

Adhesion Performance and Surface Characteristics of Low Surface Energy PSAs Fluorinated by UV Polymerization

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Acrylic pressure sensitive adhesives (PSAs) have a range of applications in industry, such as medical products, aircraft, space shuttles, electrical devices, optical products, and automobiles, etc. In this study, acrylic PSAs with fluorinated groups were synthesized using 2,2,2-trifluoroethyl methacrylate (TFMA) under UV radiation. The surface properties and adhesion strength were measured. The results showed that the addition of TFMA reduced the surface energy of the PSAs and improved the adhesion strength. POLYM. ENG. SCI., 53:1968–1978, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Pressure sensitive adhesives (PSAs) are nonmetallic materials used primarily to bond the surfaces of various materials through adhesion and cohesion [1]. The function of PSAs is to ensure instantaneous adhesion with the application of light pressure [2]. In particular, acrylic PSAs have many advantages, such as excellent aging characteristics, resistance to elevated temperatures and exceptional optical clarity. Therefore, acrylic PSAs are applied in areas, such as splicing tapes, protective foils, films for the graphics market, and a range of medical products. The common composites used in acrylic PSAs are hard segment monomer, soft segment monomers and additives. The roles of the hard segment are to control the adhesive properties of PSAs. An example is acrylic acid (AA), which has a glass

transition temperature (T_g) of 106°C. AA possesses carboxyl groups that provide cross-linking sites. Therefore, the cohesion and adhesion properties can be controlled by the AA content. Another important component for controlling tacky property of PSAs is the soft segment, which is a combination of soft and tacky polymers with a low glass transition temperature (T_g). Commonly reported monomers include alkyl acrylates and methacrylates with 4–17 carbon atoms, e.g. butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, isooctyl acrylate, or decyl acrylate. The others are additives, such as plasticizers, inhibitors, and fillers [3]. Therefore, the final property of PSAs is controlled by the optimal fractions of these components.

Although acrylic PSAs have many advantages and are used in a variety of fields, they have poor adhesion to plastic substrates, such as polyethylene (PE), polypropylene (PP), or polytetrafluorethylene (PTFE), which have low surface energy. Until now, attachment to plastics has required an additional surface pretreatment to increase the surface energy of the substrate. The previously used pretreatments to improve the adhesion between the surface and adhesive were the corona, plasma, primer, or flame treatments of the plastic surface [4]. However, pretreatments of plastics have problems, such as cost and damage to the substrate. The reason for the weak adhesion strength is the difficulty of wetting the PSAs on plastic substrates. Proper wetting does not occur when the surface energy of the substrate is lower than the surface energy of the PSAs.

A novel method for the adequate wetting of PSAs is the formation of PSAs with a lower surface energy than the substrate using their high molecular mobility [5, 6]. Therefore, suitable viscoelastic properties and low surface energy are the key factors for achieving perfect PSA wetting of the substrate surface.

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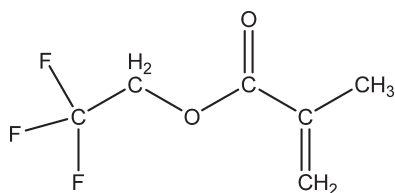


FIG. 1. Chemical structure of 2,2,2-trifluoroethyl methacrylate (TFMA).

One of the lowest surface energy monomers is the fluorinated monomer and fluorinated polymers are used widely in industry. In particular, in the coating industry, a low surface energy and resistance to most chemicals are more outstanding than other polymers [7]. As an example application, poly(tetrafluoroethene) is hydrophobic and lipophobic. Accordingly, polymers possessing a perfluoroalkyl side chain with an appropriate length are used for water and oil repellents and surface modifiers. The reason for the novel properties of fluorinated polymers is that fluorine has a small atomic radius and the largest electronegativity of all elements, so it forms a stable covalent bond with carbon [8]. As an aspect of the surface energy property, the surface energy of the constituent groups decreases in the following order: CH_2 (36 mN/m) > CH_3 (30 mN/m) > CF_2 (23 mN/m) > CF_3 (15 mN/m) [9]. This suggests that the lower surface free energy of the polymers is controlled by packing of $-\text{CF}_3$ groups [10, 11]. However, the applications of fluorine to PSAs are not common on account of their expense and difficulty in applying to a surface.

In this study, a fluorinated monomer was added to PSAs polymers to control the surface energy of PSAs by UV irradiation. UV (ultra violet) radiation polymerization is used in many applications in industry, such as the curing of inks, as well as in coatings, adhesives, and grafting to other polymers [12]. The common mechanism is that acrylates or epoxides are polymerized by radical or cationic type processes using a photo initiator. UV polymerization has advantages, such as high polymerization rates, low energy consumption, polymerization at ambient temperatures, and requiring little space for the equipment [13]. Therefore, in this study, the UV polymerization rates according to the content of the fluoro monomer were estimated by photo-DSC and real-time FTIR. In particular, the surface of fluorinated low surface energy PSAs was observed, and the correlation between the surface energy and adhesion strengths was examined using a variety of substrates with different surface energies.

EXPERIMENTAL

Materials

Acrylic monomers were selected for UV-polymerization. 2-ethylhexyl acrylate (2-EHA, 99.0% purity, Sam-

chun Pure Chemical, Republic of Korea), acrylic acid (AA, 99.0% purity, Samchun Pure Chemical, Republic of Korea) and 2,2,2-trifluoroethyl methacrylate (TFMA, 99.0% purity, TOSOH F-TECH, INC., Japan) shown in Fig. 1 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 of acrylic PSAs. Polybutene (PB1400, M_w : 1400, Daelim Chemical, Republic of Korea) was used as the plasticizer to improve the flexibility of the acrylic PSAs. The substrates used for the peel strength test were stainless steel (SUS), polypropylene (PP), Teflon, PVC, ABS, and phenolic resin.

Synthesis

Acrylic monomers (2-EHA and AA) and low surface tension acrylic monomer (TFMA) were prepared by the effect of UV radiation 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 LSE (Low surface energy) PSAs were synthesized using a high-output low-attenuation 250 W lamp (SP-9-250UB, USHIO INC. System Company, Japan). Compositions of acrylic PSAs are shown in Table 1. During photo polymerization, N_2 gas was purged 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, polybutene and a photo initiator were mixed into the PSAs without exposure to UV radiation, and the synthesis was terminated. Figure 2 shows a schematic diagram of the low surface energy PSAs.

Formation of PSA Film

Corona-treated polyethylene terephthalate (PET, SK Chemical, Republic of Korea) films, 100 μm in thickness, were coated with the acrylic PSAs swelled with ethyl acetate and polybutene using a No. 44 K-bar and cured

TABLE 1. Compositions of the low surface acrylic PSAs.

Composition (wt%)	PSAs sample at 1 st step			
	F0	F5	F10	F20
2-EHA	95	90	85	80
AA	5	5	5	5
TFMA ^a	0	5	10	20
HP-8 ^b	0.2	0.2	0.2	0.2
	PSAs sample at 2 nd step			
	Plasticizer ^b			
HP-8 ^b	10	10	10	10
	1	1	1	1

^a Surface tension of the homopolymer of TFMA is 19 mN/m.

^b Unit: parts per hundred parts PSAs.

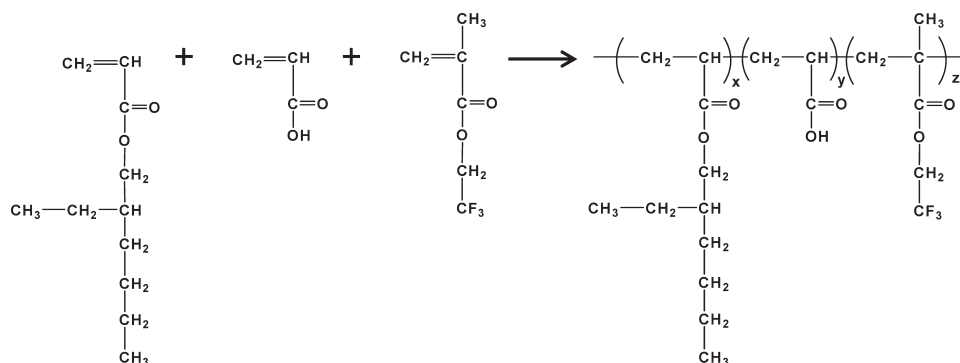


FIG. 2. Schematic diagram of the low surface energy PSAs.

using conveyor belt type UV-curing equipment with a 100 W high pressure mercury lamp (main wavelength: 365 nm). The UV doses were gauged using an IL 390C Light Bug UV radiometer (International Light, USA). The samples were dried in an oven at 80°C for 30 min. The dried films were stored at 22°C ± 2 and 60 ± 5% RH for 24 h before performing additional tests.

Kinetics of UV Synthesis of Fluorine Grafted Copolymer

Real-Time Fourier Transform Infrared Spectroscopy (Real-Time FTIR). FTIR-6100 (Jasco, Japan) with an attenuated total reference (ATR) accessory (Jasco, Japan) was used to obtain the real-time FTIR spectra. Rapid scan mode was used for the high speed measurements with a MCT-M detector. 4.0 mW/cm² intensity UV was irradiated for 600 s, and the spectra were observed for 600 s to determine the photo-polymerization behavior of the acrylic monomers to the prepolymer stage. UV spot curing equipment (SP-9-250UB, USHIO INC. System Company, Japan) was used as the light source. The spectral range was 700 to 4000 cm⁻¹. The photo-polymerization behavior was monitored from the 810 cm⁻¹ C=C double bond peak for 600 s. All mixed monomers were placed on an ATR crystal in a 10 µl volume and photo-polymerization was performed at room temperature.

Photo-Differential Scanning Calorimetry (Photo-DSC).

Photo-DSC analysis was performed using a DSC Q-1000 (TA Instrument, USA) to observe the photo-polymerization behaviors of 2-EHA, AA, and various TFMA contents. The photo-DSC experiments were equipped with a photocalorimetric accessory (Novacure 2100 at NICEM, Seoul National University), which utilized light from a 100 W Medium-pressure mercury lamp under a nitrogen atmosphere. The UV light intensity at the sample was 40 mW/cm² over the wavelength range, 300–545 nm. The sample weight was ~4 mg, and the sample was placed in an open aluminum DSC pan. The measurements were carried out at 25°C. In this analysis, the heat released during photo-polymerization was compared.

Surface Characterization of Low Surface Energy PSAs

Contact Angle Test. The surface properties were measured using a contact angle test. The surface energy was estimated from the water contact angle. Each sample was coated on glass using a 90 µm thickness applicator. Subsequently, the glass was passed through the UV conveyor belt machine with a UV dose set to 600 mJ/cm² to cure the prepolymer. Subsequently, the sample was dried in an oven at 80°C for 30 min in order to remove nonreacted monomers. The contact angle was measured using a contact angle goniometer (SEO 300A contact angle measuring device, Surface & Electro-Optics, Republic of Korea). A single drop of distilled water, diiodomethane and ethylene glycol was placed on the surface of PSA. The contact angle was observed after 5 s on PSAs surface. The surface energies of PSAs were calculated by acid/base method. The bounce of the water drop on the coated PSAs surface was observed using a high speed camera (1000 frame/s).

Fourier Transform Infrared Spectroscopy. 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 cm⁻¹ of 2.4. It had a transmission range of 700–4000 cm⁻¹. The resolution of the recorded spectra was 4 cm⁻¹ and the detector mode was TGS. All spectra were obtained with some correction, such as CO₂ reduction, H₂O reduction, and a baseline correction.

X-Ray Photoelectron Spectroscopy. The XPS experiments were performed using an UHV multipurpose surface analysis system (SIGMA PROBE, Thermo, UK) operating at base pressure <10⁻⁹ mbar. The photoelectron spectra were excited by an Al Kα (1486.6eV) anode operating at constant power of 100 W (15 KV and 6.7 mA). X-rays from the Al Kα (1486.6eV) anode were used to irradiate the samples with a 400 µm diameter spot size. Elemental survey scans from 0 to 1350 eV were acquired with a pass energy of 100 eV. High-resolution scans of the C1s and F1s regions were performed in constant analyzer energy

(CAE) mode at a pass energy of 30 eV and a step of 0.1 eV. The C and F atomic percentages were calculated from the peak areas using standard atomic sensitivity factors (SF). Additionally, the background was corrected using the Smart method in the curve fitting program (Advantage program). The spectra were referenced to the hydrocarbon component of the C1s region at 285.0 eV.

Viscoelastic Properties

Advanced Rheometric Expansion System. 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 120°C with various strains (0.05–40%) and frequencies (1 Hz). The heating rate was $5^\circ\text{C}/\text{min}$.

Adhesion Performances

The prepared acrylic PSAs films were attached to various substrates (Teflon, phenolic resin, SUS, PP, PVC, and ABS) and the samples were rolled over twice with a 2 kg rubber roller. The samples were stored at room temperature for 24 h, and the 180° peel strength was measured using a Texture Analyzer (TA-XT2i, Micro Stable Systems, UK). The test speed was 300 mm/min and the mean peel strength was measured five times. The probe tack on the Texture Analyzer was measured using a 25 mm diameter stainless steel spherical probe. The measurements were carried out at separation rates of 10 mm/s under a constant pressure of 100 g/cm² and a dwell time of 1 s. The probe tack was estimated to be the maximum debonding force.

RESULTS AND DISCUSSION

Kinetics of UV Synthesis of Fluorine Grafted Copolymer

The acrylic monomers and low surface tension acrylic monomer were synthesized by UV-polymerization using hydroxy dimethyl acetophenone as the photo initiator. In addition, the kinetics of UV synthesis of the fluorinated copolymer and the curing behavior of UV irradiation were analyzed by RT-IR, P-DSC, and temperature according to the irradiation time with various amounts of TFMA (F0 : TFMA 0 wt%, F5 : TFMA 5 wt%, F10 : TFMA 10 wt% and F20 : TFMA 20 wt%).

Real-Time Fourier Transform Infrared Spectroscopy (Real-Time FTIR)

Real time-IR can examine the specific peaks at different times. Therefore, it is possible to estimate the

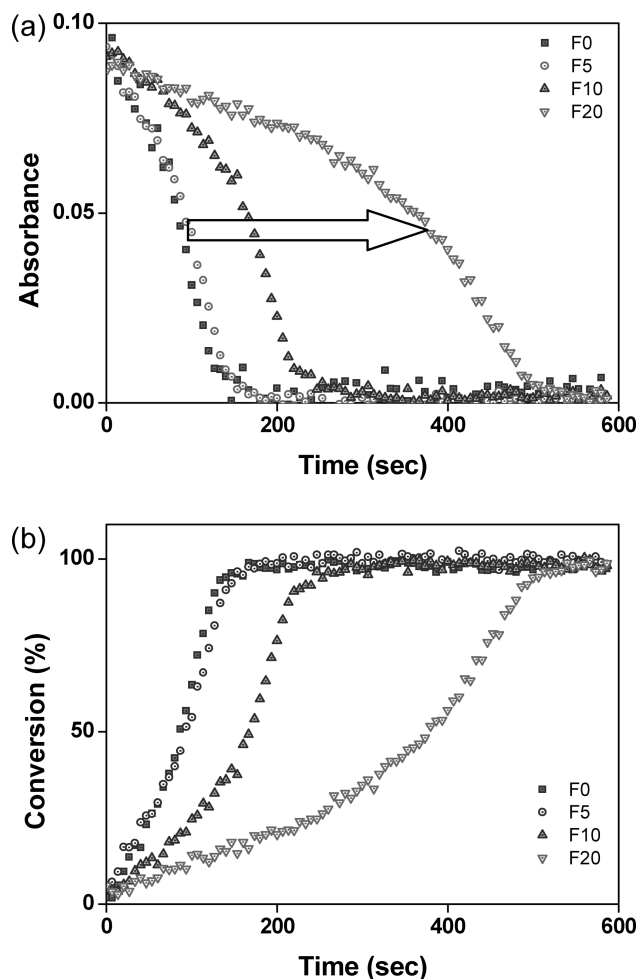


FIG. 3. Real-time FTIR data of the C=C bond (810 cm^{-1}) absorbance as a function of the irradiation time (sec) at UV $4.0\text{ mW}/\text{cm}^2$ (a), and the calculated conversion from the absorbance of the C=C bond (810 cm^{-1}) in each sample (b).

polymerization rates and conversion of polymerization, particularly with radiation polymerization. Anseth examined the measurement methodology for RT-IR and chose the absorbance peak (C=C bond 1640 cm^{-1}) whose absorbance decreased with decreasing concentration of C=C bonds [14]. Also another C=C bond is at 810 cm^{-1} [15–17]. In this study, the 810 cm^{-1} C=C bond was used to estimate the polymerization rate and conversion with various TFMA concentrations at 4.0 mW UV irradiation. In Fig. 3a, the data demonstrated a decrease in the C=C bond, which means that UV polymerization occurred at the expense of C=C bonds. Therefore, the F0 (TFMA : 0 wt%) sample showed the fastest polymerization rate among the four samples. The absorbance decreased more gradually as TFMA monomer wt% increased. In contrast, the C=C bonds in both F0 and F5 were almost diminished until 100–200 s. The time taken for the absorbance of the C=C bond to decrease to 0 in F10 and F20 was 250 and 500 s, respectively. In Fig. 3b, the conversion of the polymerization was calculated by

TABLE 2. Calculated heat flow of the low surface acrylic PSAs.

	F0	F5	F10	F20
Heat flow (J/g)	503.0	495.9	488.7	474.4

fixing the initiation absorbance value as 0% and measuring the decrease in absorbance from Eq. 1 [18]:

$$\text{Conversion (\%)} = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance of the IR peak at 810 cm^{-1} before UV irradiation and after UV irradiation during time t .

The time (s) when the conversion of each sample reached 100% was shown in Fig. 3a. The low polymerization rate was caused by the TFMA, which has a methacrylate functional group and fluorine atoms. Methacrylate creates more of a steric hindrance than acrylate. In addition, the fluorine atom is larger than hydrogen and induces more localized polarity when substituted in molecules [8].

Photo-Differential Scanning Calorimetry (Photo-DSC)

The behavior of UV polymerization was estimated by Photo-DSC. The heat of UV polymerization from the C=C bond was recorded as a function of time. The heat flow curves were measured in isothermal mode, and the reaction of the vinyl group with UV polymerization was exothermic. Therefore, the heat flow curve demonstrates the tendency of the reactions as different reactants, and the conversion of polymerization was calculated by integrating the heat flow versus time curves from equation (2) [16]:

$$C(\%) = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \times 100 \quad (2)$$

where ΔH_t is the integrated heat at the irradiation time from the heat flow curve and $\Delta H_0^{\text{theor}}$ is the calculated heat using the heat values, $\Delta H_0^{\text{theor}}$ (acrylate) = 86 kJ/mol and $\Delta H_0^{\text{theor}}$ (methacrylate) = 54.4 kJ/mol [14, 19]. Considering the copolymerization between acrylate and methacrylate, the heat of each sample, $\Delta H_0^{\text{theor}}$ (sample), was calculated using equation (3). [20]:

$$\begin{aligned} \Delta H_0^{\text{theor}} (\text{sample}) &= \frac{\Delta H_0^{\text{theor}} (\text{acrylate}) \text{ or } H_0^{\text{theor}} (\text{methacrylate})}{M_n^{\text{theor}}} \times \text{Functionality} \\ & \quad (3) \end{aligned}$$

where M_n^{theor} is the molecular weight of each monomer. Table 2 lists the calculated value of each sample.

With increasing amounts of TFMA, the heat flow curves showed a different shape during UV irradiation from 30 sec, as shown in Fig. 4a. With increasing amounts of TFMA, the peak of each curve moved to the

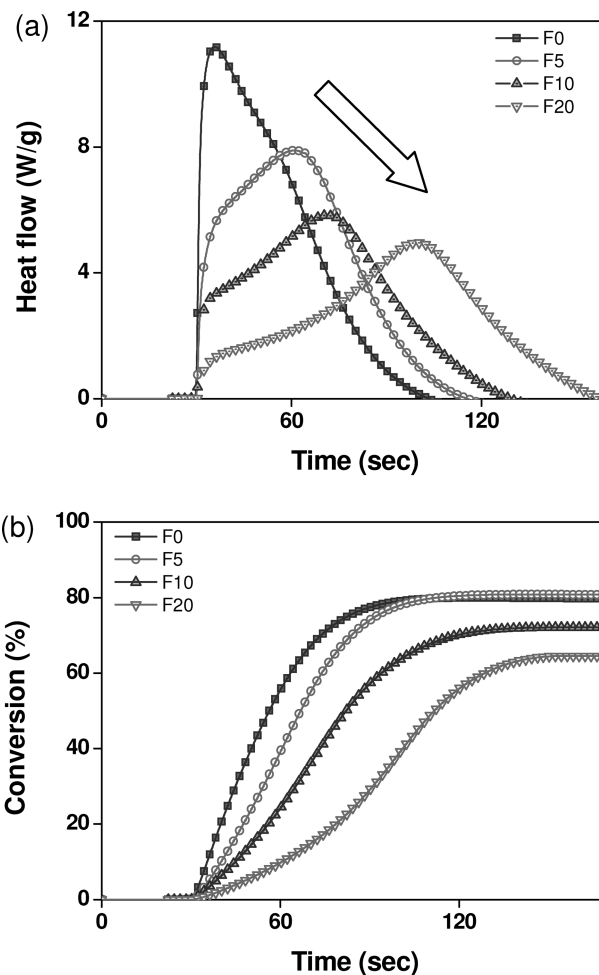


FIG. 4. Heat flows of acrylic PSAs as a function of the TFMA contents (a), conversion (%) versus UV irradiation time (b).

right and the gradient of the curve from the base to the peak decreased. This tendency means that TFMA affects the gradual polymerization rates. Moreover, the heat flow values and the height of each peak decreased with increasing amounts of TFMA. TFMA contains methacrylate, and the heat of methacrylate, $\Delta H_0^{\text{theor}}$ (methacrylate) = 54.4 kJ/mol, is lower than that of acrylate.

The conversion (%) of each sample in Fig. 4b shows a different tendency. In the case of the F0 and F5 samples, the conversion rates were similar and the final conversion of both samples was 80 %. However, with an increasing amount of TFMA, the final conversions of F10 and F20 were 72 % and 65 %, respectively. The conversion calculated from RT-IR was 100% but the conversions determined from Photo-DSC were relatively low. This difference was attributed to the difference in UV intensity and sampling weight.

Surface Characterization of Low Surface Energy PSAs

Contact Angle Test. Zisman analyzed the surface energies of a range of materials using contact angle

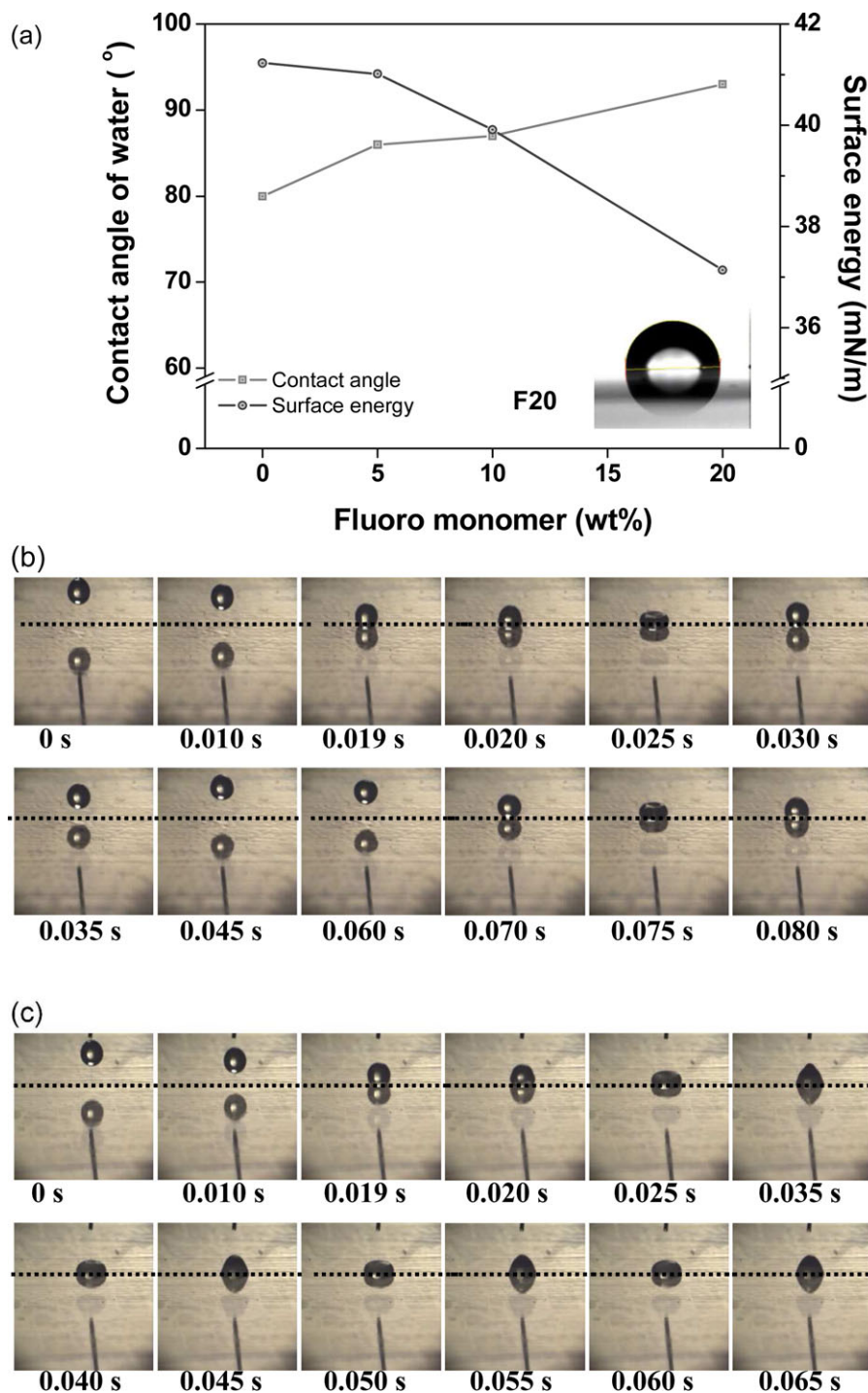


FIG. 5. Contact angle and surface energy of the water drop from F0 (angle : 80°) to F20 (angle : 93°) (a), time sequence pictures (1000 frames/s) of water on F20 (b) and F0 (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measurements and Young's equation [9]. Moreover, the common liquid used to calculate surface energy is water, which has a surface tension of 76 mN/m. If the contact angle of water on a solid surface is $< 90^\circ$, the solid surface is hydrophilic, which indirectly suggests that surface has high surface energy. In contrast to a hydrophilic surface, a hydrophobic surface has a water contact angle $> 90^\circ$ and is believed to have low surface energy [21].

TFMA has both fluorine atoms and a very low surface energy (19 mN/m). Therefore, the contact angle of water increased with increasing TFMA wt % in the samples. As shown in Fig. 5a, the contact angle of water on the F0 and F20 samples were 80° and 93° , respectively. In addition, the contact angle of each sample increased with the increasing wt% of TFMA. Moreover, the water drops bounced on the surface of the F20 sample, as observed by

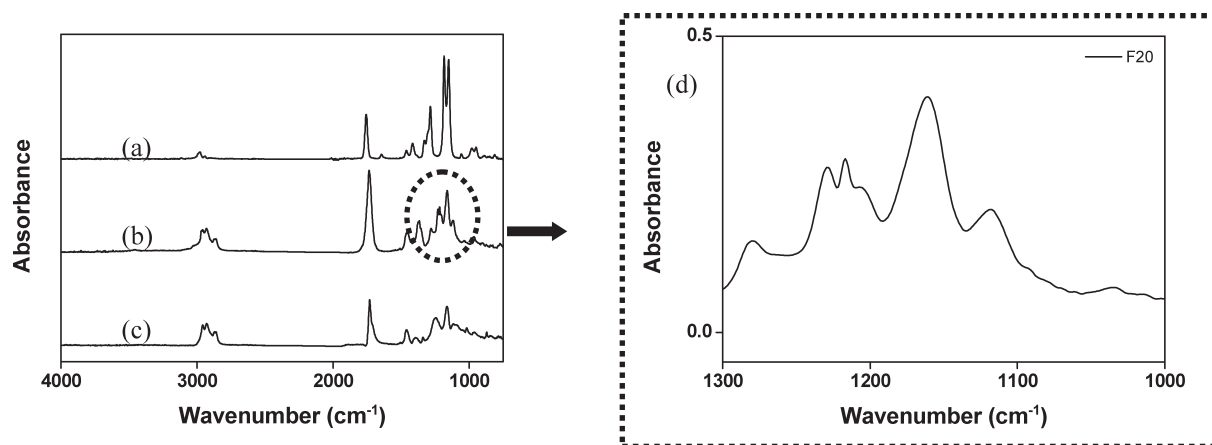


FIG. 6. FTIR peaks of the TFMA monomer (a), F20 has 20 wt% of TFMA in main polymer (b), F0 has not fluorinated functions (c) and F20 between 1000 ~1300 cm^{-1} (d).

a high-speed camera at a 1000 frame/sec (Fig. 5b). The time sequence pictures were obtained of dropping water on the F0 and F20 samples. In the case of the F20 sample, the water drop dripped down and then bounced. However, the drop did not bounce in the case of the F0 sample (Fig. 5c). The shape of the water drop on the F0 PSAs was pulled toward the down side and vibrated up and down, which suggests that the F0 PSAs attracted the drop. This was attributed to the low surface energy of PSAs except for the roughness effect of the surface [21, 22]. As a result, the surface energy of the F0 sample was larger than that of F20, which affects the attraction of the water drop.

Fourier Transform Infrared Spectroscopy (FTIR).

Figure 6 shows the FT-IR spectra of the F0, F20 and TFMA samples. The F0 sample is a copolymer of 2-ethylhexyl acrylate and acrylic acid. In contrast to F0, the F20 sample contained fluorine atoms in the polymer theoretically containing 20 wt% TFMA. Most of the peaks in both F0 and F20 were similar, even though the peaks were shifted. The peak near 3000 cm^{-1} was assigned to the C-H stretch. The C=O stretching vibration was observed at 1750 cm^{-1} and

the hydroxyl band was noted at 1340 cm^{-1} . Furthermore, the peaks at 1628 cm^{-1} and 810 cm^{-1} were assigned to C=C-C=O. These C=C bond peaks are normally detected during the radical polymerization of acrylate. However, in Fig. 6, polymerization was almost complete, so it was difficult to identify C=C peaks. In particular, a noticeable peak was observed between 1100 and 1300 cm^{-1} in the F20 sample and TFMA, which was assigned to C-F stretch peak ($1200\sim1300\text{ cm}^{-1}$) [22]. The shifts in the peaks are usually negligible due to hydrogen bonding [23]. The shift in the C-F peak was attributed to hydrogen bonding with OH in acrylic acid [8]. Accordingly, the electron withdrawing effects of fluorine induced an electron density in C-F bonding so that the C-F bond shifted to a higher frequency (higher-energy).

X-Ray Photoelectron Spectroscopy (XPS).

XPS was used as an additional surface analysis technique to RT IR because RT-IR can detect fluorine but it is difficult to detect its quantity. In this study, the atomic % of F and C were determined by XPS. Figure 7 shows the C1s XPS peak for F20. Bias hydrogen carbon was fitted to 285eV. Table 3 lists the binding energy of each sample. The peaks at 293 eV and 689 eV were assigned to C1s of CF_3 and F1s of CF_3 (the F1s curve is not shown in this figure) [24]. The 294 eV peak was detected with increasing amounts of TFMA.

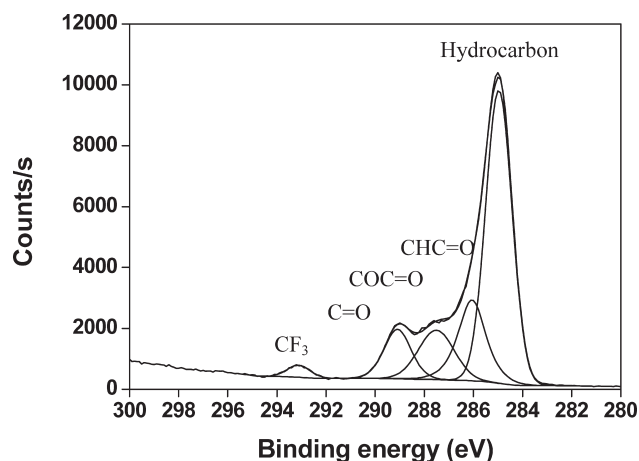


FIG. 7. The XPS raw and curve fit data of the C1s spectrum of F20.

TABLE 3. Binding energy and atomic proportion of F on the surface of PSAs.

Atom	Functional group	F0 (eV)	F5 (eV)	F10 (eV)	F20 (eV)
C1s	Hydrocarbon	285	285	285	285
	CHC=O	286.25	286.19	286.15	286.10
	COC=O	287.55	287.56	287.56	287.55
	C=O	289.09	289.12	289.13	289.13
	CF_3	—	293.07	293.13	293.15
F1s	C—F	—	689.28	689.26	689.17
F Atomic %		0	2.46	5.08	9.72

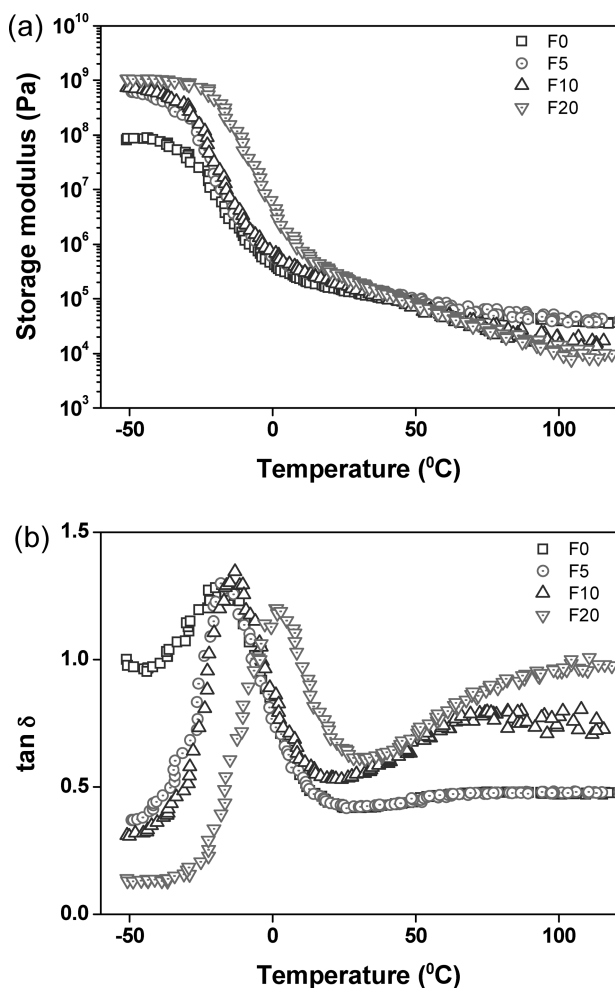


FIG. 8. Viscoelastic curves of the acrylic PSAs with different fluoro monomer contents: storage modulus curve (a) and $\tan \delta$ curve (b).

Table 3 lists the atomic % of fluorine of the samples. The F atomic % increased with increasing TFMA, which contains 3 fluorine atoms per molecule. The atomic % of F in F0, F5, F10 and F20 were 0, 2.46, 5.08 and 9.72 %, respectively. However the calculated theoretical atomic % of F was less than the atomic % of F detected. This is similar to results reported elsewhere. The lower calculated percentage of F than detected was caused the limits of the instrument and interpenetration [10]. These results suggest that fluorine atoms exist on the surface of PSAs. In addition, the quantity of F atoms increased with increasing amounts of TFMA. XPS showed that the contact angle of PSAs increases with increasing TFMA content due to the low surface energy of fluorine [9].

Viscoelastic Properties

Advanced Rheometric Expansion System (ARES). The storage modulus of PSAs is an important factor for determination of adhesion and wettability. The PSAs are considered to be in a semi solid state. The wettability of PSAs

improves with increasing flexibility. In addition, the mobility of molecules is also a key factor for improving the wettability. The storage modulus is the elastic property. Therefore, the flexibility would improve with decreasing storage modulus.

Chang *et al.* divided the PSAs into 4 viscoelastic window categories according to the storage and loss moduli. The area beside the $10^4 \sim 10^6$ Pa of both the storage and loss moduli is defined as high shear PSAs [25]. Figure 8a shows the temperature dependence of the storage modulus of the PSAs as a function of the TFMA content. The storage modulus increased with increasing TFMA until room temperature ($F20 > F10 > F5 > F0$). This means that the mobility of F20 is similar to the other samples. The storage modulus decreased sharply at the glass transition temperatures. In addition, the region where the temperature gradually decreases indicates the rubbery plateau. The rubbery plateau was observed at 25–50 $^{\circ}\text{C}$ and the storage modulus of each sample was similar, indicating that all the samples had comparable molecular weights [1]. Above 50 $^{\circ}\text{C}$, the order of the storage modulus was opposite ($F0 > F5 > F10 > F20$). This area, the terminal region, showed crosslinking or entanglement of the polymer chains. From the F20 curve, the well defined boundary of the plateau and terminal region was not observed because F20 has a lower entanglement than the other samples. The reason is that TFMA has a short chain, even though fluorine has a hydrogen bond [8]. Moreover, the phenomena of F20 decreasing more drastically above the T_g is similar to non crosslinked PSAs [26]. According to Chang, all the samples included were in the high shear PSAs region [25]. Moreover, the mobility of each sample was similar to each other at room temperature.

In Fig. 8b, at T_g , the $\tan \delta$ value moved to a high temperature with increasing TFMA content. The T_g of TFMA (80 $^{\circ}\text{C}$) is higher than that for 2-EHA (–70 $^{\circ}\text{C}$). In addition, the compatibility of the plasticizer with PSAs could be determined from the T_g . If the T_g is a well defined single peak, the plasticizer is miscible with PSAs. Moreover, if the T_g is 2 peaks, this indicates that the plasticizer is not miscible with PSAs [1]. Therefore, the well defined single peak in Fig. 8b shows that the plasticizer (polybutene) is miscible with each sample.

Adhesion Performance

The adhesion performance of the PSAs is affected by the surface energies of both the substrate and PSAs. A PSA's wettability is improved when the surface energy of the PSAs is lower than that of the substrate. The adhesion performance is improved as a result of the improved wetting of PSAs on the substrates. The flexibility of the molecules is also an important factor affecting the adhesion performance [4]. The prove tack indicates the adhesion performance, which is determined by attaching a spherical stainless steel prove for a short time (1 s) and detaching it. The prove tack

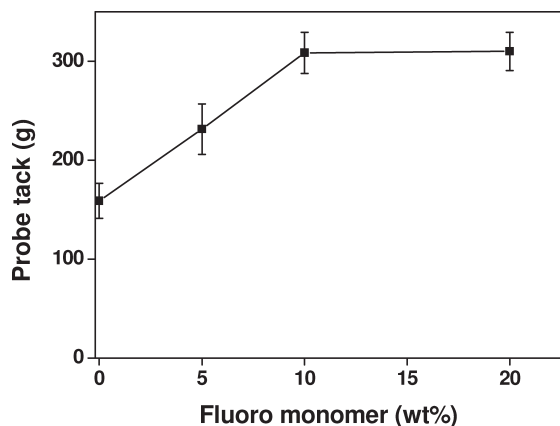


FIG. 9. Probe tack value (25 mm diameter stainless steel spherical probe) as a function of the TFMA content.

values of PSAs, which were cured using an UV dose of 600 mJ/cm^2 , as shown in Fig. 9, increased drastically from 150 to 300 g at 10 wt% of TFMA. The prove tack of the 20 wt% TFMA sample was similar to that of the 10 wt%, 300g. This suggests that the adhesion of PSAs is improved

by the lower surface energy of the PSAs due to the low surface energy of TFMA.

Figure 10 shows the peel strength on various substrates with different surface energies and attachment times (30 min. and 24 hours). The peel strength of PSAs on each substrate (PP, ABS, PVC and SUS) increased with increasing TFMA content except for PP. In the case of PP, the peel strength of the 0 wt% TFMA sample was approximately 300 g/25 mm, which increased to 1000 g/25 mm at 10 wt% TFMA. A comparison of the 30 min. and 24 hour attachment times showed no improvement in peel strength, as shown in Fig. 10a. However, in the case of ABS, the peel strength gradually increased from approximately 600 g/25 mm to 800 g/25 mm, and to more than 1000 g/25 mm with increasing attached time on ABS, as shown in Fig. 10b. Figure 10c shows the peel strength of the PSAs with different TFMA contents on a PVC substrate. The peel strength of the PSAs containing the 20 wt% TFMA after an initial 30 min attachment time was approximately 1000 g/25 mm, which increased to approximately 1200 g/25 mm after 24 hours. In Fig. 10d, higher peel

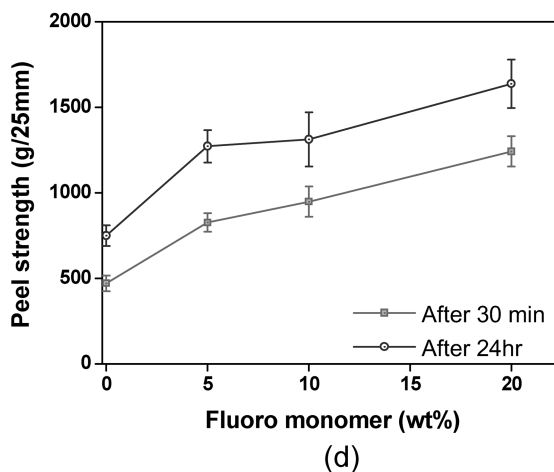
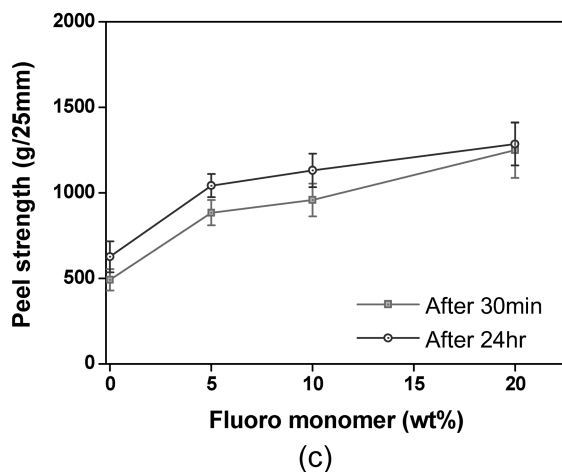
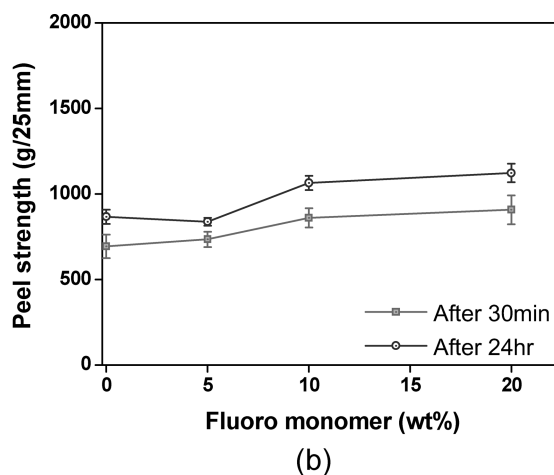
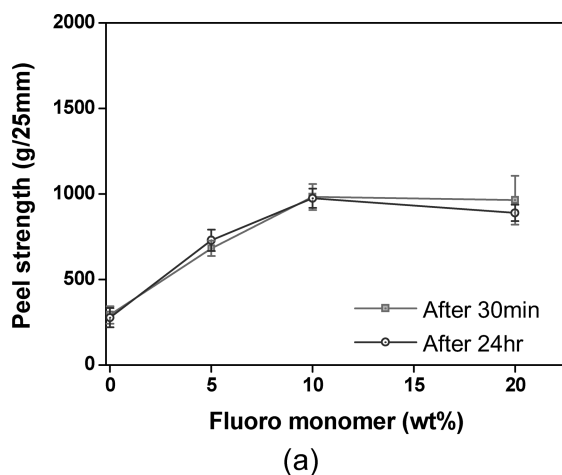


FIG. 10. Peel strength as a function of the TFMA content on PP (a), ABS (b), PVC (c), and SUS (d) (tested after 30 min, 24 h).

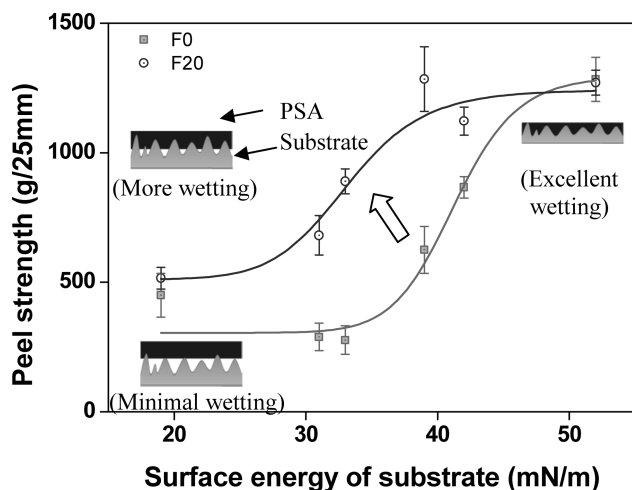


FIG. 11. Peel strength of the F0 and F20 sample with a 600 mJ/cm² UV dose on various surface energy substrates (tested 24 h after attaching the PSAs to the substrate).

strength was observed on stainless steel, which has a high surface energy (200~1000 mN/m), than on the other substrates (PP, ABS and PVC). The initial 30 min peel strength of the PSAs with 0 wt% TFMA was similar to the other substrates (500 g/25 mm) but the peel strength increased sharply to more than 1500 g/25 mm with increasing attachment time and TFMA content. Figure 11 shows the F0 and F20 peel strength curves attached to various surface energy substrates (Teflon, PP, PVC, ABS, phenol resin). From the contact angle data, F20 has lower surface energy than F0 but similar viscoelastic properties at room temperature from ARES. The peel strength was similar on the phenol resin substrate, which has a surface energy of 50 mN/m. In addition, the improved peel strength was not improved on the substrates with a surface energy > 50 mN/m. The reason for this fixed peel strength is that both F0 and F20 PSAs were already wetted on the high surface energy substrate. This shows that the peel strength on a substrate increases with increasing surface energy (PP : 33 mN/m, ABS : 42 mN/m, PVC : 39 mN/m and SUS : 200~1000 mN/m). Kim *et al* examined the peel strength of rubber-based PSAs on a range of substrates. The surface energy of the substrates affected the peel strength of PSAs [27]. In addition, the peel strength increased with decreasing surface energy of the PSAs. This suggests that the peel strength of the PSAs increases when the wettability of PSAs is improved. Overall, the peel strength, wettability and adhesion can be improved by controlling the surface energy of PSAs by using low surface energy fluorine.

CONCLUSIONS

Fluorinated acrylic PSAs were synthesized by UV polymerization using 2-EHA and AA with a fluorinated acryl monomer (TFMA). The advantage of this system is

that there is a much faster reaction rate than with solvent polymerization, and no need for added heat in the reaction. The reaction rate of polymerization using different amounts of TFMA was examined using RT-IR and Photo-DSC. The reaction rate decreased with increasing TFMA content because of the stable states of the fluoro monomer and methacrylate. XPS showed that fluorine exists on the surface of the PSAs. In addition, the surface had low surface energy and was hydrophobic. The viscoelastic property affected by fluorine was analyzed by ARES. The T_g increased due to TFMA, which has a higher T_g than 2-EHA. The storage modulus increased until 20°C but decreased at higher temperatures due to the low entanglement of PSA's molecules. TFMA has a short chain and the polarity of fluorine reduces the localization of 2-EHA molecules resulting in low levels of entanglement. In terms of the adhesion performance, the peel strength increased with increasing TFMA content. Therefore, the peel strength is affected by the surface energy of the PSAs and the substrate. The peel strength increased with decreasing surface energies of the PSAs. This means that the wettability and adhesion strength is improved by using PSAs with low surface energies.

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