UV Curable Pressure-Sensitive Adhesives for Fabricating Semiconductors. II. The Effect of Functionality of Acrylate Monomers on the Adhesive Properties

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ABSTRACT: In an attempt to control the adhesive properties of acrylic copolymer-based pressure-sensitive adhesives, a series of multifunctional acrylate monomers were added and UV cured. The adhesive compound with a difunctional monomer had increased peel strength after UV curing. On the other hand, the compound with a tri- or more functional (polyfunctional) monomer had markedly decreased strength after UV curing. Those adhesives containing any polyfunctional monomer also showed much higher storage modulus than an adhesive containing a difunctional monomer. The greater volume contraction of UV-cured polyfunctional monomer suggested microvoids at the interface between the adhesive layer and the adherent, resulting in poor strength. Estimated values of the peel strength of UV-cured adhesives according to the theoretical equations proved that the strength is approximately inversely proportional to the elastic moduli. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2889–2895, 2004

Key words: pressure-sensitive adhesives; UV curing; acrylic copolymer; multifunctional monomers, peel strength

INTRODUCTION

Various acrylic copolymers are being used in a wide range of pressure-sensitive adhesives (PSAs), and the PSA tapes for fabricating semiconductors mostly consist of the copolymers. In a previous paper,[1] we reported on the development of such dicing tapes that are convertible and easily peelable from diced chips with UV curing to facilitate further processing. The key point for this work was to mix a photocurable diacrylourethane oligomer into an acrylic copolymer. Several papers have been published concerning the same technique.[2–4]

In the fabrication of semiconductors PSA tapes are used for process other than dicing, wherein the required adhesion strength differs. Accordingly, control of the peel strength to be lower or higher by means of UV curing has the potential to facilitate the procedure and/or broaden the application fields of PSA tapes. An acrylic copolymer itself would not change its adhesion strength with UV irradiation due to the absence of any reactive site to UV irradiation.[1–4] Therefore, we investigated changes in the peel strength and viscoelastic properties on UV curing of the acrylic copolymer mixed with a series of multifunctional acrylate monomers. Furthermore, the relationship between the peeling behavior and dynamic viscoelasticity is discussed based on the theoretical equation derived by Fukuzawa.[5]

EXPERIMENTAL

Materials

The acrylic copolymer used in this study was tailor-made and composed of butyl acrylate (80 mol %), methyl methacrylate (9.7 mol %), 2-hydroxyethyl acrylate (5.0 mol %), and acrylic acid (5.3 mol %). The molecular weight of the acrylic copolymer thus obtained was 6.5×10^5, which was measured by GPC calibrated with standard polystyrenes.

Multifunctional acrylate monomers listed in Table I and other chemicals were commercially obtained and used as received. Silicon wafers were obtained from Mitsubishi Materials and were 15 cm in diameter and 650 μm thick.

Before sample adhesive tapes were prepared, the miscibility or compatibility of an acrylate monomer and the copolymer was tested with eye observation and further with a haze meter. These preliminary tests proved that a monomer is easily miscible to the copol-

TABLE I
List of the Multifunctional Acrylate Monomer

Abbrev.	Acrylate	No. of C=C	Supplier
NPGDA	Neopentylglycol diacrylate	2	a
MPDA	3-Methyl-1,5-pentanediol diacrylate	2	a
HDDA	1,6-Hexanediol diacrylate	2	a
TCDDA	Dimethylol-tricyclodecane diacrylate	2	a
TMPTA	Trimethylolpropane triacrylate	3	b
PETTA	Pentaerythylitol tetraacrylate	4	c
DPHA	Dipentaerythylitol hexaacrylate	6	b

Supplier: a, Kyoeisha Chem. Co., Ltd.; b, Nihon Kayaku. Co., Ltd.; Sartomer Co., Inc.

ymer throughout a wide range of monomer/copolymer mixing ratios from 5/95 up to 80/20 by weight, wherein the haze value was below 6.5. Then adhesive sheets were prepared as follows. An adhesive composition was formulated by mixing 0.1 mol of a multifunctional acrylate monomer, photoinitiator (1-hydroxycyclohexylphenyl ketone, Ciba Specialty Chemicals, Irgacure 184, 4 wt % of monomer), and a crosslinking agent (toluenedisocyanate-trimethylolpropane adduct) to the acryl copolymer solution (solid content, 100 g). A viscous composition was coated onto an 80-μm-thick polyethylene film to a thickness of 10 μm after air-drying at 100°C for 1 min. The dried sample was subsequently kept standing for 1 week at 23°C and 65% relative humidity for aging.

UV irradiation

UV irradiation to adhesive strips laminated onto a silicon wafer was performed with a Lintec RAD-2000 to an exposure of 180 mJ/cm^2 at the irradiance of 280 mW/cm^2. For measuring volume contraction, UV was irradiated to the adhesive samples between two quartz glass plates with an Eye Graphic UPI 150 M lamp for 4 min at the irradiance of 360 mW/cm^2.

Measurements and testing

The adhesive strength was measured in terms of 180° peel strength according to JIS Z 0237. A strip of 25-mm-wide adhesive tape was laminated on a silicon wafer with a 2-kg roller, and 20 min later the peel test was performed at a peel rate of 300 mm/min.

The dynamic viscoelastic properties of adhesives as formulated were measured for tablet samples of about 2-mm thickness with a Rheometrics RDA II at an 11-Hz frequency from -30 to 120°C. The extension storage modulus, E', was calculated from the equation[6] $E' = 3G'$, where G' is the shear storage modulus measured with this equipment. The dynamic viscoelastic properties of UV-irradiated samples were measured with a Rheovibron DDV-II EP (A and D F. E. Ltd.) at an 11-Hz frequency and a heating rate of 3°C/min from -30 to 120°C.

By reference to a ISO standard,[7] the volume contraction was determined from the thickness change of an adhesive sample before and after UV irradiation with a TMA-4000 (Mac Science) at a compression load of 2 g.

The contact angles were measured with a FACE CA-DT contact angle meter (Kyowa Interface Science Co., Ltd.) by dropping a given aliquot of H$_2$O, ethylene glycol, or α-bromonaphthalene onto each sample (silicon wafer, acrylic copolymer, formulated and UV-cured adhesive).

RESULTS AND DISCUSSION

Change of peel strength

Table II shows peel strengths of the adhesives before and after UV irradiation. Whether increasing or decreasing, the peel strength leveled off at the exposure dose shown under Experimental. Before UV irradiation, all compounded PSAs have lower peel strength than the acrylic copolymers. This suggests that the interface of a silicon wafer is covered with a thin liquid layer of an acrylate monomer. The adhesive containing NPGDA has a little lower strength than neat copolymer, probably due to better compatibility between them. UV-cured PSAs containing any difunctional monomer, HDDA, MPDA, NPGDA, or TCDDA have much higher peel strengths than before irradiation. The fact that the peel strength of UV-cured ad-

TABLE II
Effect of Mixed Monomer on the Peel Strength

Monomer	180° Peel strength (mN/25 mm)	
	As formulated	UV-cured
None	4300	4200
NPGDA	3500	4500
MPDA	1800	4800
HDDA	1100	4200
TCDDA	1200	2100
TMPTA	1000	570
PETTA	1700	520
DPHA	1400	110
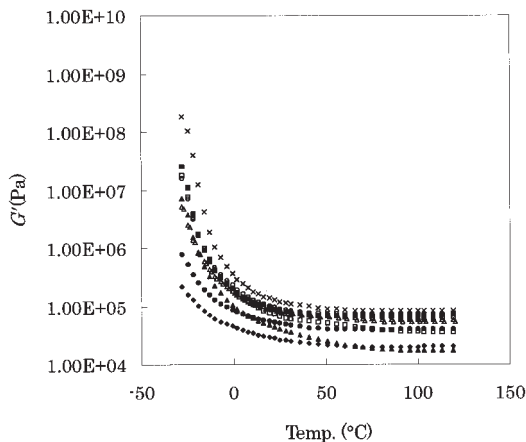
Figure 1 The thermograms of the shear storage modulus (G') for adhesives as formulated. Added monomer: ×None, △ HDDA, ○ MPDA, □TCDDA, ■ NPGDA, ●TMPTA, ◆PETTA, ▲DPHA
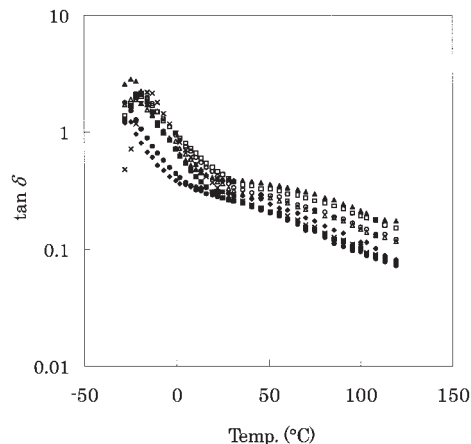
Figure 2 The thermograms of the loss tangent (tanδ) for adhesives as formulated. Added monomer: ×None, △ HDDA, ○ MPDA, □TCDDA, ■ NPGDA, ●TMPTA, ◆PETTA, ▲DPHA

hesive with TCDDA is rather low compared to other compositions can be attributed to the rigid polymer networks containing aliphatic rings.

On the other hand, a UV-cured adhesive compound containing a monomer of which functionality is more than three (polyfunctional monomer) gives decreased peel strength, and the greater the functionality the lower the peel strength. Including the above result for the TCDDA composition, these results suggest that the change of peel strength is related to the change of viscoelastic properties of adhesives with photopolymerization of added monomers.

Viscoelastic properties

To investigate the effect of adding multifunctional acrylate monomers on the rheological behavior, dynamic viscoelastic properties of the adhesive compositions were measured before and after UV curing. The thermograms of the storage modulus and the loss tangent (tan δ) before are shown in Figures 1 and 2, respectively.

In Figure 1, the shear storage modulus, G', of the adhesives containing one of the difunctional monomers decreases abruptly around at -30 and -20°C due to glass transition state and then levels off at a temperature range over 40°C showing the rubbery state. As for the adhesives containing TMPTA, PETTA, or DPHA, the rubbery state lies at a higher temperature range than 50°C. The storage modulus at around 23°C, where the peeling test was carried out, decreases with increasing number of functionality of added monomers, which suggests a more plasticizing effect with increasing functionality of the added monomer. As for the tan δ, Figure 2 shows its maximum at around -20°C for any adhesive.

Figures 3 and 4 are the thermograms of the extension storage modulus (E') and the dynamic loss tangent of the adhesive compounds after UV irradiation, respectively. As illustrated in Figure 3, all UV-cured adhesives have much higher extension storage modulus (E') than before curing. As for adhesives containing NPGDA, MPDA, or HDDA, E' decreases abruptly with increasing temperature, while the E' of the adhesive containing TCDDA moderately decreases with increasing temperature and is around 10 MPa at a temperature range more than 50°C, which is one order higher than that of other adhesives containing other difunctional monomers. Having cyclic moieties, TCDDA is thus effective to give a comparatively harder material as described previously. As for those adhesives containing monomers of which the functionality
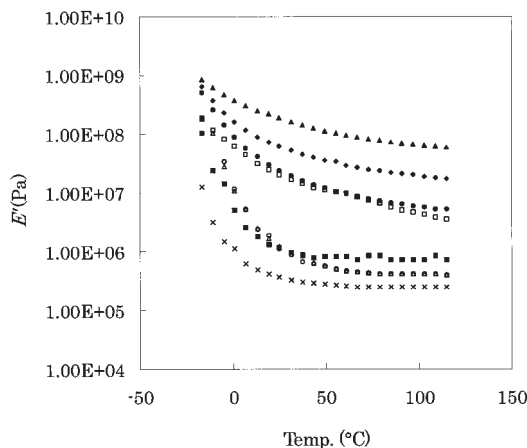
Figure 3 The thermograms of the extension storage modulus (E'') for UV-cured adhesives. Added monomer: ×None, △ HDDA, ○ MPDA, □TCDDA, ■ NPGDA, ●TMPTA, ◆PETTA, ▲DPHA
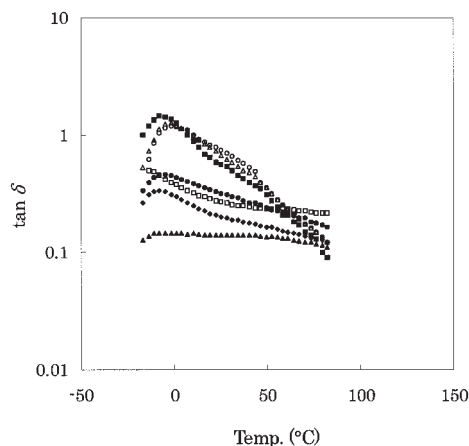
Figure 4 The thermograms of the loss tangent (tanδ) for UV-cured adhesives. Added monomer: ×None, △ HDDA, ○ MPDA, □TCDDA, ■ NPGDA, ●TMPTA, ◆PETTA, ▲DPHA
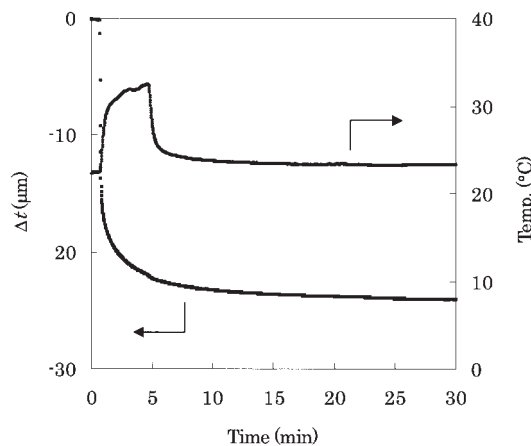
Figure 5 Thermal mechanical analysis of UV curing of the adhesive added with DPHA. UV was irradiated for 4 min at 360 mW/cm².

is more than 3 (TMPTA, PETTA, or HDDA), E' decreases slowly with increasing temperature and maintains a higher value with increasing functionality at high temperature range. Upon UV irradiation, on the other hand, the maximum value decreases with increasing functionality of the added monomers as well as a shift of the maximum point to temperatures higher than 20°C.

While the E' value at around 23°C, where the peeling test was carried out, is around 1 MPa for adhesives containing NPGDA, MPDA, or HDDA, where the peeling strength increases remarkably upon UV curing, it is more than 27 MPa for ones containing TMPTA, PETTA, or DPHA, where the strength decreases upon UV curing. Thus, a major factor for the changes in the peel strength seems to be E'. However, after UV irradiation, the adhesive containing TCDDA has an E' value as high as 22 MPa despite increased strength. This fact suggests that there are factors other than the modulus that effect the change of peel strength.

Volume contraction of UV-cured adhesives

Figure 5 shows the changes in the reaction temperature and the linear shrinkage when the adhesive composition containing DPHA, as an example, was irradiated with UV light for 4 min. Irradiation raised the temperature up to 34°C, followed by a decrease to the ambient temperature when stopped. The shrinkage started as soon as exposure to UV began and then leveled off at -16μm within 30 min. The volume contraction rates thus obtained are shown in Table III. The results show a tendency for the contraction rate to increase with increasing functionality of the added monomer. By comparing these results with those shown in Table II, it can be concluded that upon UV

irradiation the peel strength increases for an adhesive of lower contraction while it decreases for one of higher contraction. A possible mechanism for the decrease in peel strength is the generation of microvoids at the interface between the adhesive and adherent with high volume contraction of the adhesive, although this mechanism does not work for the other case.

Theoretical consideration

Among various theoretical studies[5,7–11] on the rheology of PSAs, Fukuzawa[5] derived the following simple equation for the 180° angle peel strength (P) measured at a rapid peeling rate (>200 mm/min):

$$P = bt_a f_c^2/4E_a + bW_a/2, \tag{1}$$

where P is peel strength; b is tape width; t_a is thickness of the adhesive; f_c is critical surface adhesion; E_a is the modulus of the adhesive mass; and W_a is the work of adhesion. The validity of Eq. (1) was ascertained with a series of experiments using a natural rubber-terpene resin adhesive.[5]

TABLE III
Volume Contraction of the Adhesive Formulations

Monomer	% Vol. contraction
NPGDA	0.8
MPDA	2.0
HDDA	2.3
TCDDA	3.8
TMPTA	4.0
PETTA	4.3
DPHA	5.4

TABLE IV
Parameters for Estimating Relative Peel Strength of Adhesives as Formulated and Obtained Relative Values

Monomer	E_a (MPa)	W_a (10^{-3} N/m)	E_m (MPa)	f_c (MPa)	Relative strength	
					Obs.	Calc.
None	0.39	72.3	200	170	1.0	1.0
NPGDA	0.33	67.3	180	160	0.8	1.04
MPDA	0.26	70.3	160	150	0.42	1.17
HDDA	0.24	68.4	150	140	0.26	1.11
TCDDA	0.19	65.8	140	140	0.28	1.39
TMPTA	0.26	70.2	160	150	0.23	1.15
PETTA	0.20	72.5	140	140	0.40	1.28
DPHA	0.075	68.7	86	110	0.33	2.2

According to Eq. (1), the peel strengths of the adhesives in this work were estimated. In this work the tape width (b) and thickness of the adhesives (t) are constant values, and the modulus is observed. The work of adhesion (W_a), although so small as to be in the range of 0.1 N/m according to Ref. 5, can be calculated from the surface energies of the adhesive layer and the adherent (silicon wafer), which are obtained contact angle measurements[12–14] (see Appendix). The only unknown value, the critical surface adhesion (f_c), was calculated from the equations[12]

$$f_c = M(W_a E_m / r_0)^{1/2} \qquad (2)$$

$$E_m = (G_h E_a)^{1/2}, \qquad (3)$$

where W_a is the work of adhesion; r_0 is the intermolecular distance where the potential is the minimum (5×10^{-8} cm); G_h is the modulus of the adherent (measured as 10^7 Pa); and M is a correction factor including the effective adhesion area, surface roughness, crack, and so on. The correction factor M was assumed to be constant since the major component of the adhesives is acrylic copolymer and because of its ambiguous meaning. Therefore, the peel strengths estimated are values that are relative to that of the acrylic copolymer.

Those parameters used for estimation and relative peel strength for the adhesives as formulated and the UV-cured adhesives are listed in Tables IV and V, respectively.

Table IV reveals that the estimated values for adhesives before UV curing are much greater than that of the standard, while those observed are smaller. This apparent discrepancy, as described previously, may be due to heterogeneous distribution of added monomers most provably between the interface of the adherent (silicon wafer) and the adhesive. As for UV-cured adhesives (Table V), on the other hand, the observed and estimated strengths are in the same order of magnitude. Thus, the peel strength of an UV-cured adhesive is approximately inversely proportional to its own elastic modulus, as presented in eq. (1). Minor differences between the observed and estimated strengths could also be due to heterogeneous distribution of

TABLE V
Parameters for Estimating Relative Peel Strength of UV-Cured Adhesives and Obtained Relative Values

Monomer	E_a (MPa)	W_a (10^{-3} N/m)	E_m (MPa)	f_c (MPa)	Relative peel strength	
					Obs.	Calc.
None	0.39	72.3	200	170	1.0	1.0
NPGDA	1.2	66.0	350	210	1.0	0.50
MPDA	1.3	68.7	360	150	1.1	0.50
HDDA	1.4	68.4	370	220	1.0	0.46
TCDDA	22	71.8	1500	460	0.5	0.13
TMPTA	27	70.2	1600	490	0.13	0.12
PETTA	66	77.6	2600	640	0.12	0.085
DPHA	200	68.7	4500	800	0.026	0.043

cured components and differences at the interfaces such as void formation.

CONCLUSION

The present study clearly shows that the adhesive properties of UV-cured acrylic copolymer–multifunctional acrylate blends depend on the functionality of the acrylates. An adhesive formulation with a difunctional acrylate monomer had an increased modulus and peel strength upon UV curing. Contrarily, an UV-cured adhesive with a tri- or more functional (polyfuncttional) monomer had a remarkably increased modulus and decreased peel strength. Fukuzawa's theoretical equation, that the 180° peel strength of a PSA is inversely proportional to its modulus, is applicable to the UV-cured blended PSAs although not to the PSAs as formulated. These reverse results suggest that the adhesive property of a PSA depends not only on its modulus but also on the interfacial phenomena such as local distribution of acrylate monomer or polar segments at the interface between the adhesive and the silicon wafer.

APPENDIX

The work of adhesion, W_A, between an adhesive and a substrate (silicon wafer) can be given by the equation[12–14]

$$W_a = \gamma_a + \gamma_w - \gamma_{aw}, \tag{A1}$$

where γ_a and γ_w are the surface free energies of the adhesive and wafer, respectively, and γ_{aw} is the interfacial free energy.

These energies can be determined by measuring the contact angles (represented as θ) of the respective materials (denoted by suffix "s") with the use of test liquids (denoted by suffix "1") of which the dispersion and polar force components of the surface free energies are known, and then using Young's equation:

$$\gamma \cos \theta = \gamma_s - \gamma_{s1}, \tag{A2}$$

where γ_1 and γ_s are the surface free energies of the liquid and sample (adhesive or wafer), respectively, and γ_{s1} is the interfacial free energy. The detailed mathematical way of calculating energies is described in the references. [12–14]

The test liquids used in this work were pure water, ethylene glycol and α-bromonaphthalene and energy

TABLE AI
Contact Angles and Surface Free Energies Calculated

Sample[a]	Contact angle[b] (°)			Surface free energy[c] (mN/m)		
	H_2O	EG	αBN	γ^D	γ^P	γ
Si-wafer	7	1	13	43.3	30.6	73.9
PSA as formulated						
None	110	78	52	29	≈ 0	29
NPGDA	112	83	58	26	0	26
MPDA	114	85	53	28.5	0	28.5
HDDA	111	82	56	27	0	27
TCDDA	115	86	59	25.5	≈ 0	25.5
TMPTA	105	90	57	26.5	≈ 0	26.5
PETTA	106	75	56	27	≈ 0	27
DPHA	106	92	59	25.5	≈ 0	25.5
UV-cured PSA						
None	110	78	52	29	≈ 0	29
NPGDA	118	83	65	22.5	≈ 0	22.5
MPDA	115	81	57	26.5	≈ 0	26.5
HDDA	116	95	58	27.5	≈ 0	27.5
TCDDA	101	73	55	25.5	0	25.5
TMPTA	104	74	52	29	0.1	29.1
PETTA	105	90	45	32.2	≈ 0	32.3
DPHA	103	79	57	26.5	≈ 0	26.5

[a] A PSA formulation is denoted by an acrylate monomer added.
[b] EG, ethylene glycol; αBN, α-bromonaphthalene.
[c] γ^D, dispersion force component; γ^P, polar force component.

data of these liquids were referred to reference 12. The results of contact angle measurements and calculated values of the surface free energy are shown in Table AI.

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