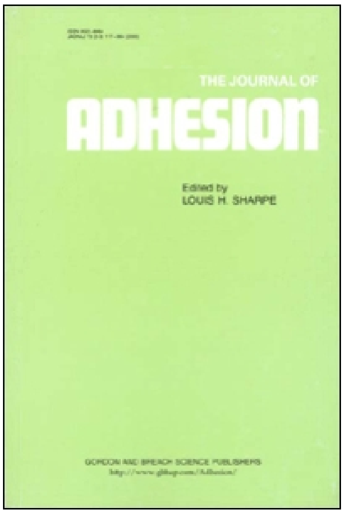


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Surface and Interfacial Structure of Release Coatings for Pressure Sensitive Adhesives I. Polyvinyl N-Alkyl Carbamates

David J. Kinning[a]
[a] 3M Company, St. Paul, MN, USA

To cite this Article Kinning, David J.(1997) 'Surface and Interfacial Structure of Release Coatings for Pressure Sensitive Adhesives I. Polyvinyl N-Alkyl Carbamates', The Journal of Adhesion, 60: 1, 249 — 274

To link to this Article: DOI: 10.1080/00218469708014422

URL: http://dx.doi.org/10.1080/00218469708014422

J. Adhesion, 1997, Vol. 60, pp. 249–274
Reprints available directly from the publisher
Photocopying permitted by license only

Surface and Interfacial Structure of Release Coatings for Pressure Sensitive Adhesives I. Polyvinyl N-Alkyl Carbamates*

DAVID J. KINNING
3M Company, St. Paul, MN 55144, USA

(Received November 30, 1995; in final form February 14, 1996)

Polyvinyl N-alkyl carbamates belong to the general class of long alkyl side chain polymers. Such polymers are commonly used as release coatings for pressure sensitive adhesive tapes. In this paper the bulk, surface, and interfacial structures of polyvinyl N-alkyl carbamates having either decyl or octadecyl side chains are examined. The bulk structures and thermal transitions were characterized using X-ray scattering and differential scanning calorimetry. Dynamic mechanical thermal analysis was used to investigate thermal transitions and rheology (*i.e.*, segmental mobility) of the polyvinyl N-alkyl carbamates. The surface energies of polyvinyl N-alkyl carbamate coatings were determined using contact angle methods, while X-ray photoelectron spectroscopy and static secondary ion mass spectrometry were employed to characterize the near-surface compositional profiles of the coatings. The peel force provided by the polyvinyl N-alkyl carbamate coatings, as a function of aging time and temperature, was measured for a tape having an acrylic acid containing alkyl acrylate based pressure sensitive adhesive. The changes in peel force with aging time and temperature were related to the ability to maintain a stable interfacial structure between the PSA and polyvinyl N-alkyl carbamate coatings. Changes in the interfacial composition upon aging were characterized by comparing the surface compositions of the PSA and polyvinyl N-alkyl carbamate coatings initially, prior to contact, as well as after aging and peeling them apart. The increase in peel force upon aging can be attributed, in large part, to a restructuring at the PSA/polyvinyl alkyl carbamate interface. Energetically favorable acid-base interactions between the basic urethane and acetate groups in the polyvinyl alkyl carbamates and the acrylic acid groups in the PSA provide a driving force for the restructuring. If the segmental mobility within the polyvinyl alkyl carbamate is sufficient, restructuring can occur, leading to increased concentrations of these groups at the PSA/polyvinyl alkyl carbamate interface, resulting in higher attractive forces and greater adhesion. The propensity for the polyvinyl N-alkyl carbamate coatings to restructure upon contact with a polar medium was also characterized by monitoring the receding contact angle of water, as a function of water contact time and temperature. A good correlation is seen between the ability of the polyvinyl alkyl carbamate coatings to provide a low peel force for the acrylate PSA tape and the ability of the coatings to maintain a high water receding contact angle.

KEY WORDS: Release coatings; pressure sensitive adhesives; polyvinyl N-alkyl carbamates; release mechanisms; surfaces; interfaces; restructuring.

---

*Presented at the Eighteenth Annual Meeting of the Adhesion Society, Inc., Hilton Head Island, South Carolina, U.S.A., February 19–22, 1995.

INTRODUCTION

Most pressure sensitive adhesive (PSA) products require the use of release coatings in one form or another. For example, the backing on tapes in roll form are often coated with a release material to provide a controlled unwind or peel force. Ideally, the peel force should not change appreciably with time, under the temperature and humidity conditions to which the tape roll will be exposed. The low adhesion provided by the release coating can be attributed to a number of factors,[1] including less than complete contact, a mechanically weak interfacial region, or weak attractive forces between the PSA and the release coating. Incomplete contact (poor wetting) between the PSA and the release coating can result from the low critical surface tension of the release coating, relative to that of the PSA, and/or from surface roughness of the release coating or PSA. A mechanically weak interfacial region is expected if there is a weak boundary layer on the surface of the release coating. Such a situation often exists for silicone release coatings.[2] Low adhesion of the PSA to the release coating also requires there to be little or no interdiffusion of the polymer molecules across the interface, so the polymers composing the PSA and release coating should be thermodynamically incompatible. In addition, in order to minimize the attractive forces across the interface (work of adhesion), specific chemical interactions such a H-bonding, polar interactions, or acid-base interactions need to be avoided.

It has been shown that the work needed to peel an adhesive from a substrate can be expressed as the product of two terms:[3,4]

$$\text{Work to Peel} \approx W_a F(R, T)$$

Where W_a is the thermodynamic work of adhesion, and $F(R, T)$ is a mechanical factor, which depends on the rate of peeling and the temperature, representing the energy dissipated in deforming the adhesive and adherends during peeling. Using the theory of fractional polarity combined with the geometric mean approximation, one can relate the work of adhesion to the dispersive and polar components of the surface energies of the adhesive and adherend.[5]

$$W_a = 2[(\gamma_1^d \gamma_2^d)^{1/2} + (\gamma_1^p \gamma_2^p)^{1/2}]$$

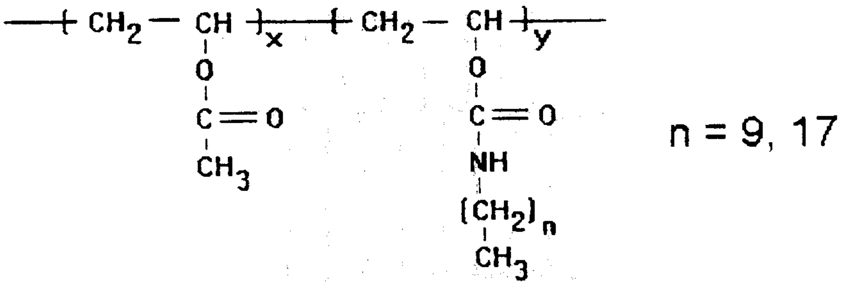
For release coatings the surface energy is typically low and entirely, or almost entirely, due to dispersive contributions. Therefore, the work of adhesion between a PSA and a release coating would be predicted to be given by

$$W_a = 2(\gamma_1^d \gamma_2^d)^{1/2}$$

Then, for a given adhesive, the work of adhesion, and thus the peel force, should decrease systematically with decreasing surface energy of the release coating. It is known, however, that various types of release coatings having similar surface energies can provide quite different levels of adhesion[2]. In addition, having low surface energy for a coating does not guarantee that the coating will provide stable low adhesion for a PSA under all aging conditions. While the surface energy of the release coating is an important contributing factor in determining the release force of a PSA, it is clear that other phenomena, which are not completely understood, can also play important roles. One of the problems in predicting the strength of adhesion from surface properties is that macromolecules have some degree of segmental mobility and can restructure upon contact with another medium[6]. Restructuring of polymer surfaces has been shown to occur for a number of multicomponent or multisegment polymeric systems, including hydrogels,[7–9] oxidized or surface-functionalized hydrocarbon[8,10,11] or fluorocarbon[12,13] polymers, graft or block copolymers,[14–24] polymer networks,[25,26] and polyurethanes.[20,27–29] Such restructuring can lead to changes in the chemical groups and, thus, changes in the strength of the chemical interactions at the interface with time,[30] leading to changes in adhesion. For this reason, it has been proposed that the static concept of polymer surface energy be replaced by the dynamic concept of "potential" surface energy to take into account the restructuring driven by the minimization of the interfacial energy between a polymer and an orienting medium.[31]

Most polymeric mateirals used for release coatings are multicomponent of multisegment, with one segment (typically alkyl, fluoroalkyl, or silicone) having low polarity and low surface energy. The low surface energy segments accumulate at the coating surface to provide the low adhesion feature. Typically, the other components present in the release material, which have higher surface energy and may have significant polar or acid-base character, are buried underneath the coating surface. In order to achieve a stable release force between the PSA and the release coating, a stable interfacial structure is required so that the higher energy or polar segments in the release coating and in the PSA are separated from each other. However, upon contact between the PSA and the release coating, restructuring can occur within the PSA and the release material near the PSA/release material interface, provided that there is sufficient segmental mobility and that there are specific favorable chemical interactions between chemical groups in the PSA and the release materials to drive the restructuring.

In this work, we examine the bulk, surface, and interfacial structure of poly(vinyl N-alkyl carbamate-co-vinyl acetate) copolymers, having either decyl or octadecyl side chains:



$$\left[CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\CH_3}}{CH}\right]_x\left[CH_2-\underset{\substack{|\\O\\|\\C=O\\|\\NH\\|\\(CH_2)_n\\|\\CH_3}}{CH}\right]_y \qquad n = 9, 17$$

These polymers are prepared from the reaction of partially hydrolyzed poly(vinyl acetate), *i.e.*, poly(vinyl acetate-co-vinyl alcohol) copolymers, with N-alkyl isocyanates, and are commonly used as release materials for PSA tapes.[1] Such release materials are generically referred to as polyvinyl N-alkyl carbamates, and in this paper the poly(vinyl N-alkyl cabamate-co-vinyl acetate) copolymers will also be referred to as such. Polyvinyl N-alkyl carbamates belong to the general class of long alkyl side chain polymers, which are known to form smectic liquid crystalline structures in which the polymer backbone is arranged in layers, separated by the side chains,[32] as shown in Figure 1. As would be expected for such a structure, the layer spacing increases with increasing side chain length. Generally, for side chain lengths less than about 10 to 12 carbon atoms, the side chains exhibit amorphous packing, while for side chain lengths greater than about 10 to 12 carbon atoms, a hexagonal packing of the side chains can develop whereby only the part of the side chains extending beyond about 10 to 12 carbon atoms participates in the hexagonal packing.[33] The side chains are then oriented perpendicular to the polymer backbone layers. As illustrated in Figure 1, both one-layer and two-layer packing have been observed depending on the specific chemical structure and thermal history of the material. Generally, increasing the distance between alkyl side chains along the polymer backbone, or decreasing the flexibility of the polymer backbone, favor one-layer packing. The surface energies of long alkyl side chain polymers are generally low, indicating a high concentration of the methyl end groups at the polymer surface.[34-36]

In the present work, the bulk structures and thermal transitions of the polyvinyl N-alkyl carbamates were characterized using X-ray scattering, differential scanning

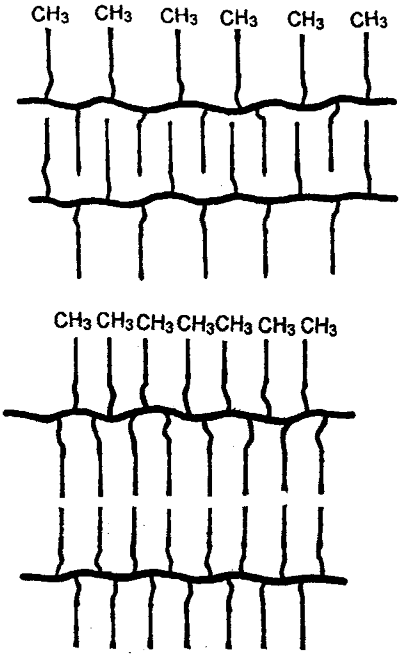


FIGURE 1 Schematic showing the structure of long alkyl side chain polymers having one layer packing (top), and two layer packing (bottom).

calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA); in addition, DMTA was used to investigate the rheology (*i.e.*, segmental mobility) of the polyvinyl N-alkyl carbamates. The surface energies of polyvinyl N-alkyl carbamate coatings were determined using contact angle methods, while X-ray photoelectron spectroscopy (XPS) and static secondary ion mass spectrometry (SIMS) were employed to characterize the near-surface compositional profiles of the coatings. The peel force provided by the polyvinyl N-alkyl carbamate coatings, as a function of aging time and temperature, was measured for a tape having an acrylic acid containing alkyl acrylate based pressure sensitive adhesive. The changes in peel force with aging time and temperature were related to the ability to maintain a stable interfacial structure between the PSA and polyvinyl N-alkyl carbamate coatings. Changes in the interfacial composition upon aging were characterized by comparing the surface compositions of the PSA and polyvinyl N-alkyl carbamate coatings initially, prior to contact, as well as after aging and peeling them apart. The increase in peel force upon aging can be attributed, in large part, to a restructuring at the PSA/polyvinyl alkyl carbamate interface. Energetically favorable acid-base interactions between the basic urethane and acetate groups in the polyvinyl alkyl carbamates and the acrylic acid groups in the PSA provide a driving force for the restructuring. If the segmental mobility within the polyvinyl alkyl carbamate is sufficient, restructuring can occur, leading to increased concentrations of these groups at the PSA/polyvinyl alkyl carbamate interface, resulting in higher attractive forces and greater adhesion. The propensity for the polyvinyl N-alkyl carbamate coatings to restructure upon contact with a polar medium was also characterized by monitoring the receding contact angle of water, as a function of water contact time and temperature. A good correlation is seen between the ability of the polyvinyl alkyl carbamate coatings to provide a low peel force for the acrylate PSA tape and the ability of the coatings to maintain a high water receding contact angle.

EXPERIMENTAL

Synthesis of Polyvinyl N-Alkyl Carbamates

Polyvinyl N-decyl carbamate and polyvinyl N-octadecyl carbamate were synthesized by reacting a partially (50 mol%) hydrolyzed poly(vinyl acetate) with decyl isocyanate and octadecyl isocyanate, respectively. The reactions were carried out at 30% solids in refluxing xylene. The completion of the reaction was determined by monitoring the disappearance of the isocyanate band at 2260 cm^{-1} in the FTIR spectrum.

Bulk Characterization of Polyvinyl N-Alkyl Carbamates

Differential Scanning Calorimetry (DSC) was performed using a Perkin-Elmer DSC-4 at a heating rate of 20°C/min. Dynamic Mechanical Thermal analysis (DMTA) was done using a Polymer Labs DMTA in shear mode at a frequency of 3 Hz, and a heating rate of 2°C/min. X-ray scattering data was obtained using a Philips vertical diffractometer, Cu Kα radiation, and proportional detector registry of the scattered radiation. Samples for DSC, DMTA, and X-ray scattering were prepared by casting films onto a silicone release liner. The films were dried first under ambient conditions and then placed in a vacuum oven at 100°C for 30 minutes. The heater of the oven was then turned off and the samples allowed to cool slowly to room temperature over a period of a few hours.

Surface Characterization of Polyvinyl N-Alkyl Carbamates

Samples for surface analysis were prepared by diluting the polyvinyl N-alkyl carbamate solution to 2 wt% with toluene, and then coating the solutions onto PET film using a #6 Mayer rod, giving a coating thickness of approximately 0.2 microns. Coatings were dried at 85°C for 10 minutes.

Contact angle measurements were made using the sessile drop method with a Ramé Hart goniometer equipped with an environmental chamber. Water and methylene iodide used for contact angle measurements were distilled, while the hexadecane was used as received. Advancing and receding contact angles were obtained by increasing or decreasing the drop volume until the three-phase boundary moved over the coating surface. The capillary pipette of the microsyringe was kept immersed in the drop during the entire measurement. The contact angles reported here are the averages of measurements made on 4 to 6 different drops.

X-ray photoelectron spectorscopy (XPS) and static secondary ion mass spectrometry (SIMS) were done using a Perkin-Elmer Physical Electronics 5100XPS/6000SSIMS instrument. For XPS, Mg $K_{\alpha 12}$ incident X-rays and a hemispherical analyzer were used. The anlge, θ, between the sample surface and the analyzer (takeoff angle) was varied between 15 and 90 degrees. The depth in the sample, normal to the surface, from which 95% of the observed signal intensity is derived, is given roughly as $3\lambda \sin\theta$ where λ is the inelastic mean free path of the photoelectrons.[37] For organic materials, and the experimental conditions used here, λ will be roughly 30 Å.[38] Therefore, sampling depths for takeoff angles of 15, 30, 55, and 90 degrees and about 25, 45, 75, and 90 Å. Atomic concentrations were determined by normalizing the areas under the high resolution spectra of each element by the atomic sensitivity factors determined for the instrument (using a series of homopolymers of known composition).

For static SIMS, a differentially pumped ion gun, a low energy electron flood gun (model 04-085), and a quadrupole mass spectrometer (m/z 0-800) were used. The analyzer was positioned to collect ions normal to the sample surface, while the ion beam was oriented at a glancing angle to the surface. The incident ions were a defocussed beam of 3.5 keV Xe^+ ions, with a beam current density of 1.5 nA/cm^2. All data was collected on samples exposed to $<10^{13}$ ions/cm^2 total ion dose in order to remain within the static regime. The neutralizer, operated at 170 V extraction potential, was oriented at a glancing angle to the ssmple surface, and its alignment was optimized for each sample before data aquisition by maximizing the total quadrupole signal above m/z 50. Both positive and negative ion spectra were obtained. The sampling depth with static SIMS has been reported to be on the order of 10 Å.[37]

Adhesion of Acrylate PSA Tape

The same coatings used for surface analysis were also used for adhesion measurements. A polypropylene-backed tape having a 1 mil (0.025 mm) thick coating of an alkyl acrylate based PSA, containing 4.5 wt% acrylic acid comonomer, was used as a test tape. One inch (2.54 cm) wide strips of tape were rolled down onto the polyviny N-alkyl carbamate coatings using 6 passes from a 2 Kg roller. Aging was done for various lengths of time (30 seconds to 4 weeks) and at various temperatures (between 21°C and 65°C) prior to peel testing, which was all done at 21°C and 50% relative humidity. For heat aging experiments, the PSA/polyvinyl alkyl carbamate composite samples were placed between preheated glass plates in the oven. After heat aging, the samples were removed from the oven and allowed to cool for 15 minutes prior to peel testing. The 180° peel force was measured at a peeling rate of 90 inches/min (2.29 m/min) using an Instrumentors Inc. slip peel tester. The reported peel force is the average over a 5 second time interval.

RESULTS AND DISCUSSION

Bulk Characterization of Polyvinyl N-Alkyl Carbamates

The DSC traces for polyvinyl N-decyl carbamate and polyvinyl N-octadecyl carbamate are shown in Figure 2. The polyvinyl N-octadecyl carbamate exhibits two broad overlapping endothermic transitions, with the minor transition centered at 48°C and the major transition centered at 65°C. These transitions can be attributed to the loss (melting) of the hexagonal packing of the octadecyl side chains. It is speculated that the two transitions correspond to the two layer and one layer packing modes illustrated in Figure 1. In contrast, the polyvinyl N-decyl carbamate shows only a glass transition centered at about 48°C. These results are consistent with previous studies[32,33] which showed that alkyl side chain lengths of at least 10 to 12 carbon atoms are typically required to obtain hexagonal packing of the side chains. The heat of the transition for the polyvinyl N-octadecyl carbamate studied here was 14 cal/gm. Following the treatment outlined by Jordan *et al.*,[33] this heat of melting would indicate that, on average, the first 12 methylene groups next to the polyvinyl N-octadecyl carbamate backbone are not involved in the hexagonal packing.

Figure 3 shows the X-ray scattering patterns for the polyvinyl N-alkyl carbamates. In the case of octadecyl side chains, a relatively sharp reflection is observed at 4.18 Å, which can be attributed to the 100 reflection of hexagonally-packed alkyl side chains.[32] At least three additional reflections are also observed at smaller angles, corresponding to spacings of 34.0, 17.0, and 10.3 Å. The relative spacings of these reflections are close to *d*, *d*/2, and *d*/3, indicating the presence of a single layered (interdigitating) type of structure, having a layer spacing of 34 Å. The structure of the polyvinyl N-octadecyl carbamate can be classified as a Smectic B type liquid crystal structure. For the case of decyl side chains, the diffraction maximum due to the side-to-side packing of the side chains is somewhat broader and centered at a larger spacing of 4.4 Å. This larger spacing is typical of amorphous melts of linear

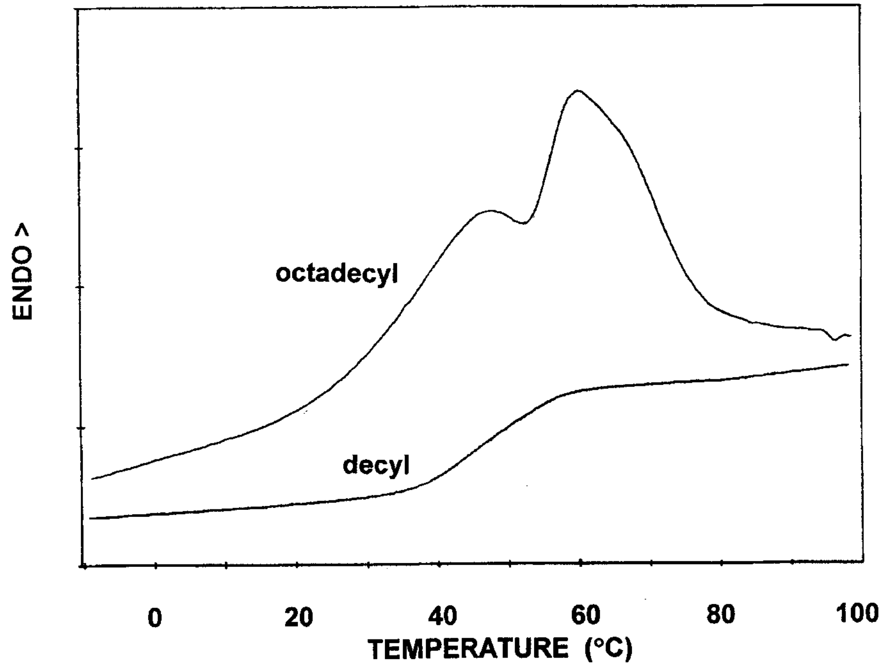


FIGURE 2 DSC traces for polyvinyl N-alkyl carbamates.

polyethylene or n-paraffins,[32] indicating a lack of hexagonal packing of the decyl side chains. This observation is consistent with the DSC results presented earlier, which showed the lack of side chain crystallinity in the case of decyl side chains. A relatively sharp reflection is observed at smaller angles, corresponding to a spacing of 27 Å, which would indicate that a layered structure is also present in the case of decyl side chains. Note the lack of higher order reflections for this spacing, which would indicate less long range order in the layered structure in the case of decyl side chains.

The storage shear modulus (G') *vs* temperature plots for the polyvinyl N-alkyl carbamates, obtained by DMTA, are shown in Figure 4. The polyvinyl N-decyl carbamate starts to soften at temperatures above about 20°C, and has a lower modulus than the polyvinyl N-octadecyl carbamate at temperatures between 20 and 70°C, presumably due to its lack of side chain crystallinity and, thus, increased segmental mobility. The drop in modulus with increasing temperature for the polyvinyl N-decyl carbamate occurs over a temperature range which is consistent with the glass transition observed by DSC. The polyvinyl N-octadecyl carbamate starts to soften at temperatures above about 40°C, and the modulus drops rapidly between 50 and 80°C, similar to the alkyl side chain melting range as determined by DSC.

Surface Characterization of Polyvinyl N-Alkyl Carbamates

The advancing contact angles of water, methylene iodide, and hexadecane on the polyvinyl N-alkyl carbamate coatings are listed in Table I. The dispersive and polar

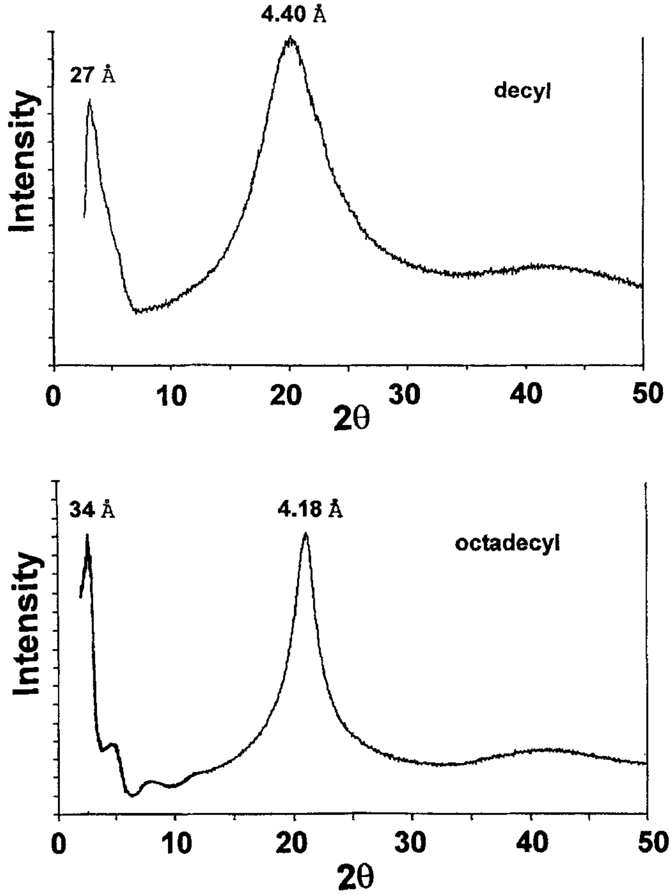


FIGURE 3 X-ray scattering patterns for polyvinyl N-decyl carbamate (top) and polyvinyl N-octadecyl carbamate (bottom).

contributions to the surface energy of the coatings were calculated for water/methylene iodide and water/hexadecane liquid pairs from the dispersive and polar surface tension components of the liquids, using the geometric mean equation.[5] The results are given in Table II. Similar results were obtained in the case of octadecyl and decyl side chains, with the calculated surface energies being almost entirely dispersive, between 21 and 22 mJ/m^2. These results are consistent with a high concentration of methyl groups at the coating surface.

The C 1s spectra obtained by XPS for the polyvinyl N-alkyl carbamate coatings, at takeoff angles of 15, 30 and 90°, are shown in Figure 5. The main peak in the C 1s spectra, centered at a binding energy of about 285 eV, can be assigned to C—C type bonding. In addition, a shoulder appears on this main peak at a slightly higher binding energy (1 to 2 eV higher) due to the carbons singly bonded to either oxygen or nitrogen. There is also a peak centered at about 289 eV due to the carbonyl carbons in the vinyl acetate and urethane groups. In general, higher surface

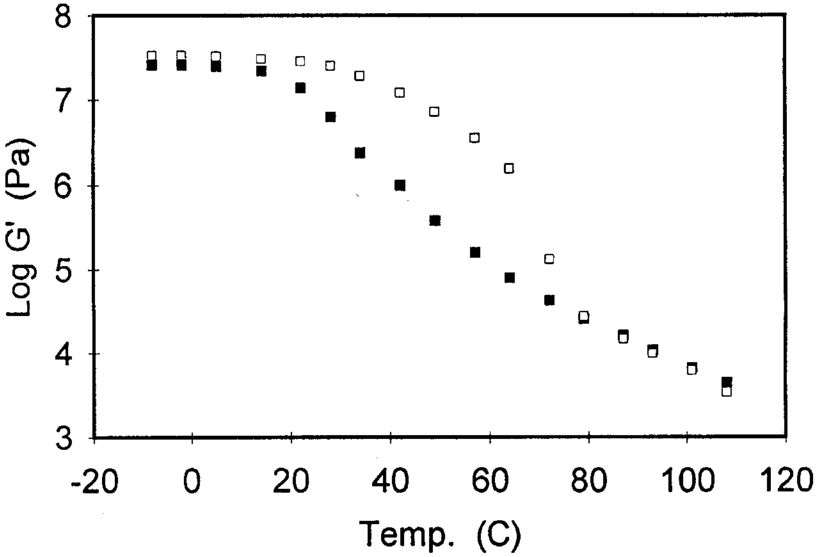


FIGURE 4 DMTA data showing Log of the shear storage modulus, *G′ versus* temperature, at 3 Hz, for polyvinyl N-alkyl carbamates. Open squares are for octadecyl side chains and filled squares are for decyl side chains.

TABLE I
Advancing Contact Angles for Polyvinyl N-Alkyl Carbamate Coatings

Coating	θH_2O	θCH_2I_2	$\theta C_{16}H_{34}$
polyvinyl N-decyl carbamate	109°	72°	40°
polyvinyl N-octadecyl carbamate	110°	72°	44°

all contact angles ±2°.

TABLE II
Surface Energy Components for Polyvinyl N-Alkyl Carbamate Coatings

Coating	Liquid Pair	γ^d (mJ/m^2)	γ^p (mJ/m^2)
polyvinyl N-decyl carbamate	CH_2I_2/H_2O	21.8	0.1
	$C_{16}H_{34}/H_2O$	21.5	0.2
polyvinyl N-octadecyl carbamate	CH_2I_2/H_2O	21.8	0.1
	$C_{16}H_{34}/H_2O$	20.5	0.2

concentrations of C—O, C—N, and O—C=O are observed in the case of decyl side chains, due in part to the higher bulk concentrations of these groups in the polyvinyl N-decyl carbamate. For both polyvinyl N-alkyl carbamates, the concentrations of C—O, C—N, and O—C=O groups decrease as the sampling depth (*i.e.*, takeoff

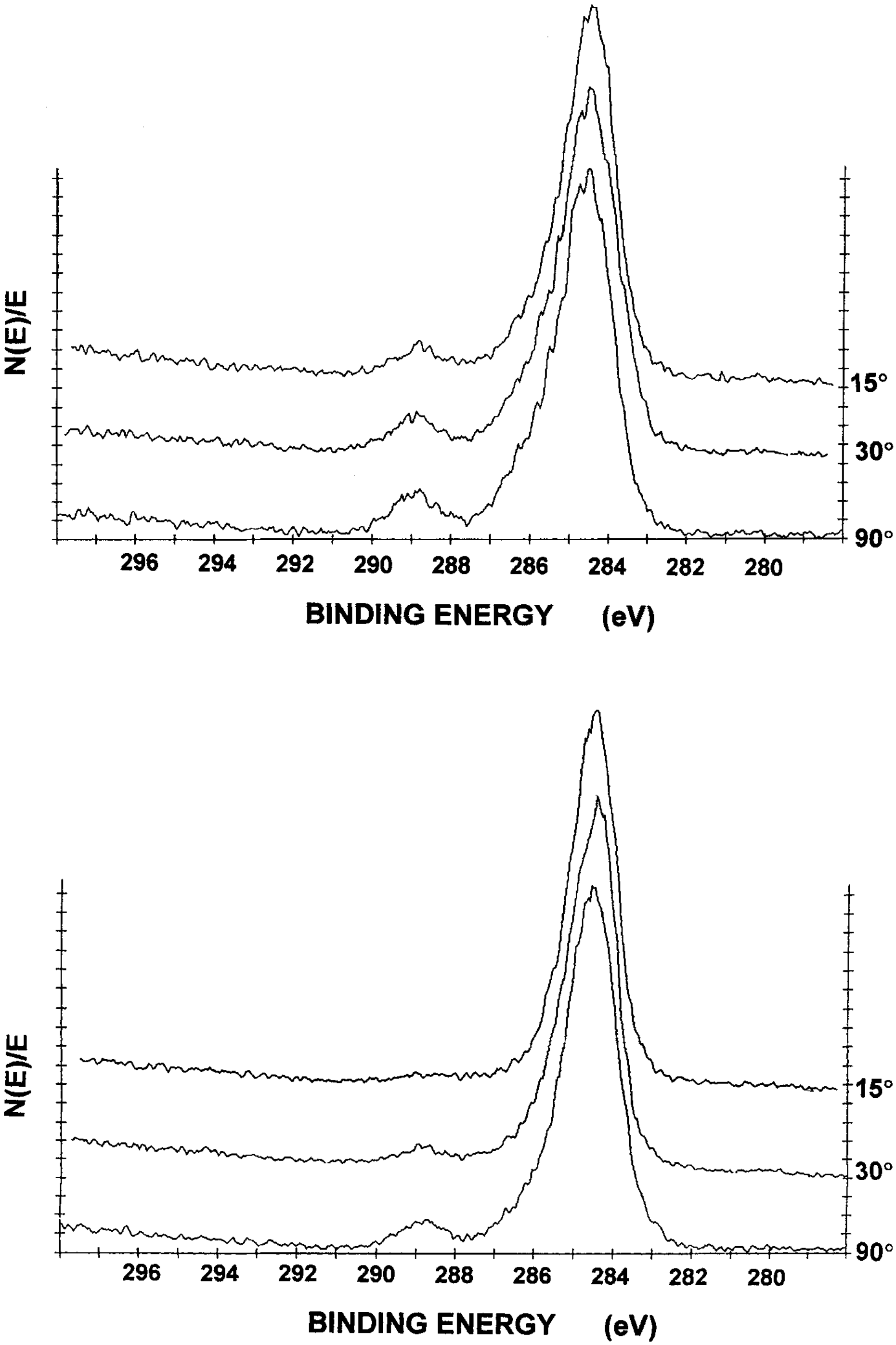


FIGURE 5 XPS C 1s spectra for polyvinyl N-decyl carbamate (top) and polyvinyl *n*-octadecyl carbamate (bottom) coatings, at takeoff angles of 15, 30, and 90 degrees.

angle) is decreased. This is especially true in the case of octadecyl side chains, for which the Cls spectrum is comprised almost entirely of C—C type bonding at a 15° takeoff angle.

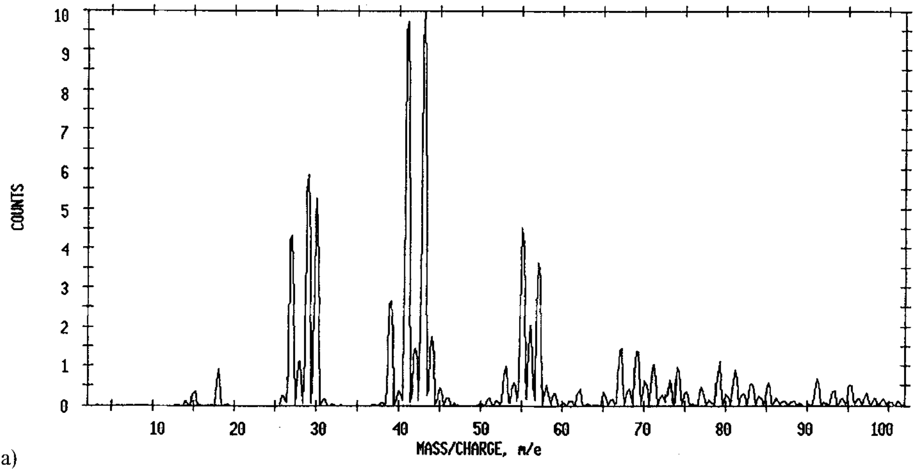
The atomic concentrations determined from angle-resolved XPS for the polyvinyl N-alkyl carbamate coatings are given in Table III. For both coatings, the concentration of oxygen and nitrogen decrease and the concentration of carbon increases as the takeoff angle (*i.e.*, sampling depth) decreases. Note however, that the decreases in nitrogen and oxygen concentration with decreasing sampling depth are more pronounced in the case of octadecyl side chains. These results are entirely consistent with the changes observed in the Cls spectra as a function of takeoff angle. Recall that the contact angle analysis indicated that the top monolayer of both polyvinyl carbamate coatings was dominated by hydrocarbon (*i.e.*, methyl) groups from the alkyl side chains. The XPS results would indicate that the hydrocarbon overlayer at the coating surface is significantly thicker in the case of octadecyl side chains, as expected, since the fully extended lengths (maximum hydrocarbon overlayer thickness) of the decyl and octadecyl side chains are 11.4 and 21.6 Å, respectively. In addition, the higher degree of side-to-side packing order for the octadecyl side

TABLE III
Atomic Concentrations vs Takeoff Angle for polyvinyl N-Alkyl Carbamate Coatings and Alkyl Acrylate PSA, as Determined by Angle-Resolved XPS

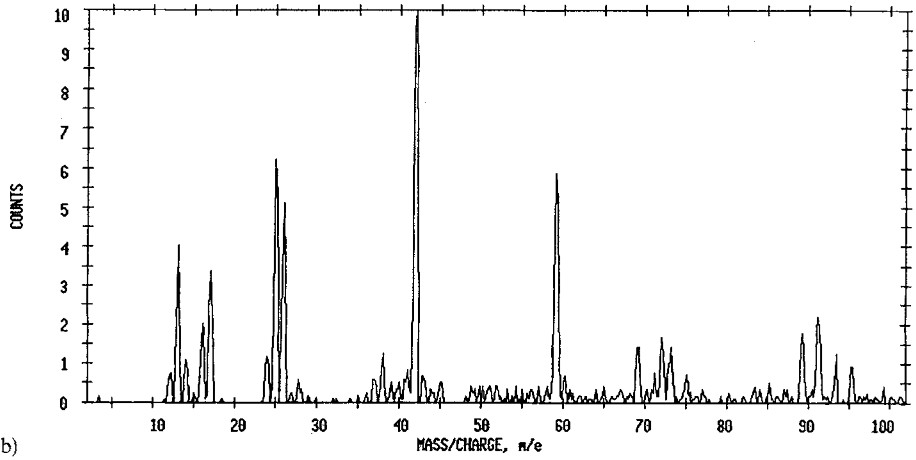
Coating	Takeoff	%C	%O	%N
Polyvinyl N-decyl carbamate	15	87	9.2	4.2
(prior to contact with PSA)	30	83	12.2	5.1
	55	81	14.4	5.2
	90	80	15.2	5.3
Polyvinyl N-octadecyl carbamate	15	94	4.5	1.4
(prior to contact with PSA)	30	91	7.1	2.3
	55	87	9.8	2.9
	90	86	11.0	3.1
alkyl acrylate PSA	15	86	14.5	–
(prior to contact with	30	85	15.3	–
polyvinyl alkyl carbamate)	55	84	16.2	–
	90	83	16.6	–
polyvinyl N-octadecyl carbamate	15	91	7.5	1.7
aged 45 seconds at 60°C	30	90	8.1	2.4
against acrylate PSA	55	85	11.7	3.0
	90	85	12.2	3.1
acrylate PSA aged	15	86	14.0	–
45 seconds at 60°C against	30	85	15.0	–
polyvinyl octadecyl carbamate	55	84	16.1	–
	90	84	16.2	–
polyvinyl N-octadecyl carbamate	15	93	5.2	1.5
aged one month at 21°C	30	91	7.3	2.2
against acrylate PSA	55	87	10.0	3.0
	90	86	11.2	3.1
acrylate PSA aged	15	86	14.4	–
one month at 21°C against	30	84	15.6	–
polyvinyl octadecyl carbamate	55	83	16.5	–
	90	83	16.6	–

chains, observed by X-ray scattering and DSC, could lead to more extended conformations of the side chains normal to the film surface, contributing to the thicker hydrocarbon overlayer in the case of octadecyl side chains.

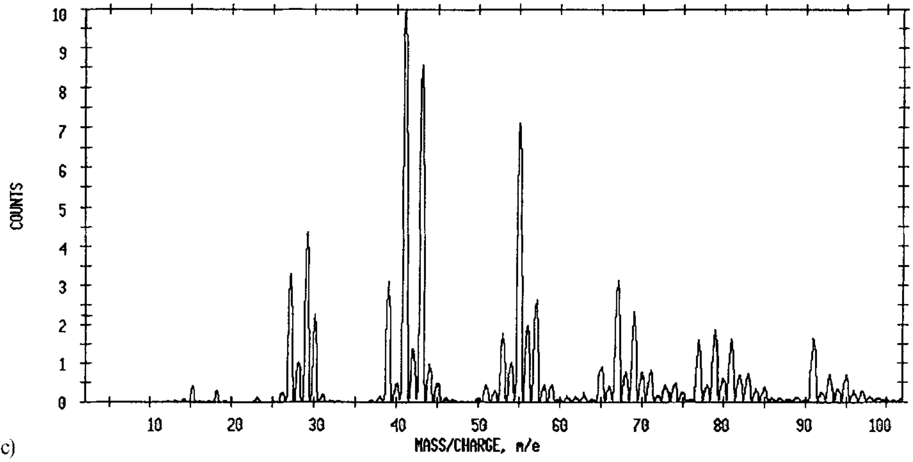
The positive and negative ion static SIMS spectra for the polyvinyl N-alkyl carbamate coatings (m/z 2 to 102) are shown in Figures 6a through 6d. The positive spectra show the characteristic envelope of mass fragments obtained with hydrocarbon polymers,[39] along with an additional fragment at 30 amu which can be attributed to either $N{\equiv}O^+$ or $CH_2{=}NH_2^+$ fragments from the urethane groups. The dominant characteristic mass fragments in the negative static SIMS spectra appear at 42 and 59 amu, and can be assigned to $^-N{=}C{=}O$ fragments from the urethane groups and CH_3COO^- fragments from the vinyl acetate groups, respectively. The



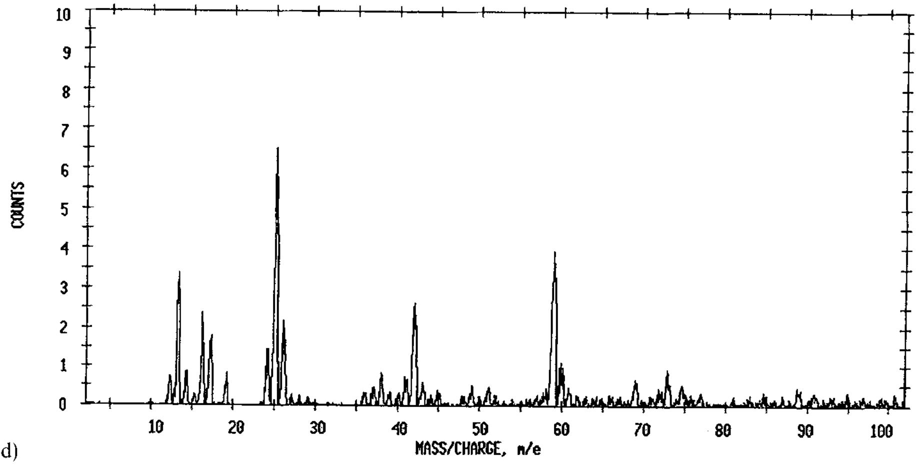
(6a)



(6b)

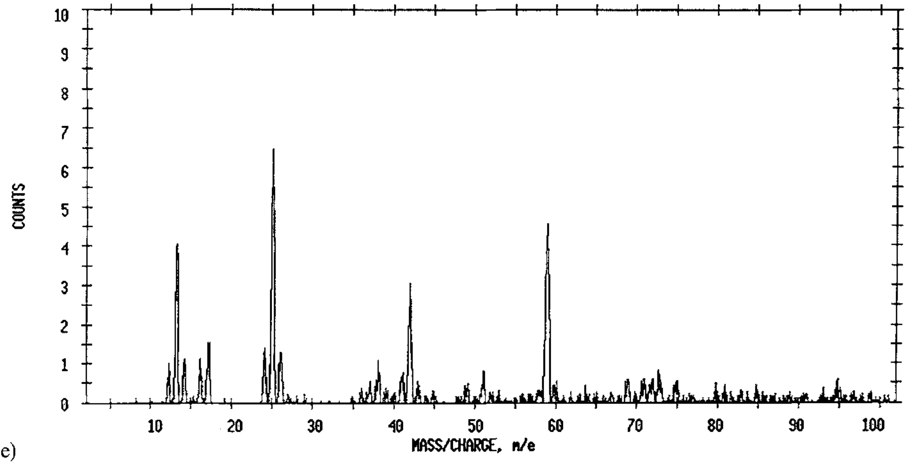


(6c)

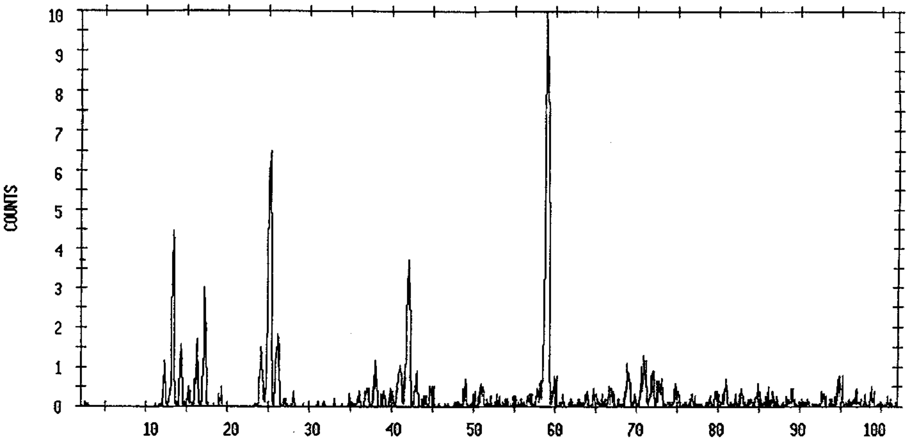


(6d)

relative intensities of the positive 30 amu fragment and the negative 42 and 59 amu fragments are given in Table IV for both polyvinyl N-alkyl carbamates. The intensity of the positive 30 amu fragment has been normalized by the intensity of the positive 41 amu fragment, and the intensities of the negative 42 and 59 amu fragments have been normalized by the intensity of the negative 25 amu fragment. Note that the relative intensities of the positive 30 amu fragment and the negative 42 and 59 amu fragments are significantly greater in the case of decyl side chains, indicating that the near-surface region (top 10 to 20 Å) of the polyvinyl N-decyl carbamate coating contains a higher concentration of the urethane and vinyl acetate groups than the polyvinyl N-octadecyl carbamate coating. These results are consistent with



(6e)



(6f)

FIGURE 6 Static SIMS spectra for polyvinyl N-alkyl carbamate coatings: a) positive ion spectrum of polyvinyl N-decyl carbamate coating, b) negative ion spectrum of polyvinyl N-decyl carbamate coating, c) positive ion spectrum of polyvinyl N-octadecyl carbamate coating, d) negative ion spectrum of polyvinyl N-octadecyl carbamate coating, e) negative ion spectrum of polyvinyl N-octadecyl carbamate coating after aging for one month at 21°C against alkyl acrylate PSA, f) negative ion spectrum of polyvinyl N-octadecyl carbamate coating after aging for 45 seconds at 60 °C against alkyl acrylate PSA.

the XPS measurements which also showed higher vinyl acetate and urethane concentrations in the near-surface region of the polyvinyl N-decyl carbamate coating.

Surface Analysis of Acrylic Acid Containing Alkyl Acrylate PSA

The atomic concentrations determined by XPS for the alkyl acrylate PSA used in these studies, as a function of takeoff angle, are shown in Table III. There is a slight

TABLE IV
Relative intensities of Static SIMS Fragments for the Polyvinyl N-Alkyl Carbamate coatings

Coating	Int_{30}/Int_{41} (+)	Int_{42}/Int_{25} (−)	Int_{59}/Int_{25} (−)
polyvinyl N-decyl carbamate	0.54	1.59	0.95
polyvinyl N-octadecyl carbamate	0.22	0.40	0.61
polyvinyl N-octadecyl carbamate aged against acrylate PSA one month at 21°C	–	0.45	0.70
polyvinyl N-octadecyl carbamate aged against acrylate PSA 45 seconds at 60°C	–	0.57	1.54

decrease in the amount of oxygen as the takeoff angle (sampling depth) is decreased, which would be consistent with a very thin overlayer of the alkyl group, from the alkyl acrylate monomer, at the adhesive surface. The negative static SIMS spectrum m/z 2 to 102) for the alkyl acrylate PSA is shown in Figure 7a. The characteristic negative ion fragments typically observed for alkyl acrylate homopolymers[40] at 41, 71 and 81 amu are clearly seen.

Adhesion of Acrylate PSA Tape

The peel adhesion of the alkyl acrylate PSA tape from the polyvinyl N-alkyl carbamate coatings, as a function of dwell time and aging temperature, is shown in Figure 8. Note that the adhesion for short dwell times (initial adhesion) is similar, and relatively low, for both polyvinyl N-alkyl carbamate coatings. This observation is consistent with the contact angle measurements, which indicated that the top molecular layer for both coatings were similar in composition, being predominantly the low energy methyl end groups. Therefore, the chemical interactions across the PSA/polyvinyl alkyl carbamate interface will also be similar for octadecyl or decyl side chains, at least intially. However, it can be seen that, in the case of decyl side chains, the adhesion of the acrylate PSA increases markedly with aging time, even when aged at 21°C. In contrast, the adhesion of the acrylate PSA to the polyvinyl N-octadecyl carbamate coating is almost constant with increasing aging time when aged at 21°C. Only when aged at temperatures above about 50°C, does the adhesion of the acrylate PSA to the polyvinyl N-octadecyl carbamate increase quickly with time.

It is proposed that the build in adhesion can be attributed, in large part, to a restructuring of the PSA/polyvinyl alkyl carbamate interface. Specifically, if the segmental mobility within the polyvinyl N-alkyl carbamate coating is sufficient, and energetically favorable specific chemical interactions can occur between the PSA and the polyvinyl carbamate, segmental rearrangements near the interface would be expected. This restructuring would lead to stronger attractive forces at the interface and higher adhesion. In the case of an acrylate PSA containing an acidic comonomer, increases in the degree of acid-base interaction between the acidic comonomer and the basic urethane and vinyl acetate groups in the polyvinyl alkyl

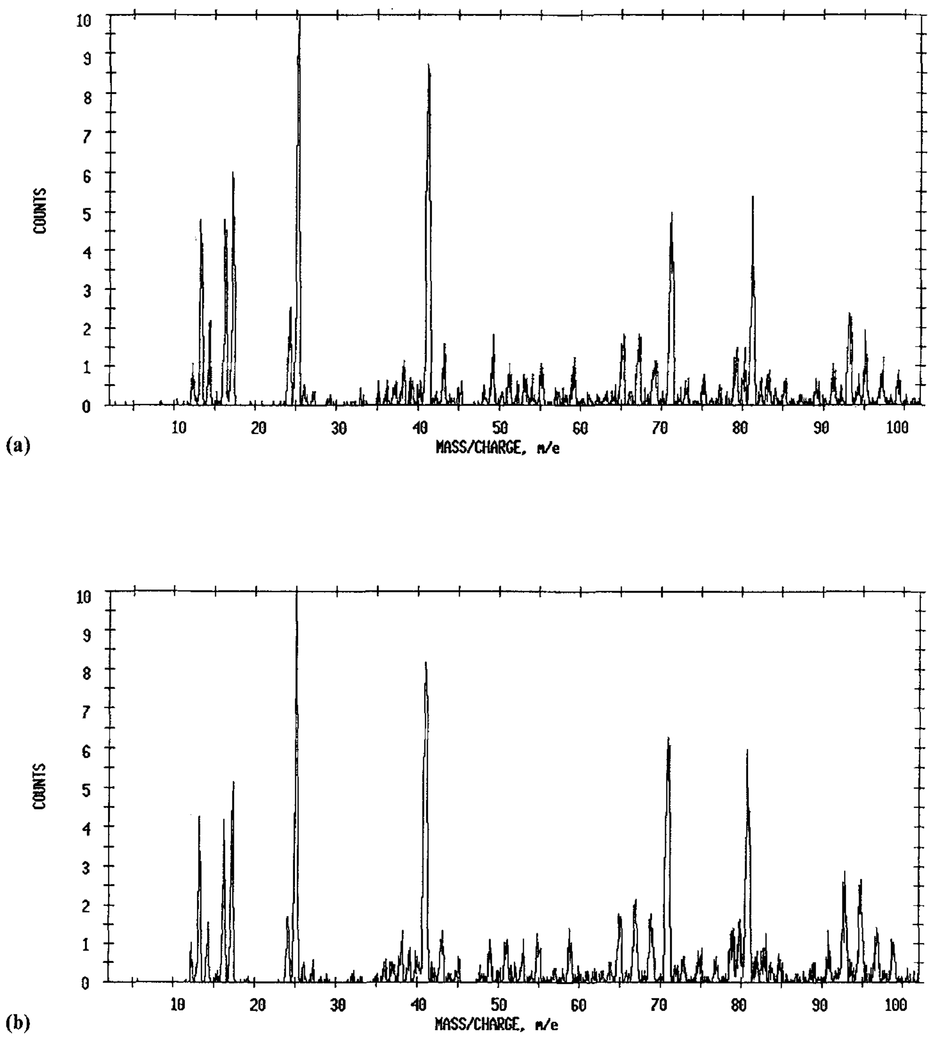
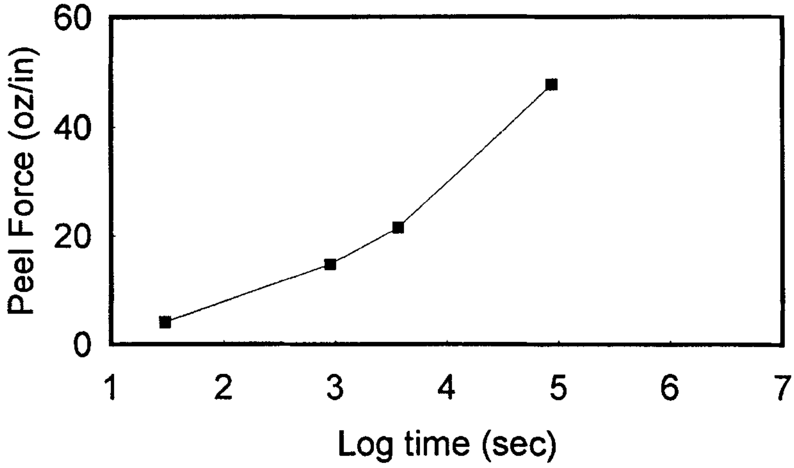


FIGURE 7 Static SIMS spectra for alkyl acrylate PSA: a) negative ion spectrum of PSA prior to contact, and b) negative ion spectrum of PSA after aging for 45 seconds at 60°C against polyvinyl N-octadecyl carbamate coating.

carbamate would be expected to increase the adhesion between the PSA and the polyvinyl alkyl carbamate.

The difference in aging behavior for the two different polyvinyl alkyl carbamates studied here can be attributed to differences in the degree of interfacial restructuring as a function of time and temperature. Recall that the DMTA measurements indicated that the modulus of the polyvinyl decyl carbamate started to decrease at temperatures above about 20°C, and that the polyvinyl decyl carbamate had lower modulus and, thus, higher segmental mobility, than the polyvinyl octadecyl carbamate at temperatures between about 20 and 70°C. While the mobility near the surface of the



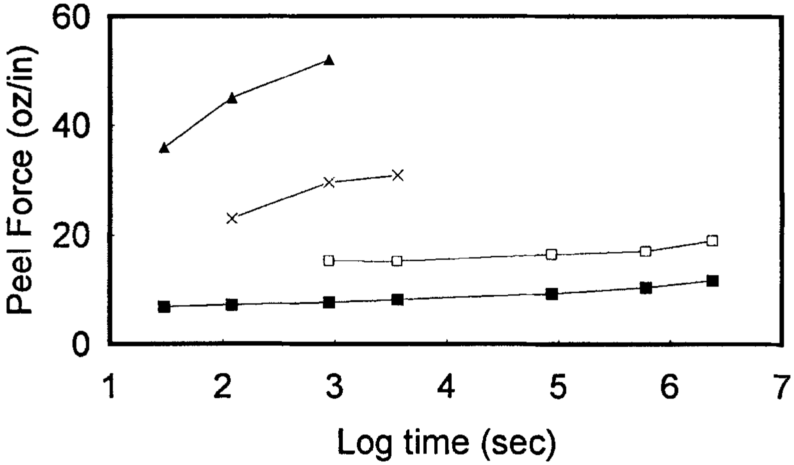


FIGURE 8 Peel force, of alkyl acrylate PSA tape peeled from polyvinyl N-decyl carbamate (top) and polyvinyl N-octadecyl carbamate (bottom) coatings, versus log of the aging time, for aging temperatures of 21°C (filled squares), 47°C (open squares), 54°C (X), and 60°C (triangles).

coatings may not be exactly the same as the mobility within the bulk, it is nevertheless expected that the ability to restructure would be greater over this temperature range in the case of decyl side chains. In addition, the XPS and static SIMS measurements showed higher concentrations of the urethane and vinyl acetate groups in the near-surface region of the polyvinyl decyl carbamate. The combination of these factors leads to a larger degree of acid-base interactions in the case of decyl side chains, and the poorer ability of the polyvinyl decyl carbamate coating to maintain the initially low adhesion observed with the acrylate PSA. For the polyvinyl octadecyl carbamate. DMTA indicated a rapid increase in the segmental mobility with increasing temperature in the temperature range of 50 to 80°C (similar to the temperature range over which the hexagonal packing of the octadecyl side chains is lost). The increase in peel adhesion of the alkyl acrylate PSA tape, upon aging at temperatures above about 50°C, is consistent with the idea of the restructuring requiring sufficient segmental mobility in order to occur. Evidence for interfacial restructuring within the polyvinyl octadecyl carbamate, upon aging against the acid containing acrylate PSA, will be presented in the next section.

Analysis of Interfacial Restructuring of Polyvinyl Alkyl Carbamates

The results of the previous section demonstrated the importance of the aging conditions, and the possible interfacial interactions between the polyvinyl alkyl carbamates and the PSA, in determining the adhesion level. It was proposed that if the segmental mobility in the polyvinyl alkyl carbamate was sufficient, restructuring near the PSA interface could occur, resulting in significantly higher levels of adhesion, attributed to acid-base interactions across the interface. In order to assess the validity of this hypothesis, two complimentary sets of experiments were conducted.

The first approach was to analyze the surfaces of the acrylate PSA and the polyvinyl octadecyl carbamate coating by XPS and static SIMS, both before and after they were put into contact and peeled apart. It was hoped that any restructuring occuring within the polyvinyl octadecyl carbamate, upon heat aging against the PSA, could be at least partially frozen in once the PSA/polyvinyl octadecyl carbamate composite sample was cooled to room temperature and the PSA peeled off. As the data in Figure 8 show, only short aging times are required to obtain significant increases in peel adhesion when aged at 60°C. The heat-aged sample chosen for surface analysis had been aged at 60°C for 45 seconds and gave a peel adhesion of 39 oz/in (435 g/cm). In addition, another sample wherein the PSA was aged against the polyvinyl octadecyl carbamate coating for one month at room temperature, and gave a peel adhesion of 11.7 oz/in (131 g/cm) was also analyzed.

Table III shows the atomic concentrations, determined by XPS, of the polyvinyl octadecyl carbamate coating and acrylate PSA before and after aging them in contact and peeling them apart. After heat aging at 60°C, there is a slight increase in the concentration of nitrogen detected at the 15 degree takeoff angle for the polyvinyl octadecyl carbamate coating, although the increase is close to the error in the measurement. However, measurable increases in oxygen content and decreases in carbon content are observed upon aging against the PSA, particularly at a 15° takeoff angle. Though not shown, the 15° takeoff angle C 1s spectra of the polyvinyl octadecyl carbamate coatings, after heat aging against the acrylate PSA, looks similar to the 30° takeoff angle C 1s spectra of the coating prior to PSA contact. The atomic concentrations of the acrylate PSA are essentially unchanged upon heat aging aginst the polyvinyl octadecyl carbamate coating. Any restructuring of the PSA surface would be difficult to capture since, once the PSA is exposed as a free surface, another restructuring step can occur in which the original lower energy surface composition would be recovered, due to the high segmental mobility of the PSA. The XPS results are consistent with a restructuring within the polyvinyl

Octadecyl carbamate coating, near the interface with the PSA, upon heat aging, whereby the concentrations of the vinyl acetate and/or urethane groups at the interface are increased. Further confirmation of this mechanism in adhesion build will come from the more surface-sensitive static SIMS and contact angle measurements. As the data in Table III demonstrate, the atomic compositions of the polyvinyl octadecyl carbamate and acrylate PSA surfaces, after one month aging at 21°C, are quite similar to their atomic compositions prior to contact. Only a very slight increase in the oxygen content, at a 15 degree takeoff angle, is seen for the polyvinyl octadecyl carbamate coating upon aging. These results are consistent with a low degree of interfacial restructuring upon aging at 21°C, leading to only a very slight increase in the peel adhesion.

The negative static SIMS spectra of the acrylate PSA, before and after aging for 45 seconds at 60°C against the polyvinyl octadecyl carbamate coating, are shown in Figure 7a and b. The static SIMS spectrum for the acrylate PSA, obtained after aging against the polyvinyl octadecyl carbamate coating, is indistinguishable from the SIMS spectrum of the PSA obtained prior to contact with the polyvinyl octadecyl cabamate. Note that no increase in the relative intensities of the characteristic mass fragments associated with the polyvinyl alkyl carbamate (42 and 59 amu) is detected upon again, indicating that there is no transfer of polyvinyl octadecyl carbamate to the acrylate PSA.

The negative static SIMS spectra of the polyvinyl octadecyl carbamate coatings, obtained before and after heat aging against the PSA, are shown in Fiures 6d and 6f, respectively. An important finding is that little increase in the relative intensities of the mass fragments associated with the acrylate PSA (*e.g.*, 41, 71, and 81 amu) are observed upon aging the polyvinyl octadecyl carbamate against the PSA, indicating that the PSA did not transfer to the polyvinyl octadecyl carbamate coating upon peeling. Combining this finding with the results of the SIMS analysis of the PSA show that the failure mode upon peeling is interfacial, at least up to peel forces of 40 oz/in (446 g/cm). The static SIMS data also show that, after heat aging against the acrylate PSA, a modest increase in the relative intensity of the mass fragment associated with the urethane group (42 amu), and a larger increase in the relative intensity of the mass fragment associated with the acetate group (59 amu), are observed for the polyvinyl octadecyl carbamate coating, indicating increased concentrations of both the urethane and vinyl acetate groups near the polyvinyl octadecyl carbamate surface. The relative intensities of the 42 and 59 amu fragments in the negative ion static SIMS spectra of the polyvinyl octadecyl carbamate, before and after heat aging against the acrylate PSA, are listed in Table IV. This result confirms that a restructuring occurred within the polyvinyl octadecyl carbamate coating near the interface with the acid-containing acrylate PSA, whereby more urethane and vinyl acetate groups come into intimate contact with the PSA. Both the urethane and vinyl acetate groups in the polyvinyl octadecyl carbamate can form acid-base interactions with the acrylic acid groups in the PSA, leading to higher attractive forces across the interface, and thus higher adhesion levels. The data presented in Table IV would indicate that the relative increase in the vinyl acetate groups at the PSA/polyvinyl octadecyl carbamate interface, upon heat aging, is more significant than the increase in urethane groups. This finding is consistent with the XPS results presented earlier, which showed a relatively large increase in the oxygen content of the polyvinyl octadecyl carbamate coating after heat aging against the acrylate PSA, and only a slight increase in the nitrogen content.

Figure 6e shows the negative ion static SIMS spectrum for the polyvinyl octadecyl carbamate coating that had been aged against the acrylate PSA for one month at 21°C. Under these aging conditions, only slight increases in the relative intensities of the 42 and 59 amu mass fragments are seen (see Table IV) upon aging. These results are consistent with the small changes in the surface composition of the coating seen by XPS, and the small increase in peel adhesion when aged under these conditions.

The receding contact angles of water on the polyvinyl octadecyl carbamate coatings were also measured both before and after aging of the acid-containing acrylate PSA against the coatings. For these measurements, aging was done at temperatures between 21°C and 65°C for various periods of time in order to obtain a wide range of peel forces. The receding contact angle was measured by advancing the liquid front and then receding the liquid front as soon as possible (*i.e.*, for as short a water dwell time as possible, being roughly 5 seconds). The water receding contact angles ranged from 98°, prior to PSA contact, to as low as 58°. Figure 9 shows a plot of the measured peel adhesion *versus* the cosine of the water receding contact angle on the polyvinyl octadecyl carbamate coating subsequent to peeling of the PSA tape. The peel adhesion increases as the cosine of the water receding contact angle increases (receding water contact angle decreases). Based on the XPS and static SIMS results presented earlier, the decrease in water receding contact angle can be attributed to an increase in the surface energy of the polyvinyl octadecyl carbamate coatings due to higher concentrations of urethane and vinyl acetate groups at the coating surface. Thus, the contact angle measurements also provide evidence of the restructuring within the polyvinyl octadecyl carbamate coating near the interface with the acid-containing acrylate PSA. It should be mentioned that the changes in surface

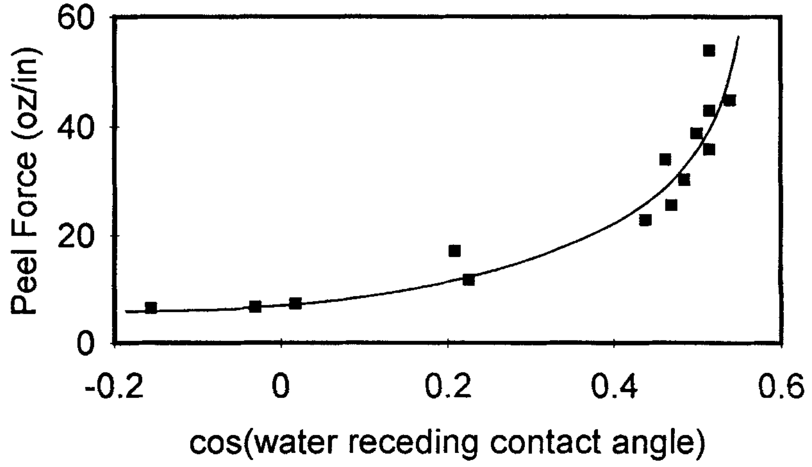


FIGURE 9 Peel force of alkyl acrylate PSA tape *versus* the cosine of the receding water contact angle, measured for the polyvinyl N-octadecyl carbamate coating after aging in contact with the acrylate PSA.

composition of the polyvinyl octadecyl carbamate coating are reversible if the coating is exposed as a free surface and sufficient segmental mobility is provided by heating the coating. For example, a coating which had been aged against the PSA at 60°C and provided a peel adhesion of 31 oz/in (346 g/cm) gave a water receding the contact angle of 62° immediately after the tape was peeled. After open face aging of this same coating at 100°C for only 10 minutes, and cooling to room temperature, the water receding contact angle had recovered to 91°, nearly the 98° contact angle exhibited by the coating prior to PSA contact.

The three-liquid contact angle analysis proposed by Good,[41] whereby the polar contribution to the surface energy can be divided into its basic and acidic contributions, has been employed to characterize the acid-base nature of the polyvinyl octadecyl carbamate coatings before and after aging against the acid containing PSA. For example, Table V gives the receding contact angles, θ_{rec}, of water, methylene iodide, and formamide obtained for the polyvinyl octadecyl coating both before PSA contact and after aging against the PSA at 60°C to obtain a peel adhesion of 31 oz/in (346 g/cm). The Lewis acid, γ^+, and Lewis base, γ^-, parameter of surface free energy, in addition to the dispersive contribution, γ^d, to the surface free energy, were calculated from the measured contact angles and the tabulated Lewis acid and Lewis base parameters of the three liquids.[41] The results are presented in Table V. Prior to PSA contact, the surface energy of the polyvinyl octadecyl carbamate coating is almost entirely dispersive, with both the acid and base parameters of the surface energy being relatively small. After heat aging against the PSA, both the dispersive component and the basic component of the surface energy are seen to increase. These results suggest that, during the heat aging, the methyl end groups of the octadecyl side chains migrate away from the PSA interface, and the basic urethane and vinyl acetate groups migrate towards the PSA, consistent with the XPS and static SIMS analysis presented earlier.

Another approach which can be used to study the susceptibility for restructuring of the polyvinyl aklyl carbamate coatings is to measure the receding contact angles of liquids having different polarity or acid-base character, as a function of liquid dwell time and temperature. Decreases in receding contact angle with increasing dwell time and/or increasing temperature can be taken as evidence for restructuring within the polyvinyl alkyl carbamate coatings. For example, Figures 10 and 11 show how the cosine of the water receding contact angle changes with the length of the

TABLE V

Three-liquid contact angle analysis of polyvinyl octadecyl carbamate surface energy components, prior to acrylate PSA contact, and after aging against acrylate PSA

Surface	θ_{rec} Water	θ_{rec} methylene iodide	θ_{rec} formamide	γ^d mJ/m^2	γ^+ mJ/m^2	γ^- mJ/m^2
polyvinyl octadecyl carbamate, prior to PSA contact	98°	65°	78°	25.7	0.048	1.6
polyvinyl octadecyl carbamate, aged against acrylate PSA at 60°C, peel force = 31 oz/in (346 g/cm)	62°	47°	51°	35.9	0.21	21

time that the water had contacted the polyvinyl decyl carbamate or polyvinyl octadecyl carbamate coating, respectively. The measurements were made using an environmental chamber at temperatures between 21°C and 65°C.

In the case the polyvinyl octadecyl carbamate, at 21°C, the water contact angle decreases slightly during the first few minutes of contact, but then remains fairly high for longer dwell times, indicating that relatively little restructuring of the coating surface had occurred. Similar behavior is observed at 40°C, although the receding water contact angle decreases slightly more than at 21°C. In contrast, at 50°C, the water receding contact angle decreases markedly during the first few

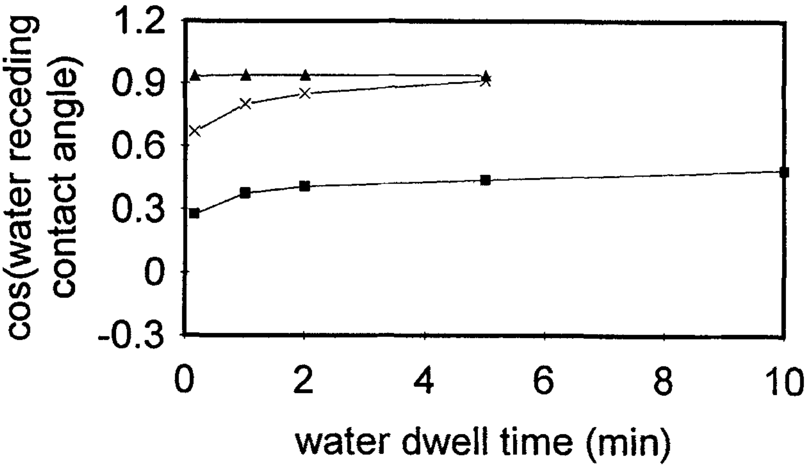


FIGURE 10 Cosine of the water receding contact angle *versus* the water dwell time, for polyvinyl N-decyl carbamate coatings, at 21°C (filled squares), 50°C (X), and 65°C (triangles).

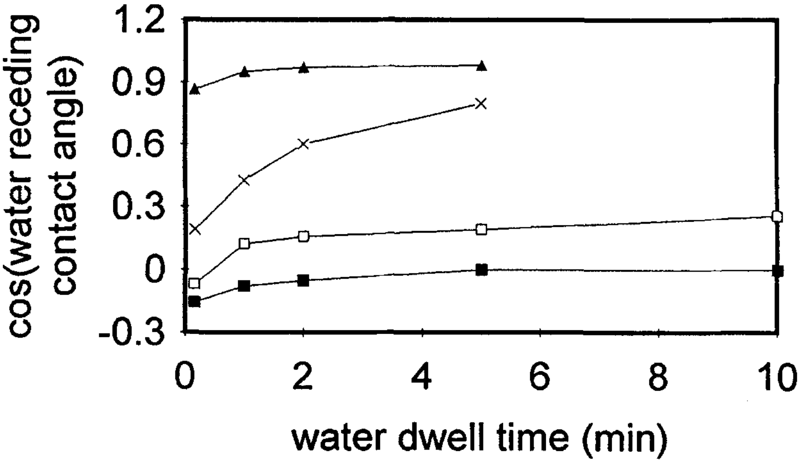


FIGURE 11 Cosine of the water receding contact angle *versus* the water dwell time, for polyvinyl N-octadecyl carbamate coatings, at 21°C (filled squares), 40°C (open squares), 50°C (X), and 65°C (triangles).

minutes of contact, indicative of a significant restructuring of the polyvinyl octadecyl carbamate near the interface with the water. At 65°C, the water receding contact angle is quite low, even when measured at very short dwell times, suggesting that the restructuring is extremely fast at this temperature. The stability of the water receding contact angle as a function of temperature is mirrored in the stability of the adhesion levels provided by the polyvinyl octadecyl carbamate coating as a function of temperature. Recall that the adhesion of the acrylate PSA increased dramatically at aging temperatures greater than about 50°C. Therefore, the ability of the coating to maintain a high water receding contact angle appears to be a good predictor of the coating's ability to maintain a stable adhesion level against the acrylate PSA. In addition, the stability in receding water contact angle and adhesion level are strongly related to the segmental mobility within the polyvinyl alkyl carbamate coating. The DMTA results, presented earlier in Figure 4, showed that the modulus of the polyvinyl octadecyl carbamate drops rapidly above about 50°C, similar to the temperature at which instabilities in receding water contact angle and adhesion levels start to appear.

For the polyvinyl decyl carbamate coating, the ability to maintain a high water receding contact angle is poor. As the data in Figure 10 show, even the initial water receding contact angle of the polyvinyl decyl carbamate coating measured at 21°C is relatively low. At the higher temperatures of 50°C and 65°C, the water receding contact angles are even lower. Evidently, significant restructuring can occur, even at room temperature, for the polyvinyl decyl carbamate coating against water. This observation is consistent with the adhesion results presented in Figure 8, which showed that the acrylate PSA exhibited a dramatic build in adhesion to the polyvinyl decyl carbamate coating when aged at room temperature. Recall that the DMTA results showed that the modulus of the polyvinyl decyl carbamate started to fall off at lower temperatures than for the polyvinyl octadecyl carbamate, and that the modulus of the polyvinyl decyl carbamate was lower over the temperature range of 20 to 70°C, suggesting higher segmental mobility in this temperature range, and a higher susceptibility for restructuring. This difference in segmental mobility can be attributed, in large measure, to the lack of crystalline side chain packing in the case of decyl side chains. In addition, the surface analyses showed that there was a thinner hydrocarbon overlayer and a higher concentration of urethane and vinyl acetate groups, in the near-surface region of the polyvinyl decyl carbamate, which are available for acid-base interactions with the acrylate PSA. The increased segmental mobility, and the higher degree of acid-base interactions with the PSA, lead to the larger increases in adhesion observed for the polyvinyl decyl carbamate coatings.

CONCLUSIONS

The studies presented here have shown that restructuring at the interface between a pressure sensitive adhesive and a release coating can occur. The restructuring results in changes in the specific chemical interactions across the interface, leading to higher attractive forces and a build in adhesion. The restructuring is driven by the minimization of interfacial energy, and requires sufficient segmental mobility in order to occur. For stable release force upon aging, in the case where there is the potential for strong specific chemical interactions between groups in the PSA and release coatings, the segmental mobility within the release coating must be kept low in order to preserve the original surface structure. For the polyvinyl octadecyl carbamate studied here, this is accomplished through the crystallinity of the octadecyl side chains. Aging at temperatures above the crystalline melting point, where the segmental mobility is high, results in rapid increases in the adhesion level. In the case of polyvinyl decyl carbamate, where the crystallinity is absent, the segmental mobility is such that low adhesion is difficult to maintain, even when aged at room temperature.

Acknowledgements

The author would like to thank Martha Jacobsen of 3M for synthesis of decyl isocyanate, and to Dr. Patricia J. A. Brandt, also of 3M, for synthesis of the polyvinyl alkyl carbamates studied here. Acknowledgement is also given to Teresa Kruger, Gary Kirsch, Myles Brostrom, and Dr. Alphonsus V. Pocius, all of 3M, for assistance with DSC, DMTA, X-ray scattering, and surface analysis experiments, respectively. Thanks are also due to Dr. Charles M. Leir of 3M, for helpful discussions concerning release coatings for PSAs.

References

1. D. Satas, in *Handbook of Pressure Sensitive Adhesive Technology*, 2nd Edition, D. Satas, Ed. Van Nostrand Reinhold, N.Y., (1989).
2. L. A. Duel and M. J. Ownen, *J. Adhesion*, **16**, 49 (1983).
3. A. N. Gent and J. Schultz, *J. Adhesion*, **3**, 281 (1972).
4. G. J. Lake, in *Proc. Int. Adhesion Conference*, (The Plastics and Rubber Institute, London), 22-1 (1984).
5. S. Wu, *Polymer Interface and Adhesion*, (Marcel Dekker, N.Y., 1982).
6. J. D. Andrade, in *Polymer Surface Dynamics*, J. D. Andrade, Ed. (Plenum Press, 1989).
7. F. J. Holly and M. F. Refojo, *J. Biomed. Res.*, **9**, 315 (1975).
8. H. Yasuda, A. K. Sharma and T. Yasuda, *J. Polym. Sci.: Polym. Phys. Ed.*, **19**, 1285 (1981).
9. S. H. Lee and E. Ruckenstein, *J. Coll. Interface Sci.*, **120**, 529 (1987).
10. S. R. Holmes-Farley, R. H. Reamey, R. Nuzzo, T. J. McCarthy and G. M. Whitesides, *Langmuir*, **3**, 799 (1987).
11. T. Yasuda, T. Okuno, K. Yoshida and H. Yasuda, *J. Polym. Sci.: Part B: Polym. Phys.*, **26**, 1781 (1988).
12. E. Ruckenstein and S. V. Gourisankar, *J. Coll. Interf. Sci.*, **107**, 488 (1985).
13. E. M. Cross and T. J. McCarthy, *Macromol.*, **23**, 3916 (1990).
14. L. Lavielle and J. Schultz, *J. Coll. Interf. Sci.*, **106**, 438 (1985).
15. Y. Tesuka, A. Fukushima, S. Matsui and K. Imai, *J. Coll. Interf. Sci.*, **114**, 16 (1986).
16. T. Teraya, A. Takahara and T. Kajiyama, *Polymer*, **31**, 1149 (1990).
17. Y. Tezuka, T. Ono and K. Imai, *J, Coll. Interf. Sci.*, **136**(2), 408 (1990).
18. Y. Tezuka, A. Okabayashi and K. Imai, *J. coll. Interf. Sci.*, **141**(2), 586 (1991).
19. Y. Tezuka, M. Yoshino and K. Imai, *Langmuir.*, **7**, 2860 (1991).
20. K. B. Lewis and B. D. Ratner, *J. Coll. Interf. Sci.*, **159**(2), 77 (1993).
21. H. Mori, A. Hirao, S. Nakahama and K. Senshu, *Macromol.*, **27**, 4093 (1994).
22. T Yasuda, M. Miyama and Y. Yasuda, *Langmuir.*, **10**, 583 (1994).
23. Y. Tezuka and A. Araki, *Langmuir.*, **10**, 1865 (1994).
24. H. Yasuda, T. Okuno, Y. Sawa and T. Yasuda, *Langmuir.*, **11**, 3255 (1995).
25. A. Magnani, R. Barbucci, K. B. Lewis, D. Leach-Scampavia and B. D. Ratner, *J. Mater. Chem.*, **5**(9), 1321 (1995).
26. D. Park, B. Keszler, V. Galiasatos, J. P. kenedy and B. D. Ratner, *Mactomol.*, **28**(3), 2595 (1995).
27. J. H. Chen and E. Ruckenstein, *J. Coll. Interf. Sci.*, **135**, 496 (1990).
28. Z. Deng and H. P. Schreiber, *J. Adhesion*, **36**, 71 (1991).

30. J. Schultz, *Proc. Adhesion Soc.*, **1**, (1995).
31. J. Schultz, A. Carré and C. Mazeau, *Intern. J. Adhesion and Adhesives*, **4**, 163 (1984).
32. N. A. Platé and V. P. Shibaev, *J. Polym. Sci,: Macromol. Rev.*, **8**, 117 (1974).
33. E. F. Jordan, Jr., D. W. Feldeison and A. N. Wrigley, *J. Polym. Sci. A-1*, **9**, 1835 (1971).
34. K. Kamagata and M. Toyama, *J. App. Polym. Sci.*, **18**, 167 (1974).
35. A. Schwarcz and R. S. Farinato, *J. Polym. Sci.: Polym. Phys.*, **10**, 2025 (1972).
36. G. Cai, M. H. Litt and I. M. Kreiger, *J. Polym. Sci.: Polym. Phys.*, **29**, 773 (1991).
37. D. Briggs, in *Encyclopedia of Polymer Science and Engineering (surface Analysis)*, Vol. **16**, (John Wiley and Sons, N.Y., 1989), p. 399.
38. M. P. Seah and W. A. Dench, *Suf. Interf. Analysis*, **1**, 2 (1979).
39. D. Briggs, A. Brown and J. C. Vickerman, *Handbook of Static Secondary Ion Mass Spectrometry (SIMS)*, (John Wiley and Sons, N.Y., 1989).
40. M. J. Hearn and D. Briggs, *Surf. and Interf. Anal.*, **11**, 198 (1988).
41. R. J. Good, *J. Adhesion Sci. Technol.*, **6**, 1269 (1992).