

Ultraviolet/Heat Dual-Curable Film Adhesives with Pendant-Acryloyl-Functional-Group-Modified Epoxy Resin

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ABSTRACT: To facilitate the fabrication of a reliable semiconductor package, the UV/heat dual curing of film adhesives was investigated. The curing system of the epoxy resin affected the film adhesive properties. As the UV/heat dual-curable epoxy resin, a modified *o*-cresol novolak epoxy resin, in which half of the glycidyl groups were substituted by acryloyl groups (OCN-AE), was applied to the film adhesive. The formulated film adhesive contained acrylic copolymer, OCN-AE, phenolic aralkyl resin as a heat-curing agent of the glycidyl groups, and 1-hydroxycyclohexyl phenyl ketone as a photoinitiator of the acryloyl groups. The formulated reference film adhesive contained unmodified *o*-cresol novolak epoxy resin

(OCN-E) in place of OCN-AE. Formulated film adhesives containing a mixture of OCN-E and *o*-cresol novolak epoxy acrylate were also used as references. The morphology and the film adhesive properties were investigated. In these investigations, the film adhesive of OCN-AE showed better adhesive properties, lower modulus, and a better stress-relaxation ability than the referenced adhesives. As a result, a reliable film adhesive for semiconductor packages was successfully developed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3466–3472, 2010

Key words: adhesion; adhesives; irradiation; thermosets; viscoelastic properties

INTRODUCTION

Information technology has emerged as a new lifestyle paradigm. This lifestyle has enlarged end users' desire to store more information inside their small mobile electronic devices. Information is stored in a device called *memory* or a storage device, both of which are semiconductor devices. A semiconductor device is protected from the external environment, that is, the outside world, by a semiconductor package.^{1,2} Semiconductor packages used to have an integrated circuit (IC) chip in a package. However, device integration by scale minimization with a single-chip packages is reaching its limit. To overcome this limitation, several IC chips are piled on top of each other and are separated by a thin layer of adhesive material.³ For this type of semiconductor package, film adhesives for bonding IC chip/IC chip or IC chip/substrate have been developed.⁴ The film adhesives are thinner and more even and stick out less than conventional epoxy liquid adhesives because they are not easily deformed.

One obtains these IC chips by cutting a circuit wafer into pieces, each made of a silicon, in a pro-

cess called *dicing*. Usually, pressure-sensitive adhesive tape, called *dicing tape*, is laminated on the back of a wafer to hold the separated IC chips during the dicing process.⁵ We attempted to transfer the pressure-sensitive adhesive layer of a dicing tape to the back of IC chips to apply the adhesive layer as a film adhesive for bonding IC chip/IC chip or IC chip/substrate,⁶ as shown in Figure 1. This film-adhesive process can simplify and shorten the semiconductor package manufacturing process.

Recently, silicon chips have become thinner, and greater numbers of silicon chips are stacked in a package because of the increasing market demand for more compact and higher performance electronic applications. This means that more vulnerable, thinner silicon chips are bonded under higher internal stress in a semiconductor package. Hence, a lower internal stress in the film adhesive is more desirable for the latest semiconductor packages, as is reliable adhesion. A low modulus and excellent stress-relaxation ability are generally dominant material properties for decreasing internal stress.

Epoxy resins are widely used as adhesives, substrates, and molding compounds for semiconductor packages because of their excellent heat, moisture, solvent, and chemical resistances. On the other hand, cured epoxy resins are brittle and have a high modulus and low stress-relaxation ability. To overcome these drawbacks, modification with

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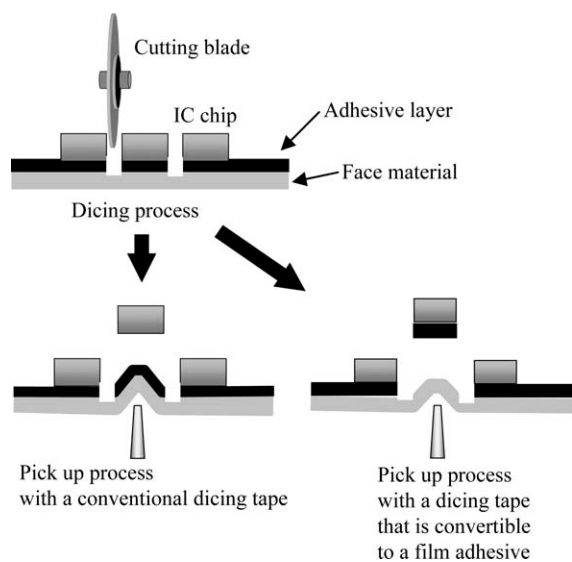


Figure 1 Conventional dicing tape and a dicing tape that is convertible to a film adhesive.

thermoplastic resins has been widely investigated.^{7–10} Acrylic copolymers are one of those thermoplastic resins used to decrease the internal stress of epoxy resins. Some authors have commented on the use of acrylic-copolymer-modified epoxy resins as dispersed particles^{11–15} or as interpenetrating polymer networks.^{16–18} The acrylic copolymers were added to the uncured epoxy resins. After the heat-curing reaction of epoxy resins, the mixture exhibited a two-phase microstructure, which had a significant effect on the internal stress, adhesion, and other mechanical properties. The two-phase microstructure depends on the curing process and the interac-

tion between the acrylic copolymers and the epoxy resins.

Acrylic copolymers are also widely used as a major component of dicing tape because of their excellent supportability of IC chips during the dicing process.¹⁹

In this study, a film adhesive for the fabrication of a semiconductor package, which was also adaptable as a dicing tape, was investigated. The investigated film adhesive was composed of acrylic copolymer; a modified *o*-cresol novolak epoxy resin, in which half of the glycidyl groups of *o*-cresol novolak epoxy resin were substituted by acryloyl groups (OCN-AE); a heat-curing agent; and a photoinitiator. The acryloyl groups of OCN-AE were cured by UV irradiation. Then, the glycidyl groups were cured with heat. This means that OCN-AE had the properties of a heat-curing resin and a UV-curable resin in one molecule. As a reference, a film adhesive composed of acrylic copolymer, *o*-cresol novolak epoxy acrylate (OCN-A) as UV-curable resin, and *o*-cresol novolak epoxy resin (OCN-E) was used. This film adhesive was cured by both UV irradiation and heating, just like the object film adhesive, but the composition was different from the object film adhesive. Film adhesives composed of acrylic copolymer and OCN-E were also used as references. These references were not cured by UV irradiation, which means that the curing system was different from that of the object adhesive.

In this article, we report how the curing system and structure of the epoxy resin influenced the morphology, mechanical properties, adhesion, and thermal stability of the film adhesive.

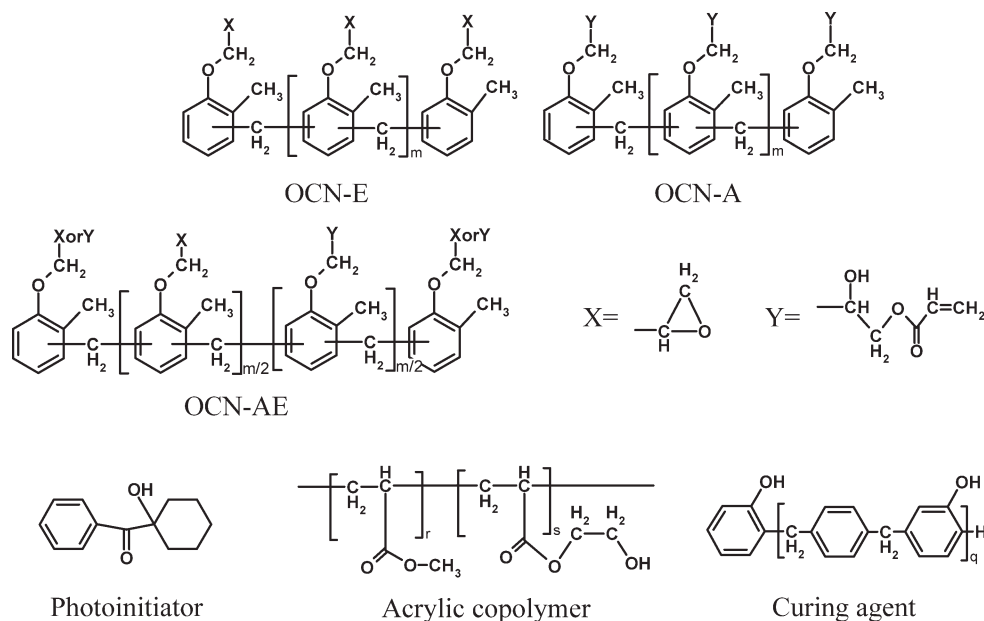


Figure 2 Materials used.

TABLE I
List of Film Adhesive Formulations

Run no.	OCN-E ^a	OCN-AE ^b	OCN-A ^c	Phenolic aralkyl resin ^d (heat-curing agent)
Run 1		23 g (44/44 mmol)		7.4 g (44 mmol)
Run 2	11 g (44 mmol)		12 g (44 mmol)	7.4 g (44 mmol)
Run 3	22 g (88 mmol)			15 g (88 mmol)
Run 4	11 g (44 mmol)			7.4 g (44 mmol)

Acryl copolymer: 70 g (0.20 mmol), 2-phenyl-4,5-dihydroxymethylimidazole: 0.10 g (0.49 mmol), and 1-hydroxycyclohexylphenyl ketone: 4.0 mol % of acryloyl groups as a photoinitiator.

^a Amount of glycidyl groups (mmol).

^b Amount of glycidyl groups to acryloyl groups.

^c Amount of acryloyl groups (mmol).

^d Amount of phenolic hydroxyl groups (mmol).

EXPERIMENTAL

Materials

The main materials are shown in Figure 2. The acrylic copolymer used in this study was tailor-made and consisted of methyl acrylate (88 mol %) and 2-hydroxyethyl acrylate (12 mol %, weight-average molecular weight = 350,000, as measured by gel permeation chromatography calibrated with standard polystyrene). OCN-E, OCN-AE, and OCN-A were obtained from Nihon Kayaku Co. (Tokyo). Phenolic aralkyl resin (XLC-4L, Mitsui Chemicals, Inc., Tokyo) was prepared as a heat-curing agent for the glycidyl group. 2-Phenyl-4,5-dihydroxymethylimidazole (Shikoku Chemicals Co., Ltd., Tokyo,) was prepared as the heat-curing catalyst for the glycidyl group. 1-Hydroxycyclohexyl phenyl ketone (Irgacure 184, Chiba Specialty Chemicals, Tokyo) was used as the photoinitiator for the acryloyl group.

The adhesive formulation is shown in Table I. The film adhesive was prepared with the following procedure. All materials were dissolved in butanone to produce a 30 wt % solution at room temperature. The solution was coated onto a poly(ethylene terephthalate) release film to a thickness of 25 μm after the film was air-dried at 100°C for 1 min to vaporize the butanone.

Curing and measurement

UV irradiation was conducted with a 200 mJ/cm² dose at a 240 mW/cm² exposure rate with a UV irradiator (RAD2000 m/12, LINTEC Corp., Tokyo, Japan) equipped with a high-pressure mercury-vapor lamp and a constant-illumination-controlling system. The exposure dose was controlled by the exposure time. A wavelength of 365 nm was used to measure the exposure dose. Heat curing was carried out at 175°C for 5 h in a heating oven. Runs 1 and 2 were cured by UV irradiation and then cured by heating. Runs 3 and 4 were cured only by heating because they did not have a UV-curable functional group. Runs 3 and 4 were also cured by UV irradiation and then cured by heating for shear testing to investigate the influence of the curing conditions.

The surfaces of the film adhesives were observed with scanning probe microscopy (SPM; SPA-300HV, SII NanoTechnology Co., Ltd., Tokyo), where an SI-DF40 (frequency = 311 kHz, spring constant = 32 N/m) was used as a cantilever in the tapping mode. The all of the domains within a 4- μm square were measured to obtain the average size and standard deviation. The haze value of the film adhesives before heat curing was measured with a haze meter (NDH2000, Nippon Denshoku Industries Co., Ltd.,

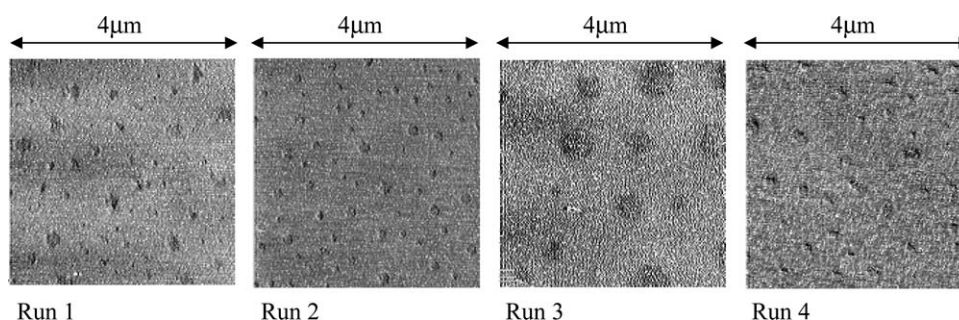


Figure 3 SPM images of the film adhesives before heat curing.

TABLE II
Domain Size (Diameter of Island) of the Pre-Heat-Cured Film Adhesives

Run no.	Average diameter of island (μm)	
	Pre-heat-cured	Post-heat-cured
Run 1	0.12 (0.05)	0.28 (0.12)
Run 2	0.13 (0.04)	0.26 (0.11)
Run 3	0.43 (0.18)	0.57 (0.27)
Run 4	0.14 (0.05)	0.29 (0.16)

The values in parentheses are the standard deviations.

Tokyo). The transmittance of the film adhesives before heat curing was measured with a UV-visible-near infrared scanning spectrophotometer (UV-3101PC, Shimadzu Co., Ltd. Tokyo).

The shear strengths of the postcuring adhesives were measured with a bond tester (series 4000, Dage Precision Industries Co., Ltd., Buckinghamshire, United Kingdom) on a $2 \times 2 \text{ mm}^2$ chip at a releasing speed of 12 mm/min, where a $10 \times 10 \text{ mm}^2$ chip was used as the adherent.

The stress versus strain curves after heat curing were measured with a tensile testing machine (Autograph AG-IS, Shimadzu) at a tensile speed of 200 mm/min.

Stress relaxation after heat curing was also measured with the same tensile testing machine. The elongation was 10% of the initial sample length.

The elastic modulus after heat curing was measured with a dynamic mechanical analyzer (DMA Q800, TA Instruments Co., Ltd., New Castle, DE) at a frequency of 11 Hz and a heating rate of $3^\circ\text{C}/\text{min}$.

The weight change after heat curing was measured with a thermogravimeter (DTG-60, Shimadzu) at a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Morphology

The SPM phase images of the adhesive surfaces before heat curing are shown in Figure 3. SPM measurement is one technique that can provide direct spatial mapping of the surface topography and surface heterogeneity with nanometer resolution. The phase images are obtained in the tapping mode. The images often provide higher contrast than the topographic images and are more sensitive to the material surface properties, such as stiffness, viscoelasticity, and chemical composition.²⁰

The darker color shows the harder region. The contrast in phase separation was low before heat curing. We believe the reason is that the uncured epoxy resin was too soft to give high contrast by phase imaging. The domain size was measured,

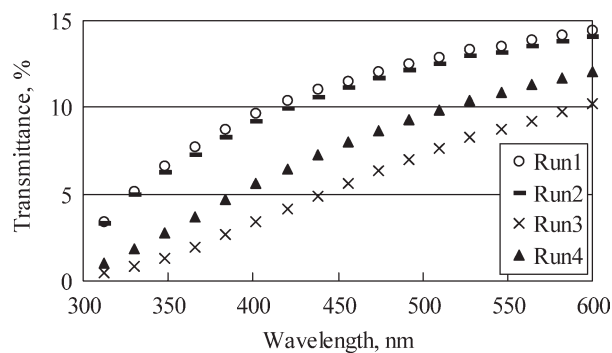


Figure 4 Transmittance of the film adhesives before heat curing.

although these images had low contrast. The average domain sizes and the standard deviations are shown in Table II. The average sizes of runs 1 and 2 were smaller than that of run 3. We believe that the acryloyl groups of OCN-AE (run 1) and OCN-A (run 2) increased the solubility in the acrylic copolymers, and the greater solubility made the domain size smaller. The domain size of run 4 was also smaller than that of run 3. Run 4 was composed of the same materials as run 3, but the amount of epoxy resin was half that of run 3. Therefore, it was natural that run 4 had a smaller domain than run 3.

The contrast of the SPM images was low, as mentioned previously. To supplement the SPM observation, the transmittance (Fig. 4) and haze (Table III) of the adhesives before heat curing were also measured. Transmittance and haze are optical properties. If the acrylic copolymer and the curable resins were miscible, the transparency of the film adhesive would have been high, and haze should have been low. Therefore, the solubility between the domains of each film adhesive could be compared by these measurements, although these measurements did not show the detailed spatial mapping information of the microphase structure shown by SPM. The transmittance was in the following order: Run 1 = Run 2 > Run 4 > Run 3. The haze was in the following order: Run 1 = Run 2 < Run 4 < Run 3 (Table III). These results indicate that the miscibilities of the domains for runs 1 and 2 were better than those for runs 3 and 4.

Figure 5 shows the SPM phase images of the adhesive surfaces after heat curing. The domain size is

TABLE III
Haze of the Film Adhesives Before Heat Curing

Run no.	Haze (%)
Run 1	10.5
Run 2	12.2
Run 3	37.3
Run 4	19.9

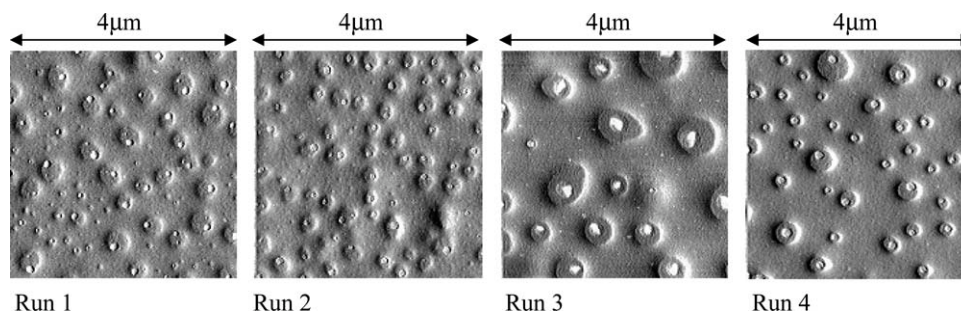


Figure 5 SPM images of the film adhesives after heat curing.

shown in Table II. The contrasts were clear, unlike those before heat curing. This indicated that the cured epoxy domain was hard enough compared with the acrylic polymer. The domains of runs 1 and 2 were smaller than that of run 3. The domain size of run 4 was also smaller than that of run 3, but scattered, relatively large domains existed. We believe that the difference in solubility affected the domain structure for the same reason as before heat curing. We also assumed that the UV curing before the heat curing of OCN-AE (run 1) and OCN-A (run 2) interrupted the growth of the phase separation during heat curing.

Adhesive properties after heat curing

The way in which the adhesive structure affected the adhesive property after heat curing was investigated. The shear strengths of the adhesives were measured after UV irradiation and heat curing or only heat curing. The purpose of measuring the shear strength of the two curing conditions was to compare the adhesive materials without the difference in curing conditions. The result is shown in Figure 6. The shear strengths of runs 1 and 2 after

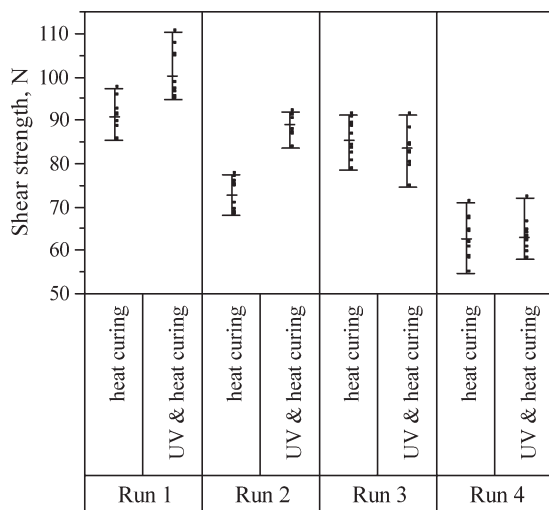


Figure 6 Shear strengths of the postcured film adhesives.

UV irradiation and heat curing were higher than those after heat curing, whereas the shear strengths of runs 3 and 4 after UV irradiation and heat curing were almost same as those after heat curing. We believe this was because runs 1 and 2 had UV-curable functions, whereas runs 3 and 4 did not have UV-curable functions. The shear strengths after UV irradiation and heat curing were in the following order: Run 1 > Run 2 \cong Run 3 > Run 4. The reason for the lowest shear strength in run 4 was believed to be that run 4 included half of the amount of reactive functions as the other adhesives. From these results, we found that the film adhesive of OCN-AE had excellent adhesion.

Modulus after heat curing

The tensile strength of the post-heat-cured film adhesives was measured to evaluate the modulus in the large deformation regime (Fig. 7). The stress versus strain curves showed that runs 1 and 4 were easier to deform than runs 2 and 3. The Young's modulus, rupture stress, and rupture strain are shown in Table IV. The Young's modulus and the rupture stress were in the following order: Run 3 \cong Run 2 >

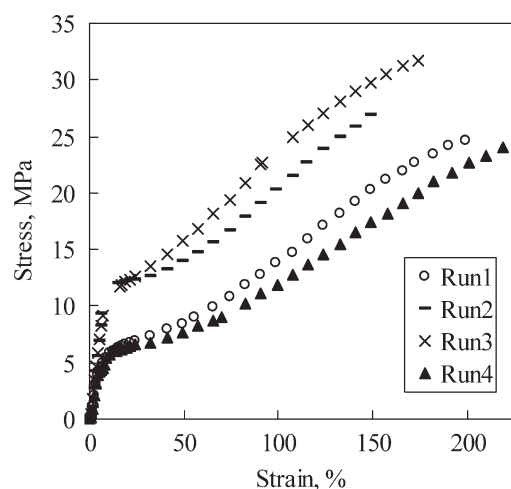


Figure 7 Stress versus strain curves of the post-heat-cured film adhesives.

TABLE IV
Mechanical Properties of the Post-Heat-Cured Film Adhesives

Run no.	Stress relaxation (%)		Young's modulus (MPa)	Rupture stress (MPa)	Rupture strain (%)
	10 s	60 s			
Run 1	84.6	90.8	127	24.7	202
Run 2	80.5	88.3	169	27.2	153
Run 3	77.6	85.4	177	31.8	176
Run 4	85.9	91.4	118	24.3	224

Run 1 \cong Run 4. We believe that the low Young's modulus in runs 1 and 4 would decrease the residual stress in a semiconductor package.

The viscoelasticity was measured to investigate how the structural difference affected the storage modulus at different temperatures. The thermograms of the storage modulus after heat curing are shown in Figure 8. The storage moduli were almost the same at room temperature. Above 50°C, the storage moduli were in the following order: Run 3 = Run 2 > Run 1 > Run 4. The result also indicates that the semiconductor packages including runs 1 and 4 had lower residual stresses than those of runs 2 and 3.

Stress relaxation after heat curing

Stress-relaxation ability is also important for decreasing the residual stress of semiconductor packages and the modulus. Bonded IC chips and the substrate are not covered with thermoset resin before molding. Therefore, the stress relaxation ability helps to reduce the internal stress between the IC chip and the substrate before molding. The stress-relaxation curves of the post-heat-cured film adhesives are shown in Figure 9. The stress-relaxation ratios after 10 and 60 s are shown in Table IV. The stress-relaxa-

tion ratio was obtained by the maximum stress or the stress after 10 or 60 s. A higher stress-relaxation ratio means superior stress-relaxation ability. The stress relaxation ratio of run 1 was almost same as that of run 4, although the number of crosslinking functional groups (glycidyl groups and acryloyl groups) of run 1 was twice that of run 4. The stress-relaxation ratios of runs 2 and 3 were lower than those of runs 1 and 4. Runs 1 and 2 had similar microphase structures, but the moduli and stress-relaxation ratios were different. Therefore, we assumed that each domain of runs 1 and 2 had different mechanical properties.

As a result, the film adhesive of OCN-AE showed a better stress relaxation ability than that of OCN-E or the mixture of OCN-A and OCN-E.

Thermal stability after heat curing

During semiconductor package manufacturing, the semiconductor package should be heated to between 240 and 260°C during the soldering process after the IC chips are bonded with the substrate and the molding process. Thus, the thermal stability of the film adhesive is critical for reliability. The results of thermogravimetric analysis are shown in Figure 10.

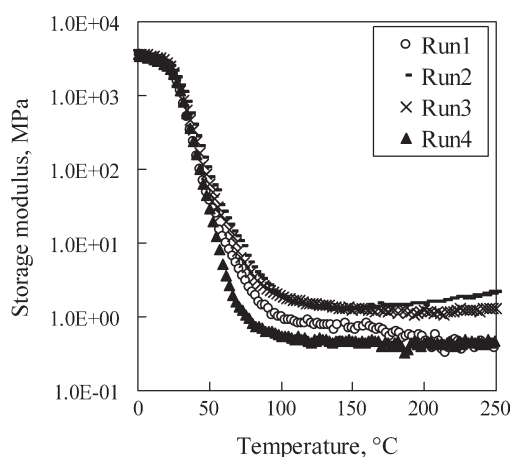


Figure 8 Thermograms of the post-heat-cured film adhesives.

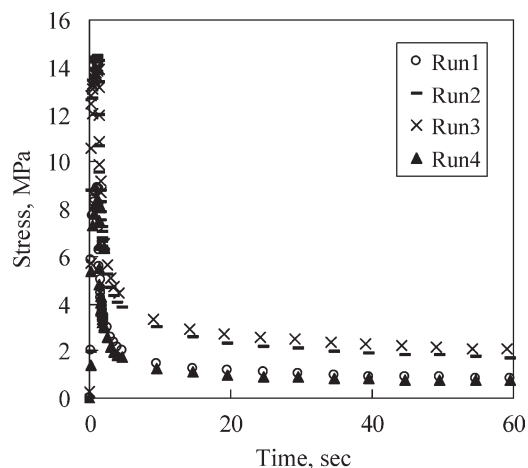


Figure 9 Stress relaxation curves of the post-heat-cured film adhesives (elongation = 10%).

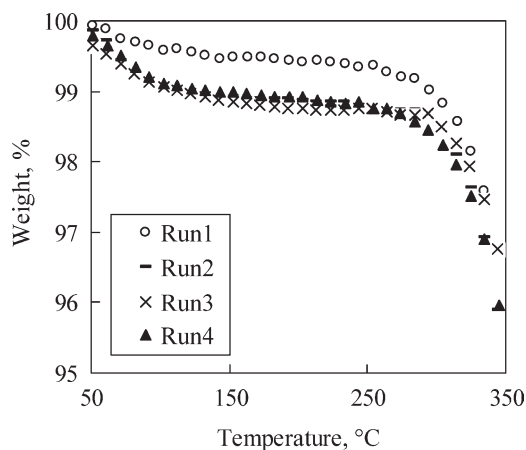


Figure 10 Weight change of the post-heat-cured film adhesives.

There was no significant difference between the samples. This result indicates that the thermal stability of OCN-AE was comparable to that of OCN-A and OCN-E.

CONCLUSIONS

To facilitate the fabrication of a reliable semiconductor package, the UV/heat dual curing of film adhesives was investigated. The investigated film adhesives had different curing systems, UV/heat and heat curing, and different curable structures, OCN-AE, OCN-A, and OCN-E. The film adhesive composed of OCN-AE and acrylic copolymer showed excellent adhesion, low modulus, and stress-relaxation ability compared with the film adhesives composed of OCN-E, OCN-A, and acrylic copolymer and the film adhesives composed of

OCN-E and acrylic copolymer. As a result, a reliable film adhesive for semiconductor packages was successfully developed.

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