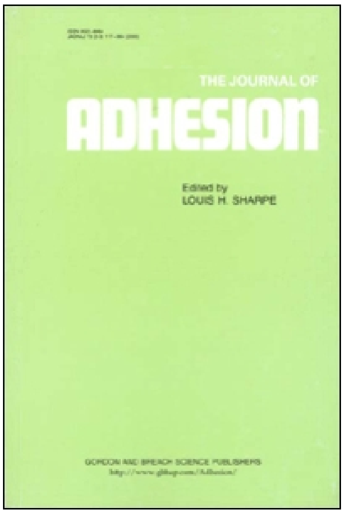

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Acrylate Copolymer/Ultraviolet Curable Oligomer Blends as Pressure-sensitive Adhesives

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For the blends of acrylate copolymer [poly(2-ethylhexyl acrylate-co-acrylic acid); P(2EHA-AA)] with ultraviolet (UV) curable oligomer [urethane acrylate oligomer; UAO], pressure-sensitive adhesive (PSA) properties, such as peel adhesion, probe tack, and holding power were examined. The values of peel adhesion and probe tack of the P(2EHA-AA)/UAO blends were dramatically reduced by UV irradiation. On the other hand, all blends had a high holding power even if these blends were cured by UV irradiation. The mechanism of reduced PSA properties was investigated *via* dynamic mechanical properties, DSC, and dynamic contact angle (DCA). The peel adhesion decreased monotonically with increasing storage modulus, E', and loss modulus, E'', for all non-UV and UV-cured blends. Since modulus values and glass transition temperatures, Tg, of these blends after UV irradiation were higher than those of these blends before UV irradiation, we judged that the reduced peel adhesion and probe tack values were caused by the modulus increase and the Tg increase due to UV irradiation. In other words, the ability of the deformation energy of UV-cured blends to influence the adhesive tests was reduced by the curing process. The DCAs of non-UV-cured blends were the same as those of UV-cured blends. We presumed that the segment mobility of the polymer chain on the surface did not contribute to the reduced peel adhesion and probe tack values.

Keywords: Blends; dicing; dynamic contact angle; dynamic mechanical property; poly(2-ethylhexyl acrylate-co-acrylic acid); pressure-sensitive adhesive; semiconductor; urethane acrylate oligomer

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INTRODUCTION

Pressure sensitive adhesive (PSA) tapes composed of acrylic copolymers have been extensively utilized in various industries, such as packaging, printing, electrical insulation, and automobiles. In general, the PSA properties (tack, peel adhesion, holding power) of acrylic adhesives have been controlled by blending with tackifiers or dissimilar polymers, by molecular weight and its distribution, and also by copolymerization with polar monomers and by curing systems. In recent years, the PSA properties of acrylic adhesive copolymers have been interpreted by considering various factors, such as dynamic mechanical properties, surface tension, and miscibility [1 – 6]. However, since the values of PSA properties are thought to be influenced by the bonding and debonding processes, the PSA properties could not be clarified.

Incidentally, ultraviolet (UV) curing technology has been already established in the painting and adhesive fields. The UV-cured adhesive can bond to an adherend in an instant at room temperature. UV-curing technology is very effective in controlling PSA properties of acrylic adhesives, because the mechanical properties, surface tension, and miscibility are dramatically changed by UV irradiation. Presumably, the level of PSA properties of UV-cured acrylic adhesives is also controlled by UV oligomers of many species, the blend ratio, and by UV irradiation conditions. Thus, the examination of the miscibility among components is very important for UV-curable PSA.

Recently, various types of PSA tapes have been utilized in semiconductor processing, such as for back-grinding and dicing processes [7 – 9]. Particularly, it is well known that UV-curable PSA tape is a very effective material for dicing process [10 – 13]. Figure 1 shows a diagram of the dicing process using UV-curable tape. In the cutting process, strong adhesion between PSA tape and wafer is necessary. If the wafer has weak adhesion to the PSA tape in the cutting process, the diced chip may separate from the PSA tape and it may fly off. On the other hand, weak adhesion between PSA tape and wafer is desired in the picking-up process. Since the UV-curable PSA is composed of blends of acrylic adhesive copolymer, UV-curable oligomer, and photopolymerization initiator, the PSA properties can be controlled by means of UV irradiation during semiconductor processing. In other words,

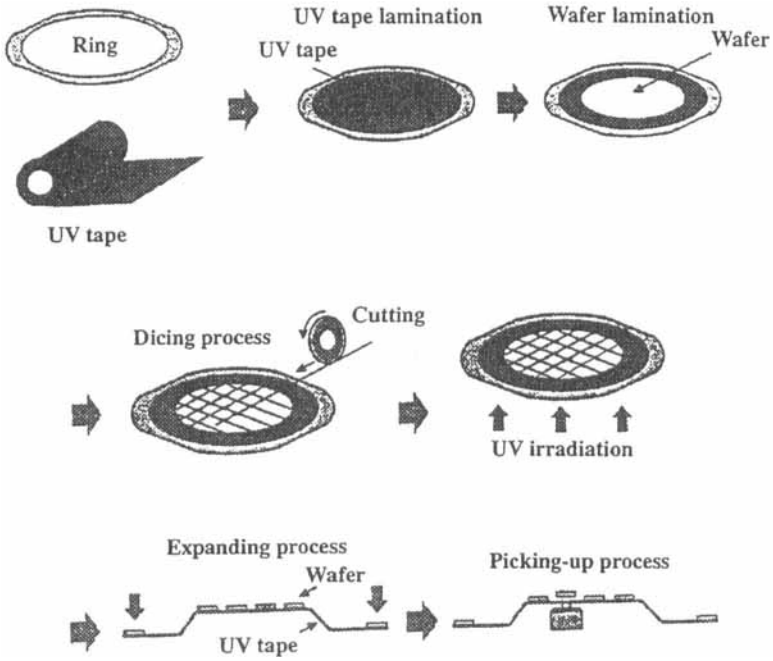

FIGURE 1 Diagram of dicing process using UV tape.

the UV-curable PSA tape is very tacky before UV irradiation but the tackiness is made to disappear *via* UV irradiation. The backbone of the UV-curable oligomer is formed of polyester, epoxy or urethane and its functional group is $CH_2=CHCO—$ or $CH_2=C(CH_3)CO—$. The photopolymerization initiator absorbs UV of $300 \sim 450$ nm. Then the initiation reaction for UV curing occurs by radical reaction through the initiator to form a UV-curable oligomer. Finally, the UV-curable oligomer is polymerized.

In this paper, for the acrylic adhesive copolymer/urethane acrylate oligomer blends, the PSA properties of non-UV-cured adhesive were compared with those of UV-cured adhesive. The effect of urethane acrylate oligomer content on the PSA properties was also investigated for the blends. Then, the mechanism of reduced PSA properties was explained *via* dynamic mechanical properties, DSC, and dynamic contact angle (DCA).

EXPERIMENTAL

Materials

The compositions of the UV-curable adhesives studied are shown in Table I. The acrylate adhesive copolymer is composed of 2-ethylhexyl acrylate and acrylic acid [P(2EHA-AA)]. The urethane acrylate oligomer [UAO] and 1-hydroxy cyclohexyl phenylketone were used as the UV-curing oligomer and photopolymerization initiator, respectively. The peak of absorption of 1-hydroxy cyclohexyl phenylketone is 327 nm. The mixtures of P(2EHA-AA), UAO, and photopolymerization initiator solutions (solvent; ethyl acetate) were coated onto a poly(ethylene terephthalate) (PET) base using a hand coating bar. After coating, the films were dried at 90°C for 2–3 min and kept at 23 ± 3°C for more than a week. The blends were 20 μm thick in their dry state. UV irradiation of 500 mJ/cm^2 was carried out with high-pressure mercury lamp.

Measurements

The PSA properties were measured according to the Japanese Industry Standard (JIS-Z0237). Peel adhesion of the UV tapes to a silicon wafer was performed at a 90° peel angle and a peel rate of 50 mm/min. The dwell time was 24 h. The probe tack of the UV tape was measured at 25°C, using a RHESCA Co. probe tack tester. The probe was made of stainless steel. For holding power measurement, the PSA tape with a 25 mm × 25 mm test area was applied on a stainless steel panel. The dwell time was 30 min. The dead load was 1 Kg and the test temperature was 25°C. In conducting the adhesion tests for the UV-cured adhesive tapes, the tapes were adherend to the test panel, then cured and finally removed.

TABLE I Composition of adhesive

Acrylic adhesive polymer	Poly(2-ethylhexyl acrylate-co-acrylic acid)	100 phr
P(2EHA-AA)	Mw = 220000, Mw/Mn = 7.3	
UV oligomer	Urethane acrylate oligomer	10, 20, 30, 40, 50 phr
Initiator	1-hydroxy cyclohexyl phenylketone	5 phr
Curing agent	Polyisocyanate	4 phr

The glass transition temperatures (Tg) of the UV-curable adhesives were determined by a Seiko Instruments Inc. RDC-220 Robot DSC at a heating rate of 10 K/min under nitrogen gas.

The dynamic mechanical properties of the UV-curable adhesive (before and after UV-curing) were measured using a Rheometrics Co. Ltd. dynamic mechanical analyzer, type RDA II and Seiko Instruments Inc. type DMA200, respectively. The temperature dependence of dynamic mechanical properties such as extension storage modulus, $E' = 3G'$, or shear storage modulus, G', extension loss modulus, $E'' = 3G''$, or shear loss modulus, G'', and dynamic loss tangent, $\tan\delta$, were measured at 1 Hz.

The dynamic loss factor, Δ, of UV-curable adhesives was measured by means of a free decay oscillation method using an Orientec Co. Ltd. rigid-body, pendulum-type dynamic mechanical property apparatus, model DDV-OPAIII, at −100 to 100°C. The heating rate was 5 K/min. The pendulum with the knife edge put in contact with the sample was used to perform the dynamic mechanical measurement.

The dynamic contact angle (DCA) was measured *via* an Orientec Corporation model DCA20 apparatus based on the Wilhelmy plate technique. Water was used as the standard liquid. The dipping velocity was 100 (mm/min) and the DCA was measured at 23°C. The acrylate copolymer P(2EHA-AA)/ultraviolet-curable oligomer UAO 50/50 blend was stirred overnight in about 10 wt% ethyl acetate solution. The aluminum plates (20 mm wide, 50 mm length, and 0.3 mm thick) were dipped into the solution withdrawn and then dried in a vacuum oven at 40°C for 24 hours. The details are described elsewhere [14, 15].

RESULTS AND DISCUSSION

The relationship between 90° peel adhesion and UAO content for P(2EHA-AA)/UAO blends is shown in Figure 2. For non-UV-cured adhesives, the value of peel adhesion increases with increasing UAO content. On the contrary, for UV-cured adhesives, the level of peel adhesion decreases with increasing UAO content. The peel adhesion of the adhesive with 40 phr UAO completely disappeared after UV-curing. Figure 3 shows the relationship between probe tack and UAO content for the blends. The value of probe tack for non-UV-cured

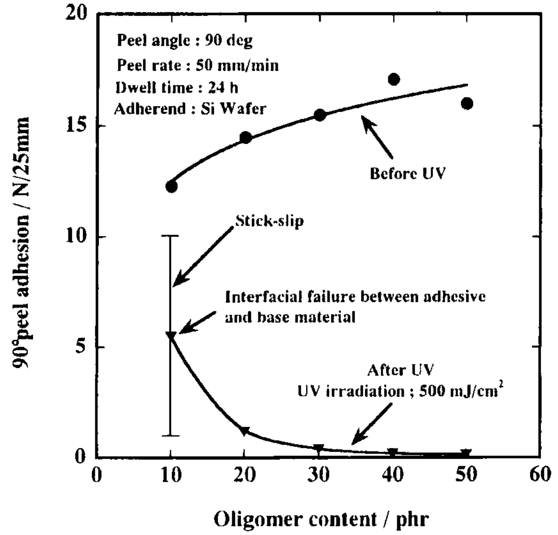

FIGURE 2 Relationship between 90° peel adhesion and UAO content for P(2EHA-AA)/UAO blends.

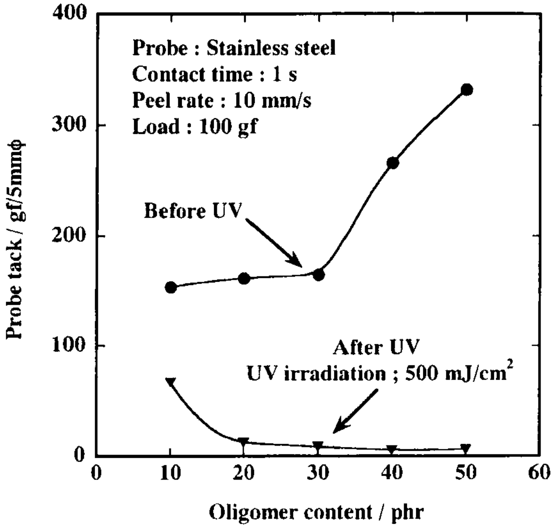

FIGURE 3 Relationship between probe tack and UAO content for P(2EHA-AA)/UAO blends.

adhesives also increases with increasing UAO content, whereas the probe tack of the UV-cured adhesive with 40 phr UAO completely disappeared. In other words, the values of peel adhesion and probe tack for P(2EHA-AA)/UAO blends were dramatically reduced by UV irradiation. These blends had a high holding power (non-creep for 80000 s). We expect that the difference of the PSA properties between the blends and the reduced PSA properties (peel adhesion, probe tack) achieved through UV irradiation are clarified by dynamic mechanical properties, surface properties and miscibility. Thus, the dynamic mechanical properties (storage moduli, G′, dynamic loss tangent, tan δ), DSC, and dynamic contact angle (DCA) were examined for the P(2EHA-AA)/UAO blends.

The relationship between PSA properties and dynamic mechanical properties for an adhesive polymer has been already investigated by many researchers [1–3, 16, 17]. For example, an original analysis of chemical and physical factors affecting PSA properties that was proposed by Dahlquist [16] is that the molecular contact between adhesive and adherend is completely established when the compressive creep compliance of the adhesive at 1 s is higher than $10^{-7}\,\text{cm}^2/\text{dyn}$ (Dahlquist criterion). Tse [1] and Yang [2] pointed out that the PSA property, T, is expressed by considering the bonding and debonding processes of adhesive as follows:

$$T = Wa \cdot B \cdot D \tag{1}$$

where Wa is the work of adhesion between adhesive and adherend, B is a function of the bonding process and depends on the plateau modulus, Ge, of the adhesive, and D correlates with the debonding process and increases with increasing loss modulus, G″, of adhesive. Therefore, we presume that the PSA properties of the P(2EHA-AA)/UAO blends are influenced by dynamic mechanical properties of the blends.

The temperature dependence of the storage modulus, G′, of non-UV-cured P(2EHA-AA)/UAO blends is shown in Figure 4. The G′ decreases with rising temperature. On the high temperature side (plateau region), the G′ decreases with increasing UAO content. Presumably, since the molecular weight (viscosity) of UAO was remarkably lower than that of P(2EHA-AA), the plateau modulus level was depressed by introducing UAO. As described above, peel adhesion and probe tack

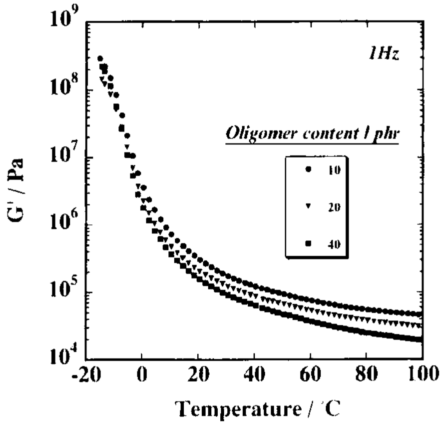

FIGURE 4 Temperature dependence of G′ of non-UV-cured P(2EHA-AA)/UAO blends.

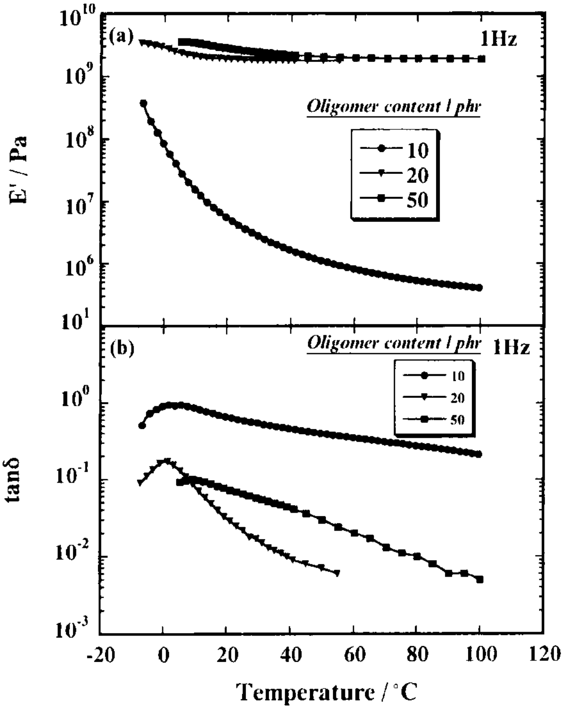

FIGURE 5 Temperature dependence of (a) extension storage modulus, E′, and (b) dynamic loss tangent, tan δ, for UV-cured P(2EHA-AA)/UAO blends.

increased with increasing UAO content for non-UV-cured blends. We think that for the non-UV-cured blends the function of bonding process reflects on the PSA properties according to Tse's equation (1).

The temperature dependences of (a) extension storage modulus, $E' = 3G'$, and (b) dynamic loss tangent, $\tan\delta$, for UV-cured P(2EHA-AA)/UAO blends are shown in Figure 5. The magnitude of E' of the P(2EHA-AA)/UAO blend with 20 phr UAO is similar to that of the blend with 50 phr UAO. On the contrary, the E' values of the blend with 10 phr UAO are remarkably lower than those of the blend with 20 phr UAO. The magnitude of the $\tan\delta$-temperature curve of the blend with 10 phr UAO is significantly larger than that of the blend with 20 phr UAO. The peel adhesion and probe tack values are also dramatically reduced for the blend with 20 phr UAO. Therefore, we judge that for UV-cured blends their PSA properties are influenced by their dynamic mechanical properties.

Secondly, for non-UV and UV-cured blends the mechanism of reduced PSA properties was explained through dynamic mechanical properties, DSC, and DCA. For the non-UV and UV-cured P(2EHA-AA)/UAO blend with 10 phr UAO, the temperature dependence of G' and $\tan\delta$ are shown in Figure 6. *Via* UV irradiation the values of G' of the UV-cured blend with 10 phr UAO are higher than those of the non-UV-cured blend with 10 phr UAO. The $\tan\delta$-temperature curve of the UV-cured blend is shifted to the high temperature side by about 5 K. Particularly, the increase of G' in rubbery, plateau region is clearly observed for the blend with 10 phr UAO. Since the rubbery plateau modulus, Gr, is influenced by entanglement of polymer chains, we presume that the molecular weight between entanglements for the P(2EHA-AA) polymer chain is decreased by UV irradiation. Figure 7 shows the temperature dependence of (a) storage modulus, E', and (b) dynamic loss tangent, $\tan\delta$, for the P(2EHA-AA)/UAO blend with 40 phr UAO. The peel adhesion (P.A.), probe tack (P.T.), and holding power (H.P.) values are also listed in the Figure. The $\tan\delta$ values are lowered by UV irradiation. The temperature of the $\tan\delta$ maximum (TDmax) is also shifted toward the high temperature side by UV irradiation. At 25°C, the E' value of the non-UV-cured adhesive is about 10^5 Pa, whereas the E' value of the UV-cured adhesive is 10^9 Pa. Dahlquist [16] suggested that tack appears when the E' value of an adhesive is lower than 10^6 Pa. In fact, the values of peel adhesion and

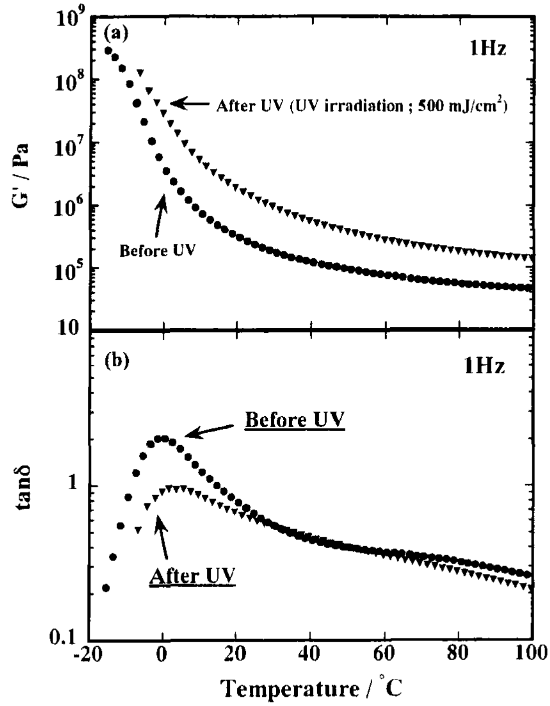

FIGURE 6 Temperature dependence of (a) G′ and (b) tan δ of P(2EHA-AA)/UAO blend with 10 phr UAO.

probe tack of the non-cured PSA tape were remarkably larger than those of the UV-cured PSA tape. Therefore, we presume that the reduced adhesion is caused by the modulus increase and the Tg increase due to UV irradiation.

The Tg increase due to UV irradiation is confirmed by DSC analysis. Figure 8 shows DSC thermograms of P(2EHA-AA)/UAO blends. The glass transition temperatures, Tg, of the non-UV and UV-cured blends are indicated in the Figure. For both blends with 10 phr and 50 phr UAO, the Tg of the UV-cured materials is higher than that of non-UV materials by about 5 K. Presumably, mobility of the segments in the P(2EHA-AA) polymer chain was depressed by UV-cured UAO. Films of all non-UV and UV-cured blends were transparent. Since the Tg of the blends also exhibited a single peak, we judge that P(2EHA-AA) is miscible with UAO.

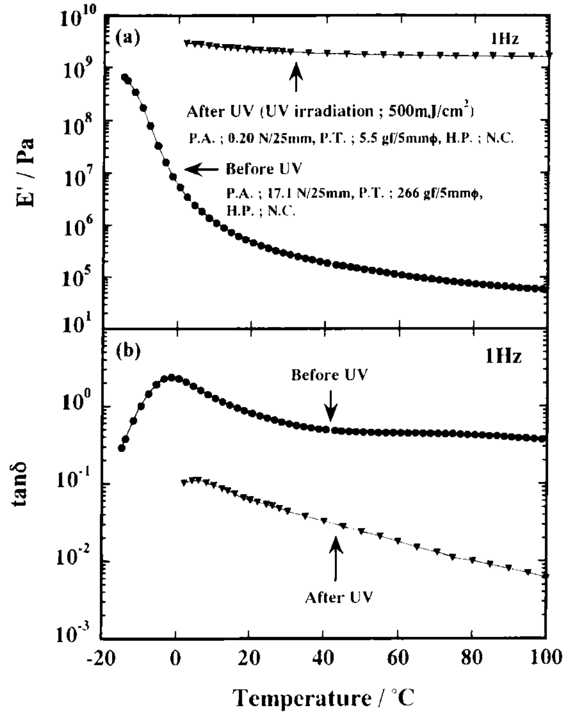

FIGURE 7 Temperature dependence of (a) storage modulus, E′, and (b) dynamic loss tangent, tan δ, for P(2EHA-AA)/UAO blend with 40 phr UAO. The peel adhesion (P.A.), probe tack (P.T.), and holding power (H.P.) values are listed in the Figure. NC.; Non-Creep 80000 sec.

The tackiness is dominated by the dynamic mechanical properties on the surface of the adhesive layer. In our previous study [18], differences of dynamic mechanical properties on the surface directly influenced the tack value. It is expected that the dynamic mechanical properties on the surface of the non-UV-cured adhesive also differs from that of the UV-cured adhesive. Thus, temperature dependence of the dynamic loss factor, Δ, for the P(2EHA-AA)/UAO blend with 40 phr UAO was measured by the free decay oscillation method as shown in Figure 9. The delineation of the curve of Δ *vs.* temperature for the non-UV-cured adhesive differs remarkably from that of the UV-cured adhesive. Therefore, we considered the difference of peel adhesion and probe tack between non-UV and UV-cured adhesives corresponded to the difference in dynamic mechanical properties on the surface.

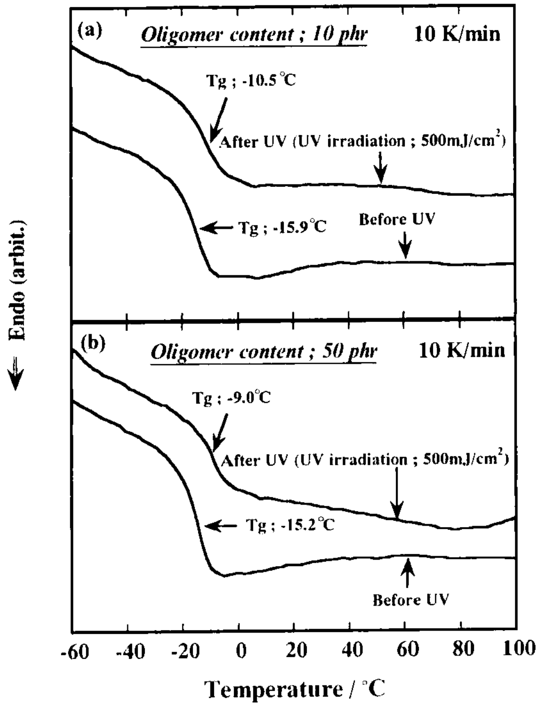

FIGURE 8 DSC thermograms of P(2EHA-AA)/UAO blends.

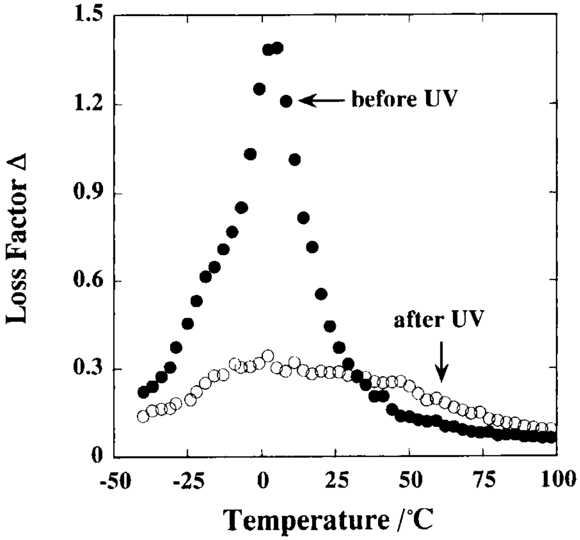

FIGURE 9 Temperature dependence of dynamic loss factor, Δ, for P(2EHA-AA)/UAO blend with 40 phr UAO. (•) non-UV, (○) after UV.

Thirdly, the mobility of the polymer chain on the surface for the P(2EHA-AA)/UAO blend with 50 phr UAO was estimated by DCA. The advancing and receding dynamic contact angles for the blend with 50 phr UAO are shown in Table II. A contact angle hysteresis about 12 deg. is observed between non-UV-cured and UV-cured blends. In general, the contact angle hysteresis of a polymer occurs because of the following factors: (a) surface contamination, (b) surface roughness, (c) heterogeneity of surface structure, (d) reorientation or rearrangement of the segment, (e) swelling, and (f) deformation. We presumed that reorientation or rearrangement of the segments of the non-UV-cured and UV-cured blends on the surface influences the contact angle hysteresis because the Tg of the blends is markedly lower than room temperature. In other words, the blends exhibit reorientation or rearrangement of a surface structure when they are moved from air into water. These blends possess a large advancing contact angle but a low receding contact angle. Presumably, the P(2EHA-AA) component can easily exhibit reorientation or rearrangement at the blend-water interface. The dynamic contact angles of the non-UV-cured blend were the same as those of UV-cured blend. This means that the segment mobility of the polymer chains on the surface was not changed by UV irradiation. We judged that the segment mobility on the surface did not influence the reduced peel adhesion and probe tack values, although the blend/water system differs from the blend/adherend system in their interfacial conditions.

Thus, we believe that the reduced peel adhesion and probe tack values were caused by the modulus and Tg increases due to UV irradiation. Figure 10 shows the relationship between 90° peel adhesion and storage modulus, $E' = 3G'$, for P(2EHA-AA)/UAO blends. The 90° peel adhesion values decreases with increasing $E' = 3G'$. The relationship between 90° peel adhesion and $E'' = 3G''$ is similar to that of 90° peel adhesion and $E' = 3G'$, as shown in Figure 11. When the function of the debonding process influences the PSA properties according to Tse's equation (1), the PSA properties increase with increasing

TABLE II Dynamic contact angle for P(2EHA-AA)/UAO blend with 50 phr UAO

	Advancing contact Angle/deg.	*Receding contact Angle/deg.*
Before UV	92.4	79.9
After UV	92.6	80.0

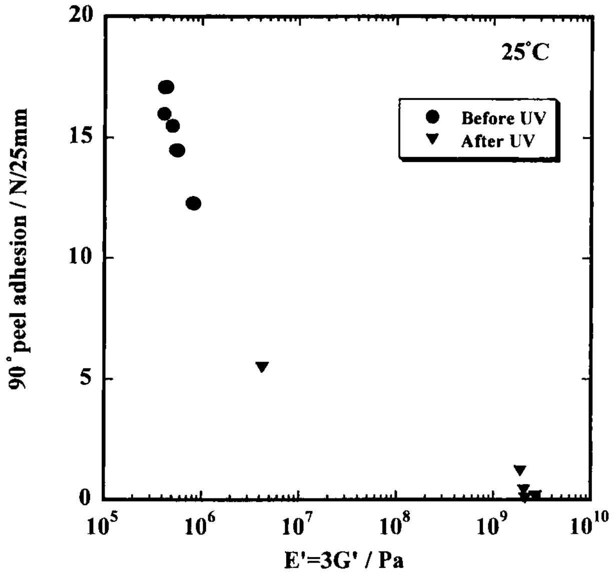

FIGURE 10 Relationship between 90° peel adhesion and storage modulus, E′ = 3G′, for P(2EHA-AA)/UAO blends.

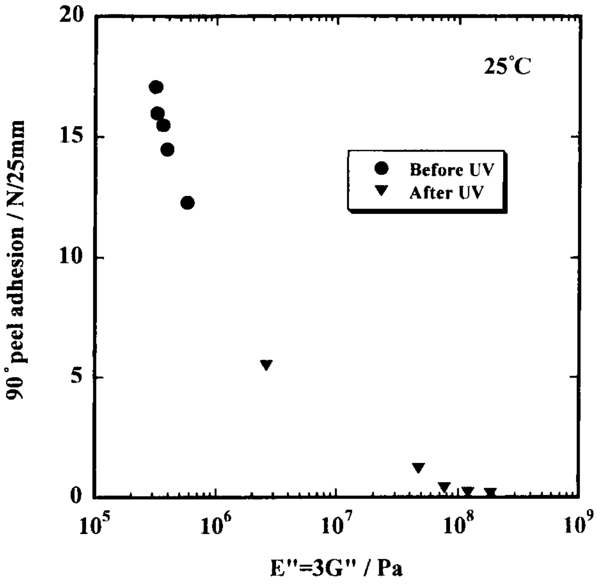

FIGURE 11 Relationship between 90° peel adhesion and loss modulus, E″ = 3G″, for P(2EHA-AA)/UAO blends.

loss modulus, $E'' = 3G''$, of the adhesive polymer. However, for P(2EHA-AA)/UAO blends the peel adhesion value decreased with increasing $E'' = 3G''$. Therefore, we believe that the ability of the deformation energy of UV-cured blends to influence the adhesive tests was reduced *via* UV irradiation.

CONCLUSIONS

PSA properties were investigated for blends of P(2EHA-AA) with UAO. The values of peel adhesion and probe tack of the P(2EHA-AA)/UAO blends were dramatically reduced by UV irradiation. The mechanism of reduced PSA properties was investigated *via* dynamic mechanical properties, DSC, and DCA. Since modulus values and glass transition temperatures of these blends after UV irradiation were higher than those before UV irradiation, we judged that the reduced peel adhesion and probe tack values were caused by the modulus and Tg increases due to UV irradiation. In other words, the ability of the deformation energy of UV-cured blends to influence the adhesive tests was reduced by the curing process. On the contrary, the DCA of non-UV-cured blends were the same as those of UV-cured blends. We judged that the segment mobility of polymer chain on the surface did not influence the reduced peel adhesion and probe tack values. Finally, we point out that the P(2EHA-AA)/UAO blends are very effective materials for dicing or back-grinding in semiconductor processing.

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