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## Effect of grafting of acrylic acid onto PET film surfaces by UV irradiation on the adhesion of PSAs

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**Abstract**—To improve the peel strength between a pressure-sensitive adhesive (PSA) and its substrate, grafting of acrylic acid (AA) onto the surface of poly(ethylene terephthalate) (PET) film was carried out. After AA was coated onto the surface of PET films using a spin coater, the coated PET films were irradiated by UV. To investigate the surface chemistry and topography of the PET-g-AA films, the grafted surface of the PET films was characterized by FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). From these investigations, the effects of grafting of AA at the surface of PET by UV irradiation were discussed. In addition, to determine the effect of grafting on the adhesion between PSA polymer and PET-g-AA films, peel strength was measured after the PSA/PET-g-AA system was cured at various temperatures. As the esterification between PSA polymer and PET-g-AA films occurred in the interfacial region, the peel strength of the PSA/PET-g-AA system generally increased with increasing curing temperature.

**Keywords:** Pressure-sensitive adhesives (PSAs); grafting; acrylic acid (AA); PET; UV irradiation; adhesion strength

### 1. INTRODUCTION

Surface modification of polymers to improve their adhesion is being investigated intensively. As the surface of a polymer generally shows a hydrophobic character, improvement of physical properties of a polymer, including its adhesion, requires modification of the polymer surface. Therefore, methods for modifying the surface characteristics of a polymer from hydrophobic to hydrophilic have received significant consideration. As the surface of a polymer is treated chemically

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and/or physically, it becomes hydrophilic with consequent improvements in surface physical properties of the polymer.

There are many useful treatment methods for the modification of a polymer surface such as treatment by plasma, electron beam radiation and UV-light-induced grafting [1–9]. Among these treatment methods for the surface modification of polymers, the photo-induced UV grafting onto polymer surfaces is a very interesting method for obtaining desired properties for specific uses, because it allows the surface characteristics to be altered without causing serious modifications to the polymer bulk mechanical properties. In addition, UV grafting is an attractive way to impart a variety of functional groups to a polymer [6–9].

In this study, we used a poly(ethylene terephthalate) (PET) film as a substrate. Although a PET film is very stable under UV irradiation, it is still efficient enough to induce grafting of vinyl monomer onto PET which is a potentially useful tool for the chemical modification of this polymer. In addition, a vinyl monomer is covalently bonded to a site on the PET surface through grafting [6].

As the purpose of the UV-induced grafting is to improve the adhesion strength, peel strength analysis is important in surface modification study. Peel strength represents the force required to peel away a tape from the substrate [10]. Resistance to peel is measured as the force required at a constant, pre-defined, peel rate and angle [10, 11].

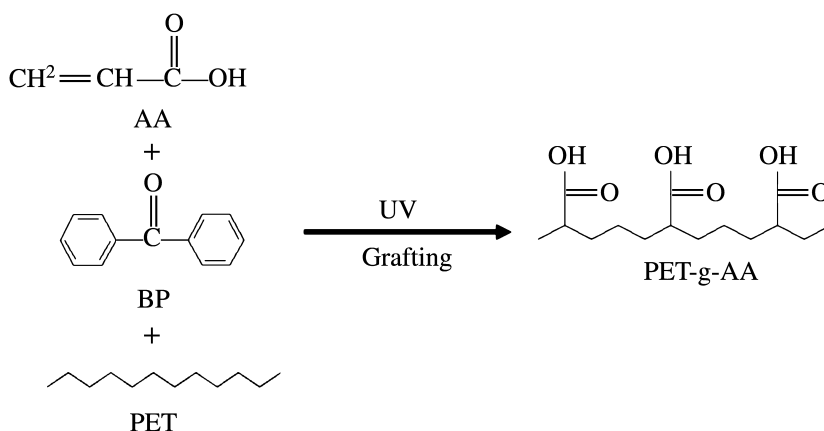
## 2. EXPERIMENTAL

### 2.1. Materials

2-Ethylhexyl acrylate (2-EHA, Junsei Chemical, Japan), vinyl acetate (VAc, Junsei Chemical), methyl methacrylate (MMA, Junsei Chemical), glycidyl methacrylate (GMA, Junsei Chemical), acrylic acid (AA, Junsei Chemical), ethyl acetate (EAc, Samjun Chemical, South Korea, analytical grade) 2,2'-azobisisobutyronitrile (AIBN, Daejung Chemicals & Metals, South Korea) and benzophenone (BP, Lancaster, UK) were used as received. PET film of 25  $\mu\text{m}$  thickness was supplied by SK Chemical (South Korea).

### 2.2. Preparation of PSA

The PSA was prepared by solution polymerization as 40 wt% solids. The synthesis method consisted in mixing 126 g 2-EHA, 10.5 g MMA, 1–3 g GMA, 10.5 g VAc, 0.3 g AIBN and 75 g EAc in a 500 ml, 4-neck flask equipped with a stirrer, a dropping funnel and a thermometer. The polymerization reaction was initiated at 70°C, and after this temperature was maintained for 30 min, a mixture of 150 g of ethyl acetate and 0.6 g of AIBN was gradually added to the flask over a duration of 2 h. The polymerization was subsequently carried out at  $65 \pm 5^\circ\text{C}$  for another 4 h.



**Scheme 1.** Process of grafting of monomer (AA) onto PET by UV irradiation.

### 2.3. Grafting on PET film

Grafting of AA onto the PET film was carried out in a conveyor belt type, UV curing machine equipped with a high-pressure mercury lamp (100 W/cm, main wavelength 340 nm) after the solution (90 wt% AA and 10 wt% BP) was coated onto the PET film using a spin coater (KPD-002, Kee-Bea, South Korea). The UV grafting times were 0, 20, 40 and 60 s. To remove the ungrafted homopolymer and the ungrafted AA, the cured films were washed successively with toluene, methanol and water. The modification process of the PET film with AA is shown in Scheme 1.

### 2.4. Characterization

The surface modification achieved was characterized using various analysis techniques [13]. Infrared spectroscopy is a very powerful tool for studying the chemical structure in bulk materials as well as for providing molecular conformational details which are inaccessible to most analytical methods [14]. After grafting, the IR spectra of PET-g-AA films were obtained using an FT-IR ATR spectrometer (Nicolet Magna 550 Series II, Midac, USA) with a resolution of  $8\text{ cm}^{-1}$ . High-resolution, three-dimensional images of the surfaces of the PET-g-AA films were obtained by a scanning probe microscope (SPM, Autoprobe CP<sup>TM</sup>, PSIA, USA) with a spring constant  $k = 3.2\text{ N/m}$  in the non-contact mode. Statistical evaluation of the surface topography was performed in a scanning area  $5 \times 5\ \mu\text{m}^2$ . Surface chemistry was characterized using X-ray photoelectron spectroscopy (XPS, ThermoVG, UK). The spectrometer utilized a monochromatic Al K $\alpha$  photon source operating at 15 kV and 15 mA. The software provided by the manufacturer was used for all XPS analyses.

### 2.5. PSA performance

The prepared PSA was coated onto the PET film using a No. 18 K-bar, kept at room temperature for 1 hr and then dried in an oven at  $60^\circ\text{C}$  for 20 min. After the dried

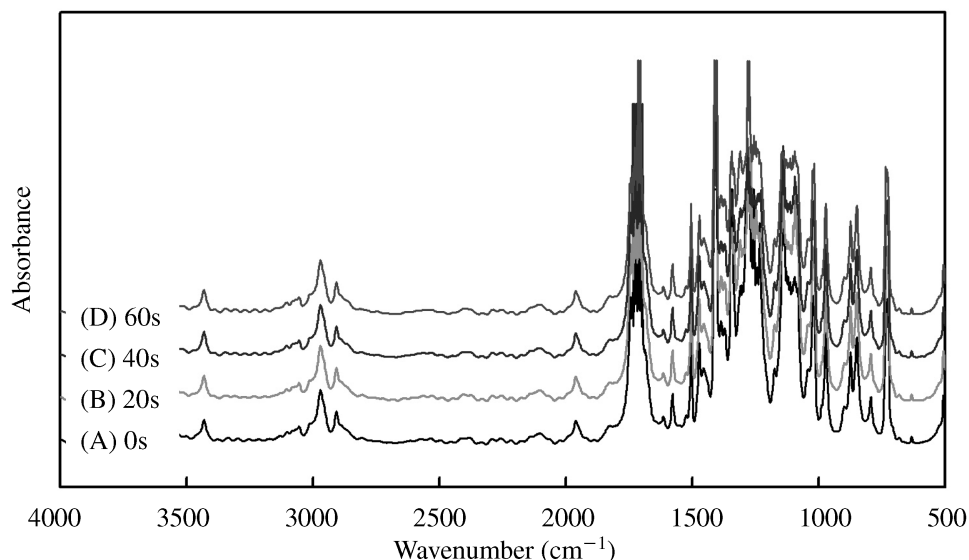
PSA films were applied onto PET-g-AA films, they were placed in an oven at 25, 60, 100, 130 and 150°C for 10 min. Finally, PSA performance was evaluated in terms of peel strength. Peel tests were conducted using a Texture Analyzer (TA-XT2i, Stable Micro Systems, UK) at an angle of 180° with a crosshead speed of 300 mm/min.

### 3. RESULTS AND DISCUSSION

#### 3.1. FT-IR analysis

FT-IR results on the PET-g-AA film with various UV grafting times are shown in Fig. 1. As only a small amount of AA was coated onto the surface of the PET-g-AA film by the spin coater, the spectra for the PET films with various grafting times were found to be close to those of the ungrafted PET film.

Although it was difficult to detect any changes in functional groups by the UV grafting, some peaks due to AA were discernible. Indeed, there was an  $\text{-OH}$  group coming from AA, at  $3430\text{ cm}^{-1}$ . To find the effect of UV grafting, we calculated the intensity ratio of the peak at  $3430\text{ cm}^{-1}$  relative to that at  $3050\text{ cm}^{-1}$ , which is assigned to the aromatic  $\text{-C=C-}$  in PET. The results are listed in Table 1. As shown in Table 1, the peak intensity ratio of the  $\text{-OH}$  group increased with increasing UV grafting time. The ratio reached a maximum at the grafting time of 40 seconds, and then decreased, possibly due to the effect of AA homopolymerization. These results confirmed that the UV grafting effect of PET-g-AA was maximum at 40 s.



**Figure 1.** FT-IR spectra of PET-g-AA films with varying UV grafting time: (A) 0 s, (B) 20 s, (C) 40 s and (D) 60 s.

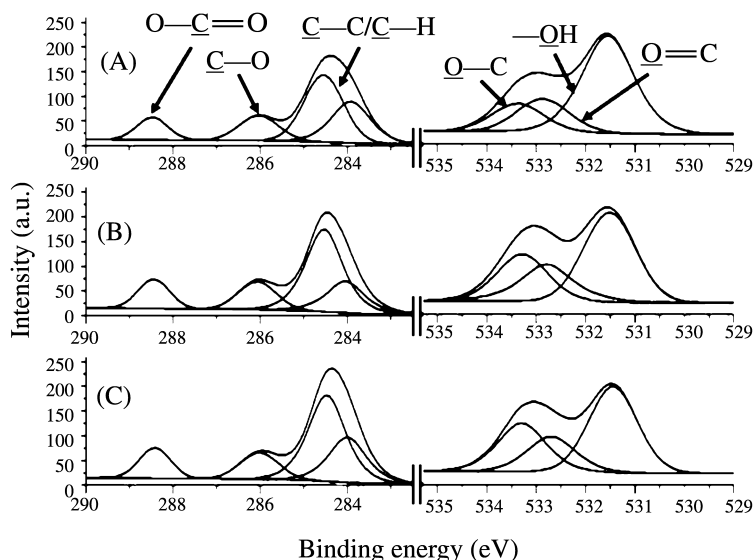
### 3.2. XPS analysis

The results of surface chemical analysis of the PET-g-AA films are presented in Fig. 2 and Table 2. According to the results obtained by XPS in Fig. 2, the  $C_{1s}$  core-level spectrum was curve-fitted with three peak components having binding energies at 284.6, 286 and 288.5 eV, corresponding to the  $\underline{C}-C/\underline{C}-H$ ,  $\underline{C}-O$  and  $O-\underline{C}=O$  functional groups, respectively [15–17]. Also evident was the peak at 283.9 eV in the  $C_{1s}$  spectra. This peak resulted from the inhomogeneous charging effect on the polymer surface due to its insulating nature [18]. As shown in Fig. 2, the peak located at 284.6 eV, which was directly related to the nature of the polymer (C–C and C–H), increased with increasing grafting time due to the grafting of AA on the PET films. On the other hand, the  $O_{1s}$  peaks were decomposed into peaks at 531.5 eV as hydroxide group ( $-\underline{O}H$ ), 532.8 eV as  $\pi$ -bonded oxygen ( $\underline{O}=C$ ) and 533.3 eV as  $\sigma$ -bonded ( $\underline{O}-C$ ) oxygen. These results were in agreement with the

**Table 1.**

OH peak intensity ratio of PET-g-AA films with varying UV grafting time

UV grafting time (s)	$I_{3430\text{ cm}^{-1}}/I_{3050\text{ cm}^{-1}}$
0	2.339
20	2.509
40	2.770
60	2.553



**Figure 2.**  $C_{1s}$  and  $O_{1s}$  XPS spectra of the PET-g-AA films with varying UV grafting time: (A) 0 s, (B) 20 s and (C) 40 s.

**Table 2.**  
Atomic concentration (%) for the PET-g-AA films as determined by XPS for varying UV grafting time

UV grafting time (s)	C <sub>1s</sub>	O <sub>1s</sub>
0	71.8	28.2
20	71.8	28.2
40	75.5	24.5

reference values [19–21]. Among the three peaks, the peak located at 533.3 eV, which was assigned to  $\sigma$ -bonded ( $\text{O}-\text{C}$ ) oxygen, increased rapidly. This is further evidence of AA grafting on the PET film.

As listed in Table 2, it was found that the amount of carbon on the PET film surface increased, while that of the oxygen decreased as a result of the grafting process.

### 3.3. SPM analysis

There are certain characteristics in the topological analysis of a surface such as the RMS roughness, average roughness and mean height. Generally, changes in the surface roughness are quantified in terms of root-mean-square (RMS) value, given as the standard deviation of the distribution of all height values within the surface area of interest and is defined as [22]:

$$R_{\text{rms}} = \sqrt{\frac{1}{L_x L_y} \int_0^{L_x} \int_0^{L_y} z^2(x, y) dx dy},$$

where  $L_x$  and  $L_y$  are the lengths of  $x$ -axis and  $y$ -axis, respectively. Although the RMS surface roughness is a useful parameter for comparing surfaces, it is insufficient to completely describe a surface and can lead to erroneous characterization for surfaces possessing a variety of feature types. Therefore, in order to provide a more meaningful description of the surface it is instructive to examine the complete height histogram of the image. A height histogram of the image can also be used to reconstruct height values and mean height, and thus it represents a superset of data contained in an RMS surface roughness value [23].

As shown in Fig. 3, the surface roughness of the PET-g-AA film increased with increasing UV-grafting time. This result supports the hypothesis that surface grafting can increase the surface roughness. In other words, the increasing surface roughness signifies occurrence of grafting reactions on the surface. However, the surface roughness of the PET-g-AA film decreased after the maximum grafting at 40 s because of the decreased graft degree due to the removal of ungrafted homopolymer and monomer. In general, homopolymer and ungrafted monomers were removed by solvent such as methanol, acetone and toluene, at the condition of excess UV irradiation times.

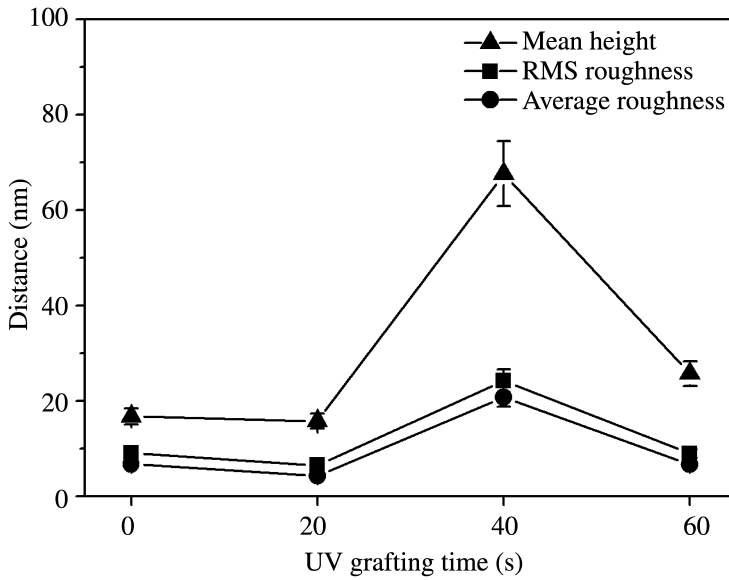


Figure 3. Surface roughness of the PET-g-AA films with various UV grafting times.

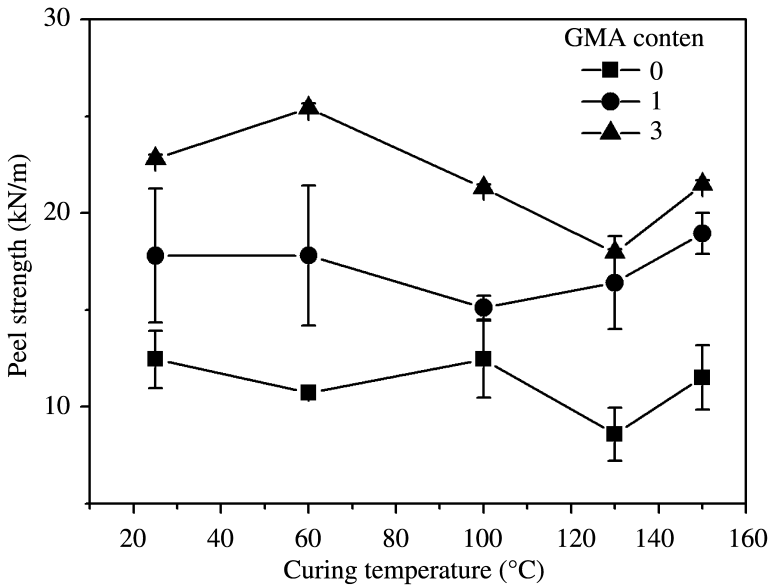
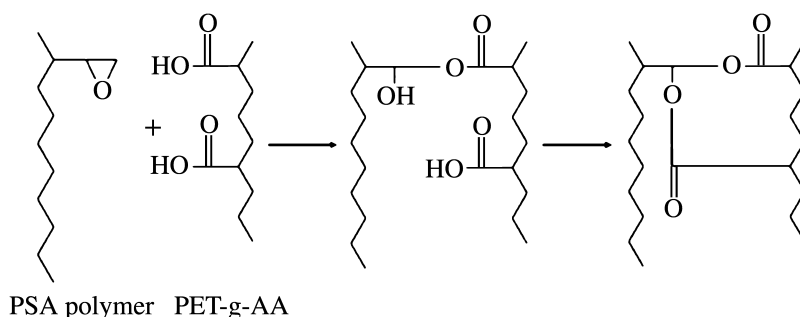


Figure 4. Peel strength of PSA/PET-g-AA films with various GMA contents as a function of curing temperature. Numbers in the upper right hand corner refer to percentage of GMA.

### 3.4. Peel strength

Figure 4 shows the peel strength of the PSA/PET-g-AA film systems with varying GMA content. With increasing GMA content, the peel strength of PSA/PET-g-AA increased because the hydroxide group of PSA reacts with the carboxylic acid





**Scheme 2.** Mechanism of esterification between PSA polymer and PET-g-AA.

group of PET-g-AA to produce esterification. The mechanism, shown in Scheme 2, consists of two steps. First, the epoxide ring of GMA is opened by the attack of the hydroxide group in AA. Due to the esterification occurring between GMA and AA, the interface between the PSA polymer and PET-g-AA becomes stronger through chemical bonding.

Although the peel strength of PSA/PET-g-AA increased with the increment of GMA, the peel strength showed an irregular relationship with the increment of UV curing temperature, as shown in Fig. 4. In fact, the peel experiments demonstrated that the failure mode of PSA/PET-g-AA depended on the curing temperature. Since the adhesion at the PSA/PET-g-AA interface was stronger than the cohesive strength of the PSA, the failure mode of PSA/PET-g-AA was cohesive rather than interfacial. However, one can see that the peel strength of PSA/PET-g-AA increased at about 150°C. It seems that the esterification between PSA and PET-g-AA affected the peel strength in spite of the cohesive failure of this system. These results confirmed that the peel strength of PSA/PET-g-AA increased with increasing GMA content due to the process of esterification.

#### 4. CONCLUSIONS

In this study, we investigated the effects of UV grafting to improve the peel strength of polymeric materials, such as PSAs. The use of AA as a vinyl monomer for UV grafting altered the surface of the substrate (PET film) from hydrophobic to hydrophilic, as confirmed by FT-IR, SPM and XPS analyses. With increasing GMA content in the PSA, the peel strength of PSA/PET-g-AA increased, but a cohesive failure occurred at curing temperatures above 130°C. The peel strength results confirmed the reaction mechanism for adhesion between PSA and PET-g-AA. The mechanism consists of two steps. The first step involves the scission of the epoxy ring in GMA. The ring is opened by the attack of the —OH group in AA. The second step is the esterification between the —OH in GMA and the —COOH in AA. These two reactions increase the adhesion at the PSA/PET-g-AA film interface. The results of this study elucidated the effect of monomer grafting and explained the increased adhesion strength observed between PSA and PET-g-AA.

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