

# Crosslinked Acrylic Pressure-Sensitive Adhesives. II. Effect of Humidity on the Crosslinking Reaction

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Received 17 September 2002; accepted 7 December 2002

**ABSTRACT:** The effect of humidity during storage on the crosslinking reactions of isocyanate groups was investigated with attenuated total reflectance Fourier transform infrared spectroscopy with pressure-sensitive adhesives composed of poly[ethyl acrylate-*co*-(2-ethylhexyl acrylate)-*co*-(2-hydroxyethyl methacrylate)] as a base resin and polyisocyanate as a crosslinker. A peak-resolving analysis of the amide II region revealed four bands. According to an analysis of the Fourier transform infrared spectra of the model compounds, these four bands were assigned to free urethane linkages, hydrogen-bonded urethane linkages, free urea

linkages, and hydrogen-bonded urea linkages. As expected, storage under humid conditions led to the formation of free and hydrogen-bonded urea linkages corresponding to the promotion of isocyanate consumption. Peak resolution of the amide II region was found to be a reasonable way of monitoring urethane and urea linkages during crosslinking reactions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3039–3045, 2003

**Key words:** adhesives; crosslinking; FT-IR

## INTRODUCTION

Although both solvent-borne and waterborne acrylic pressure-sensitive adhesives (PSAs) are derived from the same monomers, solvent-borne acrylic PSAs generally exhibit higher tack and peel adhesion because of the molecular weight difference between solvent-borne and waterborne acrylic polymers.<sup>1</sup> Solvent-borne acrylics require much lower molecular weights (ca. 100,000) than waterborne acrylics (ca. 1,000,000) to maintain a workable solution viscosity.<sup>2</sup> Because the cohesive strength remains marginal at this molecular weight level, some crosslinking mechanism is used to compensate for the low molecular weight. Typical crosslinking methods are based on chemical reactions that take place at elevated temperatures, although room-temperature curing is also known.

Polyisocyanate as a crosslinker is used in various fields because the isocyanate group has a high reactivity and can react with almost any compound possessing an active hydrogen atom, even at room temperature. Free hydroxyl groups in the polymer react with isocyanates to form urethane linkages. A three-dimensional urethane network is formed when there are two or more reactive sites on each reactant. However, reactions leading to the formation of urethane

linkages are influenced by external conditions. When water is present during crosslinking reactions, the isocyanate group reacts with water to form an amine, and the amine reacts with another isocyanate to form urea linkages. The source of water is typically a high relative humidity or water absorbed into the system. Because amines are more nucleophilic than alcohols, the formation of urea linkages will dominate the process, and the polyol will be difficult to crosslink with the isocyanate groups properly.<sup>3,4</sup> In addition, the by-products of the side reaction between isocyanate and water will affect the properties of the resulting products in various ways.

The objective of this research was to elucidate the effect of crosslinking on PSA film properties. We chose poly[ethyl acrylate-*co*-(2-ethylhexyl acrylate)-*co*-(2-hydroxyethyl methacrylate)] as a base resin and polyisocyanate as a crosslinker. We monitored the changes in the concentrations of the isocyanate groups remaining in these PSA films by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The carbonyl peak is usually used to determine the isocyanate derivatives by Fourier transform infrared (FTIR) analysis.<sup>5</sup> However, in this study, the carbonyl region is overlapped by the polyacrylate base polymer. Consequently, the amide II region was used to determine the isocyanate derivatives. The concentrations of urethane and urea linkages generated in the PSA films were also monitored by ATR-FTIR spectroscopy according to the decomposition of the amide II band with a peak-resolving technique.

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In this report, we focus on the reactions of isocyanate groups in PSA films affected by humidity during the process of crosslinking.

## EXPERIMENTAL

### Materials

A hydroxy-substituted polyacrylic resin prepared by the copolymerization of ethyl acrylate, 2-ethylhexyl acrylate, and 2-hydroxyethyl methacrylate with a ratio of 60/35/5 (w/w/w) was furnished by Hitachi Chemical Co., Ltd. (Ibaraki, Japan), in the form of an ethyl acetate/toluene solution (35/65 w/w). The glass-transition temperature of the polymer was  $-28.1^{\circ}\text{C}$ , as determined by differential scanning calorimetry. Colonate L, or trimethylpropane-1-methyl-3-isocyanato-4-carbamate (Nippon Polyurethane Industries Co., Ltd., Tokyo, Japan), was used as a polyisocyanate crosslinker in an ethyl acetate/toluene solution (20/80 w/w). These two materials were used without further purification. Other chemicals were reagent-grade in accordance with Japanese Industrial Standards.

### Preparation of the PSA films

The PSA films used in this study were prepared according to the following procedure. A polyacrylic solution was diluted to a 5 wt % solid content with toluene. The polyisocyanate crosslinker (3 phr) was added to the solution, and this gave a ratio of 1/3 NCO/OH. The mixture was stirred for 20 min and then was cast onto polyethylene films 60  $\mu\text{m}$  thick, which were the backing for the PSA films. The PSA films were dried at  $80^{\circ}\text{C}$  for 2 min and then were wound into a roll. The thickness of the PSA layers so obtained was 3  $\mu\text{m}$ . It was confirmed by gas chromatography that there was no residual solvent in the PSA films under this drying condition. The PSA layer was transparent over the experiment; this suggested that the acrylic resin and crosslinker were miscible for the aforementioned formulation. The rolls of the PSA films were left under ambient air for 2 days according to a commercial procedure. Time zero in these experiments, therefore, was 2 days after the end of the preparation of the PSA films.

The rolls of the PSA films were stored in two glass jars to simulate dry and humid atmospheres. One jar contained a saturated ammonium chloride solution and was maintained at  $20^{\circ}\text{C}$ , with 79.2% relative humidity. The other jar was desiccated with phosphorus pentoxide.

### Preparation of the model compounds

Model compounds were prepared with the polyisocyanate crosslinker as the starting material according

to the methods reported by Kaji et al.,<sup>6</sup> Kohira,<sup>7</sup> and Zhou and Frazier,<sup>8</sup> as described next.

### Urethane

Excess methanol (0.2 mol) was added to a solution of the polyisocyanate crosslinker (0.001 mol) in toluene (5 wt %). The solution was stirred for 24 h at the ambient temperature. Then, the volatiles were evaporated.

### Urea

A mixture of distilled water ( $\text{H}_2\text{O}$ ; 0.1 mol) and *N,N'*-dimethylacetamide (DMAc; 8.2 mL) was added to a solution of the polyisocyanate crosslinker (0.001 mol) in DMAc (5 wt %). The solution was stirred for 4 h at ambient temperature. The reaction mixture was poured into water, and the precipitate was filtered off and washed with water. Then, it was dried at  $85^{\circ}\text{C}$  for 24 h.

It was confirmed by FTIR measurements that there were no unreacted isocyanate groups in any of these model compounds.

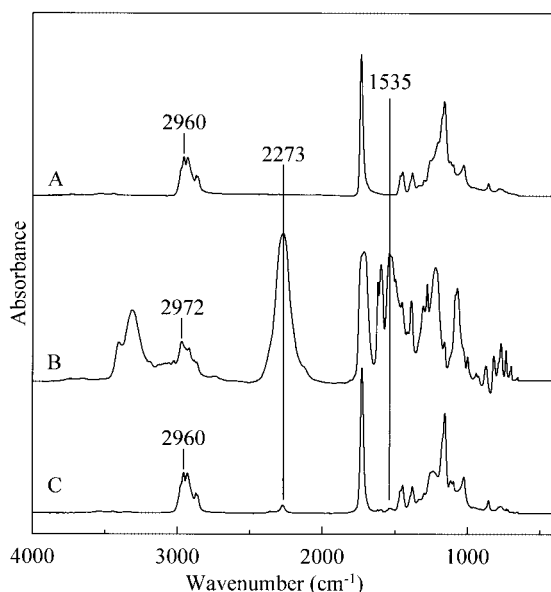
### FTIR measurements

Transmission and ATR-FTIR spectra were collected on a Nicolet Magna-IR 860 spectrometer (Thermo Nicolet Japan Co., Ltd., Kanagawa, Japan) equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride detector. An attenuated total reflectance accessory (Spectra-Tech, Inc, Shelton, CT) with a zinc selenium crystal for  $45^{\circ}$  angles of incidence was used. Transmission FTIR spectra were obtained with the potassium bromide disc technique. Transmission spectra recorded at elevated temperatures were obtained with a temperature-controlled cell, a model HT-32 heated cell (Spectra-Tech), equipped with a microprocessor programmable controller (Spectra-Tech), which had a reported accuracy of  $\pm 1^{\circ}\text{C}$ . Before each spectral measurement, the temperature was kept constant for 2 h to ensure complete temperature equilibration along the sample cell. The spectral features of overlapping bands were decomposed with peak-solving software (Peaksolve, Thermo Galactic, Salem, NH).

## RESULTS AND DISCUSSION

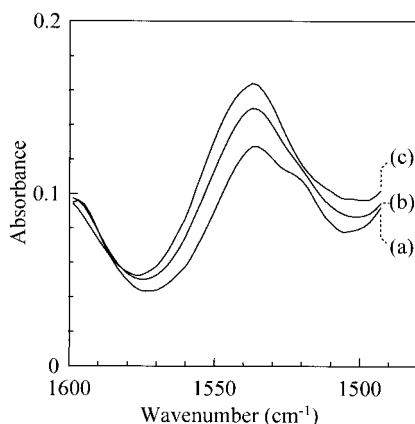
### FTIR spectroscopy

Figure 1 shows FTIR spectra of the polyacrylic resin, polyisocyanate crosslinker, and PSA film for which the crosslinker was formulated. Traces A and B in Figure 1 show transmission FTIR spectra of the polyacrylic resin and Colonate L, the polyisocyanate crosslinker, respectively. The band at  $2960\text{ cm}^{-1}$  in

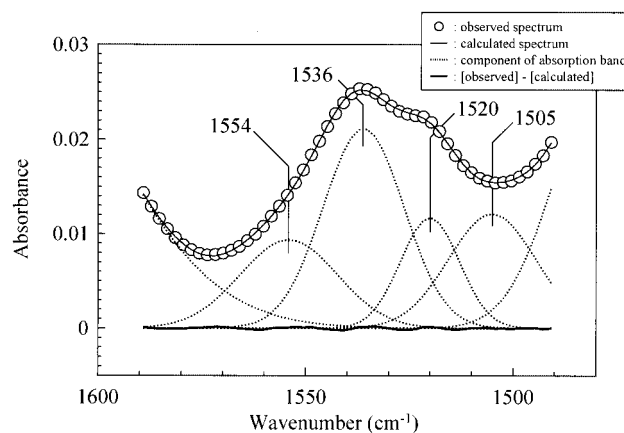


**Figure 1** (A,B) Transmission FTIR spectra of acrylic resin and Colonate L, respectively, and (C) ATR-FTIR spectrum of a PSA film after pretreatment at 80°C for 2 min.

trace A is due to the CH<sub>2</sub> stretching mode. Trace B illustrates a pronounced band at 2273 cm<sup>-1</sup> due to the NCO asymmetric stretching mode. The band at 1535 cm<sup>-1</sup> is due to the amide II band, which is a mixed mode containing contributions from the N—H in-plane bending, the C—N stretching, and the C—C stretching vibrations.<sup>9</sup> The band at 2972 cm<sup>-1</sup> is attributed to the CH stretching mode. Trace C in Figure 1 represents an ATR-FTIR spectrum of the PSA film for which the crosslinker was formulated. Of particular interest is the band due to NCO groups at 2273 cm<sup>-1</sup> because this band decreases as the crosslinking reaction proceeds.<sup>10</sup> Therefore, this band was used for the measurements of the amounts of unreacted NCO



**Figure 2** Normalized ATR-FTIR spectra in the amide II region of PSA after (a) pretreatment at 80 deg;C for 2 min and aging at room temperature for 2 days, (b) storage at 23°C for 2 days under the dry condition, and (c) storage at 23°C for 180 days under the dry condition.

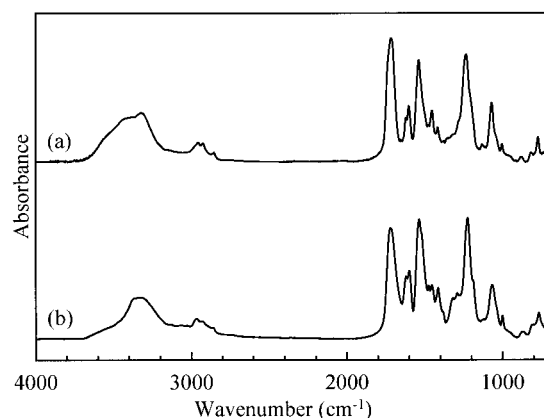


**Figure 3** Curve-fitting results in the amide II region of PSA films after pretreatment at 80 deg;C for 2 min and aging at room temperature for 2 days.

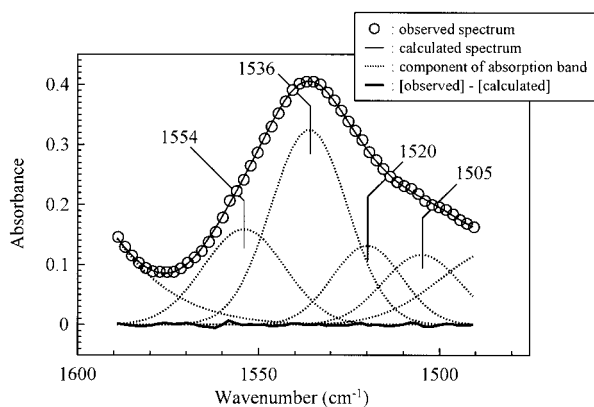
groups. The band at 1535 cm<sup>-1</sup> is due to the amide II bands of urethane and urea linkages contained in the polyisocyanate crosslinker and the products obtained from the crosslinking reaction. As shown in Figure 2, this band increases as the crosslinking reaction proceeds. Therefore, this band was used for the calculation of the amounts of isocyanate derivatives. With OMNIC, the Nicolet software, the height of this band was calculated. In an effort to minimize the effects of sample crystal coverage on the band intensity, all ATR-FTIR spectra were normalized to the CH<sub>2</sub> stretching vibrations at 2960 cm<sup>-1</sup> in the polyacrylic resin used<sup>3,4,11</sup> because the intensity of the CH stretching band at 2972 cm<sup>-1</sup> in the polyisocyanate crosslinker, charged only to 3 phr, was considered to be negligible and because the methylene groups in the resin were stable during the crosslinking reaction.

#### Peak assignments in the amide II region

In an effort to determine the relative amounts of urethane and urea linkages, the amide II band was de-



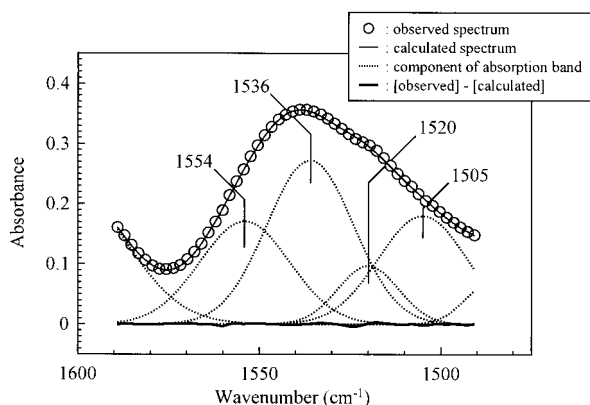
**Figure 4** FTIR spectra of (a) the model urethane and (b) the model urea.



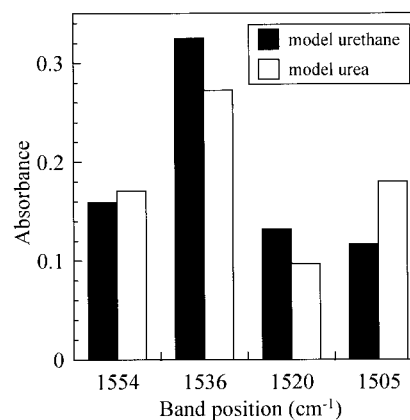
**Figure 5** Curve-fitting results in the amide II region of the model urethane.

composed into individual absorption bands with a peak-resolving method. Figure 3 shows the results of the peak resolution in the amide II region from 1590 to 1490  $\text{cm}^{-1}$  for the PSA film after pretreatment at 80°C for 2 min and at 23°C for 2 days. The spectrum in this region was resolved into four bands at 1554, 1536, 1520, and 1505  $\text{cm}^{-1}$ .

For the assignment of these four peaks, amide II bands of the model urethane and model urea, which used the polyisocyanate crosslinker as the starting material, were also decomposed into individual absorption peaks. Figure 4 shows FTIR spectra of the model urethane and model urea. Figure 5 shows the results of the peak resolution in the amide II region for the model urethane. A pronounced band appears at 1536  $\text{cm}^{-1}$  due to urethane linkages. Similarly, the peak-resolving results in the amide II region for the model urea are shown in Figure 6. The peak intensity at 1554 and 1505  $\text{cm}^{-1}$  of the model urea is stronger than that of the model urethane, as shown in Figure 7. However, the peak intensity at 1536 and 1520  $\text{cm}^{-1}$  of the model urethane is stronger than that of the model urea. Therefore, it is suggested that the bands at 1554



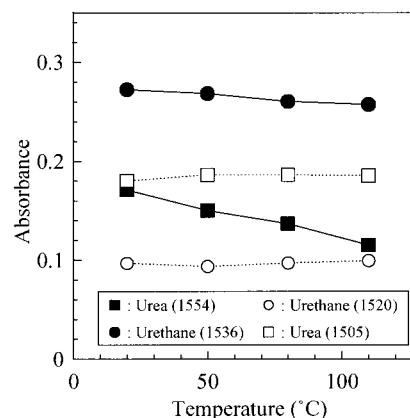
**Figure 6** Curve-fitting results in the amide II region of the model urea.



**Figure 7** Heights of each band in the amide II region for the model urethane and model urea.

and 1505  $\text{cm}^{-1}$  are due to urea linkages, whereas the bands at 1536 and 1520  $\text{cm}^{-1}$  are due to urethane linkages. The peaks at 1554 and 1505  $\text{cm}^{-1}$  due to urea linkages are observed in the amide II region for the model urethane, as shown in Figure 5. It is suggested that the polyisocyanate crosslinker reacts with water available from atmosphere as well as OH groups in methanol during the preparation of the model urethane, leading to the formation of urea linkages. However, the peaks at 1536 and 1520  $\text{cm}^{-1}$  due to urethane linkages are observed in the amide II region for the model urea, as shown in Figure 6, because these two peaks are attributed to urethane linkages contained in the polyisocyanate crosslinker.

For more information, the heights of these four bands in the amide II region of the model urea are plotted as a function of temperature, as shown in Figure 8. The bands at 1554 and 1536  $\text{cm}^{-1}$ , due to urea and urethane linkages, respectively, decrease with increasing temperature. In contrast, the bands at 1520 and 1505  $\text{cm}^{-1}$ , due to urethane and urea linkages, respectively, do not show significant changes



**Figure 8** Heights of each band in the amide II region as a function of temperature for the model urea.

TABLE I  
Band Assignments in the Amide II Region

Band position ( $\text{cm}^{-1}$ )	Assignment
1554	Urea (hydrogen bonded)
1536	Urethane (hydrogen bonded)
1520	Urethane (free)
1505	Urea (free)

with temperature. A similar tendency was also observed for the model urethane.

Coleman et al.<sup>9</sup> observed an N—H stretching band and an amide I band, which was composed of contributions from the C=O stretching, C—N stretching, and C—C—N deformation vibrations, of an amorphous polyamide with a peak-resolving method. They indicated that the hydrogen-bonded N—H band and the hydrogen-bonded amide I band decreased in area with increasing temperature, whereas the free N—H band and the free amide I band remained essentially constant with temperature. Therefore, it is suggested that the bands at 1554 and 1536  $\text{cm}^{-1}$  are attributable to the hydrogen-bonded components, whereas the bands at 1520 and 1505  $\text{cm}^{-1}$  are attributable to the free components. The assignments of individual absorption bands in the amide II region so obtained are listed in Table I and have been used to observe urethane and urea formation during the crosslinking reaction in the PSA films.

#### Effect of humidity on the NCO consumption

The relative amount of unreacted isocyanate groups [ $A(\text{NCO})/A(\text{CH})$  ratio] of the PSA films stored under the dry and humid conditions is plotted as a function of the storage time in Figure 9. The  $A(\text{NCO})/A(\text{CH})$  ratio of the PSA films decreases exponentially with an increase in the storage time under either storage condition investigated. The rate of NCO consumption in

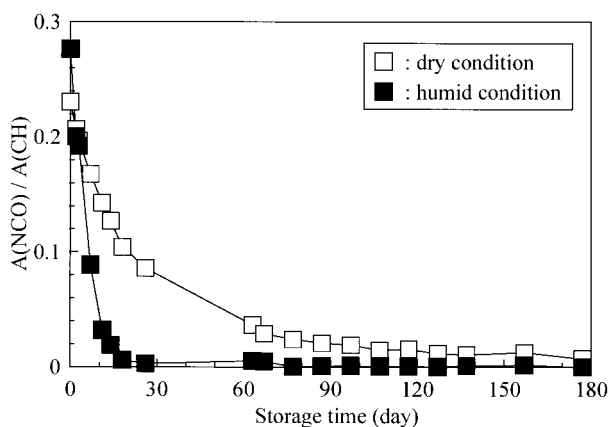


Figure 9  $A(\text{NCO})/A(\text{CH})$  ratio of PSA films as a function of the storage time.

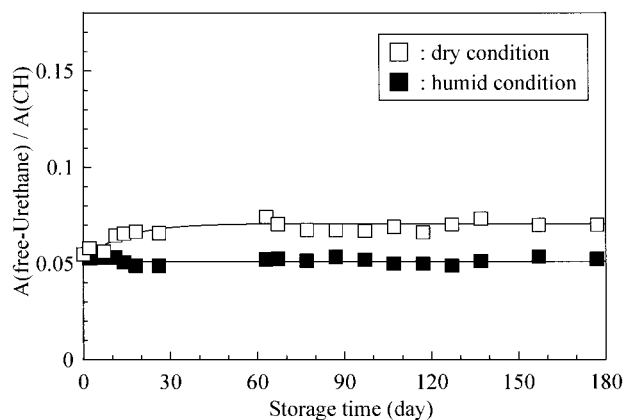
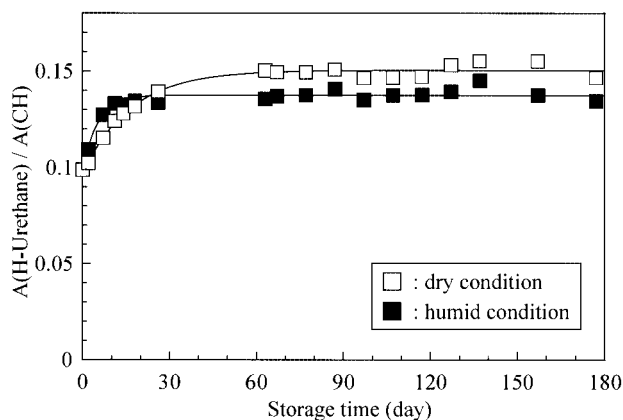


Figure 10  $A(\text{free-urethane})/A(\text{CH})$  ratio of PSA films as a function of the storage time.

the PSA films is much higher for the PSA films stored under the humid condition than for those stored under the dry condition. The storage time at which the NCO band at 2273  $\text{cm}^{-1}$  diminishes is around 20 days for the PSA films stored under the humid condition. In contrast, it is around 120 days for the PSA films stored under the dry condition. The rapid decrease in the  $A(\text{NCO})/A(\text{CH})$  ratio of the PSA films stored under the humid condition is attributed to contact with atmospheric moisture during the storage time. Cole et al.<sup>11</sup> reported that aging under humid conditions reduced the isocyanate concentration in flexible polyurethane foams faster than aging under dry conditions. Urban and coworkers<sup>3,4,12</sup> indicated for solvent-borne and waterborne polyurethane coatings that relative humidity caused an increase in the isocyanate consumption as a result of a reaction with water leading to urea formation. Our results also suggest that isocyanate groups in the PSA films react with water in the atmosphere and with hydroxyl groups in acrylic base resins under the humid condition. Now we focus our attention on urethane and urea formation in the PSA films during crosslinking reactions under the dry and humid conditions.

#### Effect of humidity on urethane and urea formation

The relative amount of free urethane linkages [ $A(\text{free-urethane})/A(\text{CH})$  ratio] in the PSA films stored under the dry and humid conditions is plotted as a function of the storage time in Figure 10. The  $A(\text{free-urethane})/A(\text{CH})$  ratio of the PSA films stored under the dry condition slightly increases up to 80 days and then holds at a constant value of approximately 0.07. However, the  $A(\text{free-urethane})/A(\text{CH})$  ratio of the PSA films stored under the humid condition holds at a constant value of approximately 0.05 during our observation period. The increase in the  $A(\text{free-urethane})/A(\text{CH})$  ratio of the PSA films stored under the dry

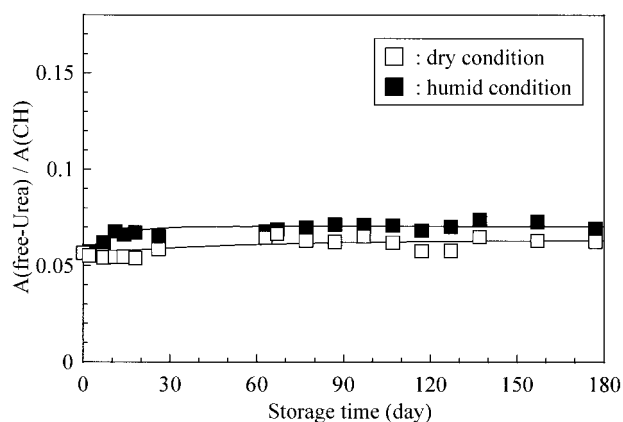


**Figure 11**  $A(\text{H-urethane})/A(\text{CH})$  ratio of PSA films as a function of the storage time.

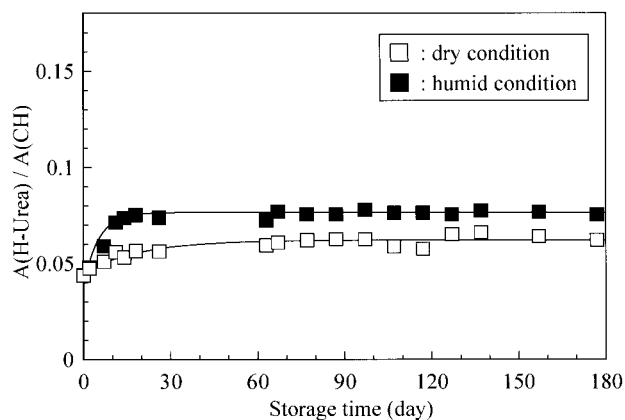
condition is higher than for the films stored under the humid condition.

Similarly, the relative amount of hydrogen-bonded urethane linkages [ $A(\text{H-urethane})/A(\text{CH})$  ratio] in the PSA films stored under the dry and humid conditions is plotted as a function of the storage time in Figure 11. The  $A(\text{H-urethane})/A(\text{CH})$  ratio of the PSA films stored under the dry condition increases up to 80 days and then holds at a constant value of approximately 0.15. However, the  $A(\text{H-urethane})/A(\text{CH})$  ratio of the PSA films stored under the humid condition increases up to 20 days and then holds at a constant value of approximately 0.135. The increment of the  $A(\text{H-urethane})/A(\text{CH})$  ratio of the PSA films stored under the dry condition is higher than that stored under the humid condition (cf. Fig. 10).

The relative amount of free urea linkages [ $A(\text{free-urea})/A(\text{CH})$  ratio] in the PSA films is plotted as a function of the storage time in Figure 12. The  $A(\text{free-urea})/A(\text{CH})$  ratio of the PSA films stored under the humid condition slightly increases up to 20 days and then holds at a constant value of approximately 0.06,



**Figure 12**  $A(\text{free-urea})/A(\text{CH})$  ratio of PSA films as a function of the storage time.



**Figure 13**  $A(\text{H-urea})/A(\text{CH})$  ratio of PSA films as a function of the storage time.

whereas those films stored under the dry condition show no significant changes during our observation period. The increase in the  $A(\text{free-urea})/A(\text{CH})$  ratio of the PSA films stored under the humid condition is higher than that for those films stored under the dry condition.

The relative amount of hydrogen-bonded urea linkages [ $A(\text{H-urea})/A(\text{CH})$  ratio] in the PSA films is plotted as a function of the storage time in Figure 13. The  $A(\text{H-urea})/A(\text{CH})$  ratio of the PSA films stored under the humid condition increases up to 20 days and then holds at a constant value of approximately 0.075. However, the  $A(\text{H-urea})/A(\text{CH})$  ratio of the PSA films stored under the dry condition increases up to 80 days and then holds at a constant value of approximately 0.06. The increase in the  $A(\text{H-urea})/A(\text{CH})$  ratio of the PSA films stored under the humid condition is higher than that for those films stored under the dry condition (cf. Fig. 12).

Urban et al.<sup>12</sup> decomposed the amide II band of the waterborne polyurethane coatings with the SS-RES maximum likelihood entropy method. They indicated that the unreacted isocyanate groups reacted with water at a higher relative humidity, and reactions between isocyanate groups and hydroxyl groups of the resin were consequently suppressed. Our results apparently indicate that unreacted isocyanate groups in the PSA films predominantly react with hydroxyl groups in the acrylic resin under the dry condition, whereas isocyanate groups react with water available from the atmosphere as well as hydroxyl groups in the acrylic resin under the humid condition. It is definite that the reaction between unreacted isocyanate groups and water available from the atmosphere leads to an increase in the isocyanate consumption rate.

## CONCLUSIONS

The crosslinking reaction between the polyacrylic PSA resin and polyisocyanate crosslinker in crosslinked

PSA films stored under dry and humid conditions was investigated by ATR-FTIR measurements.

The consumption of isocyanate groups in the PSA films was monitored by the changes in the band intensity at  $2273\text{ cm}^{-1}$  due to the NCO asymmetric stretching mode. The formation of urethane and urea linkages in the PSA films was monitored by the changes in the band intensity around  $1535\text{ cm}^{-1}$  due to the amide II band with a peak-resolving method. A peak-resolving analysis of the amide II region revealed four bands, which were attributed to free urethane linkages, hydrogen-bonded urethane linkages, free urea linkages, and hydrogen-bonded urea linkages according to the analysis of FTIR spectra of model compounds based on the polyisocyanate crosslinker.

Isocyanate groups in the PSA films stored under the humid condition were consumed earlier than the films stored under the dry condition. Consequently, more urea linkages were produced in the PSA films stored under the humid condition than in the films stored under the dry condition. As expected, the isocyanate groups in the PSA films reacted with water in the atmosphere as well as hydroxyl groups in the resin

under the humid condition, and this led to a rapid consumption of isocyanate groups. These results suggest that peak resolution of the amide II region is a reasonable way of monitoring urethane and urea linkages during crosslinking reactions.

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