post-UV-curing adhesives, as shown in Figure 2. Therefore, it can be concluded that the heat stability of the NPGDA adhesive is inferior to that of the TMPTA or DPHA adhesives.



**Figure 5** Thermogram of dual-cured adhesives.

**TABLE II**  
**Adhesive Properties between Si Chip and Copper**  
**Post-heat Curing**

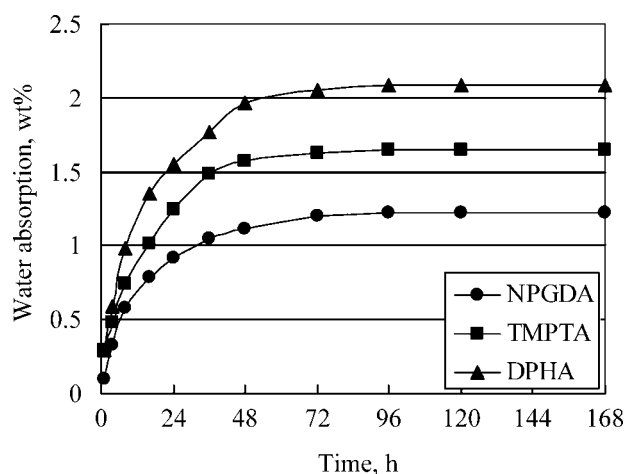
Monomer	Sheer strength (N) (250°C, 30 s)	Release force (N)	
		(23°C, 50% RH, 24 h)	(85°C, 85% RH, 168 h)
NPGDA	8.04	5.4 (If) <sup>a</sup>	4.6 (If)
TMPTA	10.29	8.0 (Cf) <sup>b</sup>	4.0 (Cf)
DPHA	8.82	8.0 (Cf)	4.4 (Cf)

<sup>a</sup> If: Interfacial failure.

<sup>b</sup> Cf: Cohesive failure.

The dual-cured adhesive properties between the Si chip and copper are shown in Table II. The releasing force of the NPGDA adhesive is lower than that of the TMPTA or DPHA adhesive. Moreover, the fracture mode of the NPGDA adhesive is an interfacial failure, while that of the TMPTA or DPHA adhesive is a cohesive failure. Again, it is clear that the adhesion between the NPGDA adhesive and the chip is inferior to the adhesion between the TMPTA or DPHA adhesive and the chip. As far as the adhesive strength is concerned, it can be concluded that the use of monomers with three or six acryloyl groups in one molecule is more suitable for the dicing and for attaining successful bonding (heat curing) processes compared with the use of bifunctional monomers.

During the IC package manufacturing, it should be heated between 240 and 260°C during the soldering process, after bonding the IC chip with the substrate and the molding process. The temperature is set high in the soldering process. Thus, the water occluded in the adhesive explosively vaporizes and often causes detachment between the IC chip and the substrate and consequently causes cracks in the Si chip.



**Figure 6** Water absorption of dual-cured adhesives.

Accordingly, the adhesive layer needs to have the water absorption rate as low as possible. Figure 6 shows the water absorption rate for dual-cured adhesives. The water absorption increased drastically up to 48 h and was stable after passage of 96 h. From this trend, the value after 168 h was defined as the rate of saturated water absorption. The rate is in the order NPGDA < TMPTA < DPHA adhesives. When NPGDA is used as a UV-curable component, the water absorption rate becomes low and adequate for the soldering process, while on the other hand; the reliability of the dual-cured adhesive becomes low.

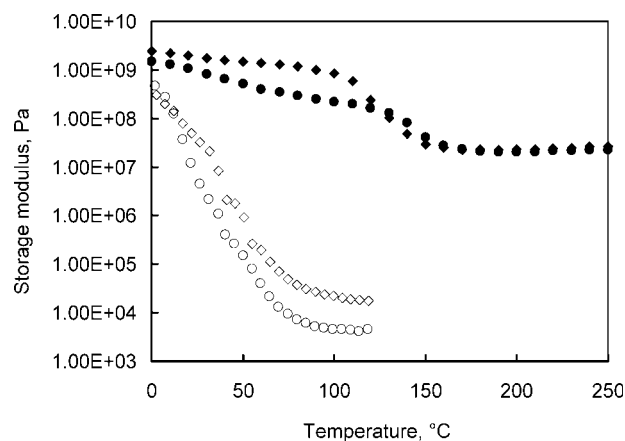
### The influence of chemical structure of UV-curable monomers

In an attempt to solve the contradictory experimental results above, the main chemical structure was investigated. NPGDA was replaced by TCDDA, which has two acryloyl groups, the same as NPGDA but containing more rigid moieties in the molecule.

Figure 7 shows the thermogram of the storage modulus of the UV-cured and dual-cured TCDDA adhesives in comparison with those of the NPGDA adhesives. Looking at the graph, you can see that in both curing systems, the storage moduli of the TCDDA adhesives were much higher than those of the NPGDA adhesives, and are comparable with those of the TMPTA adhesives shown in Figures 2 and 5. In addition, Figure 8 shows that the tangent delta of the TCDDA adhesive only has one peak.

The peel strength of the TCDDA adhesive also decreases drastically upon UV irradiation while one of the NPGDA adhesives shows only a slight decrease (Fig. 9).

In addition, the diced Si chip with the UV-cured TCDDA adhesive was bonded on a copper plate via



**Figure 7** Thermogram comparison of NPGDA and TCDDA adhesives. Open symbols: UV-cured adhesives; closed symbols: dual-cured adhesives. □: TCDDA; ○: NPGDA.

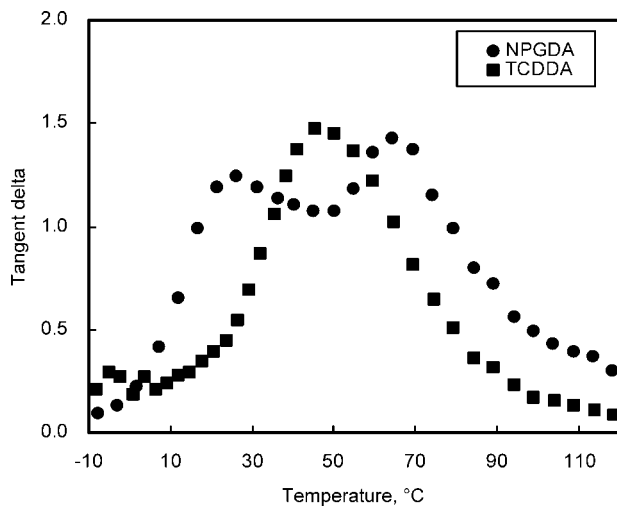


Figure 8 Tangent delta of dual-cured adhesives.

heat curing, and the adhesive strength and water adsorption were investigated. The results are shown in Table III. Compared with Table II, the dual-cured TCDDA adhesive has the same level of adhesive strength as the TMPTA and DPHA adhesives, and the failure modes of the adhesion are cohesive.

The water adsorption rate is a little higher than that of the NPGDA adhesive, but lower than that of the TMPTA or DPHA adhesive.

#### Performance tests at the manufacturing procedure

From the above evaluation, TCDDA adhesive showed better properties than the other adhesives. To prove the properties for the actual products, the performances of the tapes were examined at the practical packaging of the IC chips, which uses the procedure of Figure 1(a).

First, the adhesion to a patterned silicone wafer at room temperature was investigated and came out to

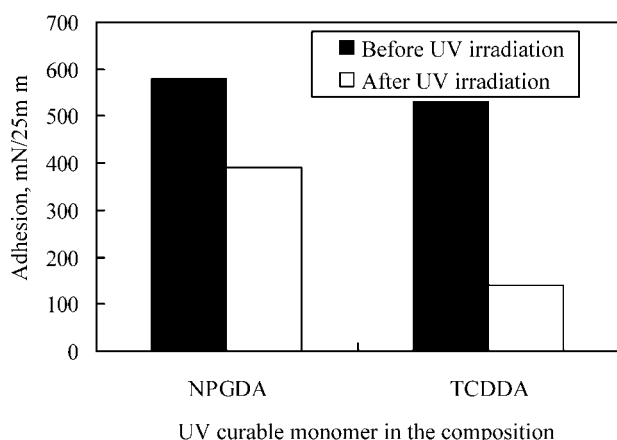


Figure 9 The effect of structure on the decrease of post-UV adhesion.

TABLE III  
Adhesion and Water Absorption of the Dual-Cured TCDDA Adhesive

Properties	Conditions	TCDDA	DPHA (Reference)
Shear strength (N)	250°C, 30 s	8.33	8.82
Release force (N)	23°C, 50% RH, 24 h	8.0 (Cf)	8.0 (Cf)
	85°C, 85% RH, 168 h	5.0 (Cf)	4.0 (Cf)
Water absorption (%)	85°C, 85% RH, 168 h	1.48	2.05

be satisfactory for dicing. That is to say, such problems as flying-off and cracking in the chips did not occur during the dicing process. Secondly, after the picking up of the diced IC chip, it was tentatively bonded onto the face material (another patterned IC chip) at 100°C, under a dead load of 100 g/chip. In such conditions, the IC chip managed to achieve fine adhesion with the uneven surface of the substrate, because of the increase in the adhesive's wettability. The NPGDA adhesive failed to be picked up because of the high adhesion after the UV irradiation. During the 160°C bonding, neither flowing-out nor rolling-up occurred for the adhesives. As a result, the stacked IC package of TCDDA adhesive sustained high temperature at the soldering process, while the TMPTA and DPHA adhesives showed defects.

#### CONCLUSION

The functionality and structure of UV-curable acrylic monomers significantly influenced not only the dicing properties post-UV irradiation, but also the heat resistance post-heat curing. Both the dicing properties and the heat resistance had been attained using the adopted monomers in this investigation. The successfully developed UV/heat dual-curable adhesives are now being used in the fabrication of commercial stacked packages of semiconductors.

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