

Improvement in Wettability of Pressure-Sensitive Adhesive on Silicon Wafer Using Crosslinking Agent with Siloxane Groups

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ABSTRACT: Acrylic copolymers are prepared by radical polymerization of 2-ethylhexyl acrylate, ethyl acrylate, and acrylic acid followed by crosslinking to manufacture the pressure-sensitive adhesives (PSAs) for silicon wafer protection. Both higher reliability and wettability are required for the protective acrylic PSAs in the semiconductor processing applications. The siloxane linkages are introduced in the acrylic PSAs via crosslinking with siloxane-containing crosslinking agent to modify the thermal and wetting properties of PSAs efficiently. The more efficient formation of crosslinked network structure was achieved with higher content of tetra-functional crosslinking agent, and the surface energy of PSAs decreased significantly with increasing the content of siloxane linkage resulting in the improved areal wetting rate. The thermal stability of PSAs was also improved significantly by incorporation of siloxane linkages. The adhesion properties such as peel strength and probe tack of acrylic PSAs decreased significantly by increasing the content of either crosslinking agent or siloxane linkage. The acrylic PSA with siloxane group showed both satisfactory wetting and clean debonding properties for the optimal protection of thin silicon wafers. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 276–281, 2013

KEYWORDS: pressure sensitive adhesive; wettability; siloxane; crosslinking; silicon wafer

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INTRODUCTION

Pressure sensitive adhesives (PSAs) are used in various fields such as masking tapes, removable labels or office notes, protective films, and medical tapes, which are used to adhere feasibly to various substrates as metal, paper, plastics, glass, wood, and skin.^{1–4} PSAs are characterized by the excellent low constant level of peel strength and tack as well as the excellent aging performance at room or higher temperatures. The inherent tackiness of PSAs allow them to wet and adhere quickly under a low pressure on a broad variety of substrates.^{5,6} With the rapid development of integrated semiconductor technology, higher reliability, and wettability are needed additionally for the manufacture of protective PSA films for thin silicon wafer.

Lower tack and peel strength, which are prerequisites for the easy debonding of protective PSAs from substrate, are generally attributed to the increased stiffness of polymeric chains of PSAs. However, the increased stiffness of polymeric chains results in the detrimental effect on the wetting of substrate with PSAs inevitably.⁷ The improved wetting of a protective PSA film on the silicon wafer surface should be accompanied with the lower tack and peel strength for easy debonding. The wetting behavior has a close relation with the surface energies of both adhesive and substrate materials. The wettability of PSAs could be

improved by introducing long aliphatic side chains to reduce the surface energy of the PSA.⁸ However, incorporation of long side chains in PSAs increased the flexibility of polymer matrix resulting in the increase of tack and the difficulty in clean debonding.

To improve the wettability of PSAs without sacrificing the clean debonding characteristics, introduction of siloxane linkages in PSAs was carried out in this study because the silicon groups are known to have versatile properties like resistance to weathering and aging, good wetting and film forming ability, low temperature flexibility, and suitable hydrophobicity.^{9–13} There are several routes to introduce the siloxane linkage in the polymeric chains of PSAs. The crosslinking agent having siloxane linkage is used to introduce the siloxane linkages in the PSAs in this study. The acrylic polymers lacking crosslink are not generally used as PSAs, because crosslinking provides the suitable thermal and mechanical properties for thermomechanical stability requirement.^{14,15} It was also known that crosslinking of polymeric chains played an important role in controlling the adhesive properties of PSAs for easy and clean debonding to a great extent.^{16–18}

In this study, acrylic copolymers were postreacted with crosslinking agents having various epoxy functionalities and

backbone structures to modify the structure of PSAs efficiently via the reaction between carboxyl and epoxy groups. The wetting and adhesion properties of the crosslinked PSAs were evaluated in terms of the variations in contact angle, areal wetting rate, peel strength, probe tack, and viscoelastic properties at various extents of crosslinking.

EXPERIMENTAL

Materials

Ethyl acrylate (EA, Samchun Pure Chemical, Korea), 2-ethylhexyl acrylate (EHA, Samchun Pure Chemical, Korea), and acrylic acid (AA, Samchun Pure Chemical, Korea) were used as monomers for radical polymerization to synthesize the acrylic copolymer. *N,N'*-azobisisobutyronitrile (AIBN, Daejung Chemicals & Metals, Korea) and ethyl acetate (Junsei Chemicals, Japan) were used as a radical initiator and a solvent, respectively. Allyl glycidyl ether (AGE, Sigma-Aldrich, USA) and 1,1',3,3'-tetramethyldisiloxane (TMHD, Sigma-Aldrich, USA) were used to synthesize the siloxane-containing crosslinking agent, 1,3-bis(3-glycidyloxypropyl) tetramethyldisiloxane (3-GTMS). *N,N,N',N'*-tetraglycidyl-*m*-xylenediamine (Tetrad-X, Mitsubishi Gas Chemical, Japan) was used as crosslinking agent containing multi-epoxy groups. The structures of crosslinking agents are presented in Figure 1.

Synthesis of 3-GTMS

3-GTMS was synthesized according to the procedures reported in the literature via Pt-catalyzed hydrosilylation reactions with AGE and TMHD.^{19,20} It was synthesized in a 500-mL four-necked glass flask equipped with mechanical stirrer, thermometer, condenser, and nitrogen inlet. The flask was charged with 67 g TMHD, 114 g AGE, and 0.2 wt % Pt catalyst followed by stirring for 8 h at 70°C. The unreacted reagents were separated using a vacuum system. ¹H-NMR spectra of 3-GTMS were obtained in CDCl₃ solution with 400 MHz FT-NMR (JNM-AL400, Jeol, Japan). ¹H-NMR peaks were identified at various chemical shifts, δ (ppm), as -0.02 and 0.00 (two CH₃Si chains), 0.42–0.48 (CH₂CH₂Si; β adduct), 1.49–1.58 (CH₂CH₂Si; α adduct), 2.45–2.47 and 2.63–2.65 (CH₂-epoxy), 2.99–3.00 (CH-epoxy), 3.24–3.40 and 3.56–3.59 (O-CH₂-epoxy and O-CH₂CH₂CH₂Si).

Preparation of Crosslinked Acrylic PSAs

The acrylic copolymer was synthesized with the fixed composition of EHA, EA, and AA in 41.7, 41.7, and 16.6 wt %, respectively. The acrylic copolymer was synthesized by solution radical polymerization with 1.5 wt % AIBN in ethyl acetate at the solid content of 32.5 wt % in a 500-mL, four-necked, round-bottomed flask equipped with a thermometer, condenser, dropping funnel, and mechanical stirrer. The flask was charged with 50% of the monomer and solvent mixture, and then polymerization was carried out at 80°C for 0.5 h followed by the addition of the remaining 50% of the monomer and solvent mixture over 1.5 h and the further reaction at 80°C for 3 h.

A given amount of the solution of crosslinking agent in ethyl acetate was added to the acrylic copolymer. The adhesive mixture was casted onto a poly(ethylene terephthalate) film to have a uniform thickness with an applicator and then dried at 80°C

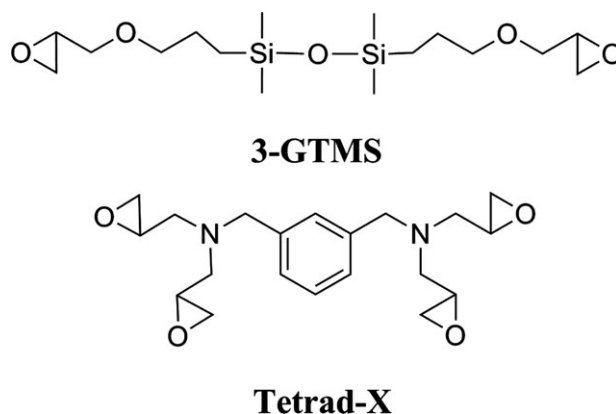


Figure 1. Structures of crosslinking agent used for the preparation of acrylic PSAs.

to remove the solvent. The thickness of the adhesive layers after drying was 20 μm . After removal of solvent, the acrylic copolymer/crosslinking agent mixture layer was stayed at 60°C for 3 days for the crosslinking reaction between carboxyl groups in acrylic copolymer and epoxy groups in crosslinking agent. The crosslinked acrylic PSA films were used for the measurements of various physical and adhesive properties.

Gel Content Measurement

The gel contents of the crosslinked PSAs were measured gravimetrically. The initial weight of sample (W_0) was measured before the immersion of sample in ethyl acetate at room temperature. The sample was filtered through a 200 mesh wire net after immersion for 3 days at 60°C followed by drying at 70°C for 24 h and then measuring the weight (W_t) at room temperature. The gel contents of crosslinked PSAs were calculated using the following equation:

$$\text{Gel content (\%)} = W_t/W_0 \times 100 \quad (1)$$

Wettability Evaluation

The contact angle measurement was carried out to evaluate the surface energies of PSAs in relation to the wettability. The contact angles on various PSA films were measured by the sessile drop method using a contact angle meter (Phoenix 300 SEO, SEO, Korea). Distilled water was used as probe liquid for the contact angle measurements. Wettability of PSA was directly measured as the time required for the complete contacting of silicon wafer with PSA film. PSA films were put on silicon wafer of $5 \times 5 \text{ cm}^2$ for the measurement of wettability as the areal wetting rate in $\text{cm}^2 \text{ min}^{-1}$.

Viscoelastic Property Measurement

The viscoelastic properties of the acrylic PSAs were determined using an advanced rheometric expansion system (ARES-FRT2000, Rheometric Scientific, UK) equipped with an 8 mm parallel plate mode. The typical temperature scan range was -60 to 120°C, and the heating rate was 5°C min^{-1} . The frequency was 1 Hz and the gap between the plates was 1 mm.

Adhesion Property Measurement

The acrylic PSAs were cut to a width of 25 mm for the adhesion tests. Each PSA film was attached to a glass substrate and a 2 kg rubber roller was passed over it thrice. The 180° peel strength was measured using a texture analyzer (Top Tack 2000, Yeon Jin, Korea) with a crosshead speed of 300 mm min⁻¹ at room temperature according to ASTM D3330. The lap shear strength was also measured using a texture analyzer (Top Tack 2000, Yeon Jin, Korea) with a displacement rate of 1 mm min⁻¹ at room temperature according to ASTM D 5868-95.

Probe tack was measured using a texture analyzer (Top Tack 2000, Yeon Jin, Korea) at room temperature. Polished stainless steel cylinder with a diameter of 5 mm was used as probe. The standard probe tack test was divided into three stages: approaching the surface of PSAs, contacting, and detaching from the surface of PSAs. Probe moved at a rate of 0.5 mm s⁻¹ and stayed on the contacting surface of PSA for 1 s under a constant force of 100 gf cm⁻² followed by debonding at a separating rate of 5 mm s⁻¹. Probe tack was obtained as the maximum debonding force during the debonding process.

RESULTS AND DISCUSSION

Crosslinking of Acrylic Copolymer

Crosslinking of polymer chains becomes more feasible when the reacting groups approach each other to increase the possibility of coupling of polymer chains. Polymer networks formed by crosslinking reaction are not soluble but just swollen in the solvent. However, other parts such as linear or branched polymers are soluble in the solvent. Therefore, the extent of crosslinking is usually evaluated by measuring the content of insoluble gel portion.^{21,22} The extent of crosslinking in acrylic PSAs was controlled by varying both the contents of crosslinking agent and the functionality of crosslinking agent. Figure 2 represents the effect of both the content and the functionality of crosslinking agent on the gel content of acrylic PSAs. The higher gel content was generally obtained for the acrylic PSAs having higher content of crosslinking agent as expected. The more efficient forma-

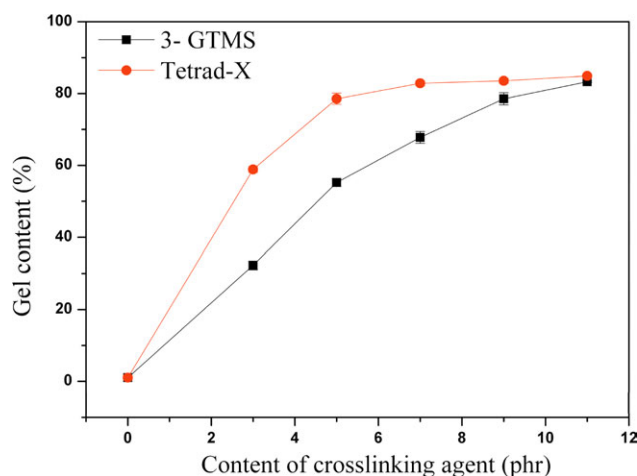


Figure 2. Variations in gel content of acrylic PSAs as a function of the content of crosslinking agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

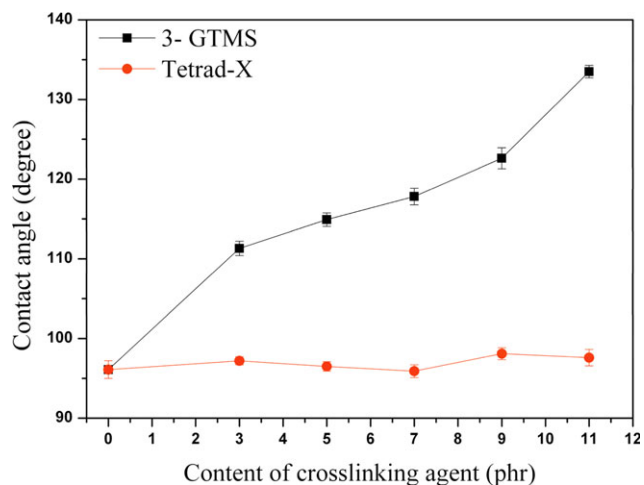


Figure 3. Variations in contact angle of acrylic PSAs as a function of the content of crosslinking agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion of crosslinked network structure was achieved with tetra-functional Tetrad-X compared to bifunctional 3-GTMS due to the higher numbers of reactive sites at the same composition of crosslinking agent.

Wettability of Crosslinked Acrylic PSAs

The siloxane linkages were introduced into the acrylic copolymer by crosslinking with 3-GTMS expecting the lowered surface energy of PSA, which would facilitate the wetting and contacting of PSA on the surface of silicon wafer. The contact angle of water on acrylic PSA increased significantly as the content of siloxane linkages increased in acrylic copolymer because the hydrophobicity of acrylic PSA increased efficiently by increasing the content of 3-GTMS as shown in Figure 3. However, the contact angle did not show big difference for the acrylic PSA crosslinked with Tetrad-X.

Contact angle measurement gives the information about the organization at the solid/liquid interface. The contact angle, θ , is related to the solid–liquid interfacial tension, γ_{SL} , solid surface free energy, γ_{SV} , and liquid surface tension, γ_L , through Young's equation²³:

$$\cos \theta = (\gamma_{SL} - \gamma_{SV}) / \gamma_L \quad (2)$$

The sessile drop method is one of the most commonly employed ways to measure the contact angles. The surface free energy decreases with the increase of contact angle. The distinction between the different wetting states is usually made by considering the equilibrium spreading coefficient, S_{eq} , which is related to the surface free energy of PSA for spontaneous wetting²⁴:

$$S_{eq} = \gamma_2 - \gamma_1 - \gamma_{12} \quad (3)$$

When S_{eq} is positive, spreading can occur spontaneously, but if S_{eq} is negative, the liquid will not spread spontaneously over the substrate. Therefore, the PSAs of lower surface tension spread on silicon wafer fast and easily as shown schematically in

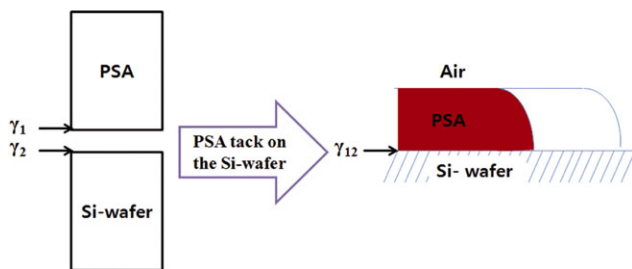


Figure 4. Scheme of spreading process of PSA on silicon wafer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. This principle is similar as the surfactants which are introduced in water. When a surfactant is added to water, it would decrease the liquid surface tension resulting in both increasing the spreading coefficient and allowing the spontaneous wetting to occur.

The contact angle characteristics of acrylic PSAs had a close relation with the wettability of PSAs on silicon wafer. The areal wetting rate of acrylic PSA increased significantly for the acrylic PSAs having higher content of siloxane linkages as shown in Figure 5. On the other hand, the wettability of acrylic PSA crosslinked with Tetrad-X remained almost constant regardless of the content of crosslinking agent due to the little variation in surface energy of PSA. As a result, the wettability of acrylic PSA was significantly improved due to the efficiently lowered surface energy of PSA by incorporating siloxane linkages in the adhesive polymer chains.

Viscoelastic Properties of Crosslinked Acrylic PSAs

The viscoelastic properties usually play an important role in the adhesion performance of PSAs.^{25–28} The storage modulus (G') and the loss modulus (G'') are associated with the elastic nature and the energy absorption of adhesive, respectively. $\tan \delta$ is determined by the following equation:

$$\tan \delta = G''/G' \quad (4)$$

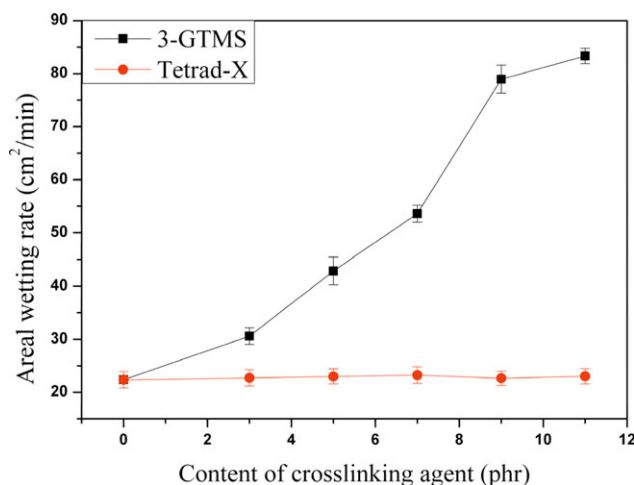


Figure 5. Variations in areal wetting rate of acrylic PSAs as a function of the content of crosslinking agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Both storage and loss moduli of acrylic PSAs showed the significantly different behavior depending on the kind of crosslinking agent as shown in Figure 6. The abrupt change in the storage modulus is related to the glass transition of acrylic PSA, which also has a close relation with the chain mobility. The variation of glass transition is also clearly seen from the variation of $\tan \delta$ peak depending on the kind of crosslinking agent. Both the storage modulus of rubbery plateau region and the glass transition temperature increased for the crosslinked acrylic PSAs compared to the noncrosslinked acrylic copolymer because of the higher extent of crosslinked network structures. The acrylic

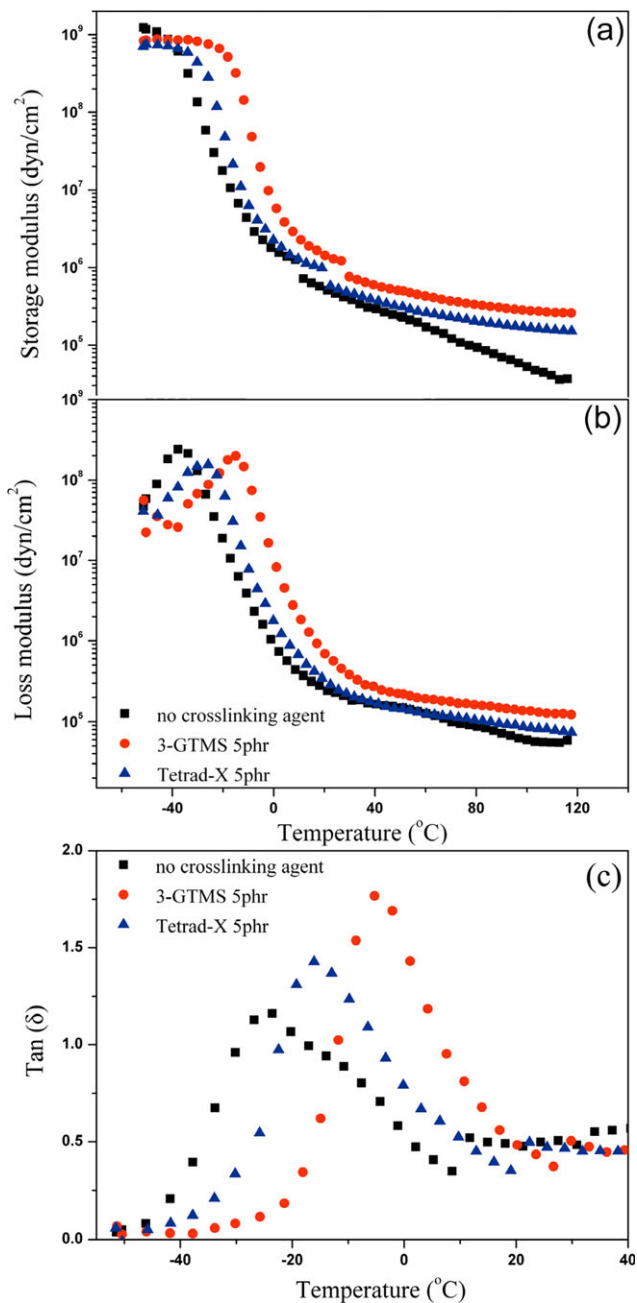


Figure 6. Variations in (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$ of various acrylic PSAs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PSA, which was crosslinked with 3-GTMA, showed the noticeable increase in the storage modulus, the glass transition temperature, and the damping characteristics demonstrating the improvement in thermal stability and elastic deformation characteristics.

Adhesion Performance of Crosslinked Acrylic PSAs

The adhesion performance such as the peel strength and probe tack of acrylic PSAs was evaluated depending on both the content and the kind of crosslinking agent as shown in Figure 7. Both peel strength and probe tack of acrylic PSAs decreased significantly by increasing the content of crosslinking agent. The variations in extent of crosslinking and glass transition temperature of acrylic PSAs are important factors for controlling the adhesion performance.²⁹ The decreases in both peel strength and probe tack are mostly attributed to the severe hindrance in chain mobility and anchoring of acrylic copolymer at the adhesion interface resulting from the highly crosslinked structures. Interfacial failure, which meant little adhesive remainder on the silicon wafer substrate, was observed for the peel tests of crosslinked acrylic PSAs. Both peel strength and probe tack of acrylic PSAs crosslinked with 3-GTMS decreased more sharply than those crosslinked with Tetrad-X demonstrating that the siloxane linkages in PSAs gave a significant effect on adhesion performance.³⁰ As a result, the acrylic PSA, which was crosslinked with

3-GTMS of more than 8 phr, showed both satisfactory wetting and clean debonding properties of acrylic PSA for the proper protection of thin silicon wafers. Probe tack test is intended to measure the tackiness of PSA. Because the tackiness indicates the ability of adhesive to adhere to substrate at low pressure, it is highly dependent on the mobility of polymer chains and the extent of crosslinking.³¹ Probe tack also decreased noticeably as the content of crosslinking agent increased especially for the acrylic PSAs crosslinked with 3-GTMS due to the same polymeric chain behavior as the case of peel strength variation.

CONCLUSIONS

The acrylic copolymer, which was prepared by radical polymerization of EHA, EA, and AA, was crosslinked with 3-GTMS or Tetrad-X to prepare the protective PSA films for silicon wafer. The extent of crosslinking of acrylic PSAs varied significantly depending on the content of crosslinking agent. The wettability of acrylic PSAs was improved significantly by crosslinking with 3-GTMS resulting from the siloxane linkages incorporation due to the decreased surface energy. The acrylic PSA, which was crosslinked with 3-GTMA, showed the noticeable improvement in thermal stability and elastic deformation characteristics. Both peel strength and probe tack of acrylic PSAs decreased significantly by increasing the content of crosslinking agent due to the severe hindrance in chain mobility and anchoring at the adhesion interface. The acrylic PSA, which was crosslinked with 3-GTMS of more than 8 phr, showed both satisfactory wetting and clean debonding properties for the optimal protection of thin silicon wafers.

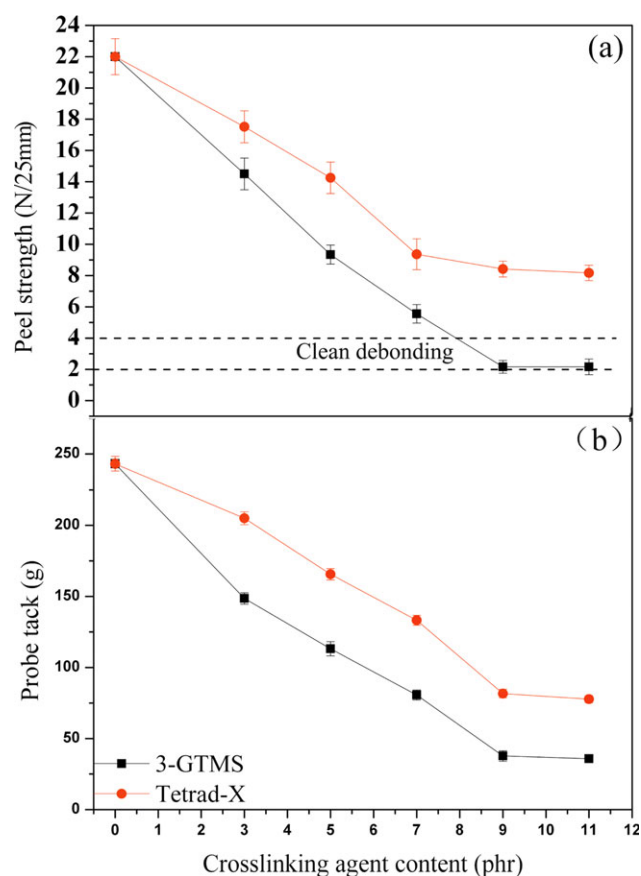


Figure 7. Variations in (a) peel strength and (b) probe tack of acrylic PSAs as a function of the content of crosslinking agent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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