Crosslinked Acrylic Pressure-Sensitive Adhesives. I. Effect of the Crosslinking Reaction on the Peel Strength

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ABSTRACT: For pressure-sensitive adhesives (PSAs) composed of poly(co-ethyl acrylate-2-ethylhexyl acrylate-2-hydroxyethyl methacrylate) as a base resin and polyisocyanate as a crosslinker, the relationship between the crosslinking reaction and peel strength was investigated. A 90° peel test of cured PSA films under various storage conditions was carried out. At the same time, the isocyanate (NCO) consumption in these PSA films was monitored by attenuated total reflectance/Fourier transform infrared spectroscopy. The peel strength of the PSA compounded with the crosslinker decreased as the NCO groups were consumed. The elevation of the aging temperature promoted the crosslinking reaction and increased the decrement in the peel strength. The peel strength of noncrosslinked and crosslinked PSA films increased with the contact time. A high storage temperature made the increment in the peel strength increase. The addition of the crosslinker to the PSA films reduced the increment in the peel strength. Furthermore, PSA films with residual NCO groups possessed stronger peel strengths than fully cured films. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1493–1499, 2003

Key words: adhesives; crosslinking; FT-IR

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are viscoelastic materials that can adhere firmly to solid surfaces upon the application of a light contact pressure and a short contact time. The commercial use of PSAs covers a broad range of labels, tapes, and medical and cosmetic products.[1]

The oldest PSA is a blend of a natural rubber and a rosin ester tackifier from a toluene and heptane solution. In the 1970s, both solution and emulsion polymerizations of low-glass-transition-temperature (T_g) acrylics such as poly(butyl acrylate) and poly(2-ethyl hexyl acrylate) gave inherently tacky PSAs without the need of an added tackifier. The absence of plasticizers and tackifiers in acrylic PSAs made them attractive choices when the migration of low molecular weight components into a substrate became a problem. Although both solvent-borne and water-borne acrylic PSAs are derived from the same monomers, solvent-borne acrylic PSAs generally exhibit a higher tack and peel adhesion, which arise from the molecular weight difference between solvent-borne and water-borne acrylic polymers.[2] Solvent-borne acrylics have much lower molecular weights (ca. 100,000) than water-borne ones (ca. 1,000,000) so that a workable solution viscosity is maintained.[3] Because the cohesive strength remains marginal at this molecular weight level, some crosslinking mechanism is used to compensate for the low molecular weight.

Crosslinking is a technique used very widely to alter polymer properties.[2] Typical crosslinking methods are based on the chemical reaction that takes place at elevated temperatures, although room-temperature (RT) curing is also known. Recently, radiation curing employing electron beams or a UV sources has also been used. Crosslinking affects most of the mechanical properties of a polymer, including adhesion-related properties. The most important effect of crosslinking on PSAs is the increase in its creep resistance. However, crosslinking in PSAs has special requirements. The crosslink density must be quite low, and the average molecular weight between crosslinks must be high for PSAs. Because PSAs must have a sufficiently low modulus of elasticity at a low rate of force application that is not compatible with a higher degree of crosslinking, control over the crosslinking reaction is of particular importance in PSAs.

The objective of this research was to elucidate the effect of crosslinking on PSA film properties. We chose poly(co-ethyl acrylate-2-ethylhexyl acrylate-2-hydroxyethyl methacrylate) as a base resin and polyisocyanate as a crosslinker. Polyisocyanate has high reactivity even at RT and is used in various fields. In Japan, PSA films crosslinked with polyisocyanate have become important. However, the relationships between the reaction of isocyanate (NCO) groups and PSA prop-

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TABLE I
Sample Formulation and Curing Conditions

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Sample code	Crosslinker (phr)	Aging condition		Contact condition	
		Time (day)	Temperature (°C)	Time (min)	Temperature (°C)
C0	3	—[a]	23,40,65	30	23
A0	0				
C2	3	2	23	—[a]	40,65
A2	0				
C95	3	95			

[a] Varying.

erties are not fully understood. Therefore, it is important to clarify the effect of the NCO reaction on PSA film properties.

We monitored changes in the 90° peel strength and the concentration of NCO groups remaining in these PSA films simultaneously with attenuated total reflectance/Fourier transform infrared (ATR–FTIR) spectroscopy under various storage conditions.

In this report, we focus on the relationship between the change in the peel strength and the consumption of NCO groups in PSA films as an index of the degree of crosslinking.

EXPERIMENTAL

Materials

A hydroxy-substituted polyacrylic resin prepared by the copolymerization of ethyl acrylate, 2-ethylhexyl acrylate, and 2-hydroxyethyl methacrylate in 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 (25/65 w/w). The T_g value of the polymer was −28.1°C according to differential scanning calorimetry (DSC) measurements. Coronate L (Nippon Polyurethane Industries Co., Ltd., Tokyo, Japan) was used as a crosslinker in an ethyl acetate/toluene solution (20/80 w/w). These two materials were used without further purification. Other chemicals used were reagent-grade in accordance with Japanese industrial standards.

Preparation of the PSA films

The PSA films for the peel test and ATR measurements were prepared with the following procedure. The polyacrylic solution was diluted to a 5 wt % solid content with toluene. Coronate L (3 phr) was added to the solution, and this gave a ratio of NCO/OH = 1/10. The mixture was stirred for 20 min and was cast onto polyethylene films 60 μm thick that acted as backing for PSA films. The PSA films were dried at 80°C for 2 min and then were wound into a roll. The thickness of the PSA layer so obtained was 3 μm. 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, and this suggested that the acrylic resin and the crosslinker were miscible in this formulation. For the control experiments, polyacrylic PSA films without a crosslinker were also prepared similarly.

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 ATR accessory (Spectra-Tech, Inc.) with a zinc selenium crystal for 45° angles of incidence was used. Dry air was purged continuously in the instruments during the measurements.

Peel tests

The peel strength of the PSA films at an angle of 90° was measured with a Tensilon RTA-100 (Orientec Co., Ltd., Tokyo, Japan) at a peel rate of 0.2 m/min at 23°C. The peel strength was defined as follows:[4]

$$1 \text{ Peel strength (N/mm)} = F/b$$

where F is the peeling force and b is the width of the strip serving as a measure of the peel strength.

The PSA film was fastened to stainless steel (SUS-430BA; 50 mm × 100 mm) by means of a rubber roll with a pressure of 6 kg/cm and a press rate of 2 m/min. Then, it was cut into strips 25 mm wide. The peel strength was measured at various aging times, aging temperatures, contact times, and storage temperatures. For convenience, the sample formulations and the curing conditions were coded as indicated in Table I. The zero aging time was defined as the time just after the pretreatment at 80°C for 2 min. However, the zero contact time was defined as the time when the PSA film adhered to stainless steel followed by aging under various conditions. All specimens were placed at 23°C for 30 min before testing. Three replicates were tested for each condition.
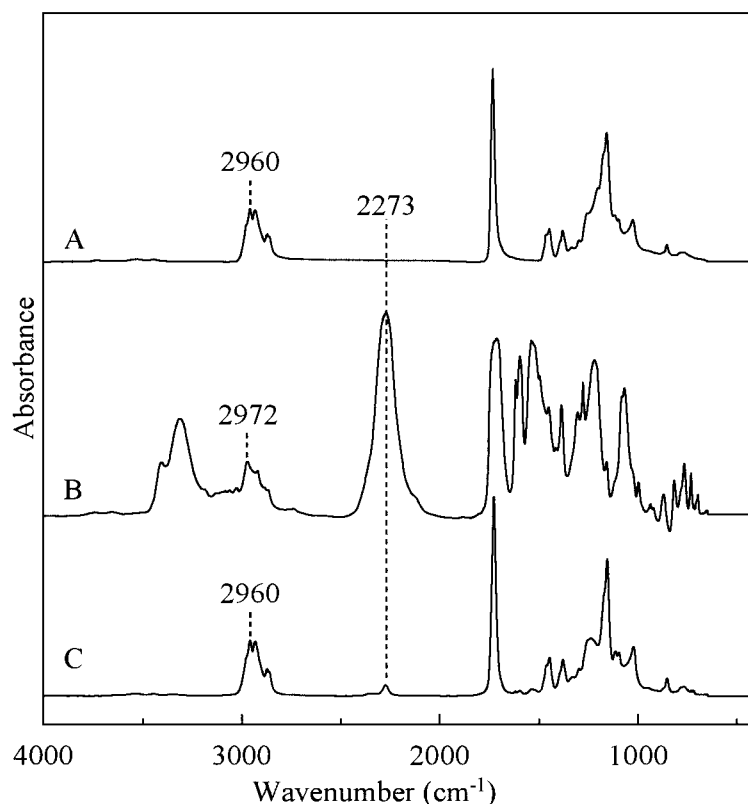
Figure 1 (A,B) Transmission FTIR spectra of acrylic resin and Coronate L, respectively, and (C) ATR–FTIR spectra of C0 after pretreatment at 80°C for 2 min.

RESULTS AND DISCUSSION

FTIR spectra

Figure 1 shows the FTIR spectra of the polyacrylic resin, Coronate L, and PSA film in which the crosslinker was formulated. Traces A and B in Figure 1 show transmission FTIR spectra of the polyacrylic resin and Coronate L, respectively. The band at 2960 cm^{-1} in trace A is due to CH$_2$ stretching modes. Trace B illustrates a pronounced band at 2273 cm^{-1} due to NCO asymmetric stretching modes. The band at 2982 cm^{-1} is attributed to the CH stretching mode. Trace C in Figure 1 represents the ATR–FTIR spectrum of C0 after pretreatment at 80°C for 2 min. Note that the band at 2273 cm^{-1} due to NCO groups is also observed even after the pretreatment at 80°C for 2 min. This band should decrease if some crosslinking reaction involving NCO groups occurred. As shown in Figure 2, this band decreases as the crosslinking reaction proceeds. Therefore, this band was used for the measurements of the amounts of unreacted NCO groups. With OMNIC (Nicolet software), the height of this band was calculated. In an effort to minimize the effects of the sample crystal coverage on the band intensity, we normalized all spectra to the CH$_2$ stretching vibrations at 2960 cm^{-1} in the polyacrylic resin used; that is, the A(NCO)/A(CH) ratio was calculated[5–7]
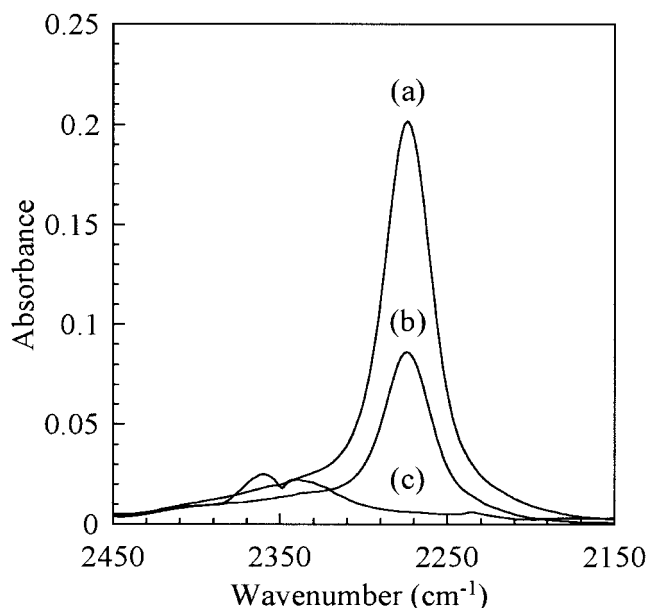

Figure 2 Normalized ATR–FTIR spectra in the NCO asymmetric stretching region of C0 after (a) pretreatment at 80°C for 2 min, (b) aging at 23°C for 2 days, and (c) aging at 23°C for 95 days.
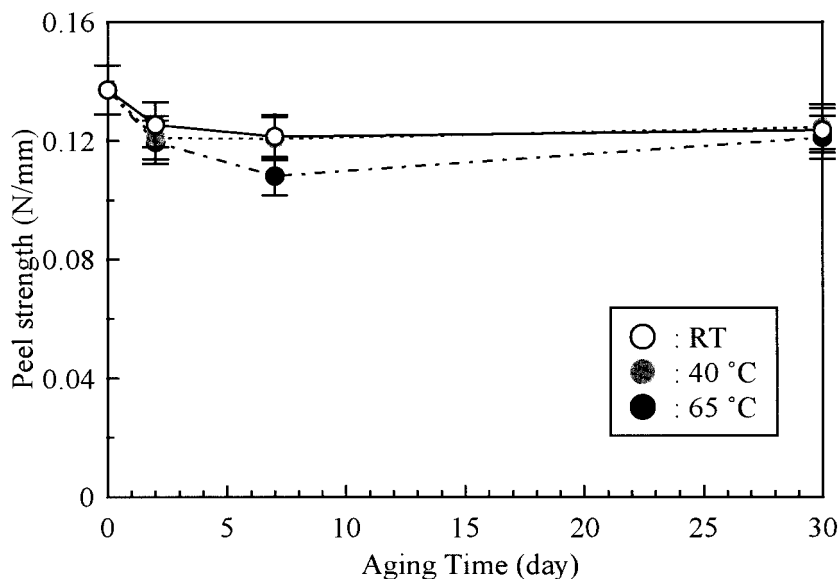
Figure 3 Plot of the peel strength of A0 as a function of the aging time.

because the intensity of the CH stretching band at 2972 cm^{-1} in Coronate L, of which only 3 phr was charged, was considered to be negligible and because the methylene groups in the resin were stable during the crosslinking reaction.

Effect of the aging condition on the peel strength

The peel strength was measured with a fixed contact time of 30 min but with various aging temperatures and times before adherence to stainless steel. Figure 3 shows a plot of the peel strength of A0, that is, a polyacrylic PSA without a crosslinker, as a function of the aging time. The peel strength of A0 slightly de-

creased with an increase in the aging time. The peel strength was apparently independent of the aging temperature. The values of the peel strength at different aging temperature were the same even after 182 days. Therefore, the change in the aging temperature had no effect on the peel strength of polyacrylic PSA without a crosslinker.

The peel strength of the C0-formulated crosslinker is plotted against the aging time in Figure 4. Over the range of 0–15 days of aging, the decrement in the peel strength was dependent on the aging temperature. As the aging temperature increased, the decrement in the peel strength increased. The peel strength, however,
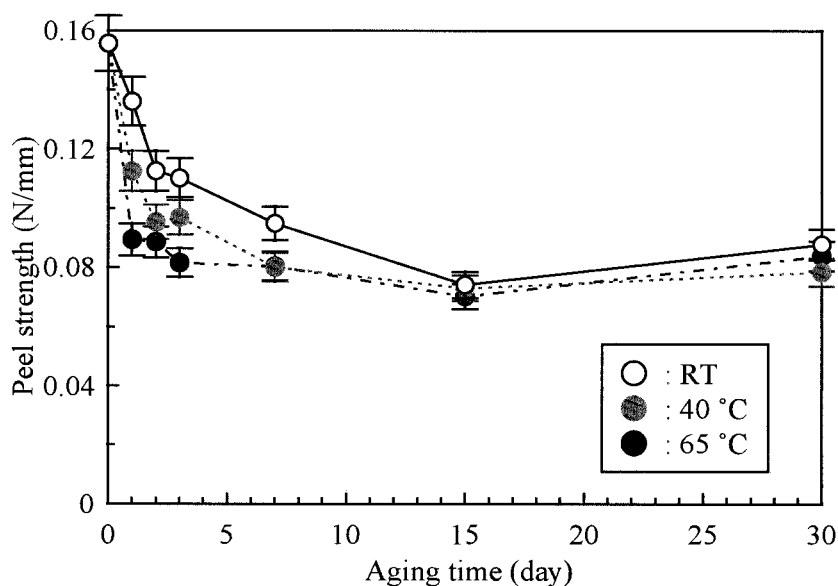

Figure 4 Plot of the peel strength of C0 as a function of the aging time.
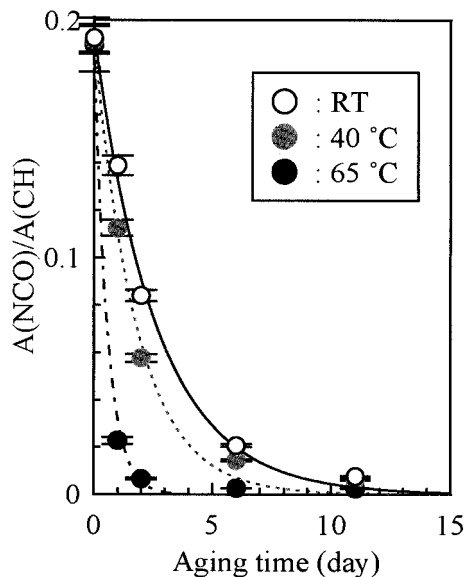
Figure 5 Plot of the A(NCO)/A(CH) ratio of C0 as a function of the aging time.

reached the same level at about 0.08 N/mm after 15 days, even if the aging temperature varied.

These findings suggest that the crosslinking reaction occurred during 0–15 days and was complete after 15 days in the films. To investigate the extent of the crosslinking reaction in these PSA films, we performed ATR–FTIR measurements for C0. Figure 5 shows a plot of the A(NCO)/A(CH) ratio in C0 as a function of the aging time. The A(NCO)/A(CH) ratio decreased exponentially, and the NCO band at 2273 cm^{-1} was diminished by an aging time of 11 days at every temperature investigated. The rate of NCO consumption in the PSA films increased with an increase in the aging temperature. The tendency observed in Figure 5 was similar to the results obtained from the peel test in Figure 4. To consider the effect of the crosslinking reaction on the peel strength, we have plotted the peel strength of C0 aged at 23, 40, and 65°C against the corresponding A(NCO)/A(CH) ratio in Figure 6. Interestingly, a linear relation was found, indicating that the peel strength decreased as NCO groups were consumed. Ozawa et al.[8] reported that peel adhesion and probe tack of UV-curable blends reduced as a result of storage and loss moduli and T_g increased by UV irradiation. Madigosky[9] also indicated that T_g of the urethane polymer increased as the crosslink density increased. In our experiment, the T_g values of the acrylic base resin and fully crosslinked resin in which the crosslinker was formulated were −28.1 and −25.5°C by DSC measurements, respectively. The storage modulus of the acrylic base resin was lower than that of the fully crosslinked resin in the rubbery region. Our results also indicate that the crosslinking reaction increased the modulus and T_g of the polymer. Therefore, the modulus of C0 was

thought to vary between those of the acrylic base resin and fully crosslinked resin, and the peel strength of C0 consequently decreased as the crosslinking reaction proceeded. Moreover, an elevation of the aging temperature promoted NCO consumption in the PSA films.

Effect of the contact condition on the peel strength

C2 had approximately 50% unreacted NCO groups in PSA films after aging at 23°C for 2 days, whereas C95 had no residual NCO groups after aging at 23°C for 95 days. This means that the crosslinking reaction of the remaining NCO groups with the hydroxyl groups of the acrylic resin in the PSA films of C2 occurred on the stainless steel. Therefore, the crosslinking reaction carried out on the stainless steel was investigated with ATR–FTIR measurements.

Figure 7 illustrates the A(NCO)/A(CH) ratio of C2 peeled off from the stainless steel as a function of the contact time. The A(NCO)/A(CH) ratio of C2 stored at 40 and 65°C exponentially decreased with an increase in the contact time. The contact times at full cure for C2 at 40 and 65°C were around 13 and 5 days, respectively.

The peel strengths of A2, C2, and C95 stored at 40°C are plotted as a function of the contact time in Figure 8. Each curve exhibits a similar shape, showing a rapid increase in the initial stage and then a plateau in the late stage. The peel strength of C2, which had residual NCO groups in the initial stage, was higher than that of C95, which was fully cured over our observation period.
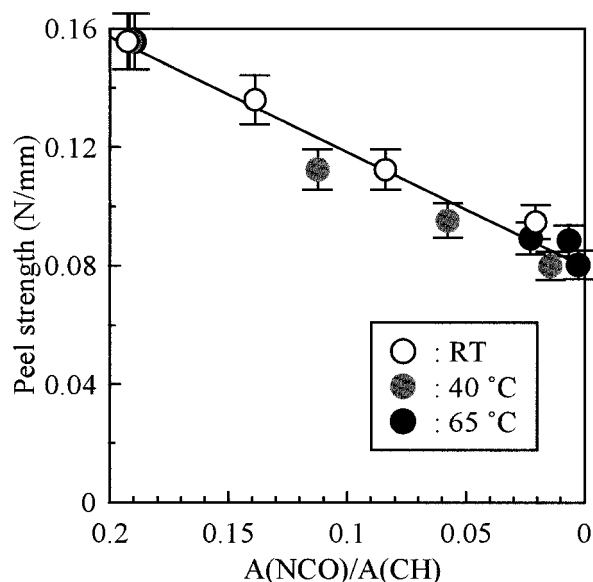

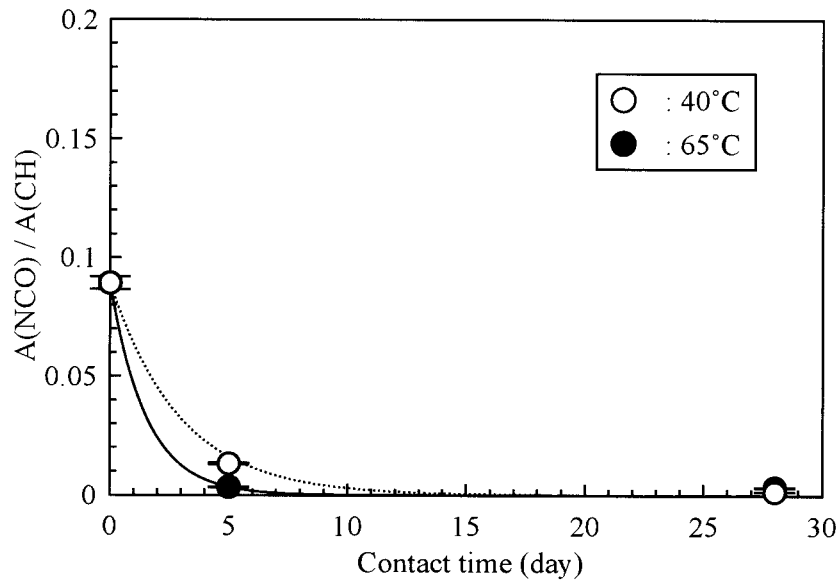**Figure 6** Plot of the peel strength versus A(NCO)/A(CH) for C0.

Figure 7 Plot of the A(NCO)/A(CH) ratio of C2 peeled off from stainless steel as a function of the contact time.

For more information, the peel strengths of A2, C2, and C95 stored at 65°C are shown in Figure 9. The curve of A2 exhibits a rapid increase up to 5 days and then a slight increase with linearity, whereas the curves of C2 and C95 rapidly increase only up to 2 days. The increments of the peel strength in the curves of A2 and C2 at the initial stage are substantially higher than for those stored at 40°C, whereas the increment in the curve of C95 is slightly higher than for that stored at 40°C. The peel strength of C2 is again higher than that of C95.

Johnston[10] reported that the separation energy of a polymer based on tack measurements increased with the contact time because of the wettability of the poly-mer and showed curves similar to those in Figures 8 and 9. Our results also indicate that the prolongation of the contact time should help a PSA to flow to stainless steel as an adherend and increase the adhesion area between the PSA resin and adherend, leading to an increase in the peel strength.

In our experiment, the storage moduli of the acrylic base resin and fully crosslinked resin continuously decreased over the range from RT to 80°C. Because the elevation of the storage temperature reduced the storage modulus of PSA films, the wetting of the PSA resin to the adherend was encouraged, leading to larger increments in the peel strength for that stored at 65°C than for that stored at 40°C.
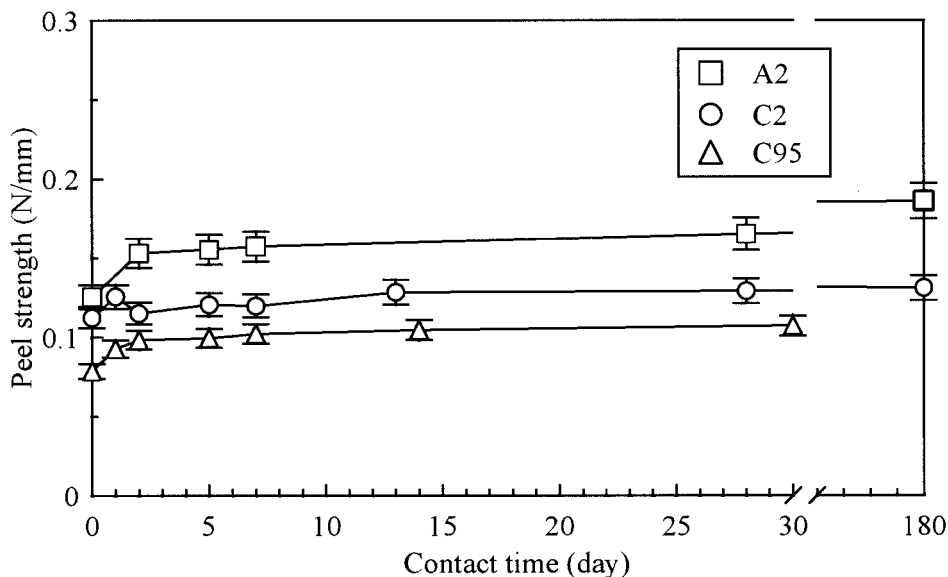

Figure 8 Plot of the peel strength of A2, C2, and C95 stored at 40°C as a function of the contact time.
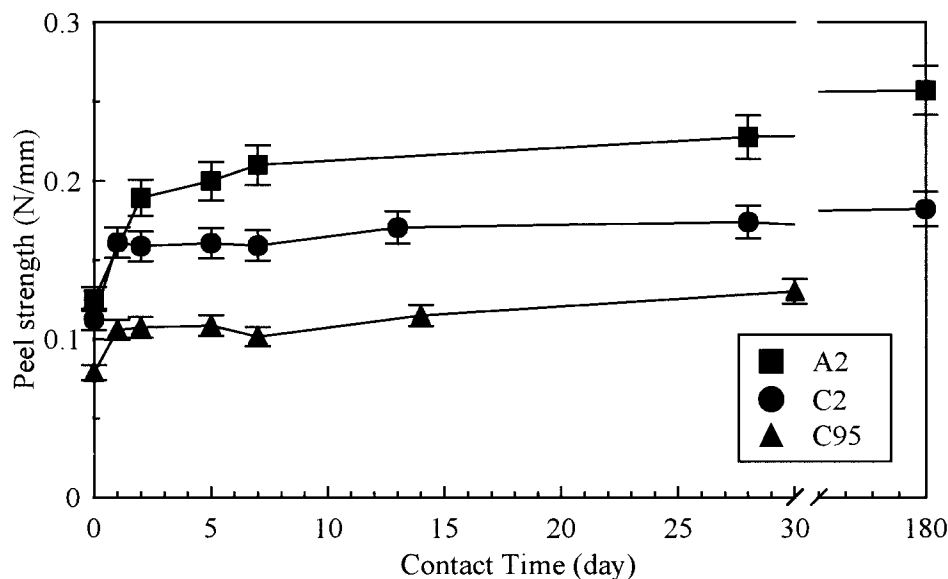
Figure 9 Plot of the peel strength of A2, C2, and C95 stored at 65°C as a function of the contact time.

As mentioned previously, the crosslinking reaction increased the storage modulus and T_g of the polymer. The storage modulus of C2 varied between those of A2 and C95 as the crosslinking reaction proceeded in C2; consequently, wettability was reduced because of the restriction of molecular movement. Because A2 provided a lower storage modulus than C95, it was reasonable that A2 exhibited a higher strength and an increasing rate of peel at the initial stage because of its better wettability. For C2, the wetting and crosslinking reaction were thought to occur simultaneously at the initial stage, and so the crosslinking structure could regulate the increment in the peel. It is interesting that the peel strength of C2, which retained NCO groups adhering onto the adherend, was higher even after the crosslinking reaction was complete. This suggests that a higher peel strength is obtainable from a PSA film with residual NCO groups in comparison with a fully cured film.

CONCLUSIONS

1. The peel strength of the crosslinked PSA films decreased with the decrease in the residual NCO groups in the PSA films as the aging time was prolonged.
2. The elevation of the aging temperature promoted the crosslinking reaction, leading to a rapid decrease in the peel strength of the crosslinked PSA films.
3. Regardless of the residual NCO groups in the PSA films, the peel strength of the PSA films tended to increase with the contact time.
4. The peel strength of the PSA films with residual NCO groups even after adhering to the stainless steel was higher than that of the PSA films in which the NCO groups were completely consumed.
5. The elevation of the storage temperature encouraged wetting of the PSA resin to the stainless steel as well as a crosslinking reaction, providing a large increment in the peel strength.

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