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# Adhesion Performance and Thermal Stability of Fluorinated PSAs as a Crosslinking System

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## Abstract

The use of pressure sensitive adhesives (PSAs) is becoming increasingly popular in many industrial fields. In the automobile industry the main reasons for using PSAs are that they reduce the overall weight of the vehicles and because they are easy to use. However, in the case of acrylic PSAs, the non-crosslinked linear chains results in low thermal stability. In this study, a fluorinated acrylic pressure sensitive adhesive was synthesized under UV irradiation and crosslinking was applied to the linear chain of acrylic PSAs to improve the thermal stability. The adhesion performance was evaluated by analyzing the peel strength, probe tack and shear adhesion failure temperature (SAFT) as a function of the type of crosslinking system. In particular, the peel strength and probe tack were measured at 25, 50 and 80°C. The viscoelastic properties, which were measured using an advanced rheometric expansion system (ARES), revealed a proper balance between the thermal stability and adhesion performance.

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## Keywords

Fluorinated pressure sensitive adhesives, crosslinking, thermal stability, adhesion performance

## 1. Introduction

Pressure sensitive adhesives (PSAs) are semi-solid phase materials with good viscoelastic properties and adhesion strength on solid substrates after applying a light contact pressure with a short contact time. The use of acrylic PSAs is increasing because of their resistance to oxidation, their transparency and because they do not discolour (yellowing) under exposure to sunlight [1]. In general, PSAs are used in

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a range of fields, which includes medical products, electronic devices, and the construction and automobile industries. The use of PSAs in the automobile industry has increased due to their light weight and thermal stability. Acrylic PSAs consist of acrylic copolymer monomers and linear chains with major components of butyl acrylate, 2-ethylhexyl acrylate and isooctyl acrylate (which are soft and tacky materials) and acrylic acid which is added to increase both the cohesion strength of the PSAs chain and the stiffness [2]. The acrylic PSAs linear chains are not crosslinked with chemical bonds but are connected by the hydrogen bonding of the carboxylic acid. This reversible hydrogen bonding of acrylic PSAs gives them poor thermal stability [1, 3].

In order to improve the thermal stability the mobility of the PSA molecular chains has to be restricted. One of methods for doing this, is to crosslink the molecular chains. In acrylic PSAs, crosslinking mechanisms are divided into two categories [4]: covalent or ionic crosslinking through functional groups such as acrylic acid; and UV crosslinking using a photo-crosslinker. A former crosslinking method involves a reaction of functional groups in the main chains with an external crosslinker. The typical functional group in the main chains is the carboxylic acid group derived from acrylic acid. Typical external crosslinkers include [5]: multifunctional unsaturated monomer, metal salts, metal chelates, amino resins, isocyanate crosslinking agents, multifunctional aziridine crosslinking agents and UV crosslinkers. Another restriction of molecular mobility of main chains is encountered when using semi-interpenetrating polymer networks (semi-IPNs) [6, 7]. Semi-IPNs are formed from the linear main chains of PSAs and networked polymers from multifunctional acrylic monomers. The crosslinked multifunctional polymer packs the linear main chains tightly [8]. Although these various crosslinking methods improve the thermal stability of PSAs by restricting the mobility of the main chains, a balance must be considered between improving the thermal stability and the adhesion strength. The reason for considering this balance between the thermal stability from crosslinking and the adhesion strength, is that crosslinking decreases the free volume of the PSAs molecules (thus improving the thermal stability) but decreases the adhesion and tack properties of the of PSAs [9].

In a previous study we showed that as a result of replacing 2-ethylhexyl acrylate (2-EHA) with 2,2,2-trifluoroethyl methacrylate (TFMA) (up to 20 wt%) the peel strength on various substrates (PP, PVC, ABS and SUS) increased from 500 g/25 mm to over 1000 g/25 mm. Moreover, the peel strength of samples increased as the bonding time increased from 30 min to 24 h because of sufficient wetting. However, the tack of PSAs decreased (at concentrations of over 30 wt% TFMA) due to the high glass transition temperature of TFMA (80°C).

In this study, fluorinated PSAs were synthesized by UV irradiation and various types of crosslinkings were applied to the PSAs to improve their thermal stability. The methods for increasing the thermal stability were: crosslinking of the main chains by aziridine; use of semi-IPN using trimethylolpropane ethoxylated (9) triacrylate (TMP(EO)<sub>9</sub>TA), which has a low glass transition temperature,  $T_g$  (−19°C),

and also provides flexibility; and combinations of the above two methods. The thermal stability and adhesion performance of these three types of molecular structures were compared.

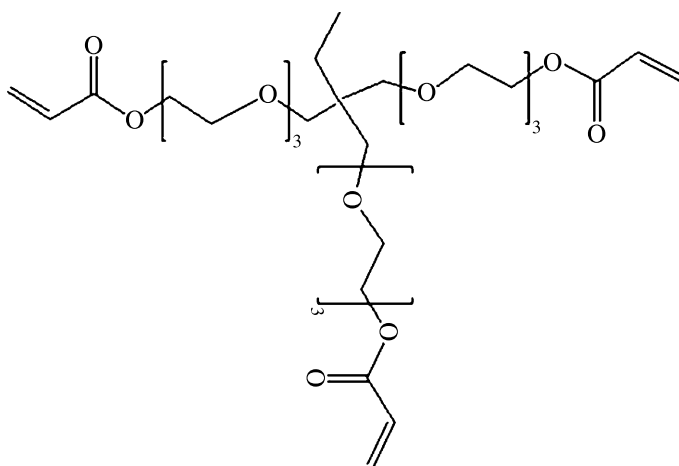
## 2. Experimental

### 2.1. Materials

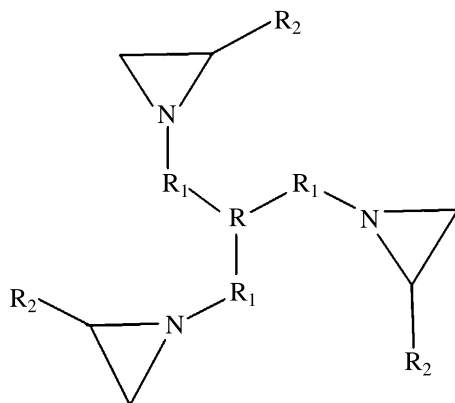
2-Ethylhexyl acrylate (2-EHA, Samchun Pure Chemical, Republic of Korea), acrylic acid (AA, Samchun Pure Chemical, Republic of Korea) and 2,2,2-trifluoroethyl methacrylate (TFMA, TOSOH F-TECH, Japan) were commercially available and used without purification. Hydroxy dimethyl acetophenone (Micure HP-8, Miwon Specialty Chemical, Republic of Korea) was used as the initiator for the UV-polymerization to synthesize the acrylic PSAs. Polybutene (PB1400,  $M_w$ :1400, Daelim Chemical, Republic of Korea) was used as a plasticizer to improve the flexibility of the acrylic PSAs. Trimethylolpropane ethoxylated (9) triacrylate (TMP(EO)<sub>9</sub>TA, Miwon Specialty Chemical, Republic of Korea) (see Fig. 1) was used as a trifunctional monomer. The crosslinker, Aziridine (see Fig. 2) was supplied by DSM Neoresins in The Netherlands.

### 2.2. Synthesis

The acrylic monomers (2-EHA and AA) and the low surface tension acrylic monomer (TFMA) were polymerized by UV-photo polymerization with hydroxy dimethyl acetophenone (Micure HP-8, Miwon Specialty Chemical, Republic of Korea) as the photo-initiator. The monomers and initiator were mixed in a 500 ml four-neck flask equipped with a condenser and a mechanical stirrer. The low surface energy (LSE) PSA was synthesized using a high-output low-attenuation



**Figure 1.** Chemical structure of trimethylolpropane ethoxylated (9) triacrylate (TMP(EO)<sub>9</sub>TA).

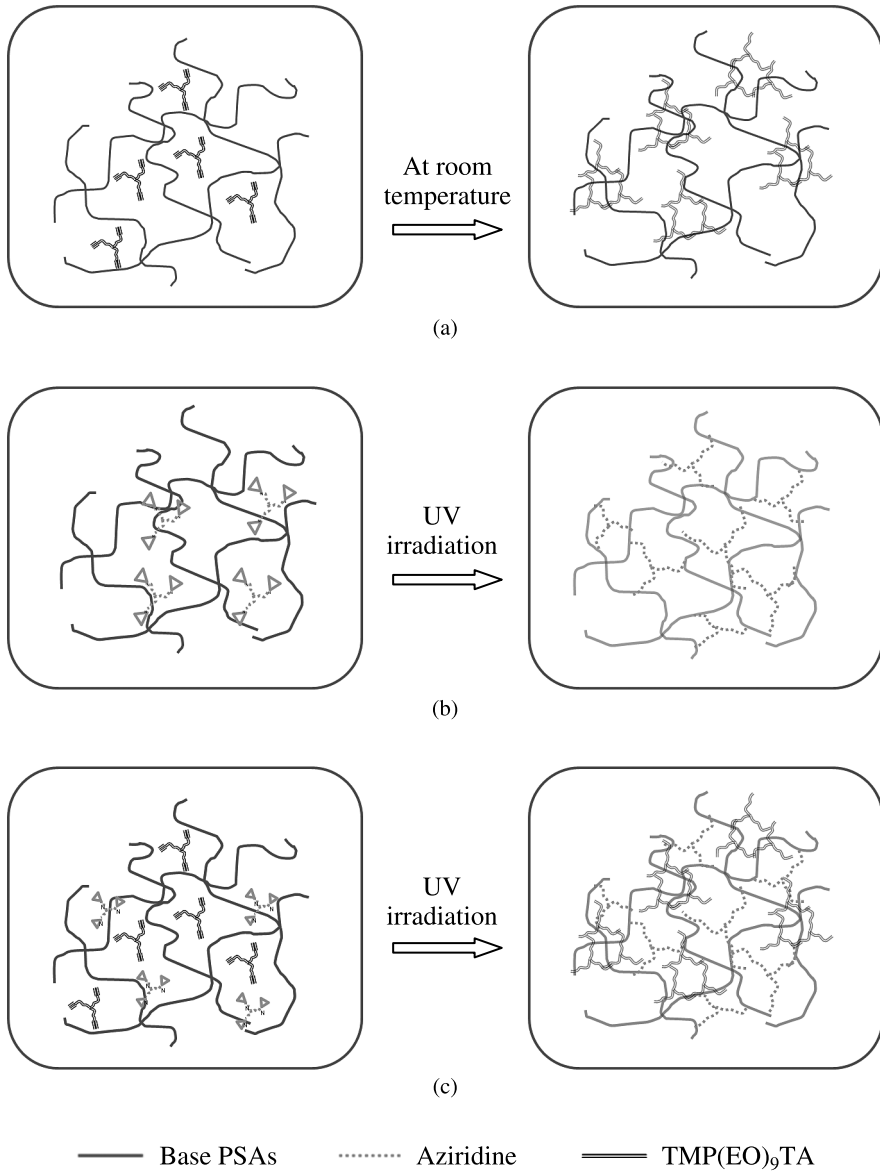


**Figure 2.** Chemical structure of methylaziridine.

250 W lamp (SP-9-250UB, USHIO INC. System Company, Japan). During photopolymerization,  $N_2$  gas was used to purge the system to prevent oxygen retarding the UV photo-polymerization process. As the viscosity of the polymer increased, a certain amount of ethyl acetate was added to swell the pre-polymer. Finally, the polybutene and the photo-initiator were added without a UV source, and the synthesis was terminated.

### 2.3. Preparation of Crosslinked Acrylic PSAs

The curing of acrylic PSAs was done by blending the UV polymerized binder with the trifunctional curing agents (TMP(EO)<sub>9</sub>TA and aziridine). The binder was polymerized by UV irradiation. The synthesized PSA (F20:non crosslinking PSA) was a random copolymer of 2-EHA (75 wt%), AA (5 wt%) and TFMA (20 wt%). The curing of the acrylic PSAs was divided into three different systems: UV curing by TMP(EO)<sub>9</sub>TA; crosslinking by aziridine; and the fusion system of UV curing and crosslinking using aziridine, as shown in Fig. 3. The amount of each trifunctional curing agent was 0.5, 1, 1.5, 2 phr (part per hundred of the resin) of the binder. The mixtures were stirred with a mechanical stirrer for 30 min. In the coating process, corona-treated polyethylene terephthalate (PET, SK Chemical, Republic of Korea) films with a 100  $\mu\text{m}$  thickness were coated with the acrylic PSAs swelled with ethyl acetate and polybutene using a No. 44 K-bar, and cured using conveyor belt type UV-curing equipment with a 100 W high pressure mercury lamp (main wavelength: 365 nm). The UV doses were measured using an IL 390C Light Bug UV radiometer (International Light, USA) at 1800  $\text{mJ}/\text{cm}^2$ . The samples were dried in an oven at 80°C for 30 min. The dried films were stored at 22°C  $\pm$  2 and 60°C  $\pm$  5% RH for 24 h before performing the other tests. Table 1 lists the composition of the crosslinked acrylic PSAs.



**Figure 3.** Scheme of curing structure using aziridine (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

## 2.4. Characterization of Acrylic PSAs

### 2.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were obtained using a FTIR-6300 spectrometer (JASCO, UK) equipped with an attenuated total reflectance (ATR) accessory. The ATR crystal was zinc selenide (ZnSe) with a refractive index at  $1000\text{ cm}^{-1}$  of 2.4. It had a transmis-

**Table 1.**

Monomer composition of the crosslinking systems (units: phr/synthesized PSA, F20)

	Aziridine	TMP(EO) <sub>9</sub> TA	HP-8
Azi 0.1	0.1	–	1
Azi 0.5	0.5	–	1
Azi 1.0	1.0	–	1
Azi 1.5	1.5	–	1
Azi 2.0	2.0	–	1
TMPTA 0.5	–	0.5	1
TMPTA 1.0	–	1.0	1
TMPTA 1.5	–	1.5	1
TMPTA 2.0	–	2.0	1
Azi 0.1_TMPTA 0.5	0.1	0.5	1
Azi 0.1_TMPTA 1.0	0.1	1.0	1
Azi 0.1_TMPTA 1.5	0.1	1.5	1
Azi 0.1_TMPTA 2.0	0.1	2.0	1
Azi 0.3_TMPTA 0.5	0.3	0.5	1
Azi 0.3_TMPTA 1.0	0.3	1.0	1
Azi 0.3_TMPTA 1.5	0.3	1.5	1
Azi 0.3_TMPTA 2.0	0.3	2.0	1
Azi 0.5_TMPTA 0.5	0.5	0.5	1
Azi 0.5_TMPTA 1.0	0.5	1.0	1
Azi 0.5_TMPTA 1.5	0.5	1.5	1
Azi 0.5_TMPTA 2.0	0.5	2.0	1

sion range from 700 to 4000  $\text{cm}^{-1}$ . The resolution of the spectra was 4  $\text{cm}^{-1}$  and the detector mode was triglycine sulphate (TGS). All spectra were obtained with some correction, such as  $\text{CO}_2$  reduction,  $\text{H}_2\text{O}$  reduction and a baseline correction.

#### 2.4.2. Gel Content

The gel content of the cured acrylic PSAs by TMP(EO)<sub>9</sub>TA and aziridine crosslinker were examined. The PSAs samples were kept in toluene for 24 h at room temperature. After 24 h, only the insoluble polymers crosslinked remained, after filtration, on a 200 mesh wire net. The insoluble polymers were dried at 80°C until a constant weight was reached. The gel content of the PSAs was calculated using the following equation:

$$\text{Gel content (\%)} = \left( \frac{W_{24}}{W_0} \right) \times 100,$$

where  $W_0$  is the initial weight of sample and  $W_{24}$  is the weight after removing the soluble polymer and drying at 80°C.

## 2.5. Viscoelastic Properties

### 2.5.1. Advanced Rheometric Expansion System (ARES)

The viscoelastic properties, such as the storage modulus, loss modulus and tangent 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  $150^\circ\text{C}$  with various strains ( $0.05\sim 40\%$ ) and frequencies (1 Hz). The heating rate was  $5^\circ\text{C}/\text{min}$ .

## 2.6. Adhesion Performances

### 2.6.1. $180^\circ$ Peel Strength

The prepared acrylic PSAs films were attached to a stainless steel substrate and the sample was rolled over twice with a 2 kg rubber roller as based on ASTM D3330. The sample was stored at room temperature for 24 h, and the  $180^\circ$  peel strength was measured using a texture analyzer (TA-XT2i, Micro Stable Systems, UK) at 25, 50 and  $80^\circ\text{C}$ . The test speed was 300 mm/min and the mean peel strength was measured five times.

### 2.6.2. Probe Tack

The probe tack was measured on the texture analyzer, using a 5 mm diameter stainless steel cylinder probe at 25, 50 and  $80^\circ\text{C}$ . The measurements were carried out at separation rates of 10 mm/s under a constant pressure of  $100\text{ g}/\text{cm}^2$  with a dwelling time of 1 s. The probe tack was estimated as the maximum debonding force.

### 2.6.3. Shear Adhesion Failure Temperature (SAFT)

The shear adhesion failure temperature (SAFT) was measured using a  $25\text{ mm} \times 25\text{ mm}$  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 500 g 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.

## 3. Results and Discussion

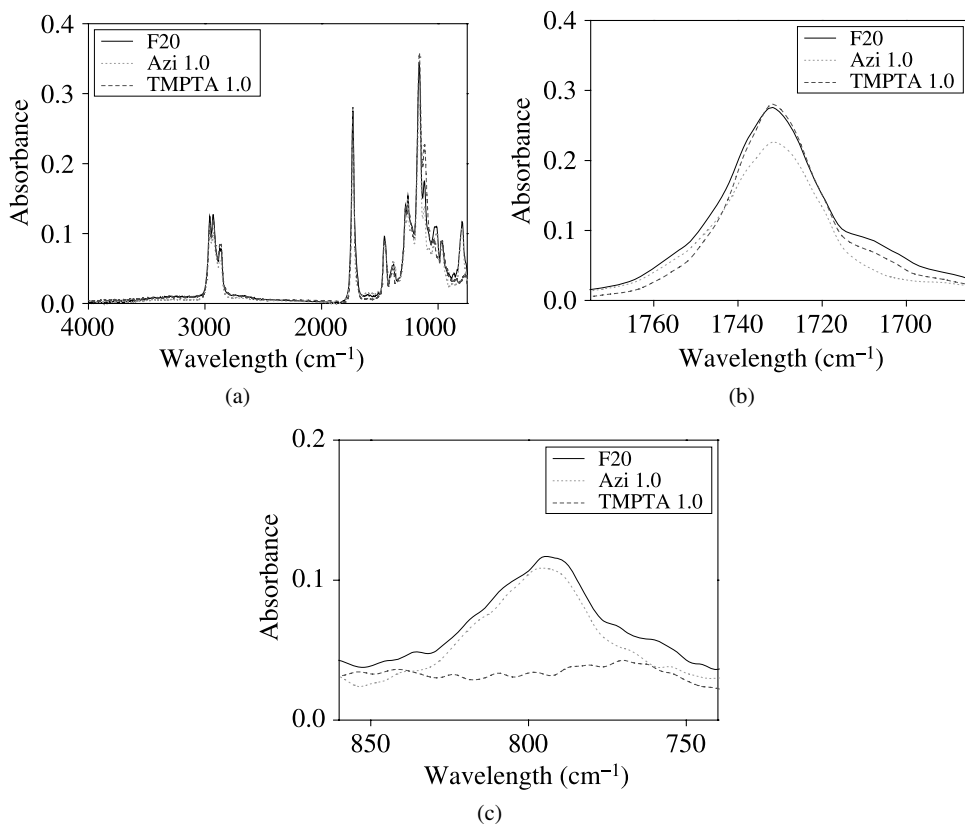
### 3.1. Characterization of the Acrylic PSAs

#### 3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The crosslinking in the blending system with aziridine and  $\text{TMP}(\text{EO})_9\text{TA}$  was measured by FTIR in a F20 binder. In the case of the crosslinking with aziridine, the carboxyl groups of the long chains in the PSAs, reacted with the aziridine crosslinker at room temperature [10]. The curing behavior of the  $\text{TMP}(\text{EO})_9\text{TA}$ , which reacted with the remaining monomers under UV irradiation, was also observed by FTIR focusing on the  $\text{C}=\text{C}$  bond twisting vibration [6].

In Fig. 4(a), F20 refers to the main binder, azi 1.0 refers to the mixture of the binder and aziridine curing agent and TMPTA 1.0 refers to the mixture binder



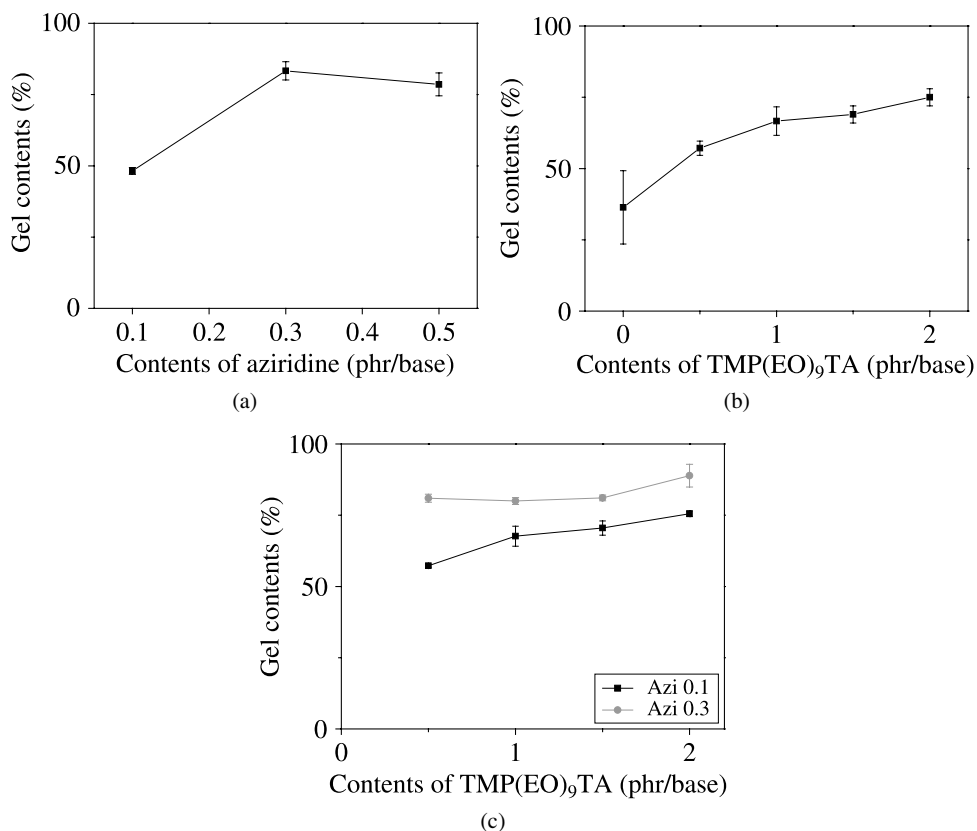


**Figure 4.** FTIR spectra of the acrylic PSAs with different curing agents (a), carboxylic group at  $1730\text{ cm}^{-1}$  (b) and  $\text{C}=\text{C}$  bond at near  $800\text{ cm}^{-1}$  (c).

and  $\text{TMP}(\text{EO})_9\text{TA}$  monomer with  $1800\text{ mJ/cm}^2$  UV irradiation. The FTIR spectra in Fig. 4(b) showed a decreasing in the  $1730\text{ cm}^{-1}$  peak which refers to the carboxylic acid group [11]. After adding aziridine, the carboxylic acid in the main long chains reacted with aziridine. Figure 4(c) shows the  $\text{C}=\text{C}$  bond peak. The  $\text{C}=\text{C}$  bond peak is commonly observed near  $810\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  [6]. In this study, the  $\text{C}=\text{C}$  bond was observed near  $800\text{ cm}^{-1}$ . In the comparison between F20 and TMPTA 1.0, F20 had acrylic monomers remaining. However, the  $\text{TMP}(\text{EO})_9\text{TA}$  added, reacted with the remaining acrylic monomers at  $1800\text{ mJ/cm}^2$  and the semi-interpenetrating polymer network was structured in TMPTA 1.0. As a result the intensity of the peak for the  $\text{C}=\text{C}$  bond decreased.

### 3.1.2. Gel Content

The crosslinking density can be measured indirectly by calculating the gel content of each sample by measuring the insoluble fraction in the polymer [6]. The insoluble fraction of the polymer indicates the three-dimensional network formed by chemical bonding. Lim and Joo *et al.* estimated the crosslinking density to confirm the UV crosslinking system as a function of the UV dose [12]. In this study, the



**Figure 5.** Gel content of the acrylic PSAs as aziridine content (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

binder F20 sample that was made up of linear long chains that were entangled by the hydrogen bonding of the carboxylic acid in the main chain, was crosslinked by using aziridine, TMP(EO)<sub>9</sub>TA and a combination of both aziridine and TMP(EO)<sub>9</sub>TA to form structured three dimensional networks. In the case of the non-crosslinked F20 sample, the gel content was 35%. With increasing aziridine content, the gel content reached more than 80% at 0.3 phr of aziridine (see Fig. 5(a)). This means that the three-dimensional network was structured by a reaction between carboxylic acid and aziridine. In addition, carboxylic acid exists in the long main chain so the crosslinking density reached a high gel content despite the low aziridine content [13]. In contrast to the aziridine crosslinking system, TMP(EO)<sub>9</sub>TA formed a three-dimensional network as a reaction of TMP(EO)<sub>9</sub>TA with the remaining monomer under UV irradiation. With increasing TMP(EO)<sub>9</sub>TA content, the gel content increased drastically until 70% at 1.5 phr of TMP(EO)<sub>9</sub>TA, and then reached 75% between 1 phr and 2 phr of TMP(EO)<sub>9</sub>TA, as shown Fig. 5(b). In the case of the TMP(EO)<sub>9</sub>TA crosslinking system, the long main chain was not crosslinked, even though TMP(EO)<sub>9</sub>TA formed a three-dimensional network, which consisted

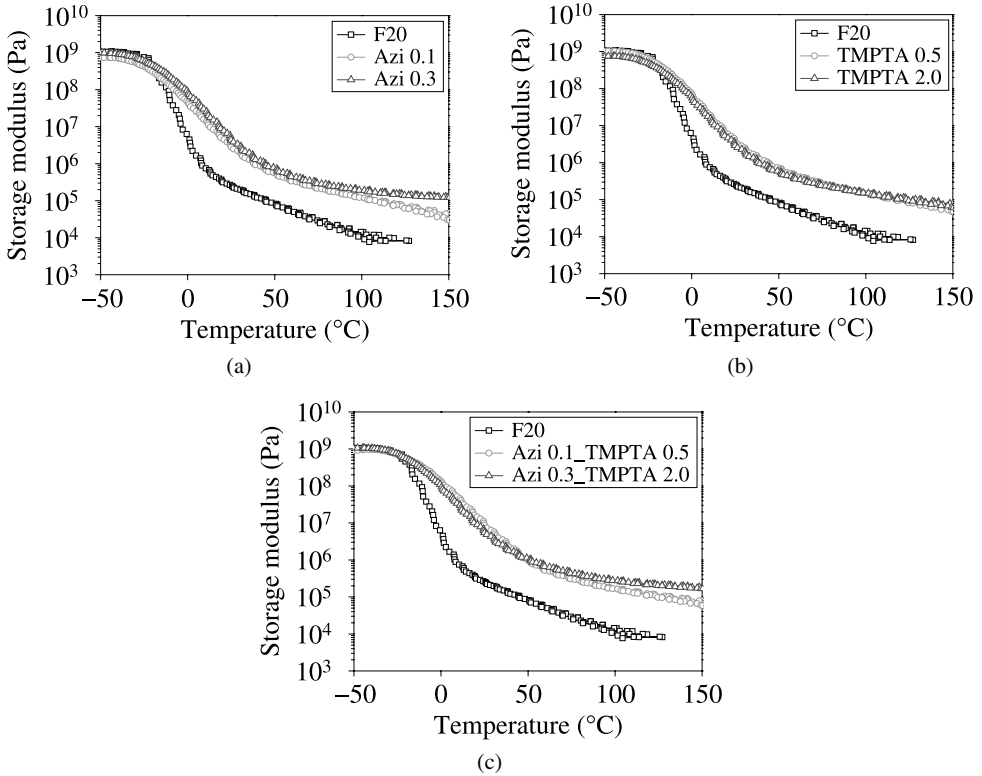
mainly of short length chains. In Fig. 5(c), it can be seen that the gel content increased to 90% with a combination of 0.3 phr aziridine and 2 phr TMP(EO)<sub>9</sub>TA. This crosslinking system consists of two types of different crosslinking networks, which formed with main chain network linked by aziridine and the short chain network of TMP(EO)<sub>9</sub>TA.

### 3.2. Viscoelastic Properties

#### 3.2.1. Advanced Rheometric Expansion System (ARES)

The PSAs have semi-solid properties and hence, for the wetting of a substrate, the viscoelastic property (a bulky property of the molecular mobility), is the main factor that determines the adhesion performance [14]. In the case of PSA, the storage modulus curve has a glassy region, a rubbery plateau and a terminal region; these curves are functions of temperature. In the glassy region, the PSAs have rigid properties, but with increasing temperature, and depending on the glass transition temperature ( $T_g$ ), the PSAs 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  $\tan \delta$  is indicative of 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 [15].

Figure 6 shows the storage modulus of the PSAs as a function of various crosslinking systems. In Fig. 6(a), F20 is compared to the aziridine crosslinking system. F20 is not crosslinked by chemical bonding. As result of physical bonding by hydrogen bonding, the storage modulus decreased sharply after  $T_g$ . In contrast to F20, the other samples were crosslinked by aziridine 0.1 and 0.3 phr, respectively. The storage modulus and  $T_g$  increased with increasing amount of aziridine. This suggests that the mobility of a molecule is limited because the main chains in a polymer are combined through chemical bonding from the aziridine crosslinking agent. In the case of adding aziridine 0.3 phr, the storage modulus was higher than that for 0.1 phr aziridine above  $T_g$ . This is caused by the higher crosslinking density due to the addition of more aziridine. In the case of adding TMP(EO)<sub>9</sub>TA (see Fig. 6(b)), a semi-IPN structure was formed by UV irradiation. With increasing TMP(EO)<sub>9</sub>TA addition, the storage modulus increased to above  $T_g$  and  $T_g$  also shifted to a higher temperature. This suggests that TMP(EO)<sub>9</sub>TA formed three dimensional structures and packed the main linear chains, resulting in the mobility of main chains being reduced. In Fig. 6(c), the combined system of aziridine crosslinking of the main chains and TMP(EO)<sub>9</sub>TA, was measured. In the case of adding TMP(EO)<sub>9</sub>TA 0.5 and aziridine 0.1, this system improved markedly compared to the aziridine 0.1 system in Fig. 6(a). However, in the glassy region, the storage modulus had similar values due to the insufficient rearrangements of the main chain in the polymer below  $T_g$ , i.e., crosslinking has no effect on the storage modulus [16]. However, the modulus in the glassy region is indicated by van der Waals forces [17].

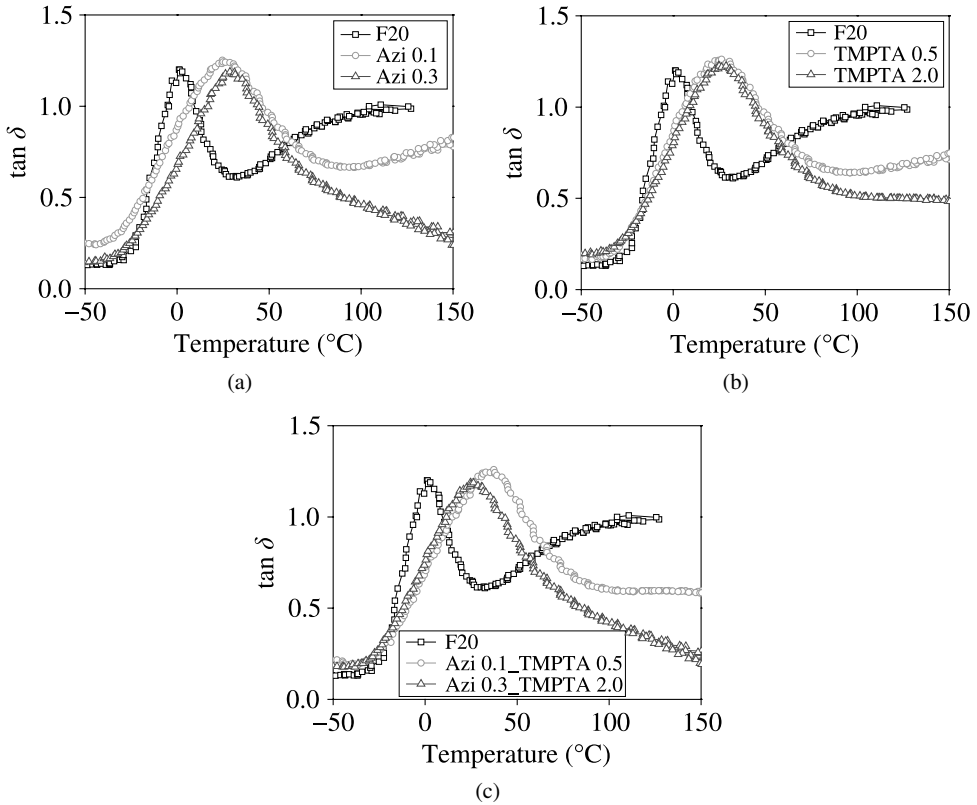


**Figure 6.** Viscoelastic curves of the acrylic PSAs with crosslinking by aziridine (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

Figure 7 shows the relationship between  $\tan \delta$  and temperature; where  $\tan \delta$  is given by the following equation:

$$\tan \delta = \frac{\text{loss modulus}}{\text{storage modulus}}.$$

In Fig. 7(a), the  $\tan \delta$  peak over 50°C was in the order of F20 > azi 0.1 > azi 0.3. The degree of crosslinking increased with increasing aziridine content in the binder. Moreover, in Fig. 7(b) it can be seen that the highest  $\tan \delta$  peak moved to a higher temperature and the  $\tan \delta$  of each sample decreased with increasing TMP(EO)<sub>9</sub>TA. In addition, with increasing degree of crosslinking, the  $\tan \delta$  was similar to previous  $\tan \delta$  curves of aziridine crosslinking systems. The higher  $\tan \delta$  curves demonstrates a more viscous property with a greater mobility at higher temperatures [12]. A comparison of the  $\tan \delta$  curves showed that the  $\tan \delta$  decreased sharply compared to TMP(EO)<sub>9</sub>TA with increasing crosslinking in the main chains. As shown in Fig. 7(c), based on aziridine crosslinking in the main chains, the added TMP(EO)<sub>9</sub>TA increases the degree of crosslinking. As a result of crosslinking, the mobility of the molecules decreases and  $T_g$  increases [18].



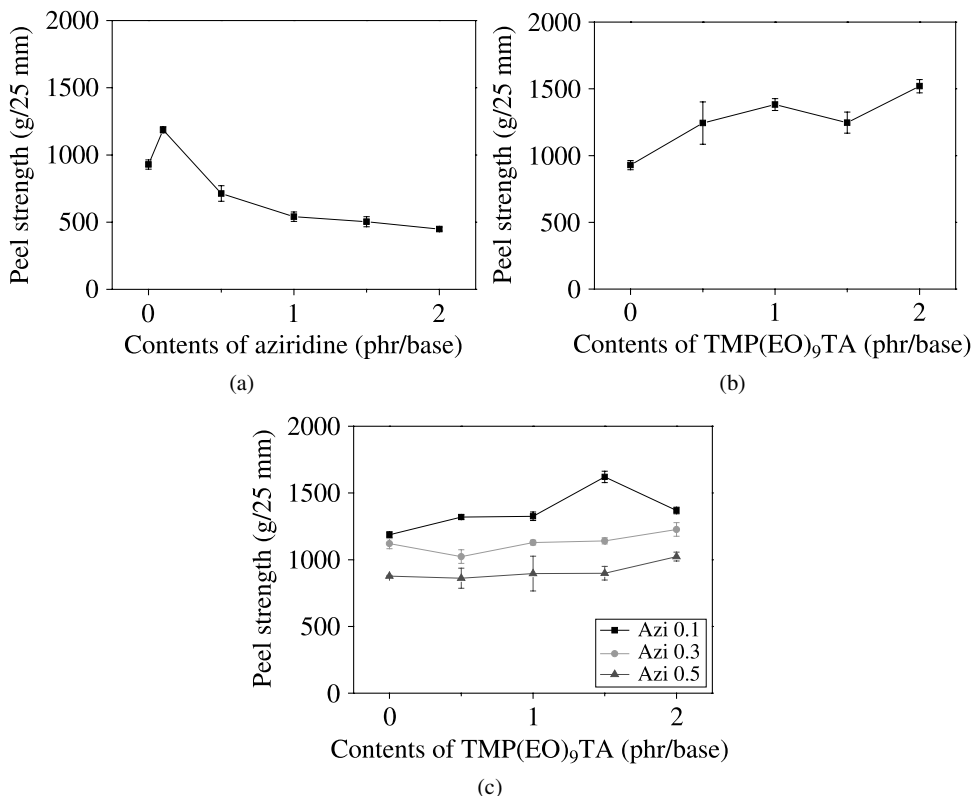
**Figure 7.**  $\tan \delta$  curves of the acrylic PSAs with crosslinking by aziridine (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

### 3.3. Adhesion Performances

The peel strength, the probe tack and shear adhesion failure temperature can give an indication of the adhesion performance of a PSA [14] and as the mobility of the molecular chains is affected by crosslinking due to the restricted free volume of molecules [19], the effect of crosslinking was estimated by the peel strength, probe tack and SAFT analysis.

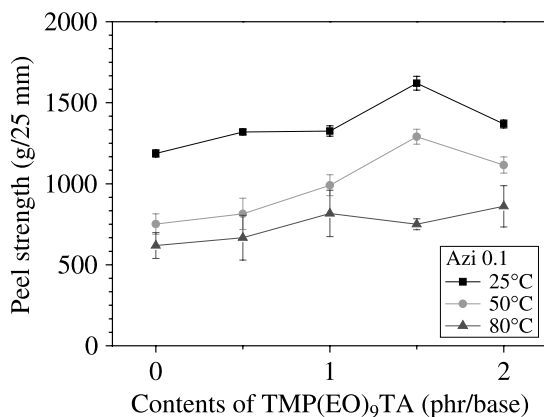
#### 3.3.1. 180° Peel Strength

The peel strength is a common method for measuring the adhesion force after attaching PSAs to substrates for a certain time. In addition, the peel strength is affected by the mobility of molecules [14]. Many researchers have examined the effect of crosslinking on the peel strength. Czech reported a decrease in peel strength as crosslinking of main chains, and Joo studied the correlation between the semi-IPN structure with the peel strength [7, 20]. In this study, three types of crosslinking were analyzed: main chain crosslinking; semi-IPN; and a combination crosslinking of both crosslinking systems. All were investigated as a function of temperature.



**Figure 8.** Peels strength of acrylic PSAs with crosslinking by aziridine (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

In Fig. 8(a), it can be seen that the peel strength increased to more than 1000 g/25 mm at 0.1 phr aziridine and then decreased sharply with further increases in aziridine content. The peel strength showed a similar tendency to other studies that reported an increasing in peel strength after the addition of a certain amount of crosslinking agent followed by a decrease in peel strength with further additions of the crosslinking agent [5]. This is caused by the increasing density of crosslinks and polymer chains at 0.1 phr aziridine. In the case of Fig. 8(b), the peel strength increased with increasing TMP(EO)<sub>9</sub>TA content. The peel strength increase was accompanied by an increase in the gel content. This shows a different tendency to that seen when the main chain crosslinking was done using aziridine. The reason for the increasing peel strength in the TMP(EO)<sub>9</sub>TA semi-IPN system was examined by Joo *et al.*, who reported that TMP(EO)<sub>9</sub>TA has a low  $T_g$  and good mobility, which resulted in the good cohesion and increased peel strength [7]. In Fig. 8(c), it can be seen that the peel strength of a combination of aziridine and TMP(EO)<sub>9</sub>TA decreased as a result of the main chain crosslinking with aziridine, whereas TMP(EO)<sub>9</sub>TA had a less pronounced effect on the peel strength than did aziridine.



**Figure 9.** Peels strength of acrylic PSAs with crosslinking by combination of aziridine and TMP(EO)<sub>9</sub>TA as a function of temperature.

The peel strength was found to be temperature dependent. The thermal stability of PSAs was determined from measurements of the peel strength at various temperatures, as shown in Fig. 9. The sample involved a combination of crosslinking main chains and TMP(EO)<sub>9</sub>TA network structures. The aziridine content was fixed at 0.1 phr and the TMP(EO)<sub>9</sub>TA content was 0, 0.5, 1, 1.5, 2 phr. The peel strength was measured as a function of temperature. The peel strength decreased with increasing temperature because the peel strength was affected by the cohesion of chains in PSAs and the adhesion force of PSAs [14]. The cohesion decreased with increasing temperature. The non-crosslinking PSAs (F20) had a lower peel strength than the crosslinking system as shown by the following results: 928 g/25 mm (at 25°C), 677 g/25 mm (at 50°C) and 663 g/25 mm (at 80°C). Moreover, the failure mode of F20 at 50 and 80°C was cohesive failure, which indicated that a non-crosslinking system had a poorer thermal stability than did the crosslinking system.

### 3.3.2. Probe Tack

In contrast to the peel strength, the probe tack is a measure of the adhesion performance over a short time (1 s). In Fig. 10(a), it can be seen that the probe tack persisted until 0.5 phr of aziridine and then decreased. However, Fig. 10(b) shows a decrease in the shoulder of the probe tack in the time–force curves. The decreased area of the probe tack means that crosslinking occurred with increasing aziridine content. As a result of crosslinking, the cohesion of PSAs increased and the tack decreased. In the case of TMP(EO)<sub>9</sub>TA (see Fig. 11(a)), the probe tack value was similar, regardless of TMP(EO)<sub>9</sub>TA content. In addition, the probe tack area increased, as shown in Fig. 11(b). This indicates that the short chain of TMP(EO)<sub>9</sub>TA and the remaining monomer reacting with TMP(EO)<sub>9</sub>TA acted as plasticizer resulting in an increase in peel strength [7]. Figure 12(a) shows that aziridine caused a decrease in the probe tack and the probe tack increased slightly with increasing TMP(EO)<sub>9</sub>TA content. The time–force curve in Fig. 12(b) shows that the probe

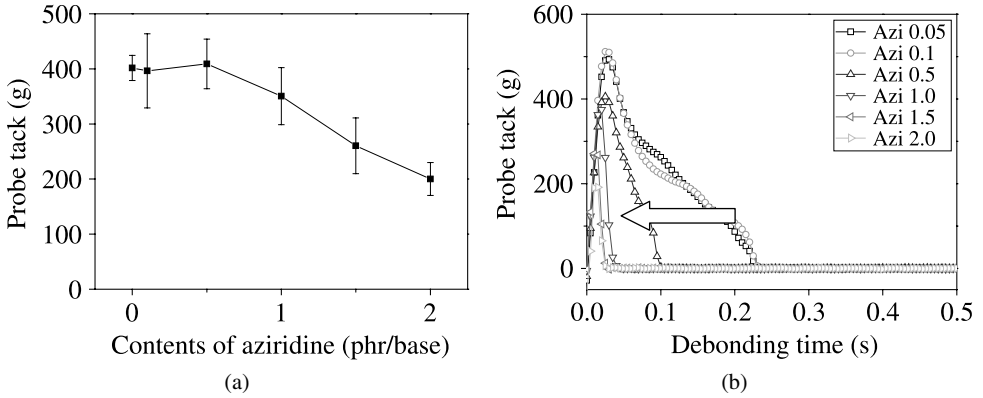


Figure 10. Probe tack of acrylic PSAs with crosslinking by aziridine (a) and time–force curves (b).

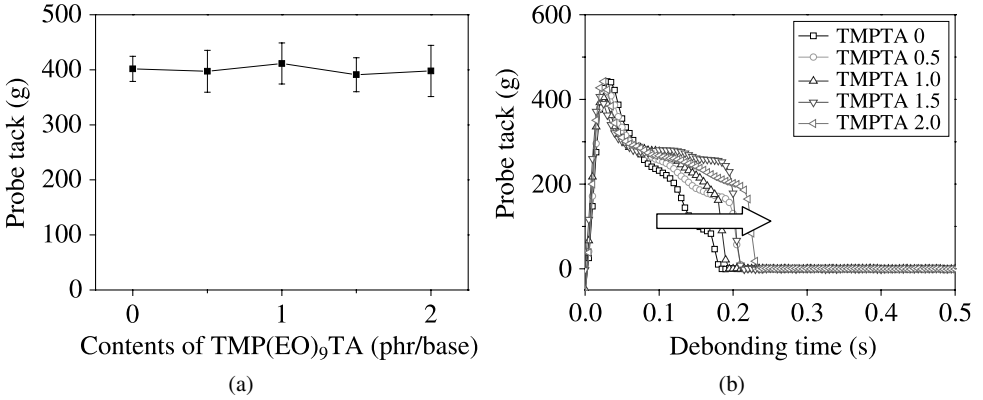


Figure 11. Probe tack of acrylic PSAs with TMP(EO)<sub>9</sub>TA (a) and time–force curves (b).

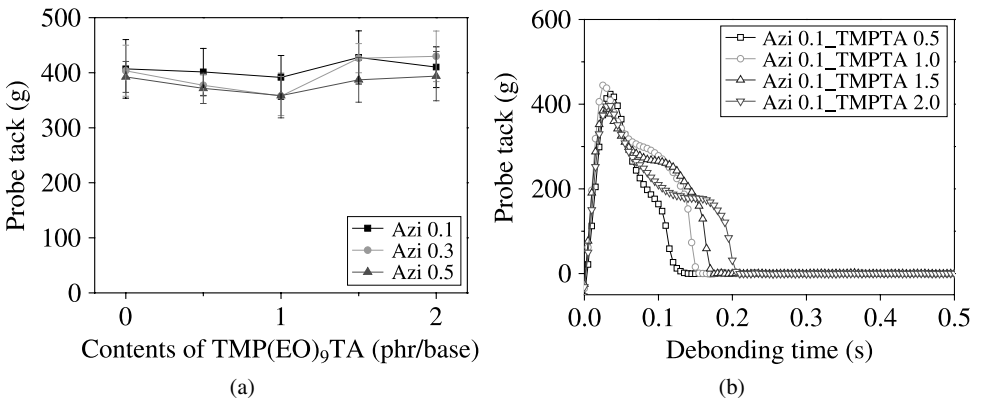
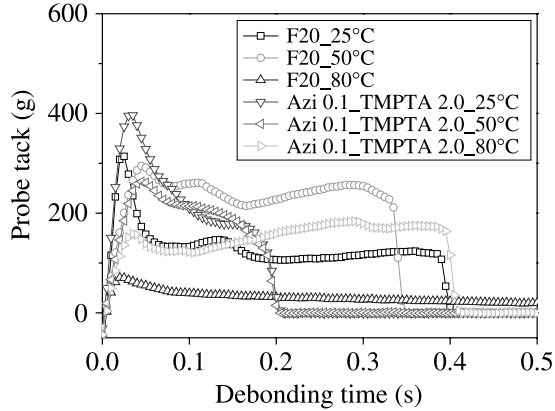


Figure 12. Probe tack of acrylic PSAs with combination of aziridine and TMP(EO)<sub>9</sub>TA (a) and time–force curves (b).





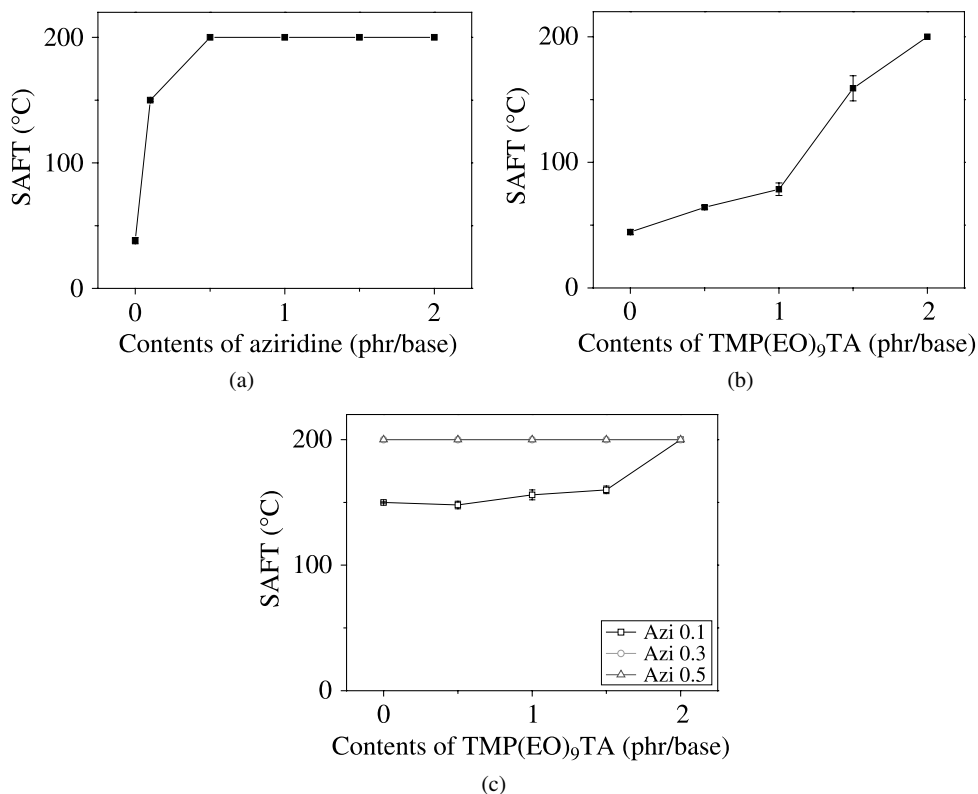
**Figure 13.** Probe tack time–force curves of acrylic PSAs with crosslinking by combination of aziridine and TMP(EO)<sub>9</sub>TA as a function of temperature.

tack area decreased with increasing aziridine content and the shoulder of the curve lagged. In addition, the time–force curve as function of temperature (see Fig. 13) shows that the non-crosslinking PSAs F20 had a flow property at 80°C and fibrillation occurred. This fibrillation phenomenon is in an agreement with the cohesive failure of F20 in the peel strength test at 80°C. Therefore, the probe tack of F20 decreased and the shoulder peak lagged, whereas crosslinked PSAs azi 0.1\_TMPTA had more elastic properties. The cohesion of PSAs was reinforced by crosslinking and the thermal stability was improved.

### 3.3.3. Shear Adhesion Failure Temperature (SAFT)

The thermal stability of acrylic PSAs can be examined by determining the SAFT; that is the upper temperature limit at which an adhesive is able to support a certain amount of weight or the temperature when the cohesion becomes weak under a constant force with increasing temperature. Joo *et al.* examined the effect of a semi-IPN structure on the SAFT and reported that the SAFT increased with increasing amount of TMP(EO)<sub>9</sub>TA due to the increased crosslinking density [7]. In this study, the SAFT of the main chain, TMP(EO)<sub>9</sub>TA and a combination of aziridine and TMP(EO)<sub>9</sub>TA were measured up to 200°C.

In Fig. 14(a) it can be seen that the F20 binder, which was not crosslinked, had a SAFT of 40°C. With increasing aziridine content in the binder, the SAFT increased to 200°C at 0.5 phr aziridine. The F20 binder became entangled by the linear chains and the three-dimensional network was structured by a reaction between aziridine and the carboxylic acid in the main linear chains of the binder. Therefore, cohesion was enforced by the chemical bonding of crosslinking and the thermal resistance was increased. In the case of Fig. 14(b), it can be seen that the TMP(EO)<sub>9</sub>TA, which has a three functional group monomer, formed a semi-IPN structure. This caused the SAFT to gradually increase until 1 phr of TMP(EO)<sub>9</sub>TA and increased drastically from 1 phr to 2 phr of TMP(EO)<sub>9</sub>TA. The results from Fig. 14(a) and 14(b),



**Figure 14.** SAFT of acrylic PSAs with crosslinking by aziridine (a), TMP(EO)<sub>9</sub>TA (b) and combination of aziridine and TMP(EO)<sub>9</sub>TA (c).

show that the crosslinking of the main chain has a larger effect on the SAFT than does the semi-IPN. The effect of the combination of the two systems can be seen in Fig. 14(c). The TMP(EO)<sub>9</sub>TA reinforced the crosslinking of the main chain and the SAFT of the azi 0.1 sample increased with increasing TMP(EO)<sub>9</sub>TA content. This SAFT data is related to the gel content and the ARES data. With increasing crosslinker concentration, the gel contents and elastic property increased [3]. This correlation between the crosslinking density and thermal stability was confirmed in this work. Kim reported that the main chain crosslinking increased the SAFT and the cohesion and Joo *et al.* reported that the semi-IPN improved the SAFT [7, 13]. The results in this paper are in good agreement with the results reported by Kim and Joo [7, 13].

#### 4. Conclusions

The chemicals 2-EHA, AA and fluorinated acryl monomer, which has low surface energy, were polymerized by a UV source and a photo-initiator. After polymerization, a plasticizer and more photo-initiator were added and the UV curing process

was continued. The non-crosslinked linear PSAs had poor thermal stability, so a crosslinking process was applied to the PSAs. However, the adhesion performance decreased with increasing degree of crosslinking density. In this experiment, the crosslinking agents were aziridine and TMP(EO)<sub>9</sub>TA. One form of crosslinking occurred as a result of the aziridine reaction with the carboxylic acid in the main chain of PSAs. Another system was the use of a semi IPN structure by TMP(EO)<sub>9</sub>TA. The third was a combination of the above two types of crosslinking systems. Aziridine crosslinking restricts the mobility of the main chains by chemical bonding between the main chains and the aziridine crosslinker. On the other hand, the semi IPN structure from TMP(EO)<sub>9</sub>TA formed short network structures consisting of TMP(EO)<sub>9</sub>TA and the remaining monomer in PSAs.

Considering the viscoelastic property, the storage modulus was significantly influenced by the aziridine, and the TMP(EO)<sub>9</sub>TA slightly improved the storage modulus at high temperatures. However, aziridine crosslinking decreased the adhesion performance. On the other hand, in the case of semi IPN from TMP(EO)<sub>9</sub>TA, the thermal stability was improved by packing the linear main chains. The TMP(EO)<sub>9</sub>TA crosslinking system also acted as a plasticizer.

As a result of these experiments, it was found that the best system was a combination of two types of crosslinking and the optimal combination of aziridine and TMP(EO)<sub>9</sub>TA was: aziridine 0.1 phr and TMP(EO)<sub>9</sub>TA 2.0 phr. Finally, the cohesive failure of the F20 was changed to interfacial failure, and the adhesion strength was increased using the combined crosslinking systems.

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