Synthesis and characterization of thermally stable acrylic PSA using silicone urethane methacrylate with a semi-IPN structure

Pan-Seok Kim, Seung-Woo Lee, Ji-Won Park, Cho-Hee Park & Hyun-Joong Kim

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of thermally stable acrylic PSA using silicone urethane methacrylate with a semi-IPN structure

Pan-Seok Kim, Seung-Woo Lee, Ji-Won Park, Cho-Hee Park and Hyun-Joong Kim*

Laboratory of Adhesion & Bio-Composites, Program in Environmental Materials, Research Institute for Agriculture & Life Science, Seoul National University, Seoul 151-921, Korea

To improve the thermal properties of acrylic PSA, silicone urethane methacrylate (SiUMA) is applied to acrylic PSA using a semi-interpenetrating polymer network (IPN) structure. Acrylic PSA was prepared by free radical polymerization and SiUMA was synthesized by additional polymerization via urethane linkage. By preparing synthetic SiUMA formed in a semi-IPN structure in acrylic PSA, the thermal stability can be verified with the shear adhesion failure temperature using 1 kg plumb weight. Normally, acrylic PSA can easily be cleared from the substrate at less than 50 °C; but when using SiUMA at 10%, it can be resistant up to 100 °C. When measuring the photo-DSC value, a 5.0 phr photoinitiator and UV intensity of 1000 mJ/cm^2 can be used to complete the curing reaction. Two types of chain polymers – short and long chain polymers – were synthesized, and the structure was confirmed through FT-IR and gel permeation chromatography. By measuring the Thermogravimetric analyses, the cross-linking effect and improvement of the thermal resistance can be checked using silicone materials. With advanced rheometric expansion system, the thermal property changes and viscoelastic changes were detected. In this study, the mobility of silicone is detected while moving onto an air interface. The result of this study can provide information with which to improve the thermal stability when using SiUMA with a semi-IPN structure and acrylic PSA.

Keywords: acrylic PSA; semi-IPN; thermal stability; silicone; urethane acrylate

1. Introduction

The term 'pressure sensitive' (or sometimes self-adhesive) is used to designate a distinct category of adhesives. They are aggressively and permanently tacky in dry form at room temperature and firmly adhere to a variety of dissimilar surfaces.[1] Pressure sensitive adhesives do not need driving force like water, solvent, light, and heat. However, they can attach to a variety of surfaces under the application of light pressure such as 'thumb pressure.' When detaching the adhesives, they do not contaminate the substrate. Acrylic PSAs have several advantages including excellent aging characteristics, resistance to elevated temperatures and plasticizers, exceptional optical clarity due to their good polymer compatibility and nonyellowing properties, the highest balance of adhesion and cohesion, and excellent water resistance.[2] Acrylic PSAs show a semi-solid state as evaluated by tack, peel resistance, and shear strength measurements. Tack is described as the ability of a material to adhere instantaneously to a solid surface

---

*Corresponding author. Email: hjokim@snu.ac.kr

when brought into contact under very light pressure. It is not a basic property of an adhesive; but a composite response of the adhesive's bulk and surface properties.

The common and widely used siloxane polymers (known in the industry as silicone) are principally based on poly(dimethylsiloxane) (PDMS). Polyorganosiloxane consists of Si-O bonds, which allow flexibility of the chain as well as good chemical resistance, corrosion resistance, water resistance, and thermal and oxidative stability. Though it has many advantages, weak points are its high price and low adhesion to porous surfaces. [3] The interesting and useful properties of siloxane polymers are a result of the somewhat unusual molecular structure of the polymer chains, which consist of alternating silicone and oxygen atoms.[4] Polyurethane (PU) is the chemistry involved in isocyanate reactions with macrodiols, diisocyanate, and chain extenders. Today, PU coatings can be found in many different applications that require different appearance and lifespan values. Examples include construction projects, floors, steel trusses, and concrete supports.[5] Thermal properties depend on the type and nature of the hard segments, the relative molecular weight, and the composition and/or ratio of the hard and soft segments. In the PSA industry, UV-curing techniques represent a major advance in the development of the coating, adhesive, and ink industries.[6] It is not state of the art, but UV curing nonetheless currently represents about 90% of the radiation-curing market in Europe. Other terms for UV photoinitiated polymerization are photopolymerization or photocross-linking.[7] Under intense illumination, reactive species such as free radicals or cations can be generated in high concentrations by the photolysis of an initiator, and thus promote the polymerization of monomers and oligomers. UV-curing formulations provide some benefits, such as a fast cure response, excellent chemical resistance, good weathering characteristics, and a broad formulating latitude range. Low VOC is certainly the most discussed aspect of UV-curing, but product performance and cost effectiveness are equally important features that lead to the decision to use UV. The rapidity of free-radical UV curing is one major advantage responsible for the constant growth of this technology: in which curing proceeds within a fraction of a second. This ultrafast transformation from a liquid phase to a solid state allows an increase in productivity on a production line while keeping the energy cost at a low level. The composition of free radical or cationic UV-curable formulations varies both in terms of the character of the oligomers and photoinitiators.

An interpenetrating polymer network (IPN) consists of an intimate combination of two or more polymers in the form of networks. However, there is no chemical linkage between these types of distinct networks. They can be synthesized by the cross-linking polymerization of two multifunctional monomers or telechelic oligomers that are polymerized by different mechanisms, e.g. radical and cationic polymerization.[8,9] A semi-interpenetrating polymer network (semi-IPN) is composed of one or more polymer networks and one or more linear polymers which penetrate on the molecular scale of at least one of the networks by at least some of the linear or branched macromolecules. [10] Through an interpenetrating network, thermally stable induction was reported.[11] Cross-linked silicone polymers have many advantages, including flexibility, low surface tension, low dielectricity, ultraviolet resistance, nonflammability, as well as high thermal and chemical stability, though some semi-IPNs based on cross-linked polysiloxanes have been reported in the literature.[12,13] In this work, an acrylic PSA/silicone semi-IPN is synthesized in which linear acrylic and a silicone urethane methacrylate (SiUMA) network are treated as the guest and host polymers, respectively. It is shown that the mixture of linear acrylic PSA with the SiUMA forms a homogeneous blend by several ratios of the two components before self-condensation cross-linking arises.

Acrylic PSAs have weak thermal properties, indicating the need to create cross-linking or to increase the molecular weight to improve their properties. To create networks, adding a multifunctional monomer or oligomer is a comparatively effective approach. SiUMA is used as a multifunctional oligomer to create networks by increasing the cohesive in acrylic PSAs. Improving the thermal properties can be expected when using silicone and dicyclohexylmethane-4,4-diisocyanate, which are known to be thermally stable materials. Through this study, acrylic PSAs are easily modified by silicone additives to demonstrate a stable thermal effect similar to that of masking tape or die attach film. A small amount of additive is enough, meaning that cost reduction and cost competitiveness can be ensured. Moreover, using the same production line used for UV operations can be useful. When the semi-IPN structure is formed with SiUMA on acrylic PSA, the chain length influences the physical and chemical properties, as a long chain changes the glass transition temperature, crystalline temperature and rheological properties. The physical property and structures were confirmed by Fourier transfer infrared (FT-IR), gel permeation chromatography (GPC), and thermogravimetric analyses (TGA). Advanced rheometric expansion system (ARES) is used to analyze the thermal property changes and viscoelastic changes. A texture analyzer and contact angle measurement show the surface conditions.

2. Experimental

2.1. Materials

Acrylic monomers were selected in order to create acrylic pressure-sensitive adhesives. 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea), acrylic acid (AA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea), and polydimethylsiloxane (PDMS, Shin-Etsu Chemical Co. Ltd, Japan) with molecular weights of 1000 were used. Dicyclohexylmethane-4,4-diisocyanate (H_{12}MDI, DESMODUR® W) was purchased from Bayer Material Science AG, Germany, and hydroxylethyl methacrylate (HEMA, 99.0% purity, Samchun Pure Chemical Co., Ltd, South Korea) was commercially available and was used without purification. Hydroxy dimethyl acetophenone (Micure HP-8, Miwon specialty Chemical Co., Ltd, South Korea) was used as the initiator for the UV-polymerization of the acrylic PSAs.

2.2. Method

2.2.1. Synthesis of basic acrylic pressure-sensitive adhesives (acrylic PSA)

The acrylic PSA was synthesized from 2-EHA, AA in an ethyl acetate solvent containing approximately 50% solid contents. The polymerization process was performed in a 500 ml, four-necked, round-bottomed flask equipped with a thermo-coupler, condenser, dropping funnel, and mechanical stirrer. The monomer resin with 0.05 wt.% AIBN was heated to 80 °C in about an hour, and the reaction mixture was kept at 80 °C until the solvent polymerization process finished in 3 h, after which 0.05% AIBN was added three more times.

2.2.2. Synthesis of silicone urethane methacrylate (SiUMA)

The SiUMA was synthesized by adding an equimolar amount of PDMS with 0.1 wt.% dibutyl tin dilaurate dropwise to H_{12}MDI (i.e. NCO:OH = 2:1) under nitrogen gas. The

reaction was maintained at room temperature with a heater. Two hours later, when the absorption peak $2250 \, cm^{-1}$ of the NCO group in the IR spectra had remained in the same state, the temperature was raised to $60 \, °C$ using a heater. An equimolar amount of HEMA with 0.5 wt.% hydroquinone as a thermal polymerization inhibitor was added dropwise to the PDMS-H_{12}MDI adduct. Five hours later, the NCO group disappeared completely. The temperature was kept at less than $60 \, °C$ to remove nonreactive sites. At this time, the absorption peak of the NCO group at $2250 \, cm^{-1}$ also disappeared completely. In the case of a long chain, one additional dropping of PDMS, followed by end-capping with HEMA, was done. (Schemes 1 and 2.)
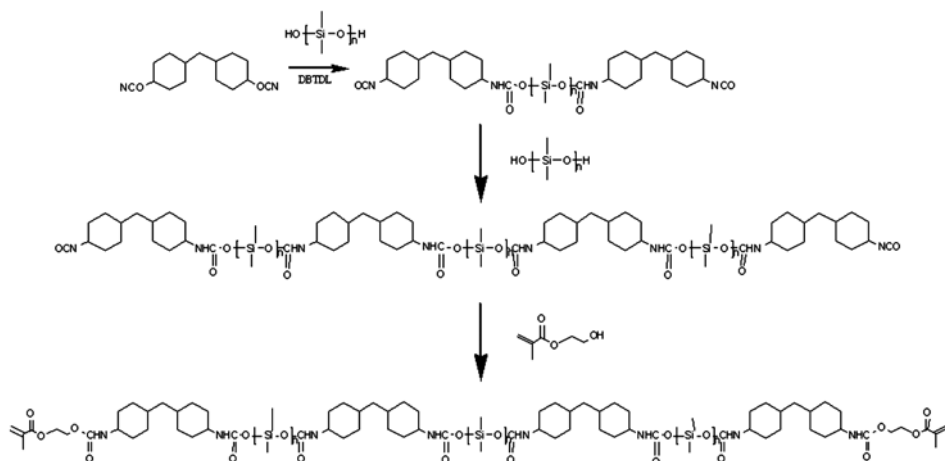
2.3. Measurements

The IR spectra were obtained on a JASCO FTIR-6100 (Japan) spectrometer equipped with attenuated total reference accessories. The spectra were recorded for 20 scans with a $4 \, cm^{-1}$ resolution over the wavelength range of $650–4000 \, cm^{-1}$. A decrease in the absorbance at different points in this range was noted. The spectra were analyzed in terms of double carbon, siloxane, and carbonyl bonds. All the results were confirmed by revising the levels of CO_2 reduction, H_2O reduction, noise elimination, smoothing, and baseline correction.

The average molecular weight (M_w) and number-average molecular weight (M_n) along with the molecular weight distribution (M_w/M_n, MWD) of the synthesized acrylic PSAs and SiUMA were determined by GPC, UK. The samples were dissolved in a tetrahydrofuran solution at a ratio of 0.5% w/v. GPC was used to obtain narrow molecular weight fractions and separation was accomplished on a column of a highly porous material that separates the polymer molecules according to size. The molecular weight and molecular weight distribution of the polymer could be measured by means of GPC. PSAs in the solution were injected into a stream of flowing solvent at the top of a packed column which consisted of a porous gel with different pore sizes. Therefore, the smaller polymer molecules could enter the pores such that their passage would be retarded, whereas the large molecules were excluded from the gel and were eluted from the column more rapidly.

Photo-DSC experiments were conducted using a TA instrument Q-200 DSC equipped with a photocalorimetric accessory (Omnicure 2000), which used light from a 100 W middle-pressure mercury lamp. The light intensity was determined by placing an empty DSC pan on the sample cell. The UV light intensity at the sample was $15 \, mW/cm^2$ over a wavelength range of 300–545 nm. The weight of the sample was
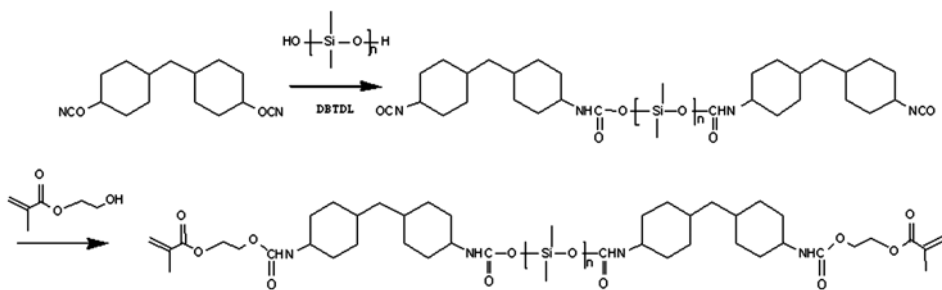
Scheme 1.　Synthesis of SiUMA (short chain: S1).

Scheme 2.   Synthesis of SiUMA (long chain: S2).

about 8 mg and the sample was placed in an open aluminum DSC pan. Measurements were carried out at 25 °C.

The acrylic PSAs films prepared were attached to a stainless steel substrate and a 2 kg rubber roller was passed over them twice. The 180° peel strength was measured using texture analyzer (TA-XT2i, Micro Stable Systems, UK) after the sample was left to stand at room temperature for 24 h. The peeling speed was 300 mm/min, and the average strength of peeling period was measured five times. The debonding speed was 0.5 mm/sec and the probe tack was measured as the maximum debonding force. Tack measurements of the PSA films were carried out with a TA-XT2i texture analyzer (Micro Stable Systems, UK) at 25 °C using a probe tack, which is a polished stainless steel (type 304) cylinder probe with a diameter of 5 mm.

The contact angle for the acrylic PSA with the semi-IPN structure was evaluated from static contact angles measured using a contact angle analyzer (Phoenix 300, Surface & Electro-Optics Corp.). The temperature and relative humidity were 23 ± 2 °C and 50 ± 3%, respectively.

The viscoelastic properties, the storage modulus, loss modulus, and tangent delta (tan δ) of the PSAs were measured using an advanced rheometric expansion system (ARES, Rheometric Scientific, UK). The PSAs were set on an 8 mm parallel plate and the gap between the plates was 1 mm. The plate was twisted at temperatures ranging from -50 to 200 °C with various strains (0.05–40%) and frequencies (1 Hz). The heating rate was 5 °C/min.

TGA were performed using a Perkin Elmer thermogravimetric analyzer (Pyris 1 TGA model). Samples were run from 30 to 600 °C with a heating rate of 10 °C/min under air.

The shear adhesion failure temperature (SAFT) was measured using a 25 mm size sample attached to a stainless steel substrate rolled with a 2 kg rubber roller twice. The samples were then stored at room temperature for 24 h. After loading with a weight of 1000 gf, the samples were held in the oven at a heating rate of 0.4 °C/min until 200 °C and the temperature at which shear failure occurred was recorded.

The tensile strength was measured using a Universal Testing Machine (Zwick Corp.) at ambient temperature with a crosshead speed of 100 mm/min. The UV-cured films

were prepared as rectangular specimens, 20 mm in length (span length), 6.6 mm in width, and with a thickness of 0.5 mm. Five measurements were taken with the mean value used for further analysis.

3.   Result and discussion

3.1.   *Fourier transfer infrared (FT-IR)*

Figure 1(a) indicates the HMDI FT-IR spectrum. The band at 2248–2264 cm^{-1} denotes the NCO group. The disappearance of the band is indicative of the completion of the reaction in (a)–(c). Figure 1(b) shows the characteristic band of PDMS, where the bands at 1015 and 1074 cm^{-1} are assigned to Si-O-Si stretching vibration. The stretching vibration at 791 cm^{-1} is characteristic of S-CH$_3$, 2248 cm^{-1} denotes the isocyanate group thus indicating a urethane reaction, though this is not visible to a greater extent than that in Figure 2(a). The result shown in Figure 1(c) is associated with the band of the acrylic double bond at 810 and 1638 cm^{-1}, but the intensity is too weak. Also, the 1720 cm^{-1} (C=O) stretching vibration shows HEMA induced in SiUMA indirectly.

   To create a long chain, the mole ratio must be controlled. Figures 2(a)–(d) depict the FT-IR spectrum of the reduced HMDI. The bands at 2248 cm^{-1} arose due to the NCO group. The disappearance of the band is indicative of the completion of the reaction in (a)–(d).

3.2.   *Gel permeation chromatography (GPC)*

The molar masses and molar mass distributions of the synthesized SiUMA01 and SiUMA02 were checked by GPC. These results are shown in Table 1. The GPC instrument was calibrated using a linear polystyrene standard. M_n value of SiUMA01 (S1) and SiUMA02(S2) are 4598 and 8942, respectively. The polydispersity indexes are 1.58 and 1.82. The value of the molar mass of S2 is double that of S1, which will be analyzed as it may offer information about the effect of the chain length. Moreover, the
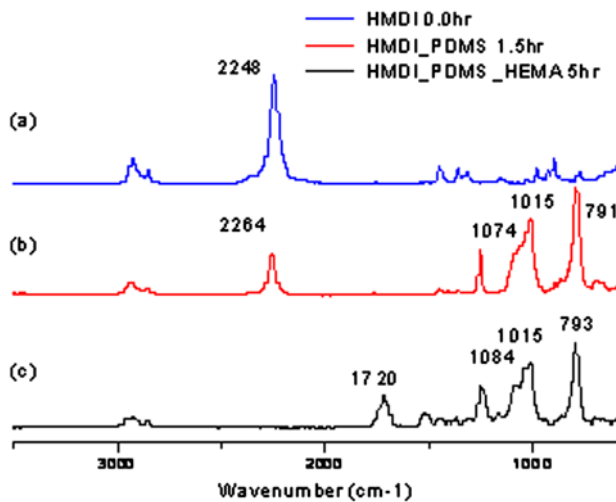

Figure 1.   FT-IR spectra of (a) HMDI, (b) addition of PDMS, and (c) addition of HEMA.
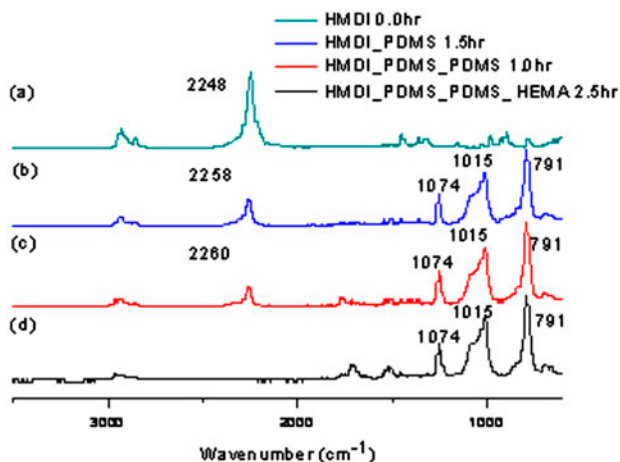
Figure 2. FT-IR spectra of (a) HMDI, (b) addition of PDMS (c) addition of PDMS, and (d) addition of HEMA.

Table 1.   Molecular weight distribution of SiUMA01(S1) and SiUMA02(S2).

Oligomers	M_n	M_w	Mp	M_w/M_n
SiUMA01(S1)	4598	7267	5264	1.58
SiUMA02(S2)	8942	16,307	9740	1.82

products showed different physical properties for the peel strength, tack, and contact angle.

3.3. *Photo-DSC (pDSC)*

The photo-DSC test is an easy method for UV-curing reactions because it can determine the kinetic parameters, degree of conversion, curing rate, and reaction enthalpy during a rapid UV-curing reaction; the behavior of which depends on the intensity and dose of the UV-light, the species, and content of the photo-initiator, the reaction temperature, and the reactivity of the functional groups.[14] In this experiment, the photo-DSC technique was used to examine the effect of the short (S1) and long (S2) chain contents depending on the amount of photoinitiator (PI). Figure 3 shows the isothermal UV-curing heat enthalpy and conversion profiles of S1 and S2 according to the photo-DSC results. The exothermic heat flow (cal/g s) vs. the curing time (Figure 3(a)) represents the important data according to the photo-DSC measurements. Auto-acceleration by the activation of radicals was confirmed to have undergone a steep increase at the beginning of the reaction, which was followed by auto-deceleration, as indicated by the rapidly dropping curves.[15] The reaction was studied by the blends S1, the photoinitiator, and different amounts of PI. Moreover, by the same method, but with different materials, S2 was blended with a photoinitiator and different amounts of PI. These reactions were performed at 0.5, 1.0, 5.0, and 10 phr at room temperature. Through this experiment, it was determined how much UV intensity was needed. From Figure 3(a), the enthalpy values were also measured under isothermal curing conditions at room temperature for 300 s at different concentrations. Through this result, it was noted that differences in the
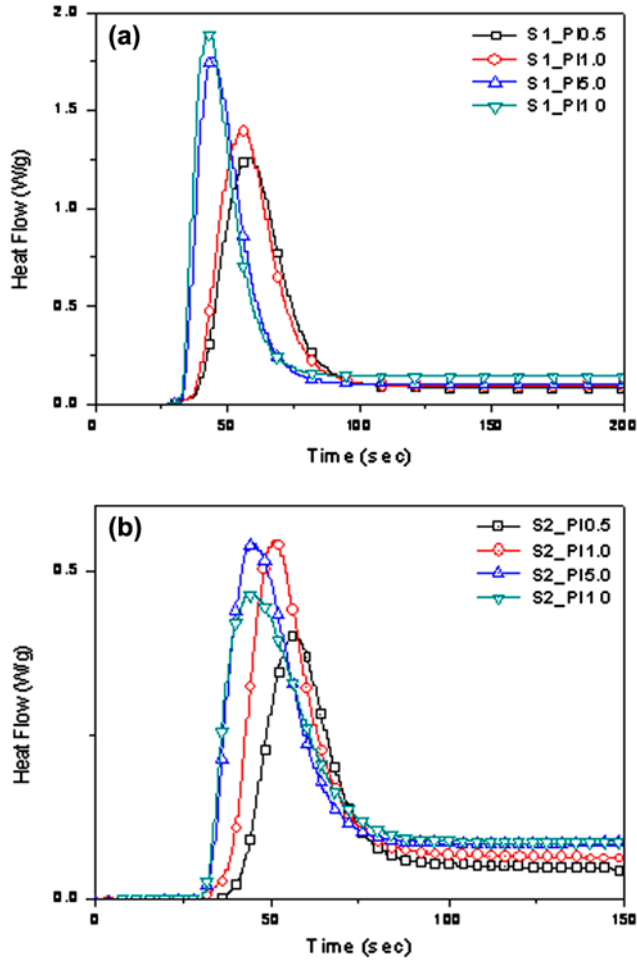
Figure 3.　The isothermal UV-curing heat enthalpy according to the photo-DSC results.

enthalpy evolve for different PI concentrations. The PI concentrations increased upon a higher conversion rate, which also explains the higher rate as the PI concentration increases in the range studied. With more than 5 phr of PIs, no significant differences were observed. Approximately, 5 phr of PIs is the proper dose for UV curing with UV irradiation of about $1000 \, \text{mJ/cm}^2$. As shown in Figure 3(b), the reactivity dropped dramatically. Given the double size (Table 1) of the chain, the effects on the enthalpy were comparatively great. The reaction rate is influenced by the viscosity, which means that a reduction in the viscosity allows greater diffusion and mobility.[16] Increasing the length of the chain increased the viscosity of S2, which reduced the reactivity. Figure 3 (b) shows that 10 phr decreased the enthalpy to less than 5 phr. When higher concentrations were used, a negative effect was observed owing to the high rate of the recombination of radicals, the higher absorption of UV light of the initiator in the top layers, and owing to some degree of incompatibility of the PIs with the molten polymer binder.[17] Figure 4 demonstrates that the mixtures of S1–S2 have no synergy between the short and long chains. The reaction rate is rather delayed by ratio of S1–S2. With

an increase in the S1 mass, the reaction rate recovers. This behavior resembles that with a long chain reaction. The long chain had an effect on the mobility of the short chain, causing S2 to increase and the S1 reactivity to decrease.

3.4. Concept drawings of UV curing

Given siloxane's low level of surface energy, the siloxane segments tended to migrate to the air–polymer interface.[18] When UV was irradiated onto the acrylic PSA-S1, the S1 segment moved to the surface of the acrylic PSA when in contact with air (Scheme 3).

3.5. Peel strength and tack

When S1 or S2 was added to the acrylic PSA, the peel strength increased depending on the dose. This fact shows that S1 and S2 influenced the surface of the acrylic PSA before UV irradiation. After UV irradiation, the peel strength declines sharply; the value is under 150 gf and almost disappeared on account of the cross-linking effect on the surface. Figure 5(a) shows a very high peel strength when the S1 and S2 are added to acrylic PSA; but at only a 1% dose with UV curing, the peel strength was very low, which indicated that S1 and S2 tend to migrate to the air–polymer interface.[18] S1–S2 mixtures show a peel strength between that of S1 and S2 and comparatively unstable variations. The probe tack is a measure of the adhesion performance over a short time. [19] In figure 5(b), it increases with the S1 and S2 amounts, but later UV irradiation decreased the value. S1–S2 mixtures had a value that was between those of their components. This is also related to cross-linking, which serves as proof that the surface is covered with S1 or S2. As a result of the cross-linking density, the short chain creates a hard surface.
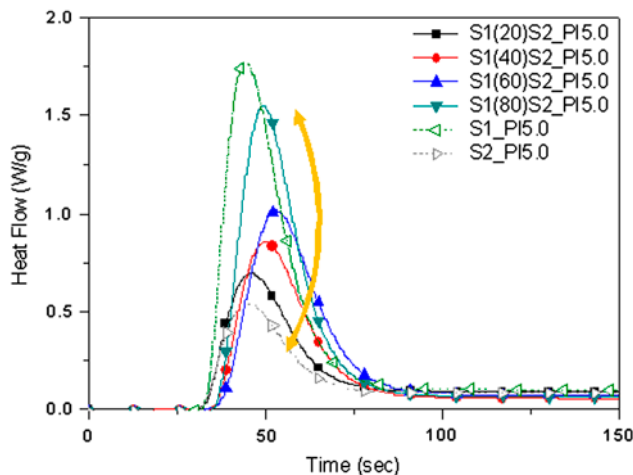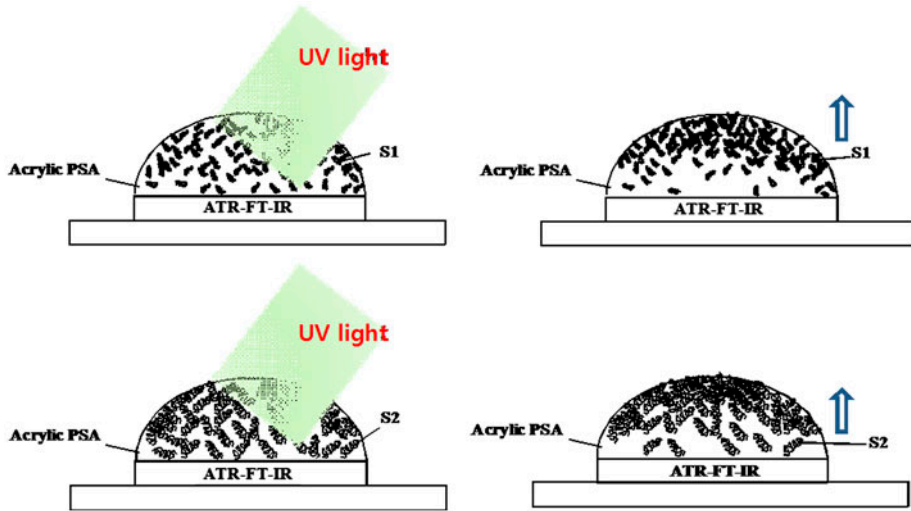

Figure 4.   Reaction heat flow profiles of the S1–S2 mixtures.

Scheme 3.   Conceptual drawings of UV curing.

3.6.   *Contact angle measurement*

Figure 6 shows the contact angles of the S1 and S2 testing liquids on each adhesive film as a function of the S1 and S2 contents with UV irradiation. Figure 6(a) shows the instant contact angle according to the S1 and S2 contents. S1 shows different behavior from S2, and S1 has the same angle with an increase in its content. However, S2 shows that the contact angle increased along with its content slightly. Nonetheless, after UV irradiation, the S1 angle increased until it was comparatively high but the S2 angle only increased slightly. This shows that the ability to create a network is better for S1 than it is for S2. Figure 6(b) shows the time-dependence for S1 and S2 according to the content levels. In the case of S1 and S2, the same angle slope appears on the time-dependence which means that siloxane, cross-linking, and the chain length do not strongly affect the incline of the time contact angle. This result shows that cross-linking is effective for changing of the surface via a short chain.

3.7.   *Rheology*

PSA has a semi-solid property. Hence, the wetting of the substrate and the viscoelastic property (a bulky property of the molecular mobility) are the important factors that control the adhesion performance.[20] In the case of acrylic PSA, the storage modulus curve has a glassy region, a rubbery plateau, and a terminal region; these curves are displayed according to the temperature. In the glassy region, the PSAs are rigid; but with an increase in the temperature as influenced by the glass transition temperature (T_g), they take on a rubbery property. The value of tan D indicates the ratio of the loss of modulus to the storage modulus; the highest peak of tan δ indicates the T_g. For a good wetting of PSAs onto substrates, the T_g of normal PSAs should be below room temperature. In addition, the rubbery plateau region existing above the T_g is related to the molecular weight and the entanglement of polymer chains.[21] Figure 7 examines the results after an increase in the ratio of the PI contents. E' and tan δ show differences in the PI contents, which increase the physical properties. In Figure 7(a), below 50 °C,
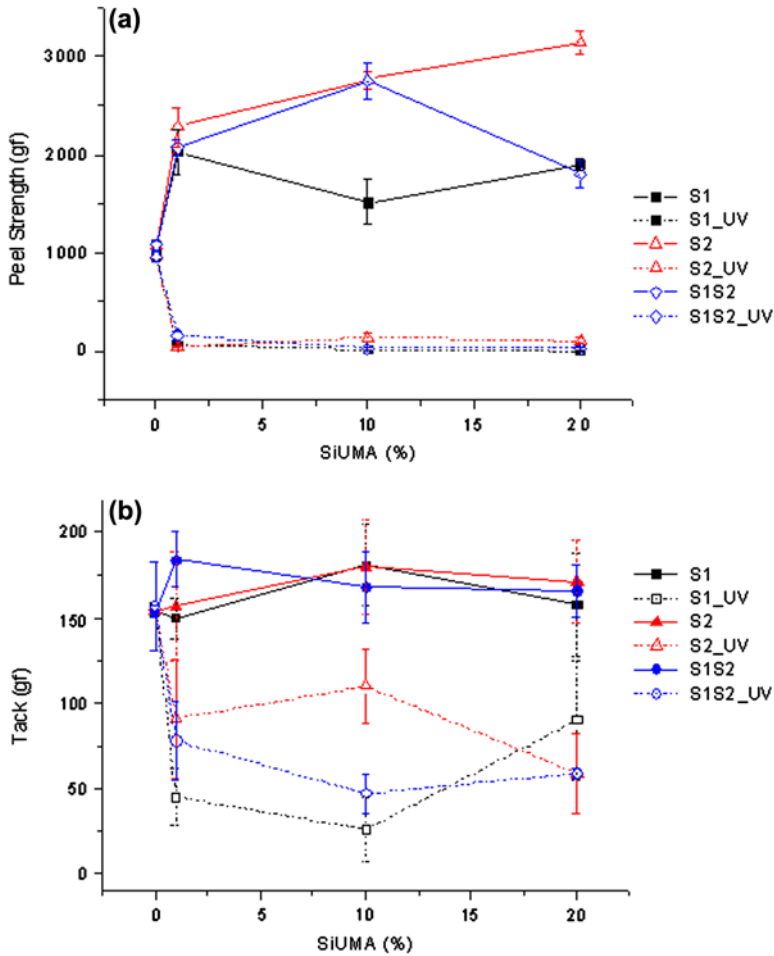
Figure 5. UV curing effects on (a) the peel strength with different SiUMA amounts (b) the tack with different SiUMA amounts.

E' is nearly identical; but over 50°C, E' is separated into three groups which use 5.0 phr as the highest value. This means that 5.0 phr PI may play a role in the creation of cross-linking. In Figure 7(b), after UV curing, E' increases with all PI concentrations with seemingly similar values. In Figure 7(c) and (d), tan D shows several peaks for which the acrylic PSA with semi-IPN has many T_gs. An examination of acrylic PSA with semi-IPN must consider compatibility and interaction with other polymers. In this study, through cross-linking, several peaks are weaker than they were before UV irradiation. This is the evidence of reduced phase separation, whereas increased phase separation leads to increased elongation upon a break.[22]

3.8. *Thermogravimetric analysis (TGA)*

The thermal stability of acrylic PSA with the semi-IPN structure was measured by TGA at temperatures ranging from 25 to 600 °C. Figure 8 shows the weight loss curves and
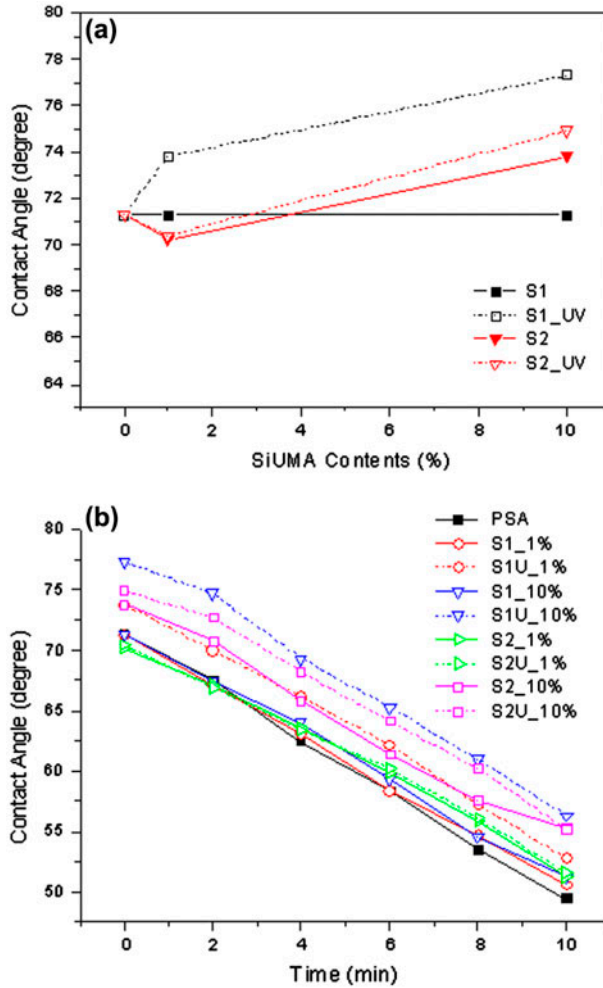
Figure 6. UV curing effect on (a) the contact angle with the S1 and S2 concentrations (b) the contact angle with S1 and the S2 time and concentrations.

the derivative of the weight profiles of each sample. Table 2 lists the characteristic thermal decomposition temperatures; the temperature of the initial 10% mass loss ($T10\%$), the temperature of the 50% mass loss ($T50\%$), and the weight percent at 480 °C (the decomposition temperature for S1). The PSA-S1 mixtures undergo depolymerization faster than acrylic PSA under 407 °C, where S1 reacts with the plasticizer in the acrylic PSA, reducing the interaction with the polymer hydrogen bond. Therefore, a higher S1 content shows a lower degradation temperature. Moreover, the thermal degradation mechanism of polyurethane is known. The urethane groups first undergo depolymerization to the individual monomers, which then react further to produce carbon dioxide. There are two stages in the thermal degradation of polyurethane. The first and second stages are due to the degradation of the hard and soft segments of the polyurethane linkages.[23,24] Over 407 °C, the soft segment becomes degraded and shows better thermal stability than acrylic PSA. The maximum decomposition of S1 occurs at approximately 480 °C.
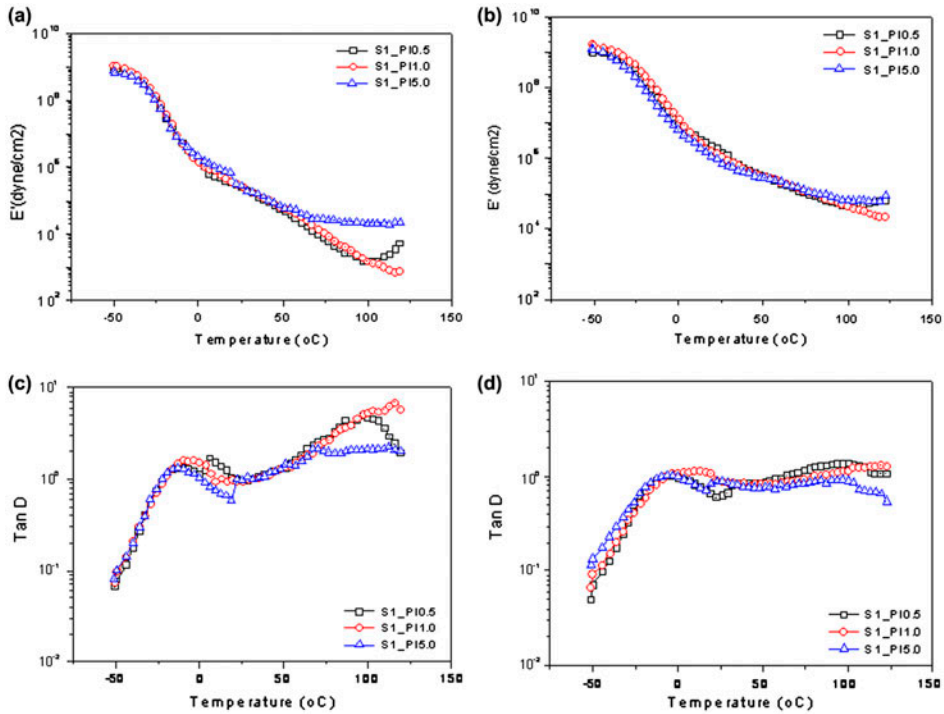
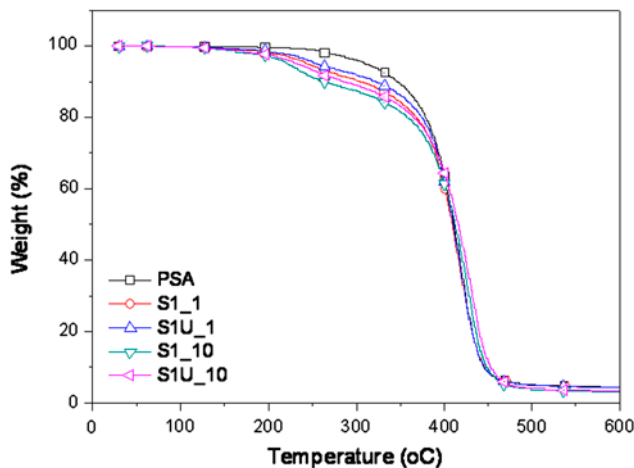Figure 7.   Viscoelastic characteristics of acrylic PSA.

Figure 8.   TGA curves with UV the curing effect on the S1 contents.

3.9.   *Shear adhesion failure temperature (SAFT)*

The thermal stability of acrylic PSAs is supported by SAFT. When the cohesion becomes weak under a constant force with an increase in the temperature, it shows a certain temperature at which the acrylic PSA is supported. In this study, the SAFT values of S1 and S2 were measured up to 200 °C. In Figure 9, except S1 and S2 UV cured

Table 2.   Thermal decomposition data of S1 and S2.

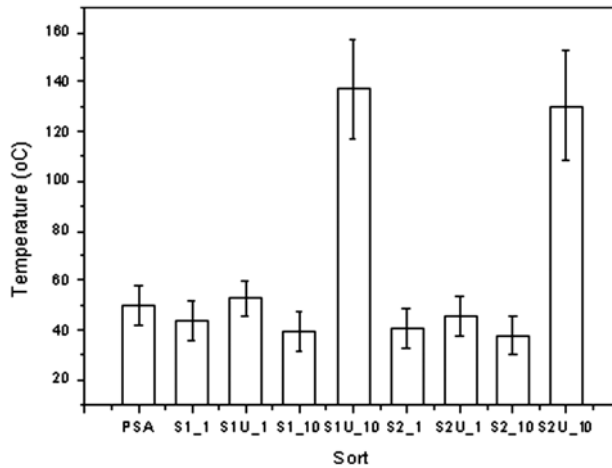| Samples	Weight loss		
	*T*10% (°C)	*T*50% (°C)	Wt.% at 480 °C
PSA	346	411	5.47
S_1	304	409	5.33
SU_1	322	410	5.33
S-10	262	412	4.26
SU_10	286	415	4.52

Figure 9.   SAFT comparison with the S1 content.

at 10%, all of them dropped to less than 50 °C. However, S1 and S2 showed good resistance to high temperature shear force. The main reason is the semi-IPN structures
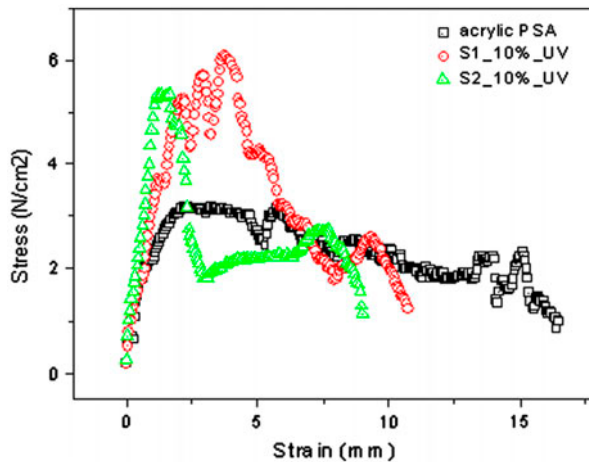

Figure 10.   Tensile behaviors of UV cured S1.

formed in the acrylic PSA, which were reinforced by the chemical bonding of the cross-linking, leading to increased thermal resistance. The results from Figure 10 show that the cross-linking of the main chain has a greater effect on SAFT than does the semi-IPN.[25]

3.10. Tensile strength

Figure 10 shows a comparison of the effects of the S1, and S2 content under UV curing behavior with acrylic PSA, which shows tensile strength and elongation upon breakage. In this experiment, the acrylic PSA indicated weak shear force that was less than S1 and S2 at 10% after UV curing. However, S1 and S2 at 10% after UV curing also do not have sufficient shear force, as acrylic PSA is 320 gf/cm^2, S1 is 610 gf/cm^2, and S2 is 540 gf/cm^2. This is the evidence which takes into consideration the fact that the samples were held in heating chamber and loaded at 1000 gf/cm^2.

4. Conclusion

In this work, SiUMA was synthesized and characterized as UV curing materials. The curing conditions of the UV intensity are photoinitiator content and chain length. The structures of the synthetic materials were characterized by H-NMR, FT-IR, and GPC. The disappearance of the band at 2250 cm^{-1}, which is assigned to the isocyanate group, signified the completion of the reaction. The reactivity of SiUMA was determined by photo-DSC measurements. The adhesion property demonstrated the state of the surface after UV curing facilitated the checking of the cross-linking effect. ARES shows that E' and tan D are indicative of the thermal properties; tan D results showed that acrylic PSA is not compatible with SiUMA due to the many T_gs. Through TGA, the thermal property of less than 407 °C is weaker than that of acrylic PSA because the SiUMA acts as a plasticizer in acrylic PSA. Over 407 °C, silicone enforces the thermal property to overcome the acrylic PSA. SAFT shows the resistance of the shear force under comparatively high temperatures, though the tensile strength data supporting the mechanical strength is not the only reason for this. With the formed semi-IPN structure in acrylic PSA, it is possible to prepare thermally stable acrylic PSA.

References

[1] Houwink R, Salomon G. Adhesion and adhesives. Vol. 1. Amsterdam: Elsevier; 1967. 32.
[2] Czech Z, Pelech R. The thermal degradation of butyl acrylate-methyl acrylate-acrylic acid-copolymers. J. Therm. Anal. Calorim. 2009;96:583–586.
[3] Kang DH, Lee BC. Preparation and characteristics of silicone modified polyacrylic hybrid elastomer. Polymer(Korea). 2007;31:86–91.
[4] Voronkvov MG, Mileshkevich VP, Yuzhelevskii YA. The siloxane bond. New York: Consultants Bureau; 1978. p. 102.
[5] Chattopadhyay DK, Raju KVSN. Structural engineering of polyurethane coatings for high performance applications. Prog. Polym. Sci. 2007;32:352–418.
[6] Pappas SP. UV curing: science and technology. Vol. 2. Norwalk (CT): Technology Marketing Corporation; 1978. p. 24–77.

[7] Glockner P. Radiation curing: coatings and printing inks. Hannover: Vincentz Network; 2008. p. 78.

[8] Drumheller PD, Hubbell JA. Polymer networks with grafted cell adhesion peptides for highly biospecific cell adhesive substrates. Anal. Biochem. 1994;222:380–388.

[9] Sperling LH. Interpenetrating polymer networks: an overview. Washington, DC: American Chemical Society; 1994. Chapter 1; p. 3–38.

[10] McNaught AD, Wilkinson A. IUPAC compendium of chemical terminology. 2nd ed. Oxford: Blackwell Science; 1996. p. 2305.

[11] Ma W, Yang C, Gong X, Lee K, Heeger AJ. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. Adv. Funct. Mater. 2005;15:1617–1622.

[12] Zeigler JM, Fearon FW. Silicon-based polymer science, Washington, DC: American Chemical Society; 1990. p. 56–72.

[13] Gilmer TC, Hall PK, Ehernfeld H, Wilson K, Biven T, Clay D, Endreszl C. Synthesis, characterization, and mechanical properties of PMMA/poly(aromatic/aliphatic siloxane) semi-interpenetrating polymer networks. J. Polym. Sci., A: Polym. Chem. 1996;34:1025–1037.

[14] Palanisamy A, Rao BS. Photo-DSC and dynamic mechanical studies on UV curable composites containing diacrylates of ricinoleic acid amide derived from castor oil. Prog. Org. Coat. 2007;60:161–169.

[15] Asif A, Shi W, Shen X, Nie K. Physical and thermal properties of UV curable waterborne polyurethane dispersions incorporating hyperbranched aliphatic polyester of varying generation number. Polymer. 2005;46:11066–11078.

[16] Nowers JR, Narasimhan B. The effect of interpenetrating polymer network formation on polymerization kinetics in an epoxy-acrylate system. Polymer. 2006;47:1108–1118.

[17] Castell P, Wouters M, Fischer H, de With G. Kinetic studies of a UV-curable powder coating using photo-DSC, real time FTIR and rheology. J. Coat. Technol. Res. 2007;4:411–423.

[18] Chiang WY, Shu WJ. Preparation and properties of UV-curable polydimethylsiloxane urethane acrylate. Die Angew. Makromol. Chem. 1988;160:41–66.

[19] Bae KY, Lim DH, Park JW, Kim HJ, Rafailovich M, Sokolov J. Adhesion performance and thermal stability of fluorinated PSAs as a crosslinking system. J. Adhes. Sci. Technol. 2012;26:361–379.

[20] Donates S. Handbook of Pressure-Sensitive Adhesive Technology. New York: Satas & Associates; 1982.

[21] Lim DH, Do HS, Kim HJ. PSA performances and viscoelastic properties of SIS-based PSA blends with H-DCPD tackifiers. J. Appl. Polym. Sci. 2006;102:2839–2846.

[22] Lee KH, Kim BK. Structure-property relationships of polyurethane anionomer acrylates. Polymer 1996;37:2251–2257.

[23] Lin YH, Liao KH, Chou NK, Wang SS, Chu SH, Hsieh KH. UV-curable low-surface-energy fluorinated poly(urethane acrylate)s for biomedical applications. Eur. Polym. J. 2008;44:2927–2937.

[24] Ge Z, Zhang X, Dai J, Li W, Luo Y. Synthesis, characterization and properties of a novel fluorinated polyurethane. Eur. Polym. J. 2009;45:530–536.

[25] Joo HS, Do HS, Park YJ, Kim HJ. Adhesion performance of UV-cured semi-IPN structure acrylic pressure sensitive adhesives. J. Adhes. Sci. Technol. 2006;20:1573–1594.