Adhesive Properties of Ultraviolet Curable Pressure-Sensitive Adhesive Tape for Semiconductor Processing (I)
- Interpretation via Rheological Viewpoint

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ABSTRACT For blends of acrylate copolymer [poly(2-ethyl hexyl 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. However, all blends had a high holding power even when cured by UV irradiation. The mechanism of reduced PSA properties was investigated via dynamic mechanical properties, DSC, and dynamic contact angle DCA. Peel adhesion decreased monotonically with an increase of storage moduli E' and loss moduli E'' for all non-UV and UV cured blends. Since moduli values and glass transition temperatures T_g of these blends after UV irradiation were higher than those of these blends before UV irradiation, we judged that reduced peel adhesion and probe tack values were caused by the moduli increase and the T_g increase due to UV irradiation. In other words, the deformation energy of UV cured blends when conducting adhesive tests was reduced by the curing process. The DCA values of non-UV cured blends were same as those of UV cured blends. We presumed that the segment mobility of polymer chains on the surface did not influence the reduced peel adhesion and probe tack values.

1. INTRODUCTION

Pressure sensitive adhesive (PSA) tapes composed of acrylic copolymers have been extensively utilized in various industries, such as packaging, printing, electrical insulation, and automobile. In general, the PSA properties (tack, peel adhesion, holding power) of acrylic adhesive have been controlled by blending tackifiers or dissimilar polymers, by adjusting molecular weight and its distribution, and also by copolymerization with a polar monomer and curing system. In recent years, the PSA properties of acrylic adhesive copolymer 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 bonding and debonding processes, the PSA properties could not be clarified.

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

Recently, various types of PSA tapes have been utilized in semiconductor processing, such as back-grinding and dicing processes 7)~9). In particular, it is well known that an UV curable PSA tape is a very effective material for dicing processes 10)~13). In the cutting process of a dicing process, strong adhesion between PSA tape and wafer is necessary. If a PSA tape adheres weakly to a wafer in the cutting process, the diced chip separates from PSA tape or flies off. On the other hand, weak adhesion between PSA tape and wafer is desired for the picking-up process of a dicing process. Since 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, an UV curable PSA tape is very tacky before UV irradiation, and this tackiness disappears with UV irradiation. The backbone of the UV curable oligomer is formed out 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 300~450nm. The initiation reaction for UV curing occurs following a radical reaction from initiator to UV curable oligomer. Finally, the UV curable oligomer is

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polymerized.

In this paper, for 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 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.

2. EXPERIMENTAL

2.1 Materials

The compositions of UV curable adhesives are shown in Table 1. 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 UV curing oligomer and photopolymerization initiator, respectively. The peak 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 a high-pressure mercury lamp.

2.2 Measurements

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

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

Table 1 Composition of adhesive

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

The dynamic mechanical properties of the UV curable adhesive (non-UV and after UV irradiation) were carried out using 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 moduli $E'=3G'$ or shear storage moduli G', extension loss moduli $E''=3G''$ or shear loss moduli G'', and dynamic loss tangent tanδ were measured at 1 Hz.

The dynamic loss factor Δ of UV curable adhesives was measured by the free decay oscillation method using an Orientec Co., Ltd. rigid body pendulum-type dynamic mechanical property apparatus model DDV-OPA III 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 dynamic mechanical measurements.

The dynamic contact angle DCA was measured with Orientec Corporation (DCA20) 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 and then dried in a vacuum oven at 40°C for 24 hours. The details were described elsewhere[14), 15)].

3. RESULTS AND DISCUSSION

Relationship between 90° peel adhesion and UAO content for P(2EHA-AA) / UAO blends is shown in Figure 1. For non-UV cured adhesives, the value of peel adhesion increases with an increase of UAO content. Conversely, for UV cured adhesives, the level of peel adhesion decreases with an increase of UAO content. The peel adhesion of UV cured adhesive with 40 phr UAO com-

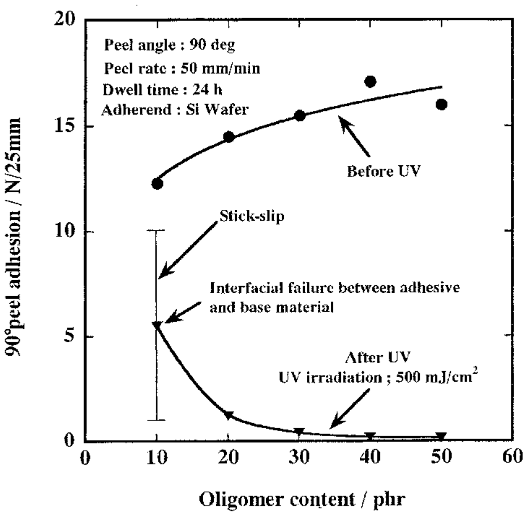

Figure 1 Relationship between 90° peel adhesion and UAO content for P(2EHA-AA) / UAO blends

pletely disappeared. The probe tack value for non-UV cured adhesives also increases with an increase of UAO content, whereas the probe tack of 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 80,000 s). We expect that the differences of PSA properties between the blends and the reduced PSA properties (peel adhesion, probe tack) through UV irradiation are clarified by dynamic mechanical properties, surface properties and miscibility. Thus dynamic mechanical properties (storage moduli *G'*, dynamic loss tangent tanδ) , 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 already been investigated by many researchers[1)~3), 16), 17)]. For example, an original analysis of chemical and physical factors affecting PSA properties was proposed by Dahlquist[16)], who found that the molecular contact between adhesive and adherend is completely established when compressive creep compliance of the adhesive at 1 s is higher than 10^{-7} cm^2/dyn (Dahlquist criterion). Tse[1)] and Yang[2)] pointed out that the PSA properties *T* are expressed by considering the bonding and debonding processes of adhesive as follows :

$$T = W_a \cdot B \cdot D \qquad (1)$$

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

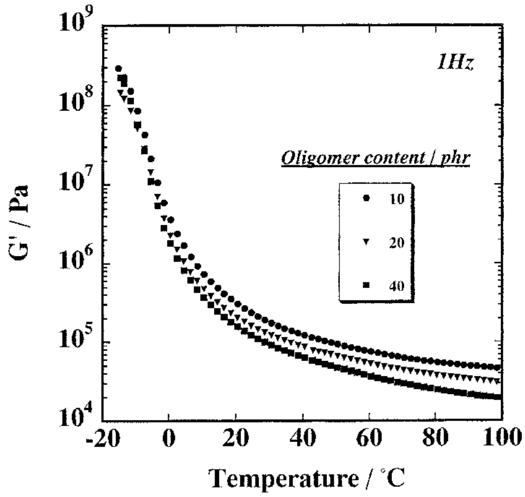

Figure 2 Temperature dependence of *G'* of non-UV cured P(2EHA-AA) / UAO blends

Temperature dependence of storage moduli *G'* of non-UV cured P(2EHA-AA) / UAO blends is shown in Figure 2. *G'* decreases as temperature rises. At the high-temperature side (plateau region), *G'* decreases as UAO content increases. Presumably, since molecular weight (viscosity) of UAO was remarkably lower than that of P(2EHA-AA), the plateau moduli level was depressed by introducing UAO. As described above, peel adhesion and probe tack increased with an increase of UAO content for non-UV blends. We think that for non-UV blends the function of the bonding process reflects on PSA properties according to Tse's equation (1).

Temperature dependence of (a) extensive storage moduli *E'* =3*G'* and (b) dynamic loss tangent tanδ for UV cured P(2EHA-AA) / UAO blends are shown in Figure 3. The magnitude of *E'* of P(2EHA-AA) / UAO blend with 20 phr UAO is similar to that of the blend with 50 phr UAO. Conversely, the *E'* values of the blend with 10 phr UAO are remarkably lower than that of the blend with 20 phr UAO. The magnitude of tanδ-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 its PSA properties are influenced by 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 dynamic contact angle DCA. For non-UV and UV cured P(2EHA-AA) / UAO blend with 10 phr UAO, temperature dependence of *G'* and tanδ are shown in Figure 4. With UV irradiation the values of *G'* of UV cured blend with 10 phr UAO are high-

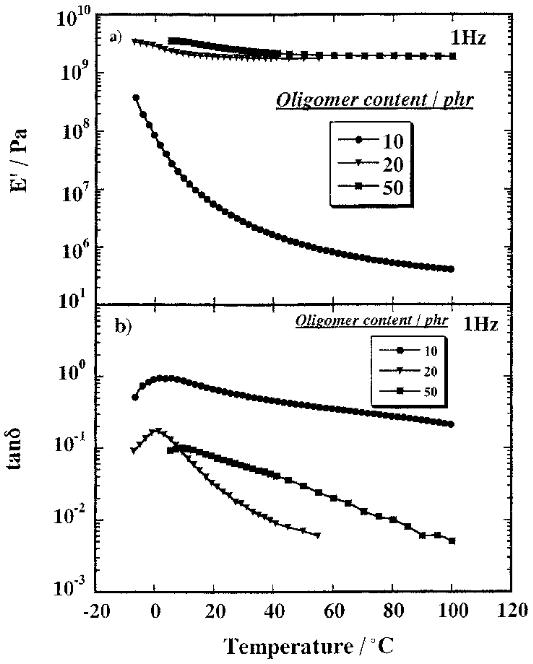

Figure 3 Temperature dependence of (a) extensive storage moduli *E'* and (b) dynamic loss tangent tanδ for UV cured P(2EHA-AA) / UAO blends

er than that of non-UV cured blend with 10 phr UAO. The tanδ-temperature curve of the UV cured blend shifted to the high-temperature side by about 5 K. In particular, the increase of G' in the rubber plateau region is clearly observed for the blend with 10 phr UAO. Since rubber plateau modulus G_r influences entanglement of polymer chain, we presume that the molecular weight between entanglements for P(2EHA-AA) polymer chain decreased with UV irradiation. Figure 5 shows the temperature dependence of (a) storage moduli E' and (b) dynamic loss tangent tanδ for P(2EHA-AA) / UAO blend with 40 phr UAO. Peel adhesion (P.A.), probe tack (P.T.), and holding power (H.P.) values are also listed in the Figure. The tanδ values are lowered by UV irradiation. The temperature of tanδ having maximum (T_{Dmax}) also shifts toward the high-temperature side following UV irradiation. At 25°C, the E' value of non-UV cured adhesive is about 10^5 Pa, whereas the E' value of 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 probe tack of non-cured PSA tape were remarkably larger than those of UV cured PSA tape. Therefore, we presume that the reduced adhesion is caused by the moduli increase and the T_g increase due to UV irradiation.

The T_g increase due to UV irradiation is confirmed by a DSC analysis. Figure 6 shows DSC thermograms of P(2EHA-AA) / UAO blends. The glass transition temperatures T_g of the non-UV and UV cured blends are indicated in the Figure. For both blends with 10 phr and 50 phr UAO, the T_g of UV cured blends is higher than that of non-UV blends by about 5 K. Presumably, mobility of the segment in P(2EHA-AA) polymer chain was depressed by UV cured UAO. All non-UV and UV cured blends films were transparent. Since the T_g of the blends also exhibited a single peak, we judge that P(2EHA-AA) is miscible with UAO.

Tackiness is dominated by dynamic mechanical properties on surface of an adhesive layer. In our previous

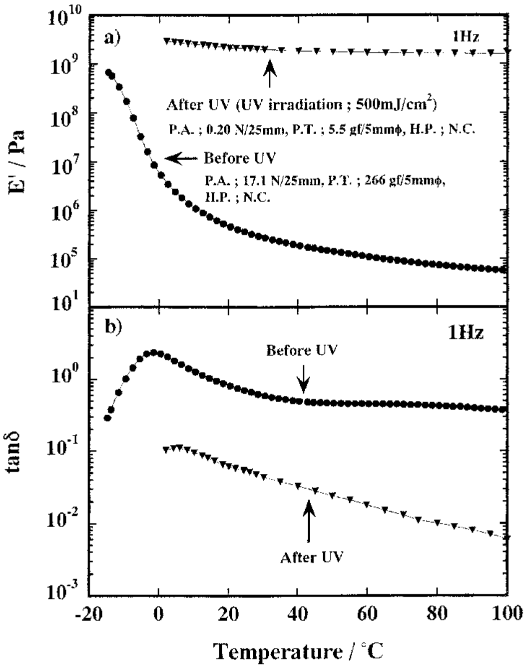

Figure 5 Temperature dependence of (a) storage moduli E' and (b) dynamic loss tangent tanδ for P(2EHA-AA) / UAO blend with 40 phr UAO. Peel adhesion (P.A.), probe tack (P.T.), and holding power (H.P.) values are listed in the Figure. N.C.; Non Creep 80000sec

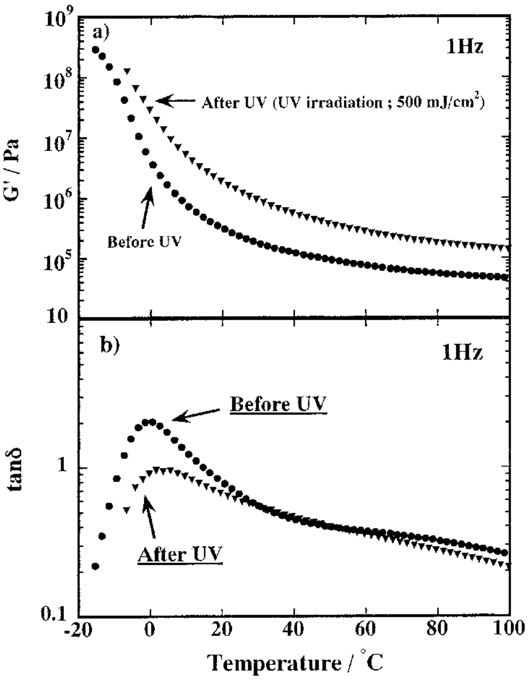

Figure 4 Temperature dependence of (a) G' and (b) tanδ of P(2EHA-AA) / UAO blend with 10 phr UAO

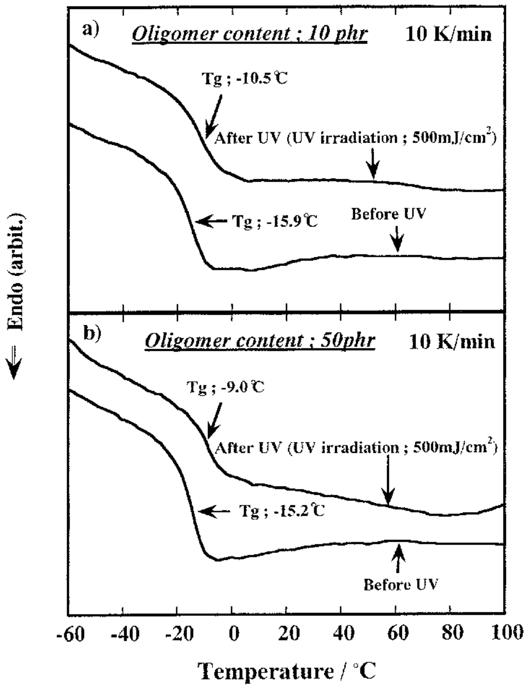

Figure 6 DSC thermograms of P(2EHA-AA) / UAO blends

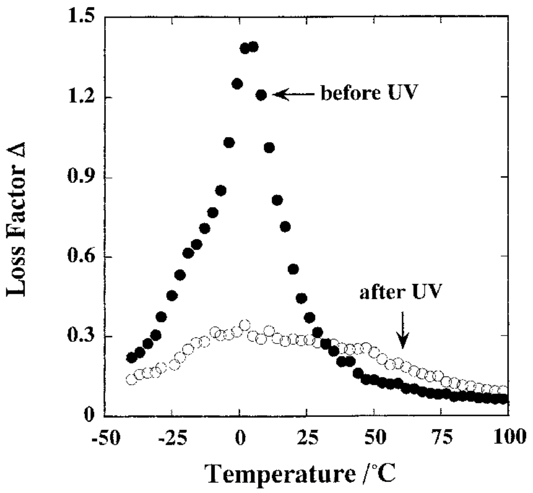

Figure 7 Temperature dependence of dynamic loss factor Δ for P(2EHA-AA) / UAO blend with 40 phr UAO. a) non-UV, b) after UV

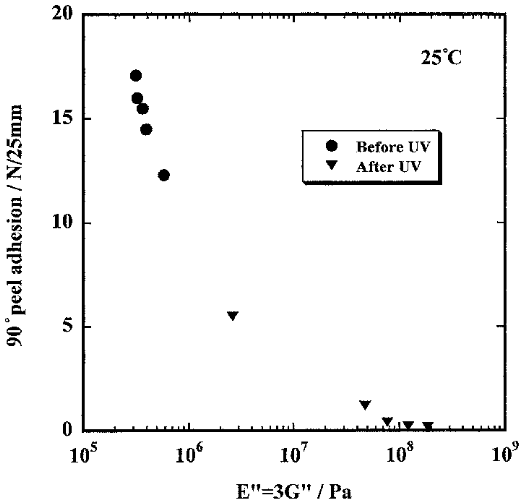

Figure 8 Relationship between 90° peel adhesion and loss moduli $E''=3G''$ for P(2EHA-AA) / UAO blends

Table 2 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

study[18], differences of dynamic mechanical properties on the surface directly influenced the tack value. It is expected that dynamic mechanical properties on the surface of a non-UV cured adhesive also differs from that of UV cured adhesive. Thus, the temperature dependence of dynamic loss factor Δ for P(2EHA-AA) / UAO blend with 40 phr UAO was measured by means of the free decay oscillation method as shown in Figure 7. The delineation of the curve of Δ and temperature for non-UV cured adhesive differs remarkably from UV cured adhesive. Therefore, we considered that the difference of peel adhesion and probe tack between non-UV and UV cured adhesives corresponded to the differences in dynamic mechanical properties on the surface.

Thirdly, the mobility of the polymer chain on the surface for P(2EHA-AA) / UAO blend with 50 phr UAO was estimated by dynamic contact angle DCA. The advancing and receding dynamic contact angles for the blend with 50 phr UAO are shown in Table 2. A contact angle hysteresis of about 12 deg. is observed for non-UV cured and UV cured blend. In general, the contact angle hysteresis of a polymer occurred 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 segment of the non-UV cured and UV cured blends on the surface influences contact angle hysteresis, because the T_g 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 and a low receding contact angle. Presumably, the P(2EHA-AA) component can easily exhibit reorientation or rearrangement at blends-water interface. The dynamic contact angles of the non-UV cured blend were same as that of the UV cured blend. This means that the segment mobility of the polymer chain on the surface was not changed by UV irradiation. We judged that segment mobility on the surface did not influence the reduced peel adhesion and probe tack values, although the blends / water system differs from the blends / adherend in terms of interfacial condition.

Thus, we thought that the reduced peel adhesion and probe tack values were caused by the moduli increase and the T_g increase due to UV irradiation. Figure 8 shows the relationship between 90° peel adhesion and loss moduli $E''=3G''$ for P(2EHA-AA) / UAO blends. The 90° peel adhesion value decreases with an increase of $E''=3G''$. When the function of the debonding process influences the PSA properties according to Tse's equation (1), the PSA properties increase while increasing the loss moduli $E''=3G''$ of the adhesive polymer. However, for P(2EHA-AA) / UAO blends peel adhesion value decreased with an increase of $E''=3G''$. Therefore, we thought that the deformation energy of UV cured blends when conducting adhesive tests was reduced by UV irradiation.

4. 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 through dynamic mechanical properties, DSC, and DCA. Since moduli values and glass transition temperatures T_g 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 moduli increase and the T_g increase due to UV irradiation. In other words, the deformation energy of UV cured blends when conducting adhesive tests was reduced by the curing process. Conversely, the DCA values of non-UV cured blend were same as that of UV cured blend. We judged that the segment mobility of the 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 processes.

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