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A THESIS FOR THE DEGREE OF MASTER OF SCIENCE

**Synthesis and Characterization of thermally stable  
Acrylic PSA using Silicone Urethane Methacrylate of  
Semi-IPN Structure**

Semi-IPN 구조의 Silicone Urethane Methacrylate 를 활용한  
열적 안정성을 가진 아크릴 PSA 의 합성과 특성

by Pan-Seok Kim

PROGRAM IN ENVIRONMENTAL MATERIALS SCIENCE

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이 논문을 농학석사학위논문으로 제출함

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# Abstract

## Synthesis and Characterization of thermally stable Acrylic PSA using Silicone Urethane Methacrylate of Semi-IPN Structure

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Program in Environmental Materials Science

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To improve the thermal stability, polydimethylsiloxane (PDMS) is used and UV curing method employed. Silicone Urethane Methacrylate (SiUMA) was synthesized and introduced into acrylic Pressure Sensitive Adhesives (Acrylic PSA) as Semi-Interpenetrating Polymer Networks (IPN) structure. Through FT-IR the structure was defined. The kinetics and behavior of SiUMA (S1) were found by adding the photoinitiator (PI) 0.5, 1.0, 5.0 and 10phr, which were examined using photo-DSC (photo-DSC). After determining the PI amount 5.0phr, 1000mJ/cm<sup>2</sup> UV intensity, added the SiUMA 20, 40, 60 and 80% to acrylic PSA which was prepared by radical polymerization and analyzed kinetic and behavior by photo-DSC, Real Time Infrared Spectroscopy (RTIR). Finally checking the peel strength shows the adhesion property. As increasing the amount of S1 and increasing the amount of PI, the reaction was greater. As increasing with the cross-linking, peel strength was dropped sharply which shows that surface change occurred. When it is applied to acrylic PSA by formed IPN

structure, it will be influenced to increase the peel strength before UV curing but peel strength decrease sharply after UV curing because of S1's mobility to the interface-air.

Next, Silicone urethane methacrylate (SiUMA) is applied to acrylic PSA using IPN structure with different chain length. Acrylic PSA was prepared by free radical polymerization and SiUMA was synthesized by additional polymerization by urethane linkage. Through urethane reaction, SiUMAs were prepared different length. Preparing of Synthetic Silicone Urethane Methacrylate formed Semi-IPN structure in the acrylic PSA, it can be verify thermal stability with the SAFT (Shear Adhesion Failure Temperature) using 1kg weights of plumb. Normally acrylic PSA easily be cleared from substrate prior to 50°C, but in case of containing S1 10%, it can resistant over 100°C. Photo-DSC shows that the 5phr photoinitiator (PI) and 1000mJ/cm<sup>2</sup> of UV intensity were available to complete curing reaction. Short and long chain 2type chain polymer structures were confirmed through FT-IR, GPC. And through measuring the TGA, it can be checked cross-linking effect and improvement of the thermal resistance using the silicone materials. By ARES, analyzed the thermal property changes and visco-elastic changes were detected. In this study, mobility of silicone is detected moving onto the interface-air. The result of the study provide an information to improve the thermally stability using SiUMA by Semi-IPN structure in acrylic PSA.

Keywords: Acrylic PSA, Semi-IPN, Silicone, Urethane acrylate, Photo-DSC, Real Time-IR,

Thermal Stability

**Student Number: 2010-21182**

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# **Chapter 1.**

Introduction,  
Literature Reviews  
and Objectives

## **1. Introduction**

### **1.1. Acrylic pressure sensitive adhesives**

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 (Houwink and Salomon, 1965). A pressure sensitive adhesives are not need driving force like water, solvent, light and heat. However, they are possible to attach to a variety of surfaces under the application of light pressure like “thumb pressure”. When detach the adhesives, they are not contaminating the substrate. Acrylic PSAs have several advantages including excellent aging characteristics, resistance to elevated temperatures and plasticizers, exceptional optical clarity due to polymer compatibility and non-yellowing, the highest balance of adhesion and cohesion and excellent water resistance(Czech and Pelech, 2009b). Commonly, acrylic PSAs often include 3-10wt.% acrylic acid and 90 – 97wt.% of alkyl soft acrylate composed of butyl acrylate, hexyl acrylate, 2-ethylhexyltyl acrylate, isooctyl acrylate or decyl acrylate. Copolymers containing butyl acrylate and acrylic acid are used for manufacture of acrylic PSAs with excellent adhesive performance(Czech and Pelech, 2009a).

Acrylic PSAs show semi-solid state is 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 when brought into contact under very light pressure. It is not a basic property of the adhesive, but a composite response of the adhesive’s bulk and surface properties. Peel force is regarded as the resistance of pressure sensitive adhesives to peel, which depends on many different factors: the test conditions, backing properties, interfacial conditions and others. The pressure sensitive adhesives must exhibit an elastic cohesiveness and a resistance to flow under stress. It is resistance to flow that is commonly associated with creep or resistance to creep(Satas, 1999).

Acrylic PSAs are cross-linked only by physical cross-linking, van der Waals forces or hydrogen bonds, thus, they exhibit limited mechanical and thermal properties(Czech,

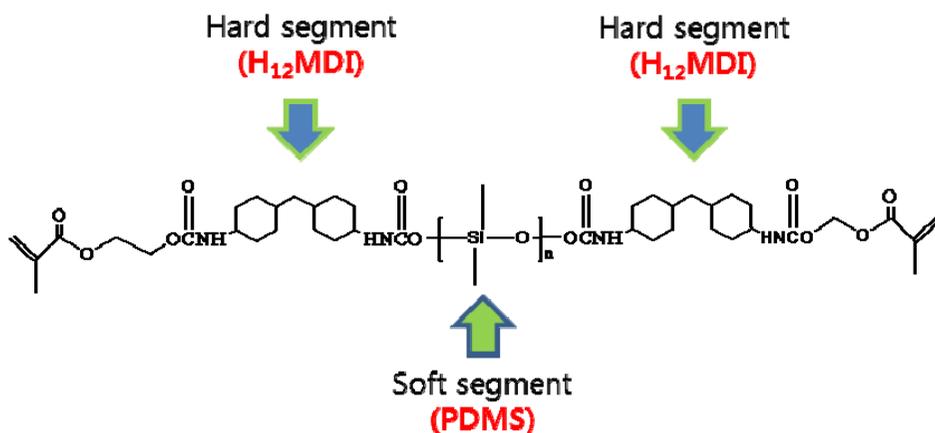
2003). Therefore it needs to induce the chemical crosslink, which will be controlled various crosslink agent or oligomer. Through this study, the effect of silicone urethane methacrylate is checked as di-functional oligomer

## **1.2. Silicone urethane methacrylate (SiUMA)**

The common and widely used siloxane polymers (so called in industry as silicone) are principally based on poly(dimethylsiloxane) (PDMS). Polyorganosiloxane consist of Si-O bond, which shows flexibility of chain, chemical resistance, corrosion resistance, water resistance and thermal, oxidative stability. Though it has many merits, still has weak point like high price and low adhesion to porous surface(Lee and Kang, 2007). The interesting and useful properties of siloxane polymers are a result of somewhat unusual molecular structure of the polymer chains that consist of alternating silicone and oxygen atoms(Voronkov *et al.*, 1978).

The repeating unit is characterized by very low molecular forces, ease of rotation and the relatively long Si-O bond length. These polymer molecules with unusual high flexibility and the ability to display properties that are fairly constant over a wide temperature range. Moreover, as a result of low intermolecular forces and flexibility, siloxane polymers possess a very low glass-transition temperature ( $T_g = -123^\circ\text{C}$ ).

Polyurethane(PU) is the chemistry involved in isocyanate reactions with macrodiol, diisocyanate and chain extender (CE). Today, PU coatings can be found on many different appearance and lifespan like construction, building floors, steel trusses and concrete supports(Chattopadhyay and Raju, 2007).



Scheme 1-1. silicone urethane methacrylate.(SiUMA)

Scheme 1-1 shows one example for SiUMA. PDMS polyurethane resins are likely to be highly separated because of the large differences in the soft and hard segment solubility parameters as well as the lack of hydrogen bonding between hard and soft segments (Chiang and Shu, 1988). Thermal properties depend on the type and nature of the hard segments, relative molecular weight, composition and/or ratio of the hard and soft segments.

Because of the siloxane segments within copolymers, thus tend to migrate to the air-polymer interface so as to form a hydrophobic surface (Gaines, 1981). The effect of migration will be expected to protect the surface of interface and give the thermal resistance.

### 1.3. UV curing

In PSAs industry, UV-curing technique represents a major advance in the development of the coating, adhesive and ink industries (Pappas, 1978). Not that is state-of-the-art but still UV curing induced currently represents about 90% of the radiation-curing market in Europe. UV curing is possible to change in other terms photoinitiated polymerization, photopolymerization or photocrosslinking (Gloeckner, 2008). Under intense illumination, reactive species such as free radicals or cations can be generated in high concentrations by photolysis of an initiator, and thus promote the

polymerization of monomers and oligomers. UV-curing formulations provide some benefits such as fast cure response, excellent chemical resistance, good weathering characteristics, and broad formulating latitude. Low VOCs are certainly the most talked about aspect of UV-curing but product performance and cost effectiveness are equally important features that lead to the decision to use UV. The energy content of a photon is defined by the equation (e.q-1).

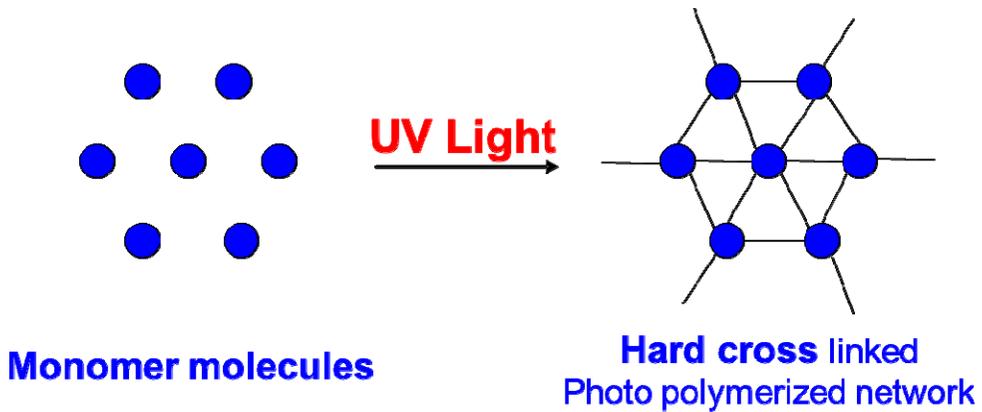
$$E = h\nu = \frac{hc}{\lambda} \text{-----(e.q-1)}$$

where  $\nu$  is the frequency and  $\lambda$  is the wavelength (nm). This equation informs that the shorter wavelength of photon reveals the higher energy. UV light in the wavelength region of 300-400 nm should already be able to cleave C-C bonds. The high energy photons of e-beam and X-ray are enough to cleave C-C or C-H bond, therefore, they do not need a photoinitiator for forming the expected radical species as initiators for polymerization. In the case of UV exposure, photoinitiators are commonly used because the direct splitting processes are not efficient (Schwalm, 2006).

Photoinitiator undergoes chemical modification leading to the formation of active species which initiate the curing process by UV radiation absorbance. Relying on the polymerization mechanism, UV-curing can be divided into two major classes; free radical UV-curing, cationic UV-curing. Each of these mechanisms displays separate benefits and limitations, so both are competitive but complementary. The rapidity of free-radical UV curing is one major advantage responsible for the constant growth of this technology: curing proceeds within a fraction of a second. This fast transformation from a liquid phase to a solid state allows increasing productivity on a production line while maintaining energy cost at a low level. Cationic UV curing involves the photo-generation of cations – usually strong Bronsted or Lewis acids – which are capable of initiating a cationic polymerization. Major advantages of cationic UV curing over a free – radical process are the insensitivity of the reaction towards oxygen inhibition

and a lower shrinkage due to the ring-opening polymerization step. Main applications for this technology can be found in printing inks, overprint varnishes and composites, requiring either high production rates under air or specific mechanical properties.

The composition of free radical or cationic UV-curable formulations varies both in character of the monomers, oligomers and photoinitiators. These formulations basically include the following components like Scheme 1-2 (Gloeckner, 2008).



Scheme 1-2. UV curing mechanism.

#### 1.4. Semi-Interpenetrating Polymer Network

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 the distinct networks. They can be synthesized by crosslinking polymerization of two multifunctional monomers or telechelic oligomers that polymerized by different mechanisms, e.g. radical and cationic polymerization (Drumheller and Hubbell, 1994; Sperling, 1981).

Semi-interpenetrating polymer network (Semi-IPN) is comprised one or more polymer networks and one or more linear polymers penetrated on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules (IUPAC, 1997) as shown in Figure 1-1.

Through interpenetrating network, thermally stability induction reported (Ma *et al.*, 2005). Cross-linked silicone polymers have many advantages, including flexibility, low surface tension, low dielectricity, ultraviolet resistance, non-flammability, as well as high thermal and chemical stability. Although some of IPNs based on cross-linked polysiloxanes have been reported in the literature (Zeigler *et al.*, 1990; He *et al.*, 1989; Gilmer *et al.*, 1996) and yet the cross-linked silicone network through self-condensation of the reactive methoxysilane groups ( $\equiv\text{Si}-\text{OCH}_3$ ), has been seldom studied. In this study, an SiUMA based on acrylic PSA with semi-IPN is synthesized in which linear Acrylic and silicone urethane methacrylate network treated as the guest and host polymers, respectively. It is shown that the mixture of linear acrylic PSA with the silicone urethane methacrylate formed a homogeneous blend by several ratio of the two components before the UV cross-linking;

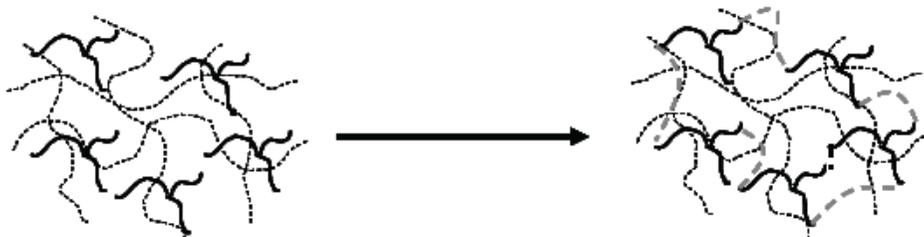


Figure 1-1. Semi-IPNs schematic diagrams (Joo *et al.*, 2006)



## 2.2. UV curing

The UV-induced cross-linking of a pressure sensitive adhesive based on an acrylic resin with copolymerized benzophenone groups was studied by real-time FTIR-ATR spectroscopy in order to simulate technical curing processes. The dependence of the conversion on the applied UV dose was investigated by irradiation with single or multiple UV pulses and with variable light intensities, (Figure 1-2) (Scherzer *et al.*, 2002).

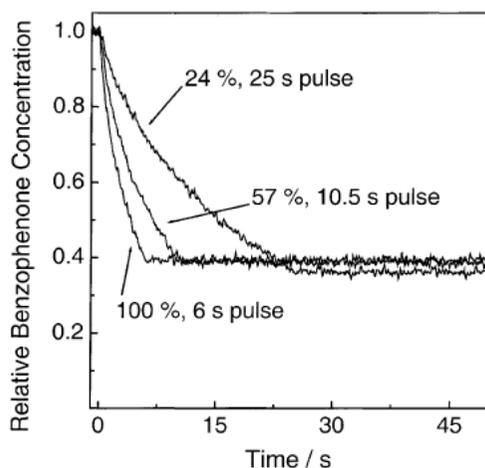


Figure 1-2. Irradiation of the adhesive with constant UV dose by exposure to single pulses of different duration and with different intensities.

FTIR-ATR spectroscopy is possible to inspect a quantitative depth profiling. For the depth of penetration of the infrared radiation from the ATR crystal into the sample conversion is able to analyze in a very thin layer about 1 mm at the bottom of the UV-irradiated coating.

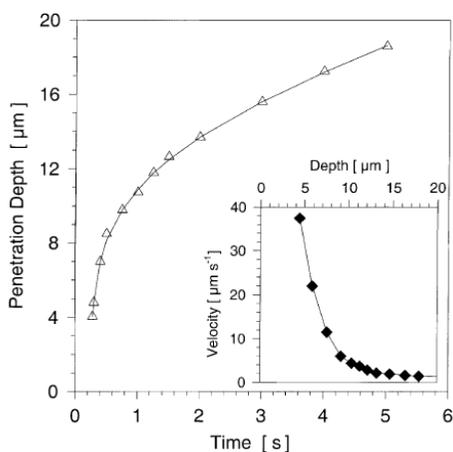


Figure 1-3. Penetration of the polymerization front into TPGDA 5 wt%

Real-time FTIR-attenuated total reflection spectroscopy was used to investigate the depth profile of the conversion during the photo-polymerization of acrylate coatings. Layers of different but well-defined thickness were deposited on the ATR crystal and irradiated by UV light, (Figure 1-3) (Scherzer, 2002).

### 2.3. Semi-Interpenetrating Polymer Networks

After UV exposure, the remaining carbon double bonding contents of all sample are shown in Figures 1-4 and 1-5 (Joo *et al.*, 2007).

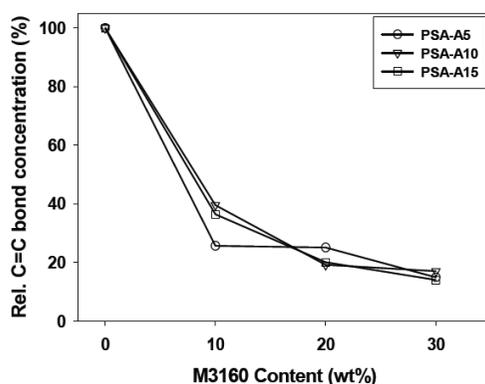


Figure 1-4. Change of relate concentration of c=c band of PSA blend with M3160

Cross-linked multifunctional acrylate produce semi-interpenetrating polymer networks (Semi-IPNs). The semi-IPN structure gives PSAs the advantages, such as improved heat resistance as well as creep resistance (Sosson *et al.*, 2005).

poly(ethylene glycol) diacrylate much faster than di-, tri-, and tetraethylene glycol diacrylates and achieve almost complete conversion because higher chain length of the monomers increased the diffusivity of the unreacted C=C bonds during the final stage of the polymerization reaction. The enhanced molecular mobility favors a higher conversion (Kristi *et al.*, 1995).

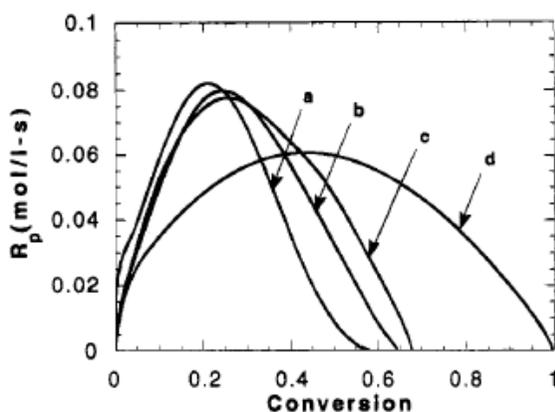


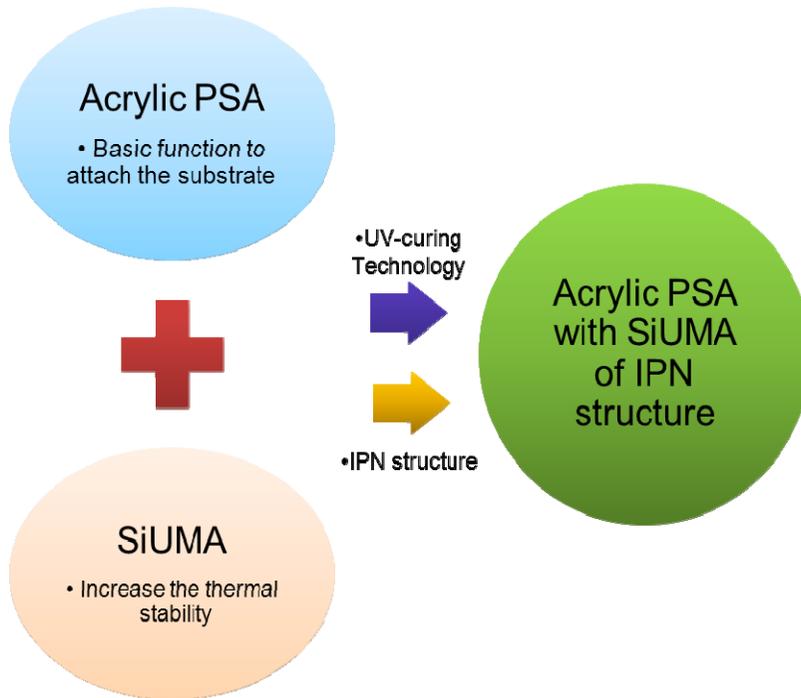
Figure 1-5. Rate of polymerization as a function of conversion for (a)DEGDMA, (b)TrEGDMA, (c)PEG200DMA, and (d)PEG600DMA. Photo-polymerizations were initiated with 0.1 wt% DMPA and  $I_0 = 0.8 \text{ mW/cm}^2$

### 3. Objectives

#### 3.1 Synthesis and characterization of thermally stable acrylic PSA using SiUMA of IPN structure

Normally acrylic PSAs have several advantages including excellent aging characteristics, resistance to elevated temperatures and plasticizers, exceptional optical clarity due to polymer compatibility and non-yellowing, the highest balance of adhesion and cohesion and excellent water resistance (Czech and Pelech, 2009a). But acrylic PSAs is weak about thermal properties, thus is need to make cross-linking or to increase the molecular weight to improve its properties. For making networks, to add

multifunctional monomer or oligomer is comparatively effective way. Silicone urethane methacrylate is used as multifunctional oligomer, to make networks by increasing cohesive in acrylic PSAs.



Scheme 1-4. Semi-IPNs concept diagrams

It is expected to improve thermal property by using silicone and dicyclohexylmethane-4,4-diisocyanate which are known as thermally stable materials. Through the study, acrylic PSAs are easily modified by silicone additives to prove the thermal stable effect like masking tape. Small amount additive is enough, thus it is expected to have like cost reduction, cost competitiveness. Moreover we can use the same production line for using UV, it is very helpful various side. Scheme 1-4 shows the total experimental concept.

### **3.2 Chain length Effect on SiUMA in Acrylic PSA achieved by IPN structure**

When semi-IPN structure is formed with SiUMA in acrylic PSA, the chain length influence to physical, chemical properties, because long chain change its glass transition temperature, crystalline temperature and rheological properties. Through this experiment, when the chain length is increased 2 times, the properties like thermal stability, peel strength, probe tack, surface condition and rheology show the differences with short chain.



## **Chapter 2.**

Kinetic and Characterization of UV-curable  
Silicone Urethane Methacrylate of  
Semi-IPN Structure in Acrylic PSA

## 1. Introduction

The UV or EV polymerization of multifunctional acrylate monomers provides an excellent method for the rapid conversion at room temperature into cross-linked polymer networks. This photo-technology provide various industry like thin film applications mainly in the coating and printing industry(Decker, 2002). The UV curing or polymerization have many advantages which is solvent free formulation, low energy consumption, and ambient temperature operation. Acrylates are very high reactive and the transformation from a liquid resin to a solid polymer exposed to light is extremely fast. This characteristic makes them very good materials for different applications(Schmidt *et al.*, 2008; Decker, 1998). Polydimethylsiloxanes (PDMSs) was well-known peculiar characteristics such as very high thermal and chemical resistance, high flexibility and hydrophobicity, stability against different types of radiation. Polysiloxanes with different organofunctional substituents were synthesized and used as starting compounds in the preparation of polymeric materials with interesting properties and applications(Harabagiu *et al.*, 1996; Simionescu *et al.*, 1996). PDMSs containing acrylic and methacrylic ester groups, linked to the siloxane chain as pendant units through aliphatic ether moieties, have been previously researched(Muller *et al.*, 1991; Muller, 1996). Until now, silicone acrylate have studied and developed for coating materials but not for adhesive materials. If silicone urethane methacrylate is induced in acrylic PSA, it is possible to make various products which emerged the characteristics of PDMS. Pressure sensitive adhesives (PSAs) are semi-solid phase materials with good visco-elastic properties and adhesion strength on solid substrates after applying a light contact pressure with a short contact time. In general, PSAs are required various physical properties under product's characteristics in a range of fields, which includes medical products, electronic devices, and the construction and automobile industries(Satas, 1999). They need to be controlled by the molecular weight, structures and side chains. The purpose of this article is to synthesize and induced an environmental friendly materials through formed Semi-IPN structure in acrylic PSA. An interpenetrating polymer network (IPN) is consists of an intimate

combination of two or more polymers in the form of networks. However, this is not chemical linkage between the distinct networks. They can be synthesized by cross-linking polymerization of two multifunctional monomers or telechelic oligomers that polymerized by different mechanisms, e.g. radical and cationic polymerization(Sperling, 1981). Homogeneous IPNs can be synthesized by means of UV curing technology(Dean and Cook, 2002). Moreover, high polymerization rates can be easily reached at room temperature under high light intensities which reduces the phase separation and improves the final properties(Lecamp *et al.*, 2005). IPNs provides the advantage to be solvent free and thus respect the environment (Lecamp *et al.*, 2005; Sangermano *et al.*, 2008). The reaction kinetics during IPN formation plays an important role in the final properties of the IPN. Reaction rates are affected by catalyst concentration, viscosity, reaction sequence and concentrations. The morphology, phase separation, and composition are determined by the reaction kinetics and chemical compatibility. Thus, understanding the reaction kinetics becomes important to engineer final material properties(Nowers and Narasimhan, 2006). In this study, The structure of SiUMA was characterized by FT-IR. UV-curing behavior of SiUMA in acrylic PSA was studied by photo-DSC, Real time infrared spectroscopy (RT-IR). The physical property of PSA was investigated through Texture Analyzer. The UV reactivity and physical properties of the cured films, through different concentration of photoinitiator, were also studied.

## 2. Experimental

### 2.1 Materials

The 2-Ethylhexylacrylate(2EHA), Acrylic Acid (AA) were purchased from Samchun Pure Chemical Co., Ltd. (Republic of Korea). 2,2-azobisisobutyronitrile (AIBN) was used as initiator from Daejung Chemicals & Metals Co. (Republic of Korea) for synthesizing acrylic PSAs. Polydimethylsiloxane (PDMS, Shin-Etsu co., Ltd), Dicyclohexylmethane-4,4'-diisocyanate (H12MDI, Bayer Material Science) were dried in 100°C 12 h prior to use and 2-hydroxyethylmethacrylate (2-HEMA, Samchun Pure Chemical Co., Ltd., Republic of Korea) was used without pretreatment. Hydroxy dimethyl acetophenone (Micure HP-8, Miwon specialty chemical Co., Ltd, Republic of Korea) was used as the photo-initiator for the UV-polymerization of acrylic PSAs. Dibutyltin dilaurate are added to allow the reaction to take place at a rapid rate as a catalyst in urethane reaction.

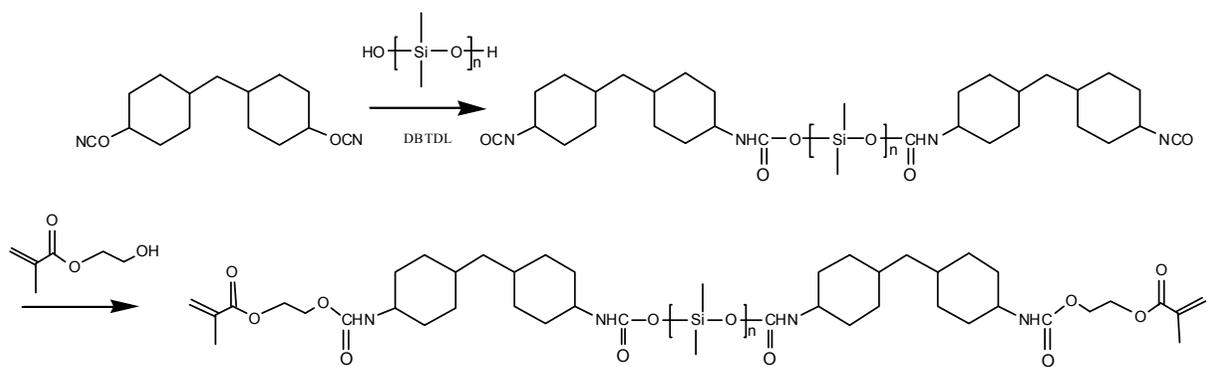
## 2.2 Method

### 2.2.1. Synthesis of Basic Acrylic Pressure Sensitive Adhesives (Acrylic PSA)

The acrylic pressure sensitive adhesive was synthesized from 2-EHA, AA in ethyl acetate solvent about 50% solid contents. The polymerization was performed in a 500 ml, four-necked, round bottom flask equipped with a thermo-coupler, condenser, dropping funnel equipped and mechanical stirrer. The monomer resin with 0.05wt% AIBN was heated up to 80°C in about an hour, afterwards, the reaction mixture was kept at 80°C until solvent polymerization finished for 3 hours and more added 0.05% AIBN three 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 (DBTDL) dropwise to H<sub>12</sub>MDI (i.e., NCO:OH = 2: 1) under a nitrogen gas. The reaction was maintained at room temperature with heater. Two hours later when the absorption peak 2250 cm<sup>-1</sup> of NCO group in infrared (IR) spectra had been stayed same state, then the temperature was maintained at room temperature until NCO band stayed. An equimolar amount of HEMA with 0.5 wt% hydroquinone as a thermal polymerization inhibitor was added a dropwise to the PDMS- H<sub>12</sub>MDI adduct. 5hours later, NCO group were disappeared completely. The temperature was kept below 60°C to remove a non-reactive site. At this time the absorption peak of the NCO group at 2250 cm<sup>-1</sup> had disappeared completely.



scheme 2-1. Synthesis of silicone urethane methacrylate

## 2.3 Measurements

### 2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The IR spectra were obtained on a JASCO FTIR-6100 (Japan) spectrometer equipped with attenuated total reference (ATR) accessories. The spectra were recorded for 20 scans with a  $4\text{ cm}^{-1}$  resolution over the wavelength range, 650 to  $4000\text{ cm}^{-1}$ . The absorbance decreases in different range. They were analyzed about double carbon, siloxane and carbonyl bond etc. All the results were confirmed by revising the level of  $\text{CO}_2$  reduction,  $\text{H}_2\text{O}$  reduction, noise elimination, smoothing and baseline correction.

### 2.3.2 Photo-Differential Scanning Calorimetry (photo-DSC)

Photo-DSC experiments were conducted using a TA Instruments Q-200 DSC equipped with a photo-calorimetric accessory (Omniscure 2000), which used light from a 100 W middle-pressure mercury lamp. Light intensity was determined by placing an empty DSC pan on the sample cell. UV light intensity at the sample was  $15\text{ mW/cm}^2$  over a wavelength range of 300–545 nm. The weight of the sample was about 8 mg and the sample was placed in an open aluminum DSC pan. Measurements were carried out at room temperature.

### 2.3.3 Real-time Fourier Transform infrared (RT-IR) spectroscopy

The effect of photo-polymerization kinetics was monitored by RT-FTIR (FTIR-6100, Jasco, Japan) equipped with an attenuated total reference (ATR) accessory and liquid nitrogen. Photo-polymerization were carried out at room temperature. The light intensity on the surface of the samples was  $7.4\text{ mW/cm}^2$ . Rapid scan mode was used for 300 seconds. UV spot curing equipment (SP-9-250UB, USINO INC. System Company, Japan) was used as the light source. The infrared spectra were collected at a rate of the 1 spectrum per second. During irradiation, the changes in the IR band for the Si-O, Si- $\text{CH}_3$ , C-O bond ( $1050$ ,  $1100$ ,  $1250$ ,  $1150\text{ cm}^{-1}$ ) because of the acrylate functional group can't be detected overlap from other peak.

#### 2.3.4 Adhesion Properties (Peel Strength)

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 sample was left to stand at room temperature for 24 hours. The peeling speed was 300 mm/min, and the average strength of peeling period was measured 5 times. 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 sample was left to stand at room temperature for 24 hours. The peeling speed was 300 mm/min, and the average strength of peeling period was measured 5 times.

### 3. Result and Discussion

#### 3.1 Silicone urethane methacrylate

##### FT-IR

Figure 2-1(a) shows the FTIR spectrum of HMDI. The bands at  $2248\text{ cm}^{-1}$  was due to NCO group. The disappearance of the band is assigned to the indicative of the completion of the reaction in (a) to (C). Figure 2-1(b) shows the characteristic band of PDMS, where the bands at  $1015$ ,  $1074\text{ cm}^{-1}$  were assigned to Si-O-Si stretching vibration, and  $791\text{ cm}^{-1}$  stretching vibration is characteristic of S-CH<sub>3</sub>,  $2248\text{ cm}^{-1}$  was isocyanate group which means urethane reaction, more disappeared than Figure 2-1(a) and (c) were associated with the band of the acrylic double bond at  $810$ ,  $1638\text{ cm}^{-1}$  but which are too weak intensity, so  $1720\text{ cm}^{-1}$ (C=O) stretching vibration shows HEMA induced in SiUMA indirectly.

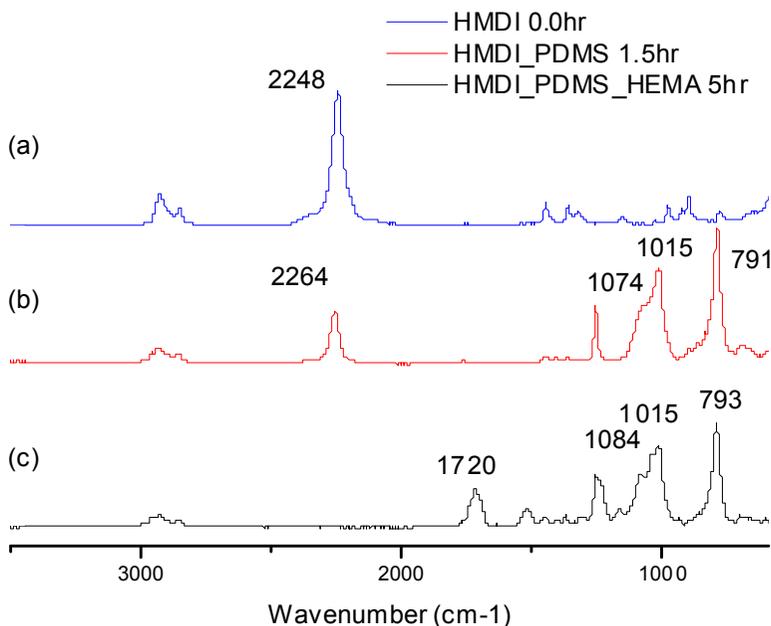


Figure 2-1. FTIR spectra of (a) HMD3, (b) addition of PDMS, and (c) addition of HEMA.

## 3.2 UV-curing kinetics

### 3.2.1. Photo-DSC (photo-DSC)

#### **Effect of Photoinitiator (PI)**

The S1 reaction was studied by the blends S1 with photoinitiator with different amounts of PIs. These reactions were carried out with 0.5, 1.0, 5.0 and 10 phr at room temperature. Through this experiment, it was determined how much UV intensity needed. Figure 2-2 gets the values of the enthalpies measured in isothermal curing conditions at room temperature during 300 sec for the Benzophenone as the photoinitiator (PI) at different contents. From figure 2-2 we can observe that differences in the evolved enthalpy are observed for the different contents studied. They increased the higher conversion and also explain the higher rate as the PIs concentration increases in the range studied. When over the 5phr of the PIs, no significantly differences were observed. So less or more about the 5phr of the PI is the proper concentration to be used and  $1000 \text{ mJ/cm}^2$  is enough UV intensity.

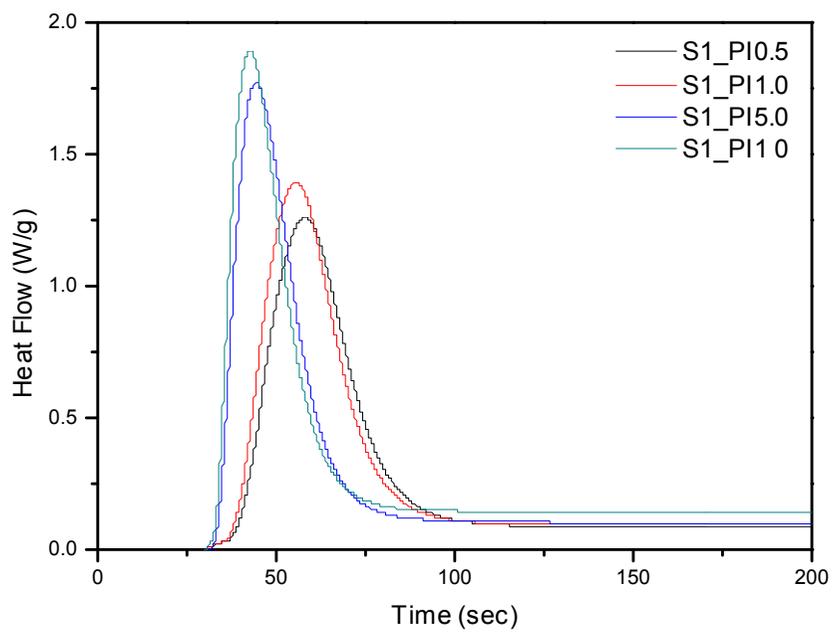


Figure 2-2. S1 reaction heat flow profiles.

### **Effect of PI's concentrations in acrylic PSA**

The PSA\_S1 reaction was studied by the blends of acrylic PSA(80%), S1(20%) and PI with different amounts. From Figure 2-3, these reactions were carried out with 0.5, 1.0, 5.0 and 10 phr at room temperature. The UV intensity was kept constant at 1000 mJ/cm<sup>2</sup>. All of the reactions were increased significantly compared with increasing amount of PI but showed to decrease dramatically when was over the 5phr of PI. Because of the high rate of recombination of radicals, the higher absorption of UV light of the initiator in the top layers and also as a result of some incompatibility of the PI with the rigid polymers. In other words, acrylic PSAs(Castell *et al.*, 2007) has a possibility to attribute to delay the blending PSAs. The reaction rate was slow due to dilution in the other monomer(Baidak *et al.*, 1997). Accordingly, it was need to calculate S1 ratio reactivity about 100% pure S1 and compared with PSA-S1 which showed the effect of the blending.

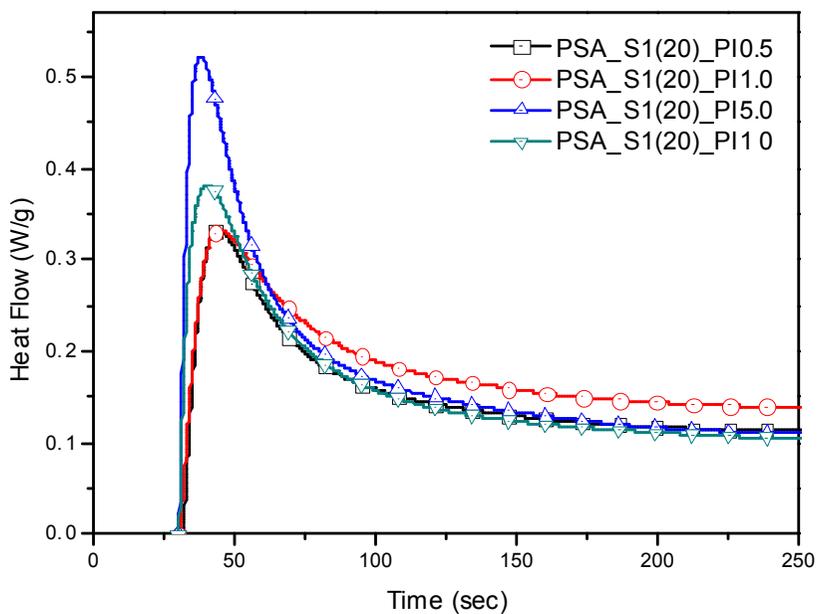


Figure 2-3. Isothermal cure at room temperature with different amounts of S1 in acrylic PSA

### **Effect of S1 concentration**

The PSA\_S1 mass fractions were studied by the blends of acrylic PSA, S1 and with different mass fraction. S1 Blends of 20, 40, 60 and 80% fraction were studied. These reactions were carried out PI 5.0%, 1000mJ/cm<sup>2</sup> UV intensity at room temperature. The reactions were increased significantly with increasing amount of S1. Figure 2-4 shows to increase S1 fraction, the enthalpy increased significantly. And increasing S1 mass fraction, the acceleration increases sharply, the deceleration increased sharply, but the decreasing S1 mass fraction, the acceleration is sharp but the deceleration is slight. This means that S1 fraction influence to acceleration but acrylic PSA influenced to deceleration. The mobility of the propagation of the S1 is reduced due to the acrylic PSA acrylate gel (Nowers and Narasimhan, 2006).

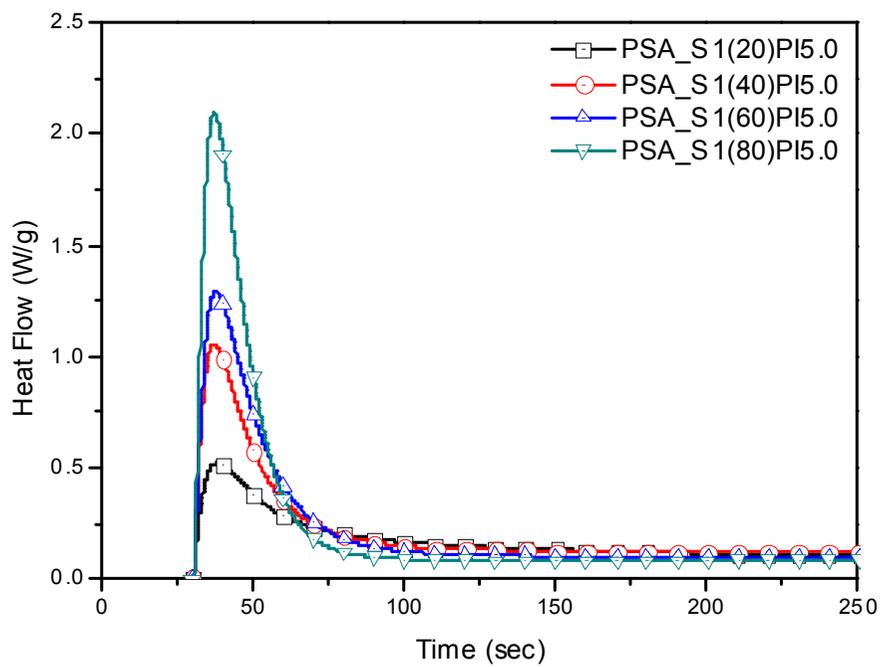


Figure 2-4. S1 different mass fraction with acrylic PSA

From Figure 2-5, Based on pure S1 as 1.0, theoretical enthalpy can be drawn from integral graph 0.2, 0.4, 0.6 and 0.8. After that, PSA:S1 = 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8 can be drawn from integral graph at the same time, then it is possible to analyze the effect of the blending acrylic PSA with S1. Each reaction increased about 20% more than theoretical values. The trends due to acrylic PSA provided by the space. The space allows S1 to move in acrylic PSA, and easy to match each other to complete reaction. And also acrylic PSA is consist of the 50% solvent which provided the mobility of S1.

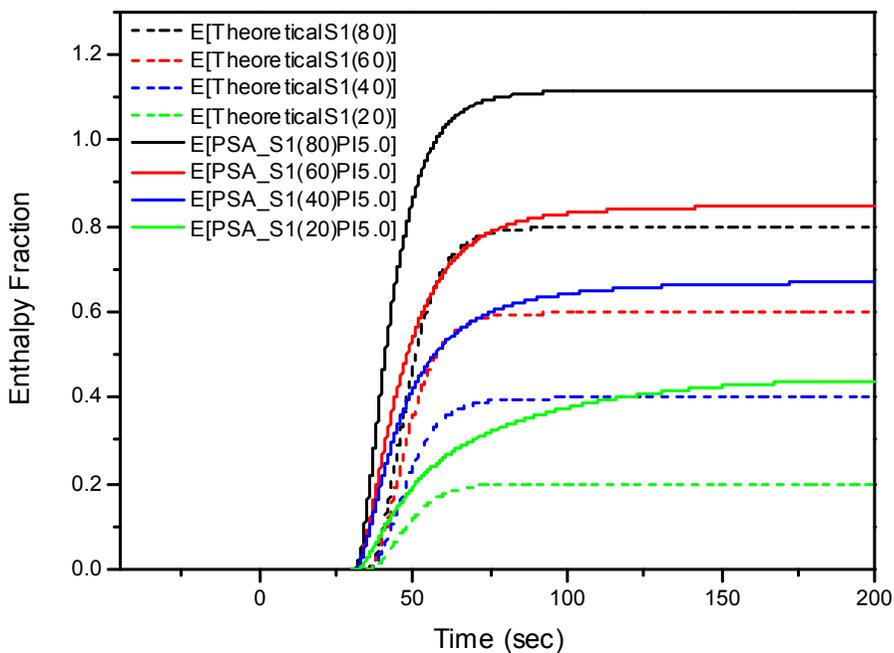


Figure 2-5. Comparison theoretical enthalpy fraction with enthalpy mixtures of PSA\_S1

### 3.2.2. Real Time Infrared Spectroscopy (RT-IR)

Figure 2-6(a), A measurement area is contacted with S1, but PI was too small amount used, there is no change of intensity in 1044, 1162, 1237  $\text{cm}^{-1}$  where the bands at 1044  $\text{cm}^{-1}$  were assigned to Si-O-Si stretching vibration, 1162 $\text{cm}^{-1}$  stretching vibration is characteristic of C-O band and 1237  $\text{cm}^{-1}$  is associated with Si-CH<sub>3</sub> band. Figure 2-6(b) There are changes of intensity in 1044, 1237  $\text{cm}^{-1}$  where the bands were assigned to Si-O, Si-CH<sub>3</sub> stretching vibration, decreased and 1162  $\text{cm}^{-1}$  is associated with C-O band which is increasing little. This means that S1 move to opposite direction to measurement area. Figure 2-6(c) is also changed little bit but almost same as (b). Figure 2-6(d) Is significantly changed. Accordingly RT-IR shows the S1 move to the interface with air(Gaines, 1981).

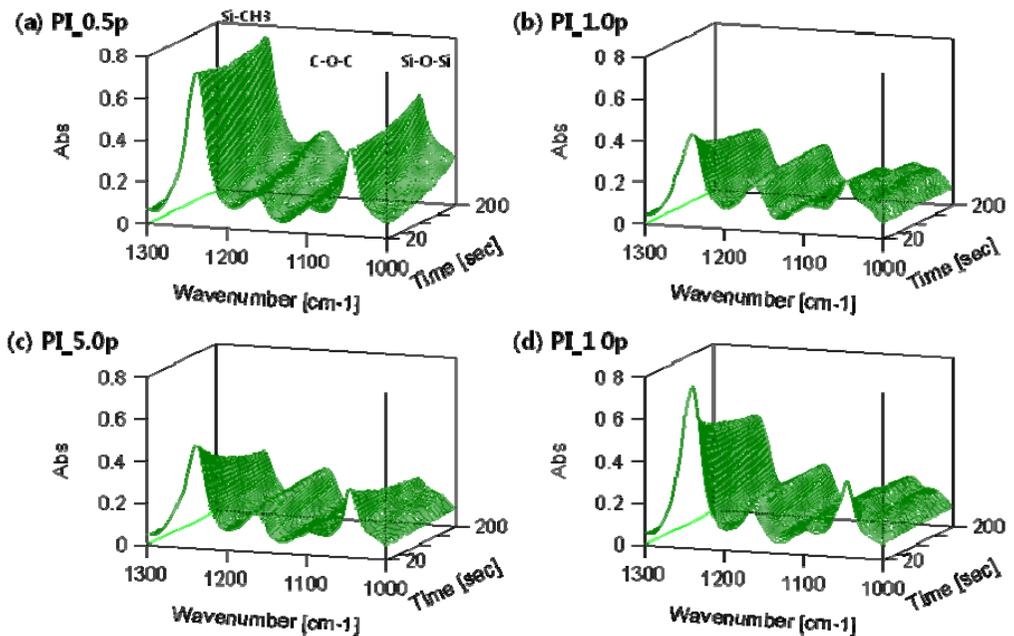


Figure 2-6. RT-IR spectra of (a) PI\_0.5phr (b)PI\_1.0phr (c)PI\_5.0phr (d)PI\_10phr

According to Figure 2-7, increasing over 20% of the S1, it is impossible to check the

mobility of Si-O band. But we could know the decrease of acrylic PSA at the measurement area through the intensity of  $1162\text{ cm}^{-1}$  was assigned to C-O-C band.

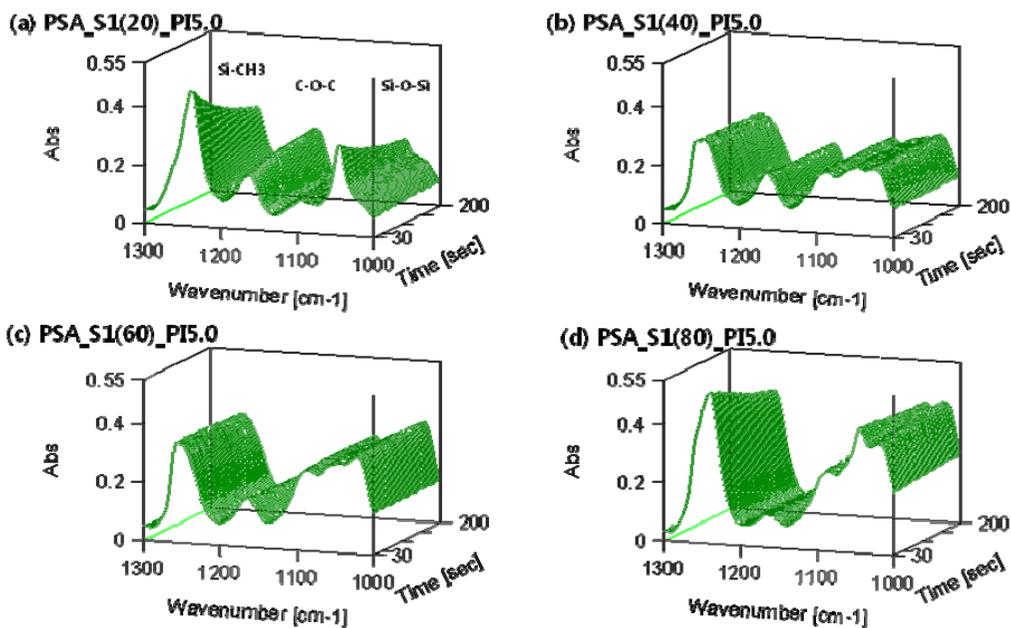
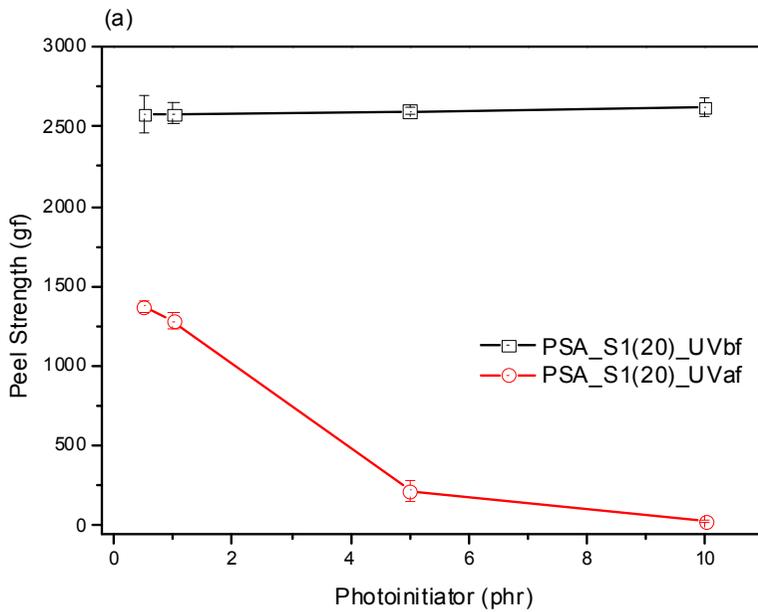


Figure 2-7. RTIR spectra of (a) PSA\_S1(20)\_PI5.0phr (b) PSA\_S1(40)\_PI5.0phr (c) PSA\_S1(60)\_PI5.0phr (d) PSA\_S1(80)\_PI5.0phr

### 3.3 Adhesion Properties

According to the concentration of PI, the cross-linking density is changed. Over the 5phr of the PI, it is in a very high cross-linking state, so peel strength is low and almost useless to add more. Over the 40% of the S1, it is impossible to use the PSA, because it is almost disappeared its peel strength. Under 40% S1, it can be controlled its various properties and degree of cross-linking.



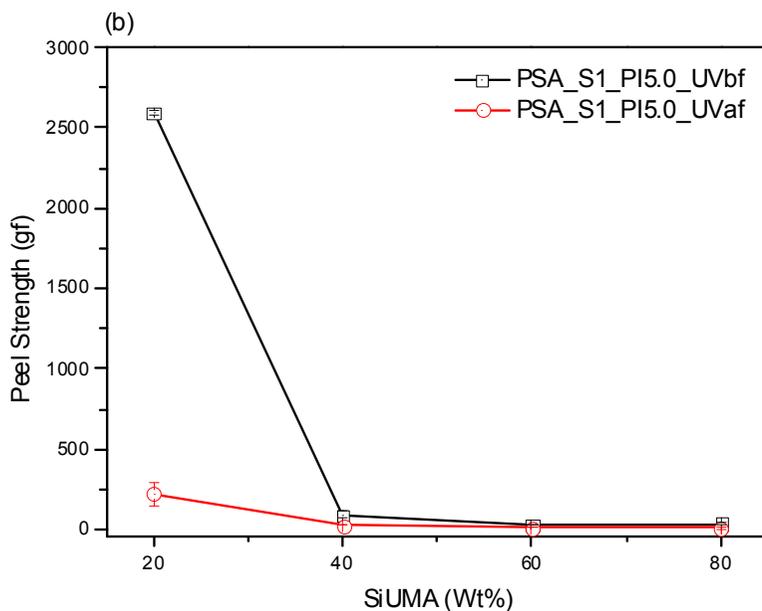


Figure 2-8. Figure 10. Changes of peel strength by (a) different PI amount (b) S1 amount

#### 4. Conclusion

In this work, synthesis and characterization of Semi-IPNs formed from radically initiated S1 and was investigated. The structure of the S1 was characterized by FTIR. The disappearance of the band at  $2250\text{ cm}^{-1}$ , which is assigned to the isocyanate group, is indicative of the completion of reaction. Reactivity of IPNs was determined by photo-DSC measurement. IPN increased with increasing content of S1 oligomer in Acrylic PSA. The IPN sample shows various compositions to analyze the physical properties. The experiments also showed that the type of reactive diluent has great effect on reactivity during curing.

## **Chapter 3.**

Synthesis and Characterization of thermally  
stable Acrylic PSA using Silicone Urethane  
Methacrylate of Semi-IPN Structure

## 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 (Houwink and Salomon, 1965). Pressure sensitive adhesives do not need driving force like water, solvent, light and heat. However, they are possible to attach to a variety of surfaces under the application of light pressure like “thumb pressure”. When detached, the adhesives 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 polymer compatibility and non-yellowing, the highest balance of adhesion and cohesion and excellent water resistance (Czech and Pelech, 2009b). Acrylic PSAs show semi-solid state is 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 when brought into contact under very light pressure. It is not a basic property of the adhesive, but a composite response of the adhesive’s bulk and surface properties.

The common and widely used siloxane polymers (so called in industry as silicone) are principally based on poly(dimethylsiloxane) (PDMS). Polyorganosiloxane consist of Si-O bond, which shows flexibility of chain, chemical resistance, corrosion resistance, water resistance and thermal, oxidative stability. Though it has many merits, still has weak point like high price and low adhesion to porous surface (Lee and Kang, 2007). The interesting and useful properties of siloxane polymers are a result of somewhat unusual molecular structure of the polymer chains that consist of alternating silicone and oxygen atoms (Voronkov *et al.*, 1978). Polyurethane (PU) is the chemistry involved in isocyanate reactions with macrodiol, diisocyanate and chain extender (CE). Today, PU coatings can be found on many different appearance and lifespan like construction, building floors, steel trusses and concrete supports (Chattopadhyay and Raju, 2007). Thermal properties depend on the type and nature of the hard segments, relative molecular weight, composition and or ratio of the hard and soft segments. In

PSAs industry, UV-curing technique represents a major advance in the development of the coating, adhesive and ink industries (Pappas, 1978). Not that is state-of the art but still UV curing induced currently represents about 90% of the radiation-curing market in Europe. UV curing is possible to change in other terms with photoinitiated polymerization, photo-polymerization or photo-cross-linking (Gloeckner, 2008). Under intense illumination, reactive species such as free radicals or cations can be generated in high concentrations by photolysis of an initiator, and thus promote the polymerization of monomers and oligomers. UV-curing formulations provide some benefits such as fast cure response, excellent chemical resistance, good weathering characteristics, and broad formulating latitude. Low VOCs are certainly the most talk about 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: curing proceeds within a fraction of a second. This ultrafast transformation from a liquid phase to a solid state allows increasing productivity on a production line while maintaining energy cost at a low level. The composition of free radical or cationic UV-curable formulations varies both in 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 the distinct networks. They can be synthesized by cross-linking polymerization of two multifunctional monomers or telechelic oligomers that polymerized by different mechanisms, e.g. radical and cationic polymerization (Drumheller and Hubbell, 1994). Semi-interpenetrating polymer network (Semi-IPN) is comprised one or more polymer networks and one or more linear polymers penetrated on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules (IUPAC, 1997). Through interpenetrating network, thermally stability induction reported (Ma *et al.*, 2005). Cross-linked silicone polymers have many advantages, including flexibility, low surface tension, low dielectricity, ultraviolet resistance, non-flammability, as well as high thermal and chemical stability.

Although some of IPNs based on cross-linked polysiloxanes have been reported in the literature (Gilmer *et al.*, 1996). In this study, an SiUMA based on acrylic PSA with semi-IPN is synthesized in which linear Acrylic and silicone urethane methacrylate network treated as the guest and host polymers, respectively. It is shown that the mixture of linear acrylic PSA with the silicone urethane methacrylate formed a homogeneous blend by several ratio of the two component after UV cross-linking. Acrylic PSAs is weak about thermal properties, thus is need to make cross-linking or to increasing the molecular weight to improve its properties. For making networks, to add multifunctional monomer or oligomer is comparatively effective way. Silicone urethane methacrylate is used as multifunctional oligomer, to make networks by increasing cohesive in acrylic PSAs. It is expected to improve thermal property by using silicone and dicyclohexylmethane-4,4-diisocyanate which are known as thermally stable materials. Through the study, acrylic PSAs are easily modified by silicone additives to prove the thermal stable effect like masking tape or Die Attach Film. Small amount additive is enough, thus it is expected to have like cost reduction, cost competitiveness. Moreover It can be useful the same production line for using UV. When semi-IPN structure is formed with SiUMA in acrylic PSA, the chain length influence on physical, chemical properties, because long chain change its glass transition temperature, crystalline temperature and rheological properties. The physical property and structures were confirmed by FT-IR, GPC, TGA. ARES analyzed the thermal property changes and visco-elastic changes. Texture Analyzer, Contact Angle Measurement shows you the surface condition.

## 2. Experimental

### 2.1 Materials

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

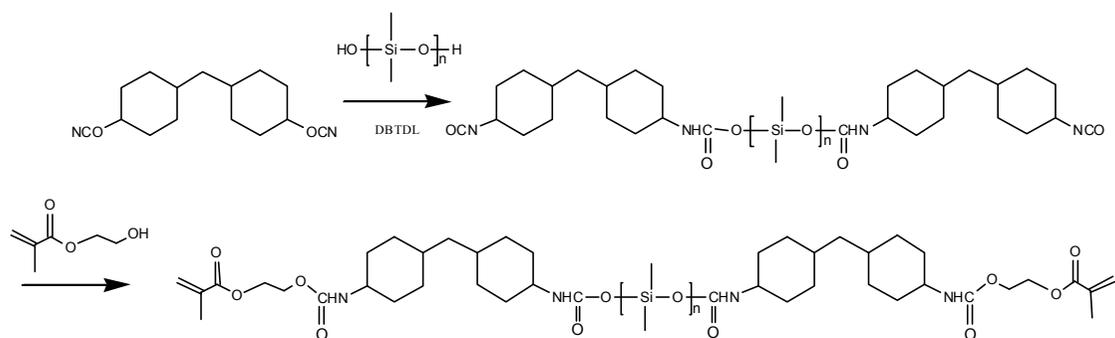
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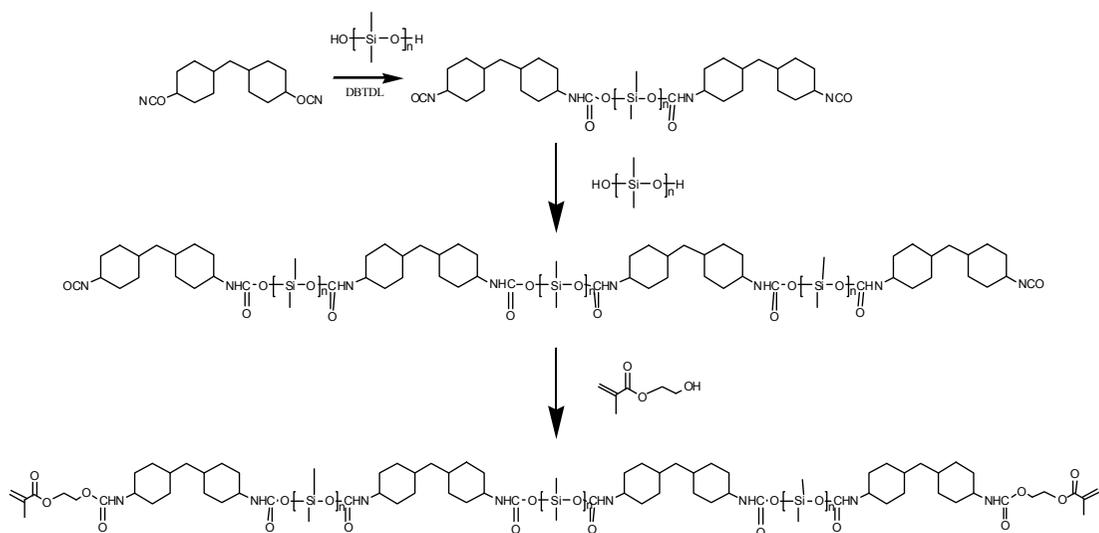
The acrylic pressure sensitive adhesive was synthesized from 2-EHA, AA in ethyl acetate solvent about 50 % solid contents. The polymerization was performed in a 500 ml, four-necked, round bottom flask equipped with a thermo-coupler, condenser, dropping funnel equipped and mechanical stirrer. The monomer resin with 0.05wt% AIBN was heated up to 80°C in about an hour, afterwards, the reaction mixture was kept at 80°C until solvent polymerization finished for 3 hours and more added 0.05 % AIBN three times.

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Scheme 3-1. Synthesis of silicone urethane methacrylate (Short Chain: S1)



Scheme 3-2. Synthesis of silicone urethane methacrylate (Long Chain: S2)

## 2.3 Measurements

### 2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The IR spectra were obtained on a JASCO FTIR-6100 (Japan) spectrometer equipped with attenuated total reference (ATR) accessories. The spectra were recorded for 20 scans with a  $4\text{ cm}^{-1}$  resolution over the wavelength range, 650 to  $4000\text{ cm}^{-1}$ . The absorbance is decreased in different ranges. They were analyzed about double carbon, siloxane and carbonyl bond etc. All the results were confirmed by revising the level of  $\text{CO}_2$  reduction,  $\text{H}_2\text{O}$  reduction, noise elimination, smoothing and baseline correction.

### 2.3.2 Gel Permeation Chromatography (GPC)

The average molecular weight ( $M_w$ ) and number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ , MWD) of the synthesized acrylic PSAs and silicone urethane methacrylate were determined by GPC (High Temperature GPC (Gel Permeation Chromatography), UK ). The samples were dissolved in tetrahydrofuran (THF) at the ratio of 0.5% w/v solutions. 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. Molecular weight and molecular weight distribution of polymer can be measured using GPC. PSAs in solution are injected into a stream of flowing solvent at the top of a packed column which consist of a porous gel having different pore sizes. Therefore, the smaller polymer molecules can enter the pores so that their passage is retarded, whereas the large molecules are excluded from the gel and are eluted from the column more rapidly.

### 2.3.3 Real-time Fourier Transform infrared (RT-IR) spectroscopy

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#### 2.3.4 Photo-Differential Scanning Calorimetry (photo-DSC)

Photo-DSC experiments were conducted using a TA Instruments Q-200 DSC equipped with a photo-calorimetric accessory (Omniscure 2000), which used light from a 100W middle-pressure mercury lamp. Light intensity was determined by placing an empty DSC pan on the sample cell. UV light intensity at the sample was 15 mW/cm<sup>2</sup> over a wavelength range of 300–545 nm. The weight of the sample was about 8 mg and the sample was placed in an open aluminum DSC pan. Measurements were carried out at room temperature.

#### 2.3.5 Adhesion Properties (Peel Strength & Tack)

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 sample was left to stand at room temperature for 24 hours. The peeling speed was 300 mm/min, and the average strength of peeling period was measured 5 times. 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 sample was left to stand at room temperature for 24 hours. The peeling speed was 300 mm/min, and the average strength of peeling period was measured 5 times. The debonding speed was 0.5 mm/sec and the probe tack was measured as the maximum debonding force. Tack measurements of PSA films is 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 5 mm of diameter.

### 2.3.6 Contact Angle Measurement

The Contact Angle for acrylic PSA with IPN structure was evaluated from the static contact angles measured using a contact angle analyzer (Poenix 300, Surface & Electro-Optics Corp, Republic of Korea). The temperature and relative humidity were  $23 \pm 2$  and  $50 \pm 3$  %, respectively.

### 2.3.7 Advanced Rheometric Expansion System (ARES)

The visco-elastic properties, such as the storage modulus, loss modulus and tan delta ( $\tan \delta$ ) 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  $200^\circ\text{C}$  with various strains ( $0.05 \sim 40$  %) and frequencies (1 Hz). The heating rate was  $5^\circ\text{C}/\text{min}$ .

### 2.3.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) were performed using a Perkin Elmer Thermogravimetric Analyzer Pyris 1 TGA model. Samples were run from 30 to  $600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$  under air.

### 2.3.9 Shear Adhesion Failure Temperature (SAFT)

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

### 2.3.10 Tensile Strength

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 SiUMA PSAs were prepared as rectangular specimens, 25 mm in length (span length), 25mm in width and 50  $\mu\text{m}$  in thickness. Five measurements were taken with the mean value used for further analysis.

### 3. Result and Discussion

#### 3.1 Silicone Urethane Methacrylate

##### FT-IR

Figure 3-1(a) indicate the FTIR spectrum of HMDI. The bands at 2248-2264  $\text{cm}^{-1}$  was to mean NCO group. The disappearance of the band is assigned to the indicative of the completion of the reaction in (a) to (C). Figure3-1(b) shows the characteristic band of PDMS, where the bands at 1015, 1074 $\text{cm}^{-1}$  were assigned to Si-O-Si stretching vibration, and 791 $\text{cm}^{-1}$  stretching vibration is characteristic of S-CH<sub>3</sub>, 2248  $\text{cm}^{-1}$  was isocyanate group which means urethane reaction, more disappeared than (a). (c) were associated with the band of the acrylic double bond at 810, 1638  $\text{cm}^{-1}$  but which are too weak intensity, so 1720  $\text{cm}^{-1}$ (C=O) stretching vibration shows HEMA induced in SiUMA indirectly.

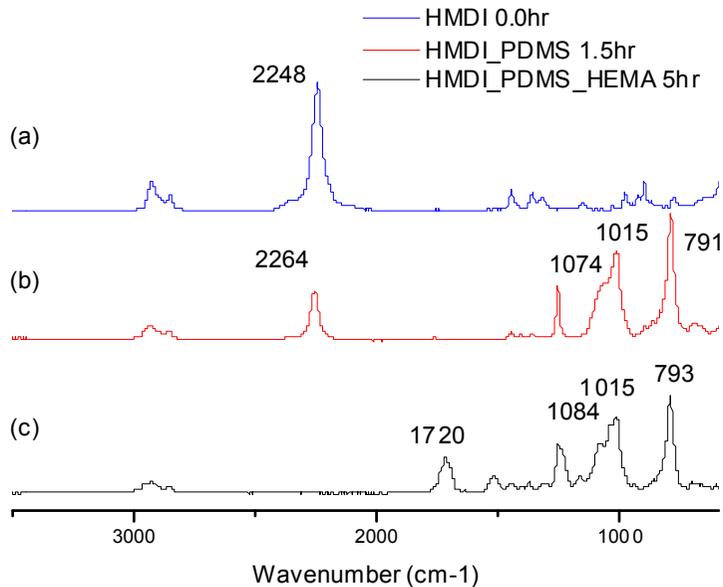


Figure 3-1. FTIR spectra of (a) HMDI, (b) addition of PDMS, and (c) addition of HEMA.

To make long chain, control the mole ratio. Form Figure 3-2(a) to (d) shows the FTIR spectrum of HMDI reduced. The bands at  $2248\text{ cm}^{-1}$  was due to NCO group. The disappearance of the band is assigned to the indicative of the completion of the reaction in (a) to (d).

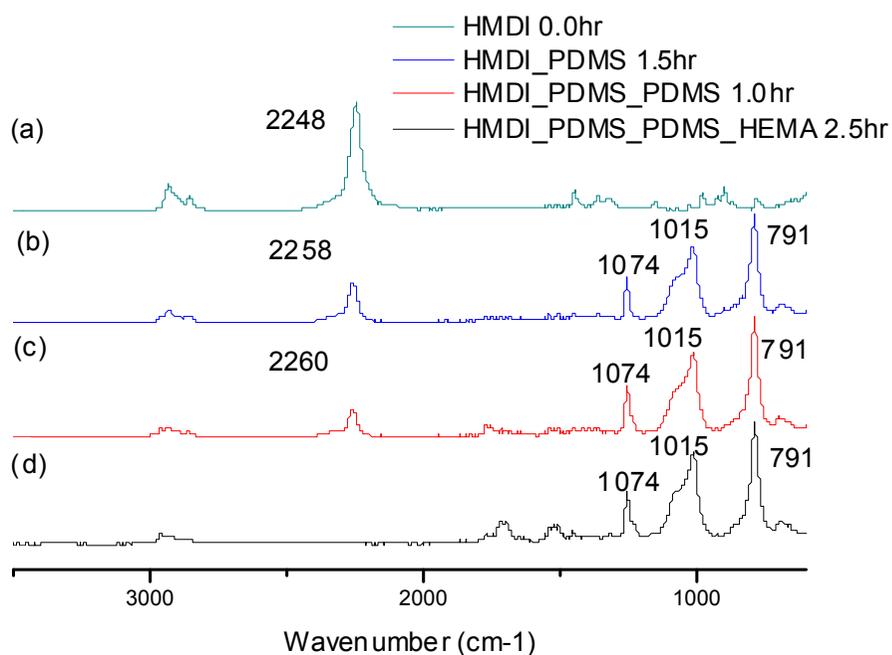


Figure 3-2. FTIR spectra of (a) HMDI, (b) Addition of PDMS (c) Addition of PDMS, and (d) Addition of HEMA

## GPC

The molar masses and molar mass distributions of the synthesized SiUMA01 and SiUMA02 were checked by GPC and the results were shown in Table I. The GPC instrument was calibrated using linear polystyrene standard. Mn of SiUMA01(S1) and SiUMA02(S2) are 4598, 8942. and polydispersity index are 1.58, 1.82 both of them. The values of molar masses of S2 is double size about S1 which will be analyzed and may be attributed to get the information of the effect of chain length. Moreover, the products showed the different physical properties like peel strength, tack, contact angle.

TABLE 3-1 Molecular weight distribution of SiUMA01(S1) and SiUMA02(S2)

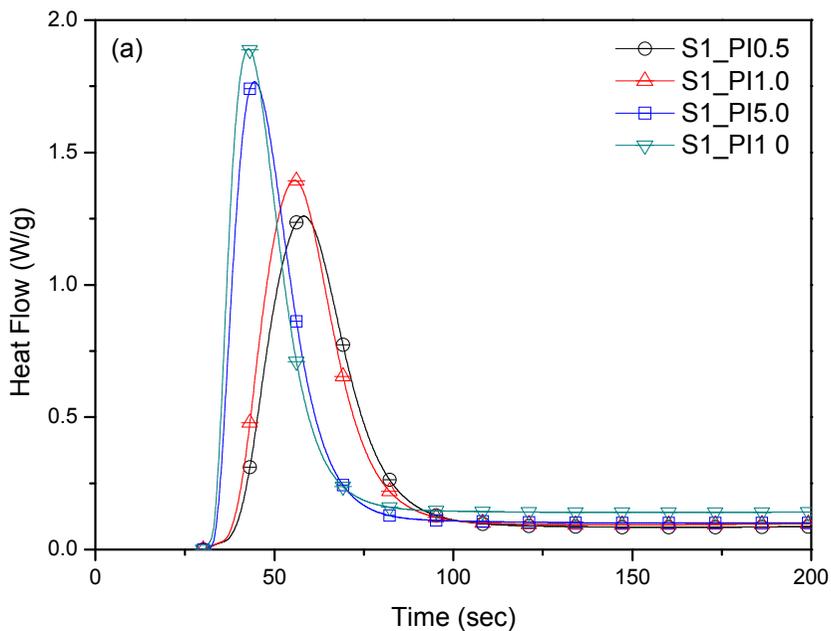
Oligomers	Mn	Mw	Mp	Mw / Mn
SiUMA01(S1)	4598	7267	5264	1.58
SiUMA02(S2)	8942	16307	9740	1.82

### 3.2 UV curing Kinetics

#### **Photo-Differential Scanning Calorimetry (Photo-DSC)**

Photo-DSC test is a easy method for UV-curing reactions because it can determine the kinetic parameter, degree of conversion, curing rate and reaction enthalpy during an rapid UV-curing reaction which behavior depends on the intensity and dose of UV-light, species and content of photo-initiator, reaction temperature, and reactivity of the functional groups (Palanisamy, 2007). In this experiment, photo-DSC technique was used to examine the effect of the short (S1) and long(S2) chain contents depend on Photoinitiator (PI) amounts, . Figure 3-3 shows the isothermal UV-curing heat enthalpy and conversion profiles of S1, S2 by photo-DSC. The exothermic heat flow (cal/g s) vs. curing time is the important data by photo-DSC measurements. The auto-acceleration by the activation of radicals was confirmed to be a steep increase at the beginning of the reaction and then was followed by auto-deceleration, as indicated in the rapid dropping curves (Asif *et al.*, 2005). The reaction was studied by the blends S1, photoinitiator and different amounts of PIs. And also by the same method but different material, S2, blend with photoinitiator and different amounts of PIs. These reactions were performed as 0.5, 1.0, 5.0 and 10 phr at room temperature. Through this experiment, it can be determined how much UV intensity needed. From Figure 3-3(a), the values of the enthalpies is measured in isothermal curing conditions at room temperature during 300 sec at different concentrations. Through this figure, it can be observed that differences in the enthalpy are evolved for the different PIs concentrations. PIs concentrations increased the higher conversion and also explain the higher rate as the PIs concentration increases in the range studied. When over the 5phr of the PIs, no significantly differences were observed. So more or less than the 5phr of the PI is the proper dose for the UV curing and the UV irradiation is about 1000mJ/cm<sup>2</sup> enough. In the case of Figure 3-3(b), its reactivity dropped dramatically. Though double size (Table 3-1.) chain, its effects on the enthalpy is comparatively great. Because the reaction rate is influenced by viscosity, which means that a reduction in viscosity allows greater diffusion and mobility (Nowers and Narasimhan, 2006).

Increasing the length of chain, S2 increased its viscosity. So it is reduced the reactivity. Figure 3-3(b) shows 10phr decreased the enthalpy less than 5phr. When higher concentrations were used a negative effect was observed, because of high rate of recombination of radicals, the higher absorption of UV light of the initiator in the top layers and also as a result of some incompatibility of the PIs with the molten polymer binder (Castell *et al.*, 2007). Figure 3-4 shows the mixtures of S1-S2 have no synergy between short and long chain. It is rather delayed the reaction rate by ratio of S1-S2. Increased S1 mass, it is recovered the reaction rate. This behavior resembled with long chain reaction. Long chain effect on the mobility of short chain, so S2 increased, S1 reactivity decreased.



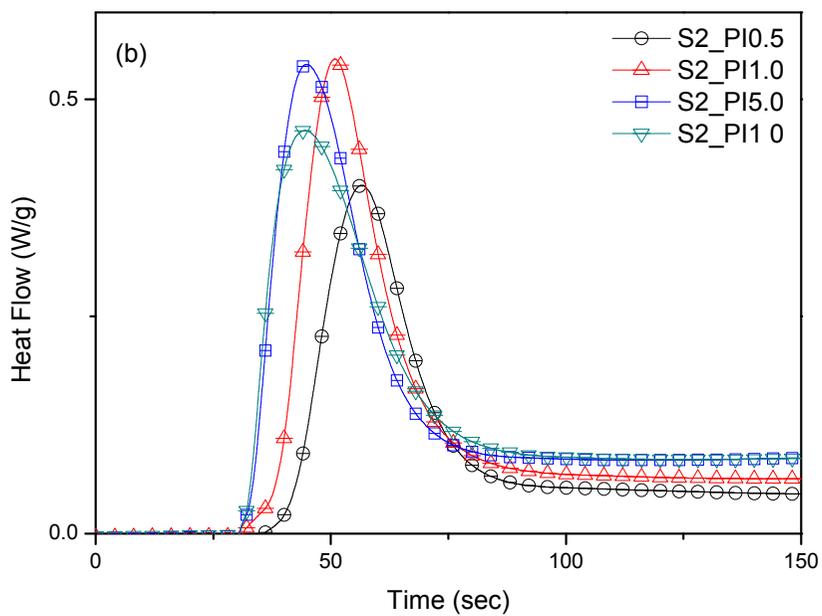


Figure 3-3. Reaction heat flow profiles (a) short chain (S1) (b) long chain (S2).

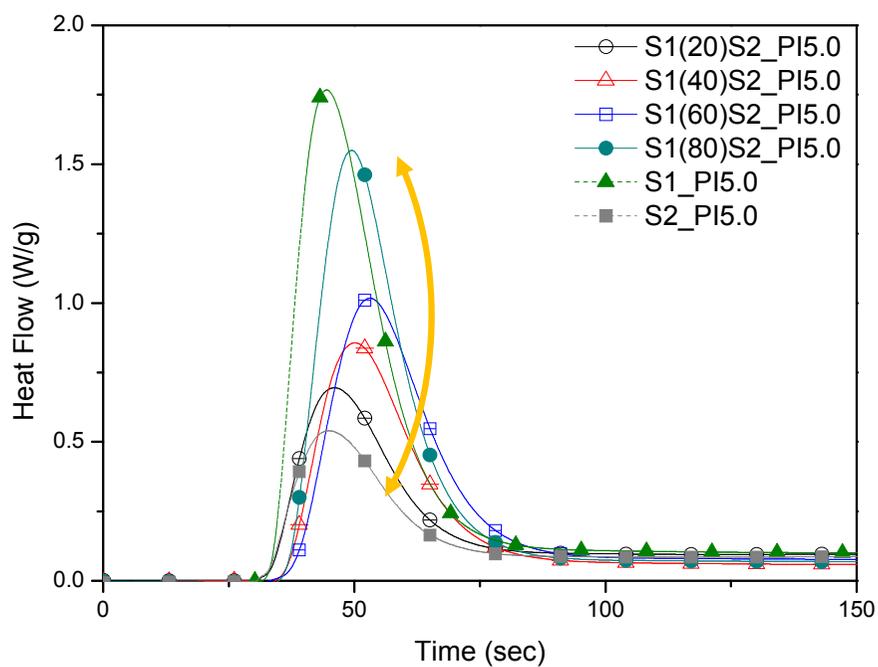
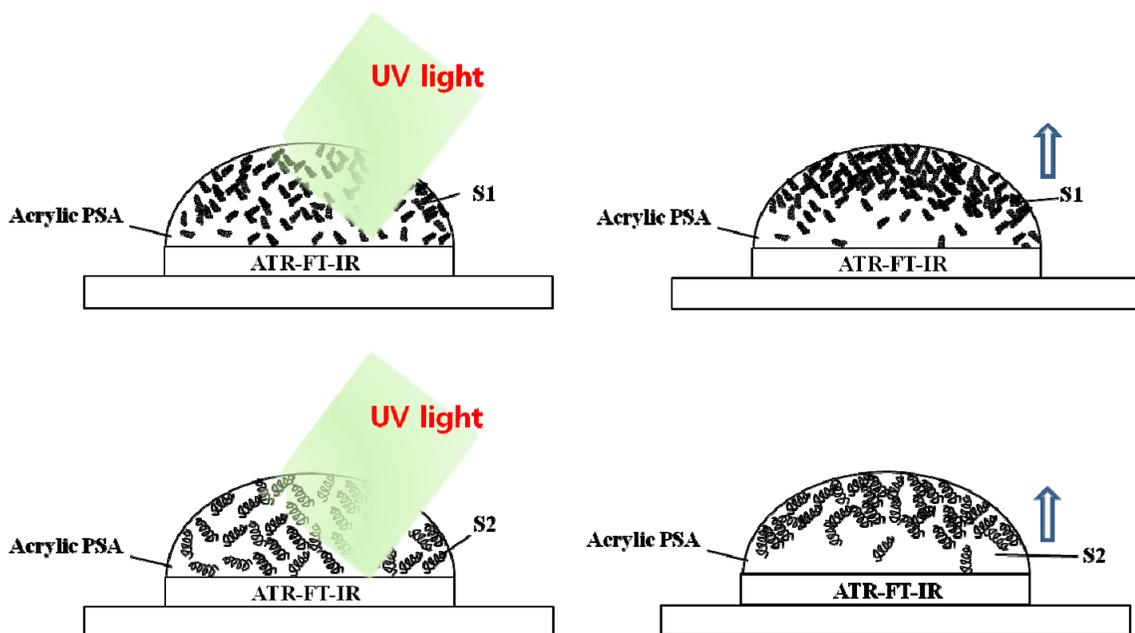


Figure 3-4. S1-S2 mixtures reaction heat flow profiles.

### Concept Drawings of UV Curing

Siloxane's low surface energy, the siloxane segments tended to migrate to the air-polymer interface (Gaines, 1981). When the UV irradiate to the acrylic PSA-S1, S1 segment moves to the surface of the acrylic PSA contacted with air. S1 segment tends to be gathered tightly better than S2.



Scheme 3-3. Concept drawings of UV curing

### 3.3 Adhesion Properties

#### **Peel Strength and Tack**

When the S1 or S2 added the acrylic PSA, the peel strength increased with their dose. This fact shows the S1, S2 influenced on the surface of the acrylic PSA before UV irradiation. After UV irradiation peel strength declines sharply, the value is under 150 gf almost disappeared because of cross-linking effect on the surface. Figure 3-5(a) shows very high peel strength when the S1, S2 added in acrylic PSA but just 1% dose with UV curing, the peel strength was very low, which indicated that S1, S2 tend to migrate to the air-polymer interface (Chiang and Shu, 1988). S1-S2 mixtures show the middle peel strength of S1, S2 and comparatively unstable variations. The probe tack is a measure of the adhesion performance over a short time (Bae *et al.*, 2012). Figure 3-5(b) is increasing with S1, S2 amount but after UV irradiation decreased the value. S1-S2 mixtures had the middle value. This is also related to cross-link. A proof for the surface is covered with S1 or S2. As a result of cross-linking density, short chain makes hard surface.

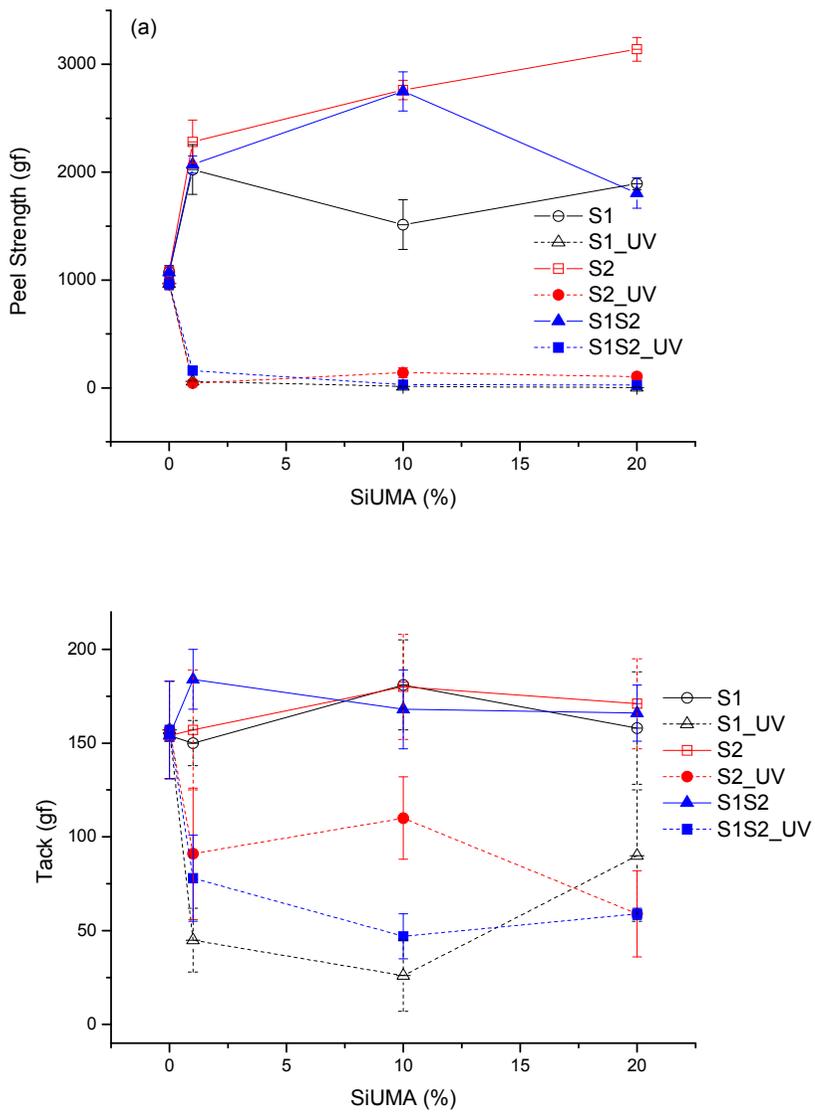
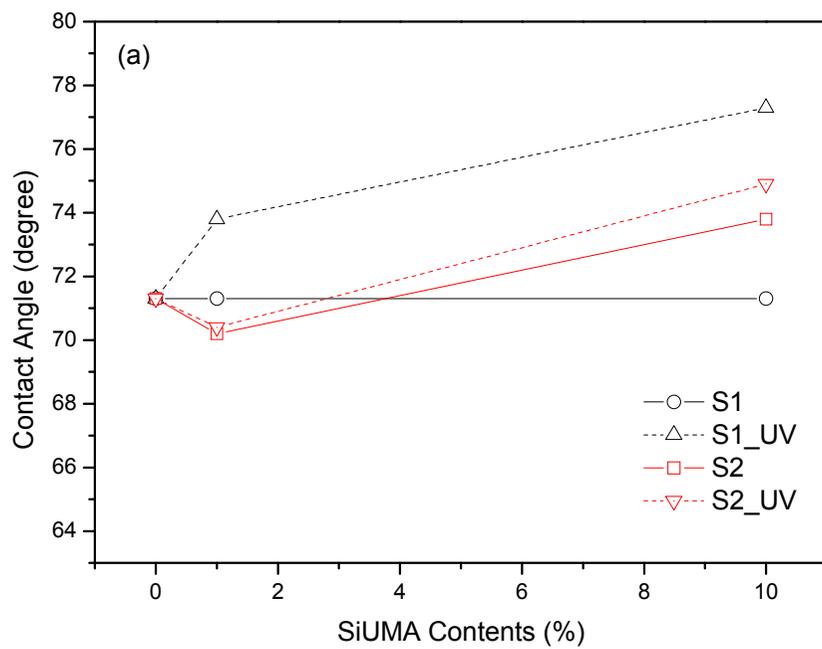


Figure 3-5. UV curing effect on (a) peel strength by different PI amount (b) tack by different PI amount

### 3.4 Contact Angle Measurement

#### **Contact Angle Measurement**

Figure 3-6 shows the contact angles of S1, S2 testing liquids on each adhesive film as a function of the S1, S2 content with UV irradiation. Figure 3-6(a) shows instant contact angle by S1, S2 contents. S1 shows different behavior with S2, S1 was same angle with increasing its content. But S2 shows contact angle increased with its content slightly. But after UV irradiation, the S1 angle increased comparatively high but S2 angle shows increasing slightly. This represents that ability to make network is better S1 than S2. Figure 3-6(b) checked the time dependence on S1, S2 by contents. In the case of S1 and S2 shows same angle slope on time dependence which means siloxane, cross-linking and chain length are not so affect on the incline of time-contact angle. The result shows cross-linking effective on the change of the surface by short chain.



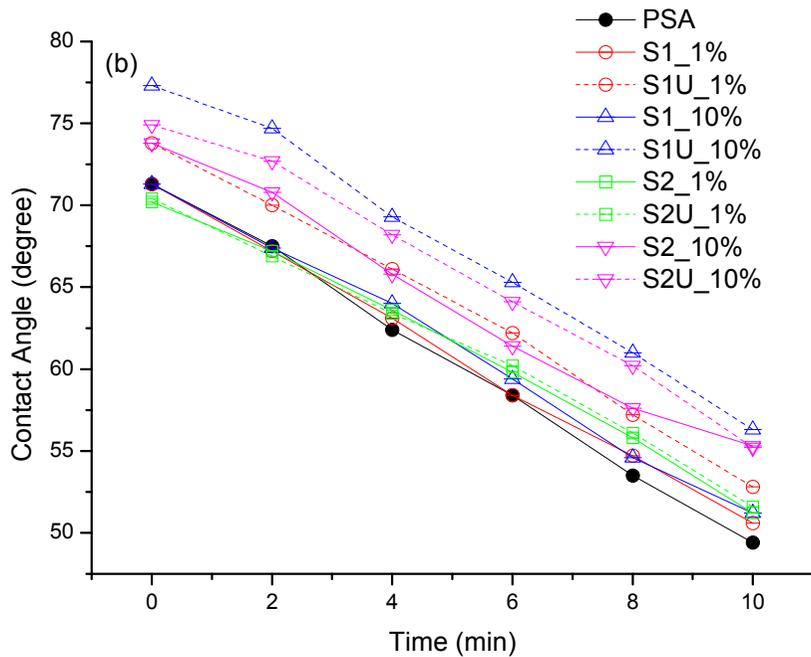


Figure 3-6. UV curing effect on (a) contact Angle with S1, S2 concentrations (b) contact angle with S1, S2 time and concentrations

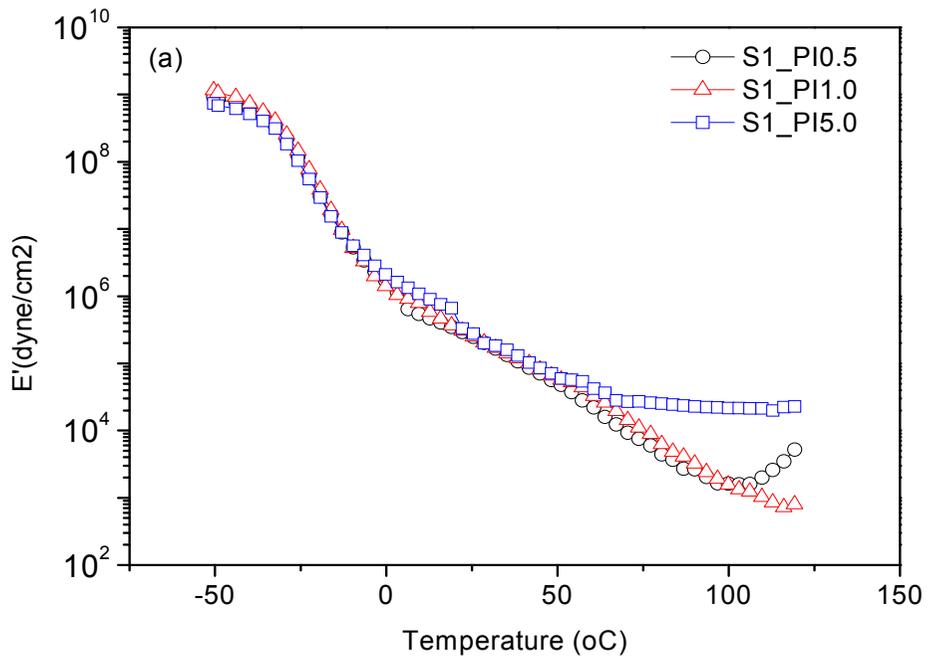
### 3.5 Thermal Properties

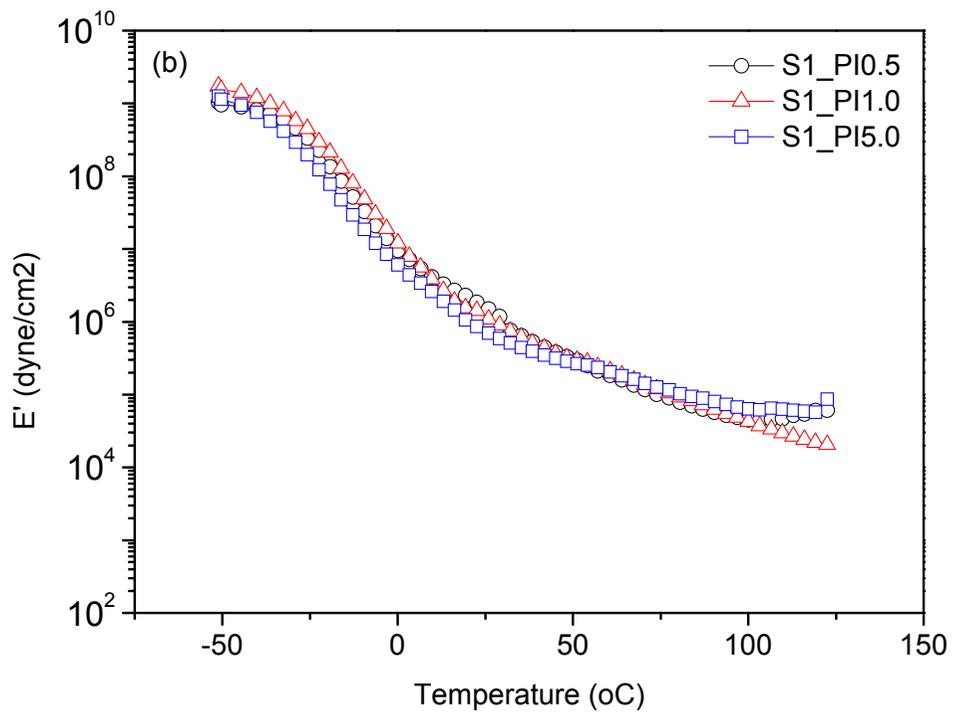
#### 3.5.1 Advanced Rheometric Expansion System (ARES)

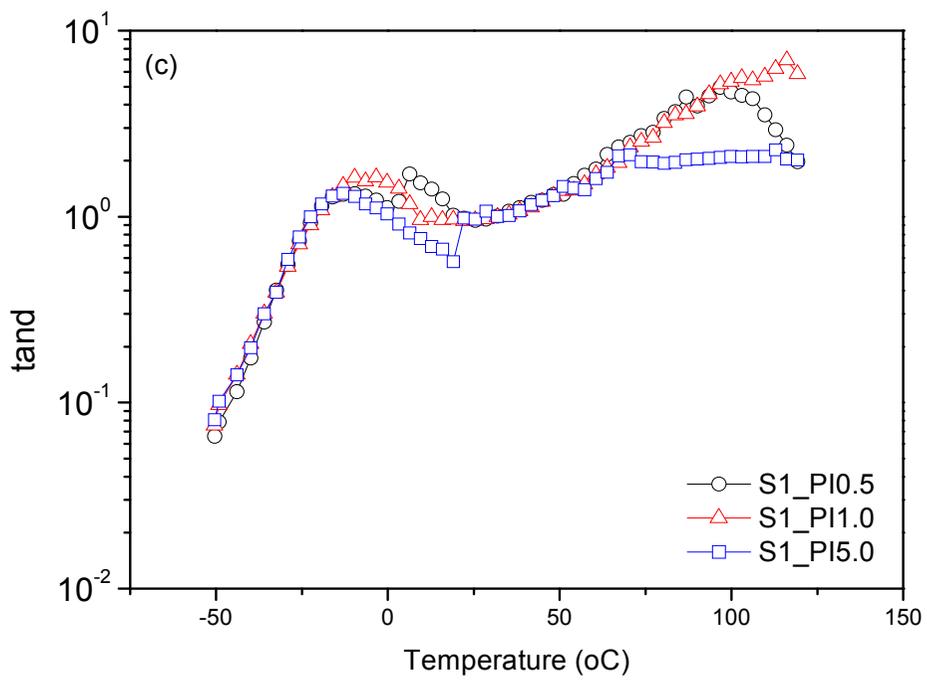
##### Viscoelasty

The PSA have a semi-solid properties and hence, the wetting of a substrate, the viscoelastic property (a bulky property of the molecular mobility), is the important factor that control the adhesion performance (Satas, 1999). In the case of acrylic PSA, the storage modulus curve has a glassy region, a rubbery plateau and a terminal region; these curves display by temperature area. In the glassy region, the PSAs have rigid properties, but with increasing temperature, and are influenced on the glass transition temperature ( $T_g$ ), the next take on a rubbery property. The value of  $\tan \delta$  indicates the ratio of the loss of modulus to the storage modulus; the highest peak of  $\tan \delta$  means

the  $T_g$ . For 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 (Lim *et al.*, 2006). Figure 3-7 is examined by increasing the ratio of PI contents.  $E'$  and  $\tan \delta$  shows differences of PI contents which is increasing the physical property. In Figure 3-7(a), before 50 °C,  $E'$  is almost same but over 50 °C,  $E'$  is separated 3 group which contained 5.0 phr is most high value. This means that 5.0 phr PI have a possibility to have a role to make cross-linking. In Figure 3-7(b), after UV curing,  $E'$  increased with all PI concentrations and the value seems similar. In Figure 3-7(c) and (d),  $\tan \delta$  shows several peaks which the acrylic PSA with IPN have many  $T_g$ s. Acrylic PSA with IPN needs to consider the compatibility and interaction with other polymer. In this study, through cross-linking, the several peaks are weaker than before UV irradiation, we can know the reduced phase separation whereas increased phase separation leads to the increased elongation at break(Lee and Kim, 1996).







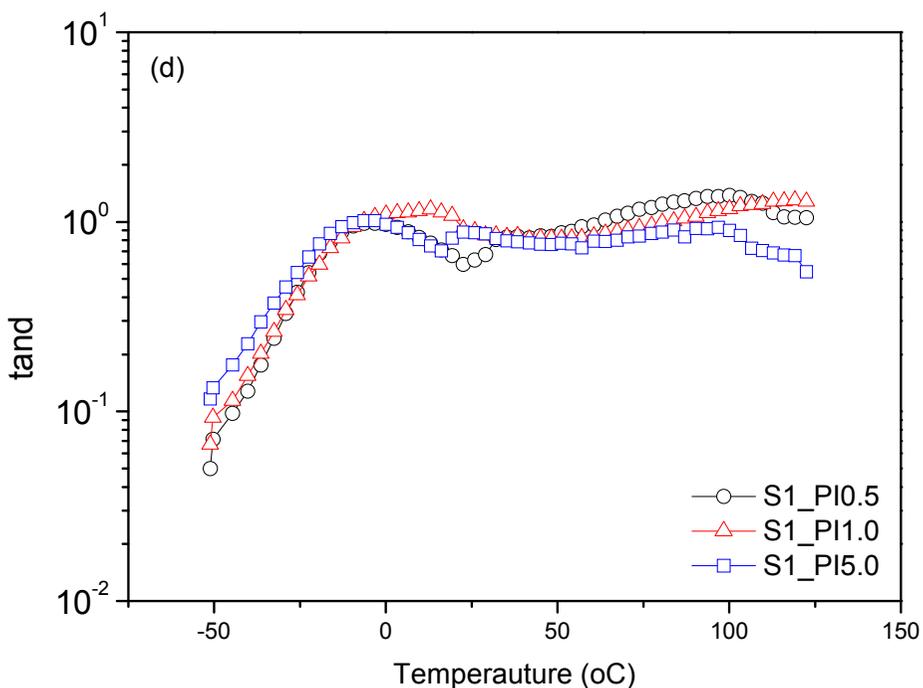


Figure 3-7. UV curing effect on (a)  $E'$  by PI contents before UV (b)  $E'$  by PI contents after UV (c) tan delta by PI contents before UV (d) tan delta by PI contents after UV

### 3.5.2 Thermogravimetric Analysis (TGA)

#### TGA

The thermal stability of acrylic PSA with IPN structure was measured by TGA at temperatures ranging from 25 to 600 °C. Figure 3-8 shows the weight loss curves and derivative of the weight profiles of each sample, respectively. Table 3-2 lists the characteristic thermal decomposition temperatures: the temperature of the initial 10% mass loss (T10%), temperature of 50% mass loss (T50%), weight percent at 480 °C (decomposition temperature about S1). The PSA-S1 mixtures undergo depolymerization faster than acrylic PSA under 407 °C, which S1 reacts plasticizer in

acrylic PSA reducing the interaction with polymers hydrogen bond. So much higher S1 content, That shows lower degradation temperature. And there is another reason. The thermal degradation mechanism of polyurethane is already announced. The urethane groups first undergo de-polymerization 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 degradation of the hard and soft segments of polyurethane linkages (Lin *et al.*, 2008; Ge *et al.*, 2009). Over 407°C, soft segment degraded and shows thermal stability better than acrylic PSA. The maximum decomposition of S1 occurred at approximately 480°C.

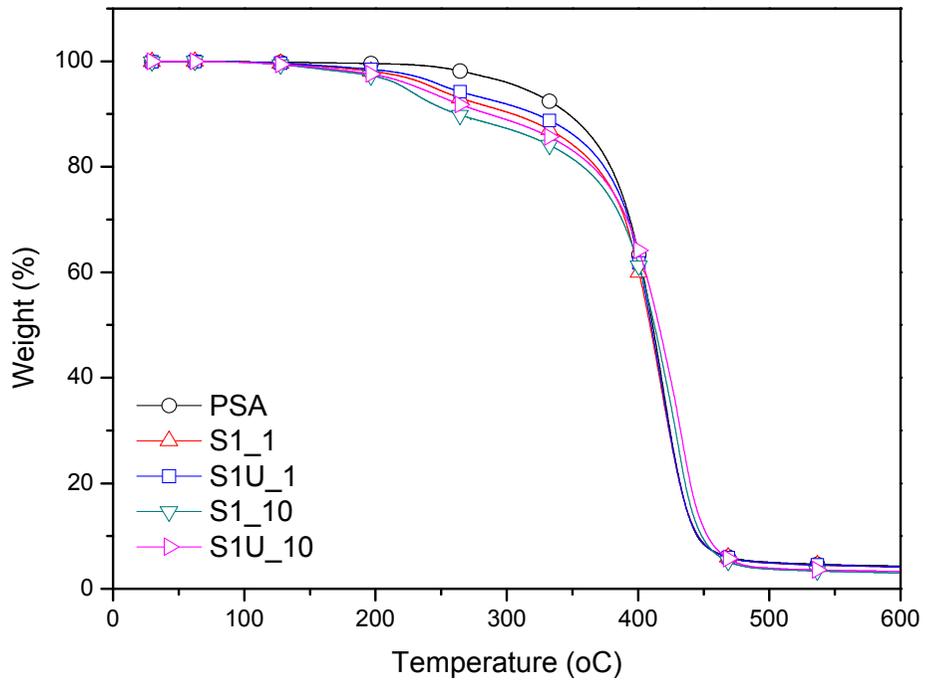


Figure 3-8. TGA curves with UV curing effect on S1 contents

TABLE 3-2 Thermal decomposition data of S1 and S2

Samples	Weight loss		
	T10% (°C)	T50% (°C)	wt.% at 480°C
PSA	346.9	411.1	5.47
S_1	304.8	409.6	5.33
SU_1	322.1	410.1	5.33
S-10	262.5	412.4	4.26
SU_10	286.1	415.8	4.52

### 3.5.3 Shear Adhesion Failure Temperature (SAFT)

#### SAFT

The thermal stability of acrylic PSAs is supported by the SAFT. When the cohesion becomes weak under a constant force with increasing temperature, it shows certain temperature which temperature is the acrylic PSA supported. In this study, the SAFT of S1 and S2 was measured up to 200°C. In Figure 3-9, except S1, S2 10% UV cured, all of them dropped under 50 °C. But S1, S2 showed a good resistance high temperature shear force. Main reason is to formed IPN structures in acrylic PSA which was reinforced by the chemical bonding of cross-linking and the thermal resistance was increased. The results from Figure 10 shows that the cross-linking of the main chain has a larger effect on the SAFT than does the semi-IPN (Joo *et al.*, 2006).

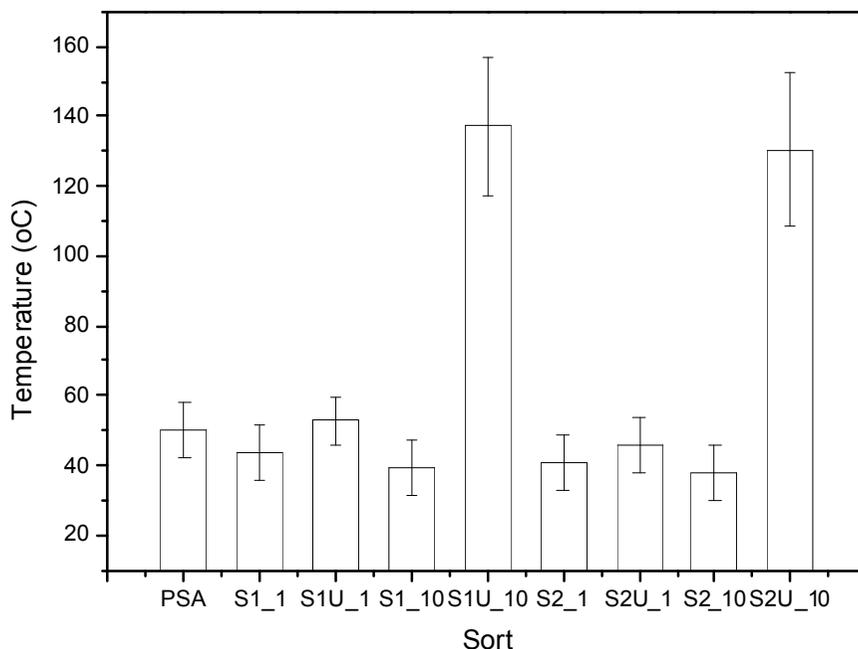


Figure 3-9. SAFT comparison with S1 contents

### 3.5.4 Tensile Strength

#### Tensile Strength

Figure 3-10 shows the comparison of effects of the S1, S2 content under UV curing behavior with acrylic PSA which shows tensile strength and elongation at break. Through this experiment, acrylic PSA indicate weak shear force less than S1, S2 10% after UV curing. But S1 and S2 10% after UV curing materials also don't have enough shear force, which are acrylic PSA is 320 gf/cm<sup>2</sup>, S1 is 610 gf/cm<sup>2</sup>, S2 is 540 gf/cm<sup>2</sup>. This is one proof which takes into consideration for the samples were held in the heating chamber loading with a 1000 gf/cm<sup>2</sup>.

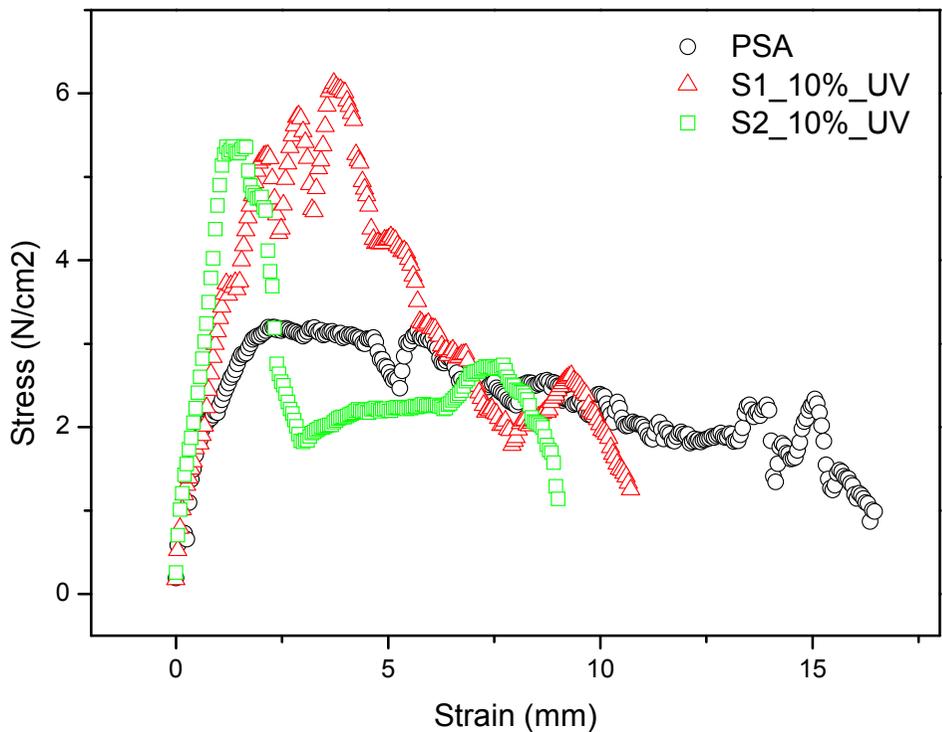


Figure 3-10. Tensile behaviors of UV curing S1

#### 4. Conclusion

In this work, Silicone Urethane Methacrylate was synthesis and characterized for UV curing materials. After then, it was determined the cuing conditions like an UV intensity, photoinitiator contents and chain length. The structures of the Synthetic materials were characterized by H-NMR, FTIR and GPC. The disappearance of the band at  $2250\text{ cm}^{-1}$ , which is assigned to the isocyanate group, is represent about the completion of reaction. Reactivity of Silicone Urethane Methacrylate was determined by photo-DSC measurement. Adhesion property demonstrated the state of surface after UV curing and is possible to check the cross-linking effect. ARES shows that  $E'$  and  $\tan \delta$  are indicative of thermal property and  $\tan D$  explain that acrylic PSA was not compatible with Silicone Urethane Methacrylate because of many  $T_g$ s. Through TGA, thermal property under  $407^\circ\text{C}$  is weaker than acrylic PSA because Silicone Urethane Methacrylate are like plasticizer role in acrylic PSA. Over  $407^\circ\text{C}$ , silicone enforced thermal property to overcome the acrylic PSA. SAFT shows the resistance of shear force under comparatively high temperature, Tensile strength data support mechanical strength is not only reason. Though the formed IPN structure in acrylic PSA, we can prepared the thermally stable acrylic PSA.

# **Chapter 4.**

## **Concluding Remarks**

Acrylic Pressure-sensitive adhesive with Semi-IPN structure is able to permanently tacky in dry form (solvent-free) at room temperature and adhesion is possible with a light pressure for short time. PSAs are used for various industrial fields such as medical, packaging, electrical devices and office and house-hold uses, etc. Recently, research about thermally stable adhesives containing various materials have been studied with growing interest about the field of electron & electric products.

The principal objectives of this research were synthesized the acrylic polymer with SiUMA and evaluated kinetics, adhesion performance, thermal property, viscoelastic property and etc.

#### 1. Kinetic and Characterization of UV curable Silicone Urethane Methacrylate of Semi-IPN structure in acrylic PSA

In this work, synthesis and characterization of IPNs formed from radically initiated S1 and was investigated. The structures of the S1 was characterized by FTIR. The disappearance of the band at  $2250\text{ cm}^{-1}$ , which is assigned to the isocyanate group, is indicative of the completion of reaction. Reactivity of IPNs were determined by photo-DSC measurement. Semi-IPN increased with increasing content of S1 oligomer in Acrylic PSA. The Semi-IPN sample shows various compositions to analyze the physical properties. The experiments also showed that the type of reactive diluent has great effect on reactivity during curing.

#### 2. Synthesis and Characterization of thermally stable Acrylic PSA using Silicone Urethane Methacrylate of Semi-IPN Structure

In this work, Silicone Urethane Methacrylate was synthesis and characterized for UV curing materials. After then, it was determined the cuing conditions like

an UV intensity, photoinitiator contents and chain length. The structures of the Synthetic materials were characterized by H-NMR, FTIR and GPC. The disappearance of the band at  $2250\text{ cm}^{-1}$ , which is assigned to the isocyanate group, is represent about the completion of reaction. Reactivity of Silicone Urethane Methacrylate was determined by photo-DSC measurement. Adhesion property demonstrated the state of surface after UV curing and is possible to check the crosslinking effect. ARES shows that  $E'$  and  $\tan \delta$  are indicative of thermal property and  $\tan \delta$  explain that acrylic PSA was not compatible with Silicone Urethane Methacrylate because of many  $T_g$ s. Through TGA, thermal property under  $407^\circ\text{C}$  is weaker than acrylic PSA because silicone urethane methacrylate are like plasticizer role in acrylic PSA. Over  $407^\circ\text{C}$ , silicone enforced thermal property to overcome the acrylic PSA. SAFT shows the resistance of shear force under comparatively high temperature, Tensile strength data support mechanical strength is not only reason. Though the formed IPN structure in acrylic PSA, we can prepared the thermally stable acrylic PSA.



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## 한글초록

본 연구는 내열성을 향상시킨 아크릴 점착제 개발을 위한 연구로, 열 안정성을 개선하기 위해 polydimethylsiloxane은 (PDMS)를 사용하였고, IPN 구조를 아크릴 내부에 형성시키는 UV 경화 방식은 채용하였다. 실리콘 우레탄 메타크릴레이트 (SiUMA)는 Interpenetrating Polymer Network 구조로 활용하였고, 합성된 물질은 FT-IR을 통해 구조를 확인하였다. SiUMA (S1)의 Kinetic과 광경화 특징은 photo-Differential Scanning Calorimetry (photo-DSC)를 사용하여 확인하였다. photoinitiator (PI)의 양을 0.5, 1.0, 5.0 및 10phr로 달리하여 광반응성을 확인하였고, 5.0phr, 1000mJ / cm<sup>2</sup>의 광개시제와 광량을 결정하였다. SiUMA 20, 40, 60, 80에 각 PSA와 블렌딩하여 photo-DSC와 Real Time Infrared를 통해 경화거동을 확인하였다. 이 때 표면의 점착력은 가교 특성 및 점착력의 변화거동을 보여준다. S1 양과 PI의 양을 늘리면 crosslinking로 증가로 인해 그 강도가 떨어지고, 단단해진다. 가교로 인한 영향은 실리콘의 영향 보다는 가교의 영향이 매우 큰 것을 확인할 수 있었다.

다음으로, 실리콘 우레탄 메타크릴레이트(SiUMA)의 길이가 다른 것

을 사용하여 IPN 구조를 아크릴 PSA 내부에 형성시켜 적용하였다. 아크릴 PSA는 free radical 중합에 의해 제조되었고 SiUMA은 우레탄 부가 중합으로 합성하였다. SAFT (Shear Adhesion Failure Temperature)와 TGA는 열적 성질을 파악하는데, 활용하였다. SAFT 결과, 일반적인 Acryl 점착제는 50℃ 이전에 기재에서 떨어지지만, SiUMA를 10% 사용하여 경화시킨 경우 100℃를 뛰어 넘는 것을 확인할 수 있었다. ARES를 통해 점탄성적인 변화 및 열적 성질에 대해 역시 파악할 수 있었다. SiUMA를 사용하는 경우 상용성이 좋지 않아 여러 지점에 Tg가 나타나는 것을 확인할 수 있었다. 길이가 짧은 SiUMA가 보다 좋은 반응성과 물성을 나타내는 것을 알 수 있었다. 본 연구를 통해 SiUMA를 사용하는 경우 가교도로 인한 표면의 열적 성질이 향상되는 결과를 확인할 수 있었고, 실리콘이 고온의 영역에서 영향을 주는 것을 확인할 수 있었다.

Keywords : 아크릴 점착제, Semi-IPN, 실리콘, 우레탄아크릴레이트, Photo-DSC, Real Time-IR, 열적안정성, 실리콘 우레탄아크릴레이트