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UV-curing and thermal stability of dual curable urethane epoxy adhesives for temporary bonding in 3D multi-chip package process

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ABSTRACT

Multi-chip packages (MCP) refers to a packaging configuration, connected via wirebonds to a multilayer circuit board, and protected by either a molded encapsulant or a low-cost ceramic package. As it requires high processing temperature, the adhesives for MCP need to show proper adhesion and thermal stability at high temperature. This study employed semi-interpenetrated (semi-IPN) structured polymer networks using UV-curing with acrylate terminated dual-curable urethane epoxy adhesive, a dipentaerythritol hexacrylate (DPHA), using hydroxydimethyl acetophenone as photo-initiator. UV-curing and thermal stability focused on different photo-initiator contents were investigated using photo-DSC, FTIR-ATR spectroscopy, gel content and TGA. The results show that UV-curable acrylic formulations with different content of photo-initiator affects UV-curing and thermal stability.

1. Introduction

Wafer- and chip-level bondings are crucial process steps for three-dimensional microelectromechanical system (MEMS) integration and packaging. Today a wide variety of bonding processes are available, such as direct fusion bonding, direct plasma-assisted bonding, anodic bonding, solder bonding, eutectic bonding, thermocompression bonding, and low temperature melt glass bonding. These processes have different shortcomings such as the need for high temperature, high voltage, or special surface preparation. Adhesive bonding provides an inexpensive alternative to fabricate bonds at low temperatures with a high surface roughness tolerance [1].

Nowadays, the wafer thinning process has increased attention due to its promising application in device miniaturization and packaging. The key factors for thinned wafers are improved heat dissipation, three-dimensional stacking, reduced electrical resistance and substrate flexibility. A reduction in wafer thickness combined with an increasing wafer diameter produces to wrap and fold of wafer and hence creates a demand for new methods of wafer handling. The thinned substrates need to be supported during the backside grinding process and through the subsequent processes such as lithography, deposition, etc. Using temporary adhesives to bond the processed device wafer to a rigid carrier wafer offers an efficient solution and is becoming increasingly important in both integrated circuit board and MEMS applications, mainly due to its low cost, ease of processing, and adaptability. The process for temporary wafer bonding is shown in Fig. 1 [2]. The front side of the carrier wafer is coated with the adhesive, and the wafer undergoes an initial bake to remove the solvent. The device wafer (possibly after the application of a protective layer) is brought into contact with the adhesive-coated carrier wafer under vacuum and pressure. Adhesives for the bonding process must adhere to a variety of semiconductor substrates such as silicon, gallium arsenide, indium phosphide and different metals, insulators and dielectrics. The adhesive layer between device and carrier wafers provides the mechanical strength required for thin-wafer handling. Adhesives should possess flow properties to flow into structures on the front side of the device wafer to provide good bonding properties. In addition, the adhesives must be easy to apply; have suitable mechanical strength, thermal stability and chemical resistance; and exhibit thickness variation across large wafers. Also, temporary wafer bonding requires the adhesive to be easily removed without damaging the features on the active side of the device wafer over a short debonding time. At present, a few number of adhesives are available for this type of application. The tapes currently used for temporary wafer bonding have limited thermal stability at higher temperatures and can be used only up to 170–200 °C [2–6].

UV-curing technology has been considered as an alternative to traditional solvent-borne coatings, due to its eco-compatible

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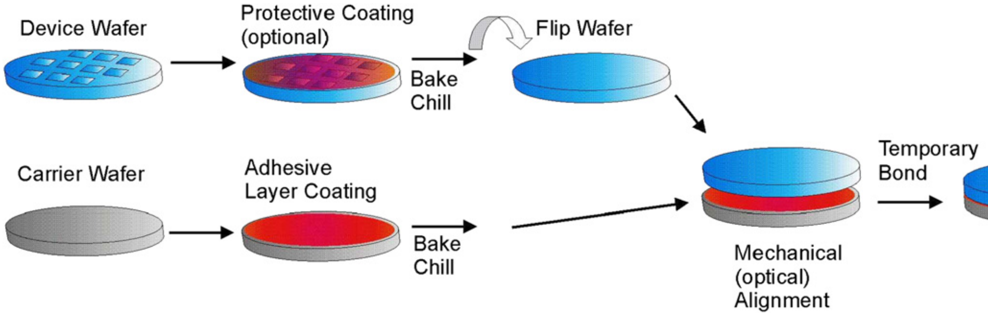

Fig. 1. Temporary bonding process flow [2].

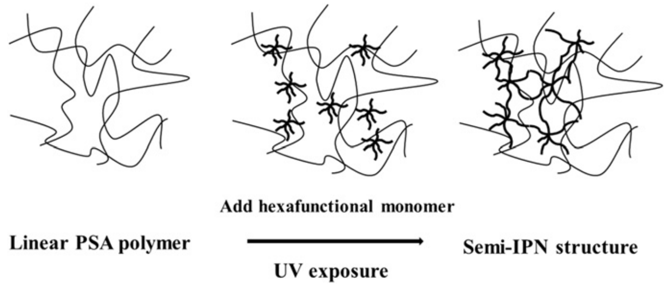

Fig. 2. Process of producing a semi-IPN structure in UV-cured acrylic adhesives [11].

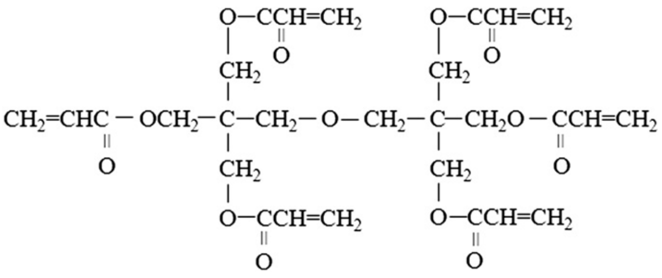

Fig. 3. Structure of dipentaerythritol hexacrylate (DPHA).

Fig. 4. Cleavage of hydroxydimethyl acetophenone as the photo-initiator in presence of UV light [20].

process and excellent properties resulting from the high cross-link density. On the other hand, acrylic monomers and oligomers are used widely. However, they have poor thermo-mechanical stability. Therefore, the cross-linking of multifunctional acrylates is needed to increase their thermo-mechanical stability [7–9].

However, the creep resistance increases greatly in more cross-linked adhesive [8,9]. Multifunctional acrylates cross-link rapidly by radical and cationic polymerization, and their kinetics and properties have been investigated [10]. Cross-linked multifunctional acrylates produce semi-interpenetrated structured polymer networks (semi-IPNs) as shown in Fig. 2. Semi-IPN structured PSAs have advantages, such as improved heat resistance [8,9,11]. Athawale [12] reported that photo-polymerization was effective in obtaining networks with a high degree of interpenetration. The curing kinetics and peel strength of dual-curable adhesives based on acrylic resins were previously reported [13,14].

To combine the functionalities of UV and heat curing in an epoxy acrylate oligomer-based system, a thermal-curing agent should be introduced. Recently, thermally latent curing agents such as dicyandiamide, which exhibit long-term stability at ambient temperature and can be transformed into activated species at high temperature, have been studied by many researchers in an attempt to obtain epoxy based resins affording one part handling and good storage stability [15–19].

In this study, semi-IPN structured urethane epoxy adhesives as temporary bonding adhesives in wafers were introduced using a hexafunctional acrylate monomer with a UV-curing system. Emphasis was placed on the optimal conditions such as photo-initiator contents and UV doses. It was obtained by using photo-DSC, FTIR-ATR spectroscopy and gel content. Also, thermal stability was studied by TGA analysis.

2. Experimental

2.1. Materials

Polydimethylsiloxane (PDMS, Shin-Etsu cp., Ltd) and isophorone diisocyanate (IPDI, Bayer Material Science) were dried in 100 °C 12 h prior use and 2-hydroxyethylmethacrylate (2-HEMA, Samchun Pure Chemical Co., Ltd., Republic of Korea) was used without pretreatment. About 0.1 wt% of dibutyltin dilaurate is added to proceed the reaction to take place at a rapid rate as a catalyst in urethane reaction. Dipentaerythritol hexacrylate (DPHA, Miwon Specialty Chemical, Republic of Korea) was used as hexafunctional monomer (Fig. 3). Hydroxydimethyl acetophenone (Micure HP-8, Miwon specialty chemical Co., Ltd, Republic of Korea) was used as the photo-initiator for the UV curing in Figs. 4 and 5 [20]. A diglycidyl ether of bisphenol A (DGEBA) (EEW: 184–190 g/eq) was supplied by Kukdo Chemical Co., Ltd, Republic of Korea). Methyltetrahydrophthalic anhydride (MeTHPA, Kukdo Chemical Co., Ltd, Republic of Korea) and triphenylphosphine (TPP, Fluka, Switzerland) were used as curing agents. All samples used in the synthesis were extra pure or reagent grade.

2.2. Synthesis of silicone urethane methacrylate (SiUMA)

The silicone urethane methacrylate was obtained by adding an equimolar amount of PDMS with 0.1 wt% dibutyl tin dilaurate (DBTDL) dropwise to IPDI (mole ratio, NCO:OH=2:1) under a nitrogen gas. The reaction was maintained at room temperature for 3 h. An equimolar amount of HEMA with 0.5 wt% hydroquinone as a polymerization inhibitor has been added a dropwise to the PDMS-IPDI adduct for about 5 h. Then the absorption peak of the NCO group at 2250 cm^{-1} had disappeared completely.

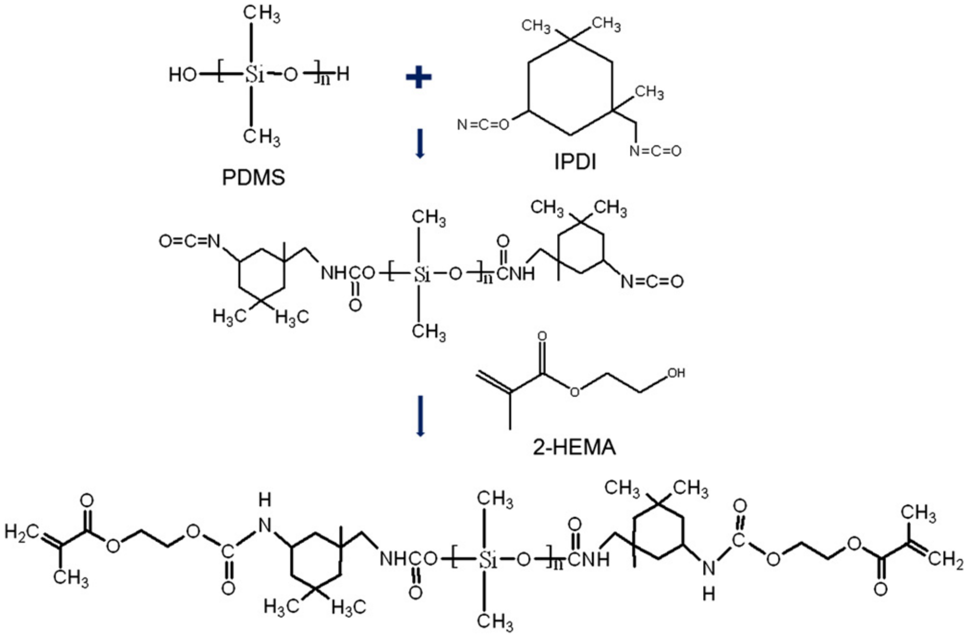

Fig. 5. Synthesis process of UV-curable Silicone Urethane Methacrylate (SiUMA).

2.3. *Preparation of dual-curable adhesive*

Diglycidyl ether of bisphenol A (DGEBA), dipentaerythritol hexacrylate (DPHA) and a photo-initiator were blended first and then latent curing agent and curing acceleration agent were mixed using a paste mixer (Daewha Tech, South Korea) at room temperature. Table 1 shows the blend ratios of the various dual-curable adhesives. The blending processes were performed in two steps to make a homogeneous mixture and to remove the air bubbles in the adhesives. In the first step, the stirring rate was 1200 rpm for 20 min and then in the second step it was 1000 rpm for 10 min.

2.4. *Curing process*

2.4.1. *Fourier transform infrared spectroscopy (FT-IR)*

The IR spectra were obtained using a JASCO FTIR-6100 (Japan) equipped with an attenuated total reflectance (ATR) accessory. In order to obtain the IR spectra of dual curable adhesives, the cured adhesive samples were cut into $0.5 \times 0.5\,\mathrm{cm}^2$ pieces. The ATR prism was diamond and its refractive index at $1000\,\mathrm{cm}^{-1}$ was 2.4 with a transmission range from 4000 to $650\,\mathrm{cm}^{-1}$. The resolution of the spectra recorded was $4\,\mathrm{cm}^{-1}$. The curing behavior of the dual curable adhesives was analyzed by observing the changes in the C=C bonding bands at $810\,\mathrm{cm}^{-1}$. All FTIR-ATR spectra were modified by baseline correction.

2.4.2. *Gel fraction*

The gel fractions of the dual-curable adhesives after UV curing and subsequent thermal curing at different temperatures, 120 and 150 °C, were determined by soaking in toluene at 50 °C for 1 day. The insoluble part was removed by filtration and dried at 50 °C to a constant weight. The gel fraction was calculated by applying the following equation:

$$\text{Gel fraction }(\%) = (W_1/W_0) \times 100$$

where W_0 was the weight before filtration and W_1 was the weight after filtration. The test was replicated three times.

Table 1
Blend ratio of dual-curable adhesives (unit: phr).

DGEBA	100	100	100
DPHA	5	5	5
Photo-initiator (phr in DPHA)	1	2	5
Latent curing agent (Dicyandiamide-type)	10	10	10
Curing acceleration agent (Sunmide LH-210)	10	10	10

2.4.3. *UV-curing behavior by photo differential scanning calorimetry (photo-DSC)*

Photo-DSC experiments were conducted using a TA Instruments Q-200 DSC equipped with a photo-calorimetric accessory (Omnicure 2000), which used light from a 100 W middle-pressure mercury lamp with a wavelength range of 300–400. Light intensity was determined by placing an empty DSC pan on the sample cell. UV light intensity at the sample was $15\,\mathrm{mW/cm}^2$ over a wavelength range of 300–400 nm. The weight of the sample was about 5 mg and the sample was placed in an open aluminum DSC pan. Measurements were carried out at room temperature in flowing N_2 gas at 50 ml/min.

2.5. *Thermogravimetric analysis*

The thermal stability and decomposition profiles of the dual curable adhesives were measured using a thermogravimetric analyzer (Perkin Elmer Thermogravimetric Pyris 1 TGA model). The sample was loaded into a ceramic pan, and heated from 30 °C to 600 °C at a constant heating rate of 10 °C/min in an inert nitrogen atmosphere.

3. Results and discussion

3.1. *Photo-differential scanning calorimeter (photo-DSC)*

Photo-DSC offers a simple method of characterizing the UV-curing kinetics for the photopolymerization of UV-cured materials. By monitoring the rate at which heat is released from the photopolymerized sample, the reaction rate can be measured. Therefore, the profiles for the heat of reaction versus time provided by photo-DSC can be used to characterize the photo-induced kinetics and to evaluate the polymerization rate constants [11,21,22]. Fig. 6 shows the isothermal UV-curing heat enthalpy and conversion profiles of UV-curable PDMS-modified urethane epoxy adhesives. The heat flow (W/g) plotted in Fig. 6(a) can be acquired by photo-DSC measurements. The photo-DSC experiments were performed at same temperature and light intensity, 25 °C and 50 mW/cm^2. At the beginning of the reaction, the early onset of auto-acceleration by activation of radicals occurred as a steep increase. A difference in activity between photo-initiator contents was observed. Fig. 6(a) shows that maximum is displaced to higher time by decreasing the photo-initiator contents. It means that the reactivity increased with increase in the concentration of radicals in the UV-curable adhesives. Because the broadening of the peak suggests that the curing has been proceeded more spread out. So a longer time was needed for its end. The exothermic area increased with increasing photo-initiator contents, as shown in Fig. 6(b). Minor difference was shown between 1 and 2 phr of photo-initiator contents. But a greatly increasing area was shown in 5 phr of photo-initiator contents. The dual curable adhesives showed a higher exothermic area with increase in concentration of free radicals due to the increase in the reaction energy [11].

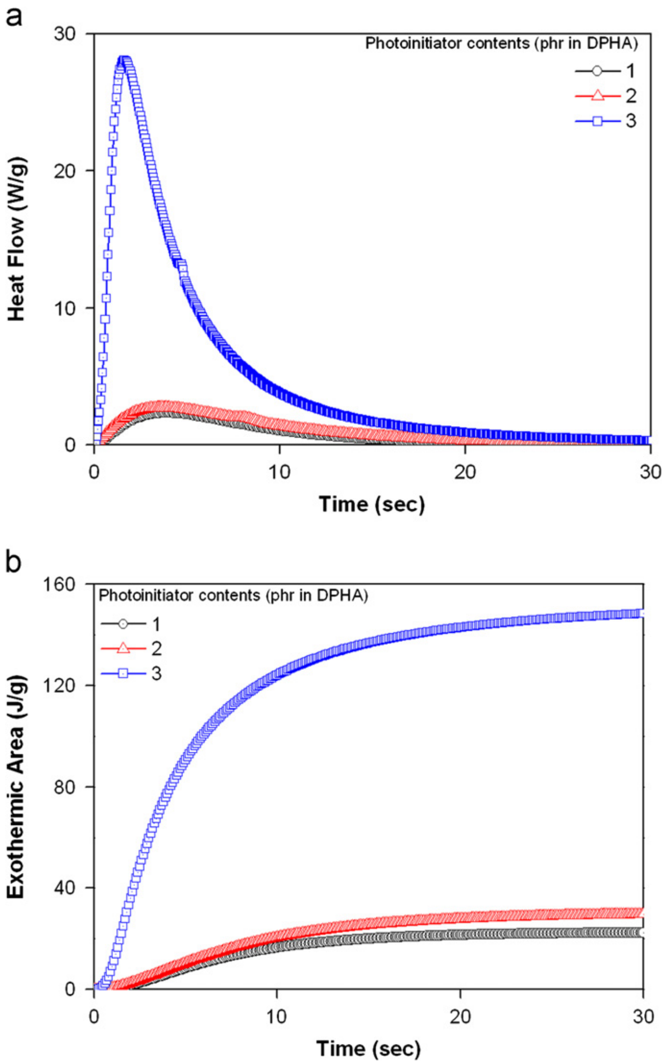

Fig. 6. (a) Photo-DSC thermograms and (b) exothermic area which was calculated by integration of heat flow with different contents of the photo-initiator.

3.2. *FTIR-ATR spectroscopy*

The cure of the photo-induced cross-linking was measured by FTIR-ATR spectroscopy. After the photo-initiation of adhesives by UV irradiation, the specific bands of the functional monomers and/or oligomers indicated that the polymerization was carried out. The curing reaction can be measured using FTIR-ATR spectroscopy because the C=C bonds in the functional monomers participate in the cross-linking reaction by photopolymerization. Previous study showed that the absorption bands at 810 cm^{-1} related to the C=C twisting vibration of the acrylate groups decrease with increase in UV exposure [11,23]. These double bonds have a planar conformation, but UV irradiation deforms them into an out-of-plane conformation [13]. FTIR spectra of the UV-curable mixture, DPHA and photo-initiator (5 phr in DPHA) were investigated, as shown in Fig. 7(a). Providing the conversions and/or absorbance data in this method makes thickness of the samples on ATR not important [24]. The relative conversion of C=C bonds decreased sharply as the UV dose increases to 200 mJ/cm^2 regardless of the photo-initiator content, as shown in Fig. 7(b). Entanglement and/or orientation of multifunctional monomers around the acrylic copolymer may induce a rapid radical chain reaction, resulting in fast reactivity [25]. As above mentioned, the photo-initiator content accelerates the cross-linking reaction. But the relative conversion of C=C bonds was not zero %. The remaining C=C bond might have remained unreacted after the action of the photo-initiator because they were trapped in the cross-linked polymer network [8]. The uncured polymer has an effect on thermal stability of adhesives.

3.3. *Gel fraction*

Gel fraction determination is a convenient method of measuring the insoluble fractions, such as the fractions of cross-linked or network polymers [13]. In this study, hexafunctional monomer in organic solvents was turned into insoluble cross-linked structures by UV-curing. The gel fraction increased with increase in photo-initiator contents, due to the cross-linking reaction of the unreacted multifunctional monomers as shown in Fig. 8. The gel fraction was relatively constant regardless of the photo-initiator contents for UV dose higher than 400 mJ/cm^2. And it showed that the gel fraction of adhesives with 1 phr of photo-initiator in DPHA increased with increasing UV dose up to approximately 50% of the gel fraction at a UV dose of 1600 mJ/cm^2. But the gel fraction increased up to around 75% in 5 phr of photo-initiator in DPHA. In other words, at a low content of photo-initiator, the gel content conspicuously increased, owing to the existence of unreacted DPHA, but the rate of increase of the gel fraction decreased with increase in the UV dose, because the amount of unreacted DPHA decreased. When a photo-initiator content of 5 phr was used to the adhesives, the gel fraction did not reach 100% irrespective of the UV dose. This indicates that the unreacted DPHA were remained in the cross-linked structure formed by UV-curing. Also, a cross-linked structure similar to a semi-interpenetrated structured polymer network was formed by all the components [8]. The initial gel fraction rate sharply increased at a UV dose of 100 mJ/cm^2 due to rapid cross-linking which induced free radical initiation of multifunctional monomer. Furthermore, these results corresponded to the FTIR results in that more contents of photo-initiator accelerates the cross-linking reaction among DPHA.

3.4. *Thermal property*

Fig. 9 indicates the thermal stability of UV-cured adhesives at temperatures ranging from 25 °C to 600 °C. Table 2 lists the

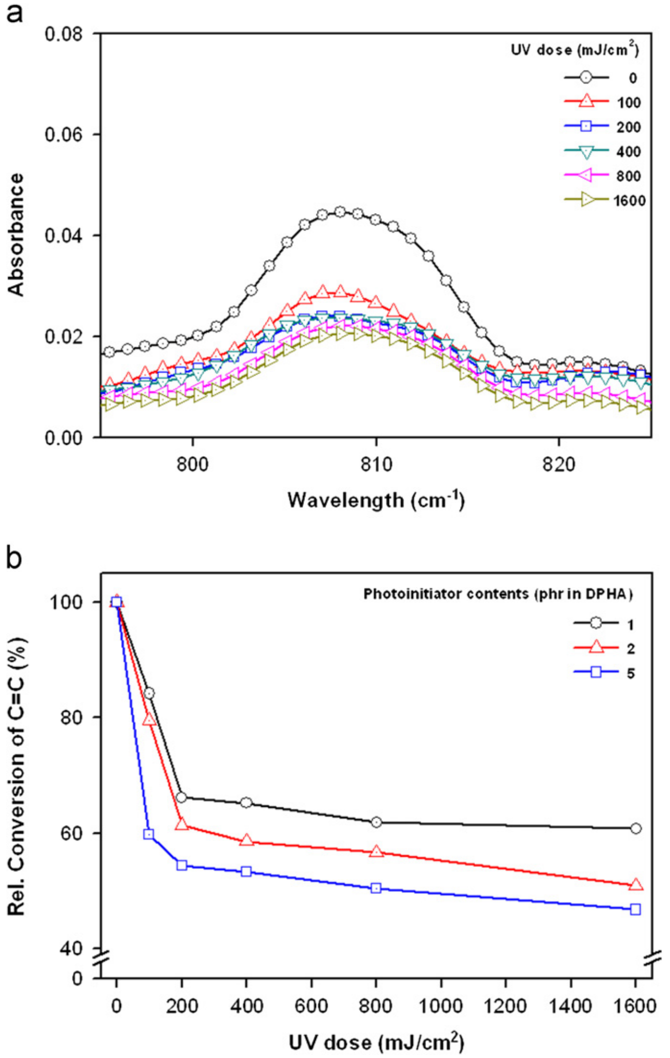

Fig. 7. FTIR-ATR spectra of UV-curable adhesives with (a) 5 phr of photo-initiator contents, as a function of the UV dose at 810 cm^{-1}, and (b) relative conversion vs. UV dose.

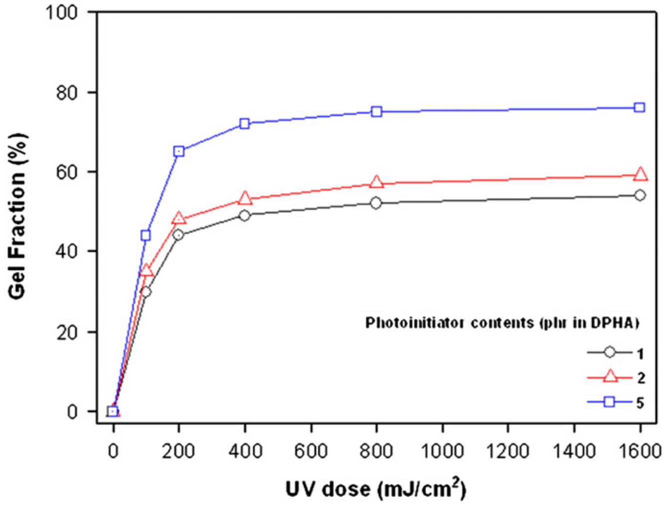

Fig. 8. Gel fraction of UV-curable adhesives after UV-curing.

characteristic thermal decomposition data of each cured adhesives. The maximum thermal degradation peak temperatures of the samples are also listed [26].

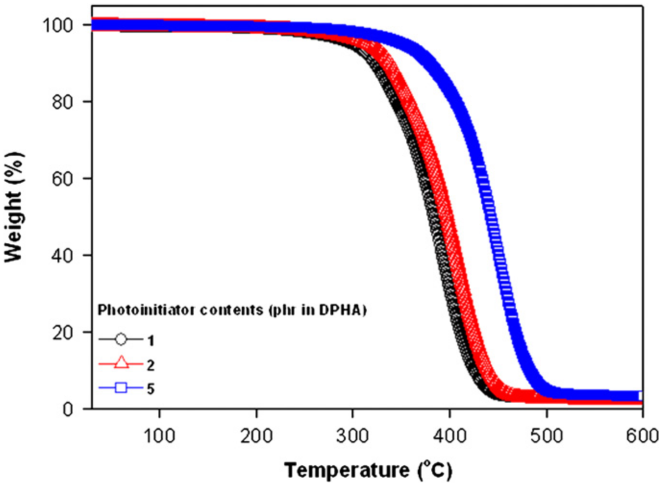

Fig. 9. Thermogravimetric analysis of the UV-cured adhesives.

Table 2
Characteristic thermal decomposition data of the UV-cured adhesives.

Photo-initiator contents (phr in DPHA)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	wt% at 600 °C	T_o (°C)	T_{max} (°C)	T_f (°C)
1	322	383	2	285	390	440
2	338	397	2	292	399	451
5	379	442	3	301	442	497

$T_{10\%}$, 10 wt% loss temperature; $T_{50\%}$, 50 wt% loss temperature.

T_o (initial decomposition temperature); T_{max} (temperature of maximum rate of weight loss); T_f (final decomposition temperature).

The main decomposition takes place at higher than approximately 300 °C corresponding to the advanced fragmentation of the macromolecules formed in reactions of dehydrogenation, thermal cracking, disproportionation and gasification processes [19]. Major differences have shown between 2 and 5 phr of photo-initiator content. This result suggests that thermal stability might have been dependent on photo-initiator content due to increased density of three-dimensional networks corresponding to FTIR analysis and gel fraction data above shown.

4. Conclusion

An attempt has been made to indicate how best the points can be established in assessing the performance of UV-curing bonding process in 3D multi-chip package process. The practical data obtained from some of the essential test based on different content of photo-initiator were discussed according to certain criteria. The data show that UV-curable acrylic formulations with different contents of photo-initiator affects not only curing behaviors on UV doses but also thermal stability. Because UV-curing behavior depended mainly on the photo-initiator. When UV light is irradiated on the curable adhesives, both the maximum curing and the exothermic areas under the thermogram curves are affected by photo-initiator content.

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