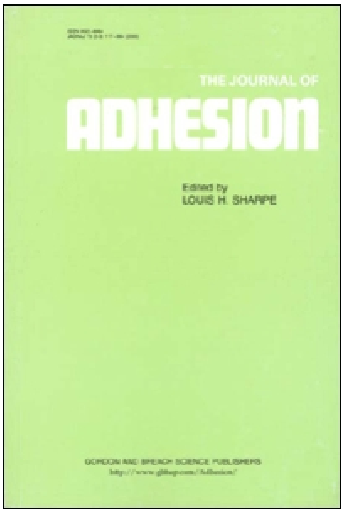

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Interfacial Energy and Adhesion between Acrylic Pressure Sensitive Adhesives and Release Coatings

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Interfacial Energy and Adhesion between Acrylic Pressure Sensitive Adhesives and Release Coatings

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The interfacial adhesive behavior between acrylic pressure sensitive adhesive-like networks (PSA-LNs) and poly(vinyl N-alkyl carbamate) release coatings was studied using a contact mechanical method and peel tests. Surface energy and interfacial energy were directly measured in JKR tests using a novel sample construction. The surface energy of the poly(vinyl N-alkyl carbamates) was found to be around $20\,\mathrm{mJ/m^2}$. Interfacial energies between PSA-LNs and the release coatings were found to be quite high — between 7 and $24\,\mathrm{mJ/m^2}$. Changes in adhesion dynamics were governed by acid-base interactions between the carbamate in the release coating and the acid groups in the PSA-LN. The length of the alkyl chain in the release coating moderated this effect. We also found a correlation between fundamental adhesion energy and peel strength. Examination of this phenomenon provides a basis for understanding the poor storage stability of PSA tapes made using alkyl carbamates and acid-containing PSAs.

Keywords: Interfacial energy; Release coating; Pressure sensitive adhesives; Peel adhesion

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INTRODUCTION

Release coatings are important components of pressure sensitive adhesive tapes (PSATs). One factor in controlling performance of a PSAT is its ability to release from its backing and yet to provide good adhesion to the substrate on which it is applied [1]. Some of the pressure sensitive adhesives (PSAs) used in PSATs are made from co-polymers of acrylic monomers yielding soft and tacky polymers of low glass transition temperature (T_g). Tapes, labels, or adhesive-coated sheets must be protected from unintended contact with other surfaces. Protection with a release sheet or, in the case of tapes, winding upon its own backing are the methods used to prevent the tacky mass from accidental sticking.

Many different polymers and compounds may be used as release agents for pressure sensitive tapes. Various polymers of critical surface tension lower than that of the adhesive and of different polarity than that of the adhesive are useful as release coatings. Silicones, fluorine-containing polymers and compounds, and long alkyl chain branched polymers and compounds are useful as release coatings [2]. Poly(vinyl 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 and are the subject of this study.

While the surface wettability, as determined by the critical surface tension of the release-coated surface, may be an important factor, the phenomenon is much more complex and not completely understood. Various types of silicone coatings exhibit the same critical surface tension, but their release level varies depending on the degree of coating cross-linking: highly cross-linked coatings exhibit an easier release than uncross-linked ones. Furthermore, coatings, such as some fluoropolymers, exhibit a lower critical surface tension, yet the release from such surfaces is not as easy as that from poly(dimethylsiloxane) coated surfaces. This suggests an additional mechanism perhaps related to the rheological properties of the coating. Newby and Chaudhury show that the special slip behavior of silicone might contribute to the good release property [3]. They contend that it is due to the propensity of slippage of the PSA on the silicone that silicone-containing polymers exhibit their unusually low adhesion to most materials. In the case of polyethylene film, however, a weak boundary layer is suspected to contribute to lower adhesion in comparison with polypropylene, which has a lower critical surface tension [4].

Surfaces exhibiting excellent release properties are of tremendous technological importance in areas spanning from anti-stick surfaces to fouling control coatings. Low surface energy is a prerequisite for these surfaces. However, it is important to consider the dynamic processes at the interface as well. Most polymeric materials used for release coatings are multicomponent or 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 a PSA containing polar groups and a release coating, restructuring can occur within the PSA and the release material near the PSA-release material interface after prolonged aging time or at elevated temperatures.

Some polymers with long side chains are waxy compounds and exhibit sharp melting points, quite unlike corresponding polymers with short side chains. In some cases, the long chains crystallize. Poly(vinyl carbamates) having long alkyl side chains have found many important applications as release agents for pressure sensitive adhesive tapes, especially on film backings.

The interfacial energy and intrinsic work of adhesion between PSAs and release coating is unknown. Interfacial energy at the liquid-liquid and liquid-gas interface can be measured by techniques such as the pendent drop method, the pendent bubble method, and the sessile bubble method. The interfacial tension between some polymer pairs in the melt state has been measured [5]. However, interfacial energy measurement between solids has been a challenge. The emergence and applications of contact mechanics in adhesion studies has offered a new route for interfacial energy studies on solid materials [6, 7]. Peel tests have been used to study the adhesion between PSAs and release coatings [2]. We attempt to connect solid-solid interfacial properties with the more normally measured peel strengths of adhesive bonds.

Direct measurement of surface energies *via* contact mechanics methods based on the JKR theory has proven to be successful and accurate for surfaces and interfaces of elastic materials [8,9]. According to the JKR theory, the contact radius a between contacting spherically symmetric bodies under an applied load, P, is given by

$$a^3 = \frac{\mathrm{R}}{\mathrm{K}}\left[\mathrm{P} + 3\pi\mathrm{WR} + \sqrt{6\mathrm{WRP} + (3\pi\mathrm{WR})^2}\right] \tag{1}$$

In which:

$$\frac{1}{K} = \frac{3}{4}\left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}\right) \tag{2}$$

$$\frac{1}{\mathrm{R}} = \frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2} \tag{3}$$

where the E_i are the moduli of the materials that comprise the samples and the ν_i are their Poisson's ratios. K, then, is a composite modulus and R is a composite radius of curvature for samples 1 and 2. We prepare our samples in the form of cylinders. In the case of contact between two crossed cylinders of equal radii of R_c, the situation is identical to a sphere of $\mathrm{R}_\mathrm{s} = \mathrm{R}_\mathrm{c}$ in contact with a flat surface of $\mathrm{R}_\mathrm{f} = \infty$, *i.e.* [9],

$$\frac{1}{\mathrm{R}} = \frac{1}{\mathrm{R}_\mathrm{s}} + \frac{1}{\mathrm{R}_\mathrm{f}} = \frac{1}{\mathrm{R}_\mathrm{c}} \tag{4}$$

Due to the action of the attractive forces, a finite tensile load is required to separate the surfaces from contact. This tensile load is called the pull-off force, P_s. When there is thermodynamic equilibrium and no adhesion hysteresis, the pull-off force is related to the thermodynamic work of adhesion, W, and the radius of the curvature, R, according to Eq. (5) for a displacement-controlled apparatus [10].

$$\mathrm{P}_\mathrm{s} = -\frac{5}{6}\pi\mathrm{RW} \tag{5}$$

If there is adhesion hysteresis between loading and unloading, then W will correspond to the effective adhesion energy, instead of the intrinsic work of adhesion. The effective adhesion energy, G, can be calculated using Eq. (6), when the crack propagates at the interface and gross displacements are purely elastic, *i.e.*, non-elastic behavior is limited to a small region near the crack tip [10, 11]. This parameter is similar to the fracture mechanics concept of strain energy release rate [10–13].

$$G = \frac{\left(P - \frac{a^3K}{R}\right)^2}{6\pi K a^3} \tag{6}$$

In the case of self-adhesion, W, the thermodynamic or intrinsic work of adhesion, is twice the surface energy, γ, as shown in Eq. (7). In the case of adhesion between dissimilar materials, the work of adhesion is described by Eq. (8), where γ_1, γ_2, and γ_{12} are, respectively, the surface energy of material 1 and 2, and the interfacial energy between 1 and 2.

$$W_{11} = 2\gamma_{11} \tag{7}$$

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{8}$$

A desirable feature of contact mechanical experiments is the very low crack propagation speeds that are accessible. Another feature is its capability to reveal both equilibrium and dynamic information for the same assembly through loading and unloading cycles. Thus, more precise connection can be found between equilibrium and non-equilibrium processes.

In this paper, we describe the measurement of the work of adhesion between PSAs and release coatings using the JKR method. One challenge is the high elastic modulus of release coatings at room temperature. To get around this problem, a thin layer of release coating is coated onto cross-linked Pressure Sensitive Adhesive-like Networks (PSA-LNs). Both the self-adhesion behavior of release coatings and the work of adhesion between release coatings and PSA-LNs were studied using the JKR method. The interplay of the effect of acrylic acid, temperature and dwell time on the interfacial adhesive behavior of PSA-LNs and release coatings was studied systematically to address a known storage problem [2]. Interfacial adhesion energy measurements are compared with the results of standard peel tests using very similar materials.

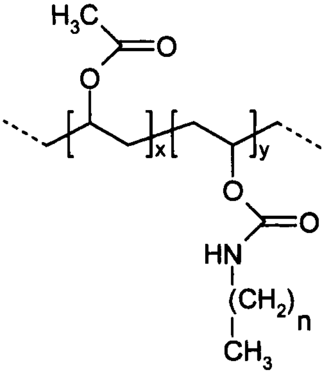
MATERIALS AND EXPERIMENTAL METHODS

Release Materials

Poly(vinyl N-octadecyl carbamate) (PVNODC) and poly(vinyl N-decyl carbamate) (PVNDC), the structure of which is shown in Fig. 1, were donated by 3M and are the same materials as used by Kinning [2]. They were synthesized by reacting hydrolyzed poly(vinyl acetate) with octadecyl isocyanate and decyl isocyanate, respectively [14]. The reactions were carried out at 30% solids in refluxing xylene. A thin film of release coating is obtained by spin coating 2 wt% poly(vinyl N-alkyl carbamates) in toluene solution at rotation speeds ranging from 1000 to 1200 rpm.

Synthesis of Pressure Sensitive Adhesive-Like Networks (PSA-LNs)

In this study, acrylic acid (AA) was co-polymerized with 2-ethyl hexyl acrylate (2-EHA) as described in Table 1. In order to provide elasticity necessary for simple contact mechanics, 10% 1,6-hexane diol diacrylate (HDDA) di-functional monomer was used to cross-link the material. The choice of HDDA as cross-linker was based upon reactivity ratios of monomers. Use of HDDA as a cross-linker



n = 9, decyl, PVNDC; n = 17, octadecyl, PVNODC

FIGURE 1 The chemical structure of the polycarbamate release coatings.

TABLE 1 The composition of PSA-LN samples

Sample Designation	*Monomer* (*wt*%)	*Co-monomer* (*wt*%)	*Cross-linker* (*wt*%)
	2-EHA	AA	HDDA
PSA-LN-NoAA	90	0	10
PSA-LN-10AA	80	10	10

provides the best chance to have a random copolymer with minimal blockiness. The detailed information on PSA-LNs cylinder preparation is described in a previous paper [15].

Preparation of Composite Samples

Oxygen plasma-treated PSA-LN-NoAA cylinders were used as the elastic foundation of the release coatings. The function of O_2 – plasma was to increase the surface energy of PSA-LN-NoAA by introducing polar groups into the surface region of the foundation. A thin layer ($\sim$200 nm) of the release coating was spun-coated on newly cleaved flat mica sheets. The release coating film was floated from the mica sheet in deionized water. The polymer film was picked up onto the plasma-treated PSA-LN cylinders. The samples were dried first at room temperature in a laminar flow hood for about two hours before they were placed in a vacuum oven at 80°C for 30 minutes. Thus, a thin layer of release coating was placed on the surface of an O_2 – plasma modified PSA-LN-NoAA cylinder resulting in the formation of a composite, as shown in Fig. 2. The composite has a modulus close to the PSA-LN foundation but having the surface character of the release coating, making it possible to use the JKR measurement directly for the study of release coatings.

Preparation of Pressure Sensitive Adhesive Tapes

Pressure Sensitive Adhesive Tapes (PSATs) were generated using monomer formulations as close as possible to the PSA-LNs but having cross-link density similar to that used in commercial acrylic PSATs. To accomplish this, 2-ethyl hexyl acrylate or a combination of 90% 2-ethyl hexyl acrylate and 10% acrylic acid were dissolved at 50 wt% in ethyl acetate in a glass bottle. Each bottle was flushed with nitrogen for 10 minutes in order to reduce dissolved oxygen in

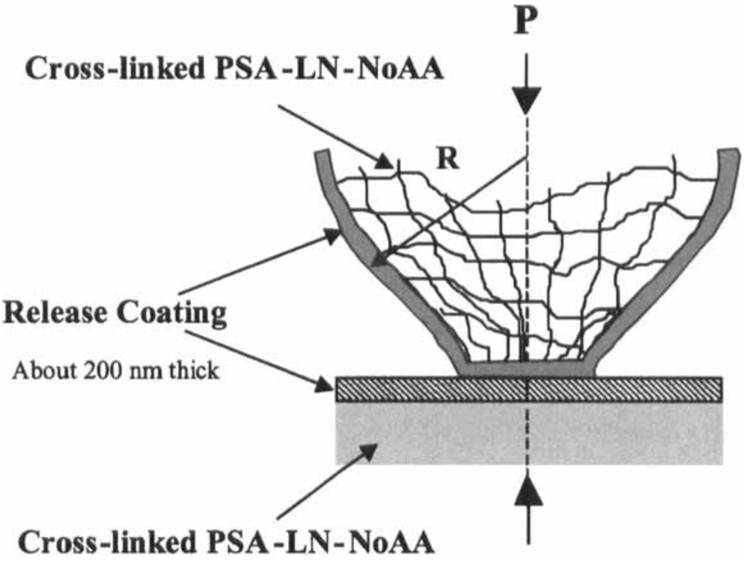


FIGURE 2 Schematic of a polymer coated PSA-LN-NoAA cylinder in contact with a polymer-coated flat surface, which is equivalent to the actual geometry of two cross cylinders with release coatings used in the JKR tests.

the reaction mixture. The containers were sealed and placed in an Atlas "Launderometer" (Atlas Electric Device Co., Chicago, IL) for 48 hours at 80°C.

One wt% benzoyl peroxide was dissolved into each polyacrylate/ ethyl acetate solution. Within a day, each ethyl acetate solution was coated onto a piece of poly(ethylene terephthalate) film (0.051 mm thick). The coated adhesive was allowed to air dry for 30 minutes before being placed in an oven pre-set at 150°C. The adhesive was allowed to dry and cross-link under these conditions for 45 minutes. The adhesive thickness on the poly(ethylene terephthalate) film was 32 microns. The PSATs made in this fashion were stored in a constant temperature (75°F) and constant humidity room (85% RH) for at least 24 hours before assembling the test specimens.

The JKR Apparatus and Environmental Cell Design

A homemade, automated JKR apparatus, as shown in Fig. 3, was used in this study to perform adhesion tests using a contact mechanical

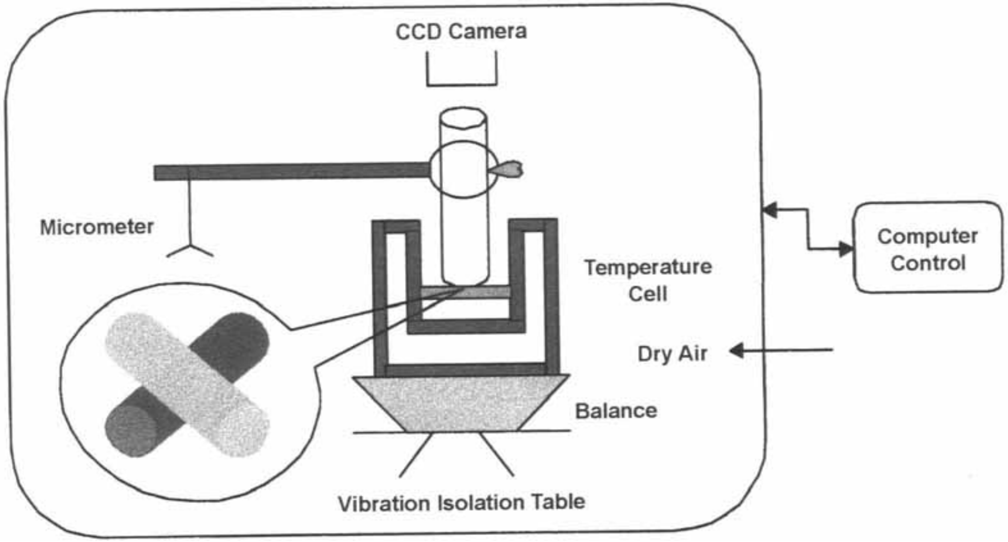


FIGURE 3 The schematic of the JKR apparatus with an environmental cell.

approach. A complete diagram of this apparatus is available in Reference [15]. A micrometer is connected to a precision translation stage to control the displacement. An analytical balance measures the corresponding load. The CCD camera captures the contact area. Adhesion tests were performed at controlled humidity, close to zero. The temperature cell has precise control of the sample temperature to within ± 0.5°C and enables us to run adhesion tests at temperatures as high as 250°C. The whole assembly is mounted on an anti-vibration table.

Adhesion Measurement Procedure: A Contact Mechanical Approach

Cross-cylinder geometry is employed in our JKR measurements. Half-cylindrical samples were glued to supporting surfaces by applying small amounts of thoroughly mixed, fast-setting epoxy. PSA-LN-10AA, due to its lower elastic modulus and tackiness, can adhere to the glass plate without an adhesive. After reaching thermal equilibrium and complete curing of the epoxy, samples were crossed by close examination at low magnification. A slight contact was made in order to align the video-zoom with the center of contact. Cylinders were then separated and the system was allowed to equilibrate mechanically and thermally for at least 3 hours. Samples were compressed stepwise allowing time for equilibration between each step. After a 10-step compression of 1 μm at each step and equilibration at the maximum load for 30 minutes, samples were decompressed in a similar stepwise fashion. For crack propagation rate studies, steady unloading at vertical separation speeds ranging from 1 nm/s to 100 nm/s was used. In dwell time studies, both loading and unloading were in steady mode at a relatively fast speed of 50 nm/s to have a better control of the contact time at the maximum testing load. Experiments were run at both 25°C and elevated temperatures of 48°C, 65°C, 75°C, 85°C and 95°C. The displacement, load and contact area were recorded on a computer for analysis. The radius of the cylinders was measured sideways under a light microscope. Each test was repeated two times using the same sample and two samples were examined for each condition. Thus, all contact mechanics adhesion data reported here are an average of at least four measurements.

Practical Adhesion Tests

Glass plates of nominal 1/4″ (0.64 cm) thickness were cleaned by scrubbing under solvent and then under Alconox^{TM}/water. The surfaces were rinsed with de-ionized water and finally reagent-grade acetone. The glass plates were further subjected to 10 minutes of oxygen plasma using a hospital instrument sterilizer (Harrick PDC-32G) set at "HI". Release coating solutions (2% solids in toluene) were coated onto glass plates using a #6 Meyer rod yielding a dry coating thickness of about 100 microns. The coated glass plates were placed in an oven at 150°C for 45 minutes.

In the constant temperature/constant humidity room described above, strips of PSAT (1.27 cm wide) were cut from the larger coated pieces (as described above.). The tape was tacked to one end of the release polymer coated glass plate and a rubber roller (nominal weight of 5 lbs. (2.3 kg)) was passed over the tape three times. The sample was immediately attached to an Instron 4501 tensile testing machine that had been equipped with a 90° peel fixture. This tensile testing machine is computer controlled and was capable of measuring force at a range of pre-determined crosshead speeds. The crosshead speeds used in these measurements were (in inches/minute): 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1, 5, and 10 (0.0025, 0.013, 0.025, 0.13, 0.25, 1.3, 2.5, 13 and 25 cm/min). The average peel force was measured at each of these peel rates. The instrument was zeroed and calibrated before each run.

Surface Composition Characterization

Surface compositions of the PSA-LNs and coated release coatings were measured using a Surface Science Labs XPS instrument with small spot capability (the spot size can be as small as 25 microns.) Because the samples are hemi-cylinders, there was no specific take-off angle and the measured values must be considered an average surface composition over approximately the first 50 Angstroms in depth. The small spot size and imaging capability of this XPS apparatus allowed us to make sure that only the sample was interrogated. The chemistry of the sample surface was determined near the "crown" of the sample.

The surface chemistry of the PSATs was measured using a Physical Electronics Model 5400 ESCA at a 20° take-off angle. The area analyzed is approximately 1 cm × 1 cm. The analysis depth is approximately 20 Angstrom units.

Film Thickness Characterization

A Sopra ES4G Spectroscopic Ellipsometer was used to measure the release coating film thickness spun coated on a silicon wafer and was found to be about 140~200 nm. Atomic Force Microscopy (AFM) was used to determine the surface topography of the release coating samples. The AFM imaging indicated that the samples were generally smooth with root mean square (r.m.s.) roughness over the interrogated surface of about 1.5 nm.

EXPERIMENTAL RESULTS

Surface Energies of Release Coating: Comparison between Two Release Coatings with Different Alkyl Side Chains

As shown in Fig. 4 (a) and (b), the works of adhesion, W, of self-contact for PVNDC and PVNODC are 40.4 ± 1.2 and 38.3 ± 2.2 mJ/m^2, respectively.

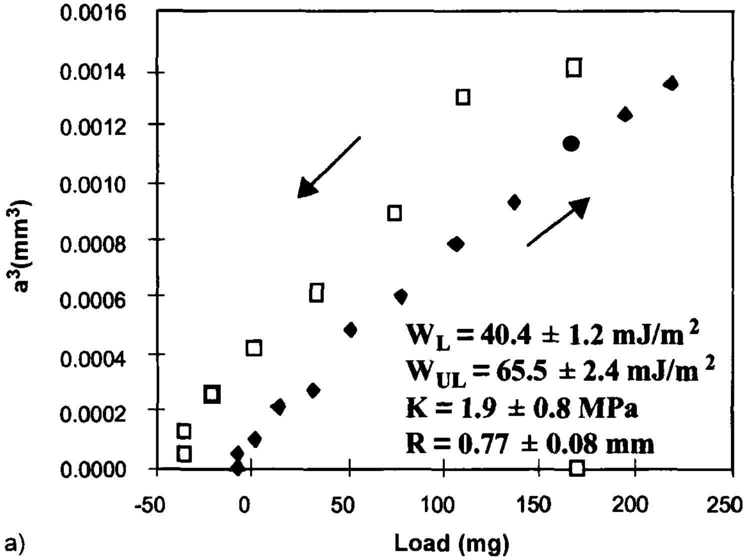


FIGURE 4 JKR plots for self-adhesion of release coatings coated on PSA-LN-NoAA elastic foundation at room temperature. Step loading (◆) and step unloading (□) modes were used. (a) PVNDC-PVNDC (b) PVNODC-PVNODC.

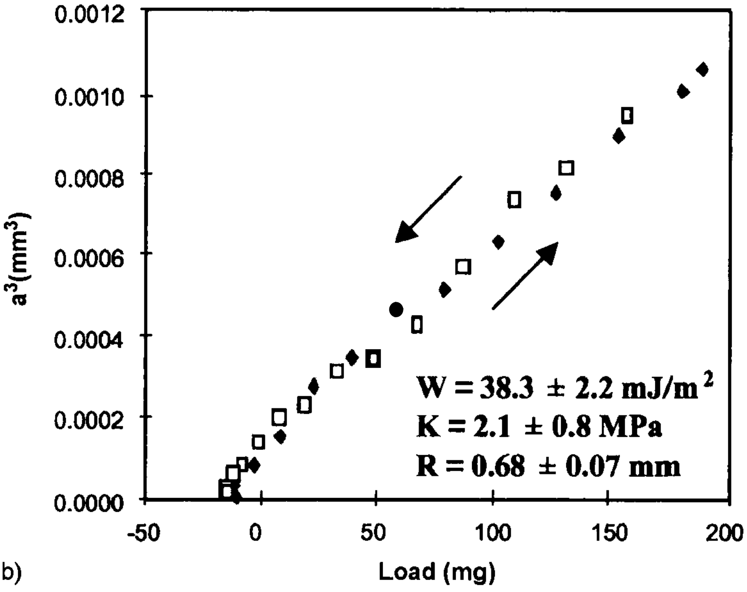


FIGURE 4 (Continued).

These values of work of adhesion were obtained by a two-parameter fit to the loading data, with the work of adhesion and composite elastic modulus as adjustable parameters. Then the energy release rate, or effective adhesion energy from unloading was obtained using the composite elastic modulus fitted from loading data using Eq. (6).

An alternative method of analyzing data is to determine the modulus independently using the displacement data, in addition to the load and contact radius. The basic assumption made by applying the JKR analysis to calculate G is that displacements are elastic, *i.e.*, that nonelastic behavior is limited to a small region near the crack tip [11]. In order to test the validity of the JKR analysis, we measured the lens displacement, δ, independently. These results agree well with the displacements predicted by the JKR theory when the aspect ratio is less than 0.1, in which case the approximation of the lens as an infinite half-space did not introduce significant error. However, in the case of the aspect ratio higher than 0.5, as observed by Shull *et al.* [13], the finite size effects result in $\delta_{JKR} > \delta$ for $P > 0$, and $\delta_{JKR} < \delta$ for $P < 0$. The net effect of finite size on G is uncertain. To avoid the complication of the finite size effect, we did not use this method for the data analysis.

According to Eq. (8), surface energies of PVNDC and PVNODC are, respectively, 20.2 ± 1.2 and $19.2 \pm 1.1\,\mathrm{mJ/m^2}$, which are quite similar to each other. These values are consistent with the surface energies of $21 \pm 1\,\mathrm{mJ/m^2}$ obtained by Kinning [2] using contact angle measurements. This indicates that the top molecular layer for both coatings was similar in composition, being predominantly the low energy methyl end groups. Low energy components in copolymers or blends tend to orient preferentially to the surface, similar to small-molecule liquids, as this will lower the overall free energy of the system. PSAs have surface energies of $25-30\,\mathrm{mJ/m^2}$ [15, 16]. Thus, release coatings used in this work satisfy the "poor wetting" prerequisite for release coatings, as described above.

Data from XPS analysis of the release coated PSA-LN-NoAA cylinders are shown in Table 2. The PVNODC, as may be surmised from its structure, has higher carbon content than PVNDC. There were no detectable contaminants.

An interesting observation is the difference in hysteretic behavior between the self-adhesion of PVNDC and PVNODC at room temperature. Self-adhesion of PVNDC gives hysteretic adhesion curves, while self-adhesion of PVNODC is non-hysteretic. Lack of hysteresis means lack of surface restructuring. The fact that PVNODC is non-hysteretic indicates that the distance provided by the octadecyl side chain is enough to screen interactions between the more polar portion of the polymer.

The non-hysteretic behavior of PVNODC might be due to the hexagonal packing of the octadecyl chain in its crystalline state [2]. When surface groups are in the solid crystalline state they are effectively immobilized. No interdiffusion occurs on contact and the adhesion should not increase with contact time. A layered structure is still present in the case of decyl side chains; however, there is a lack of

TABLE 2 The surface elemental composition of release coatings on PSA-LN-NoAA as determined by small spot size XPS

Release Coating	*C* (%)	*O* (%)	*N* (%)
PVNDC	83.82	11.71	4.47
PVNODC	87.51	9.55	2.94

hexagonal packing of the decyl side chains. With a shorter chain and higher segmental mobility, surface rearrangement can take place. This phenomenon apparently leads to measurable hysteresis for PVNDC. The hysteretic behavior difference at room temperature provides an impetus to investigate self-adhesion at elevated temperatures.

Temperature Effect on Surface Energies of Release Coatings

The intrinsic work of adhesion as a function of temperature can be obtained from quasi-static loading curves at different temperatures. The temperature effect on the intrinsic work of adhesion of the two release coatings is compared in Fig. 5. It is seen that the surface energy decreases with temperature for both polymers. The temperature coefficients of surface energy of PVNDC and PVNODC are 0.1 and 0.15 mJ/m^2/K, respectively. A lower intrinsic work of adhesion and higher temperature coefficient are observed for PVNODC.

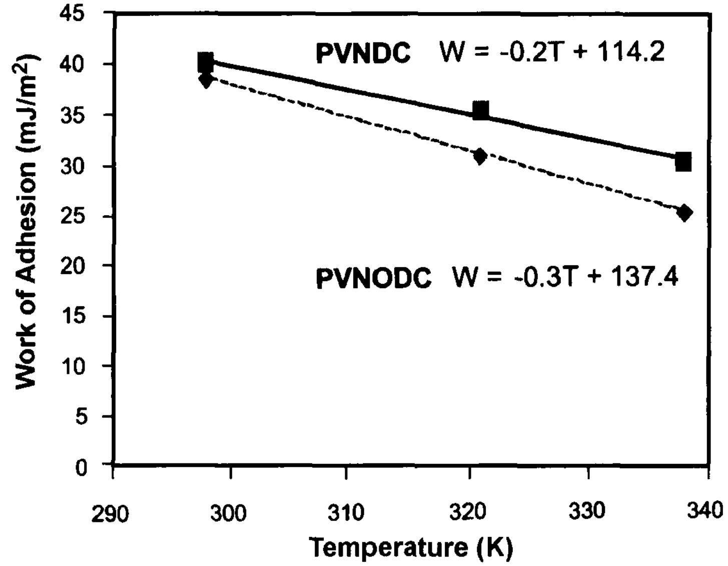


FIGURE 5 The comparison between temperature effect on surface energies on PVNDC (■) and PVNODC (◆). The values of work of adhesion are obtained from the loading experiments. The linear fit suggests that, in the temperature range tested, the work of adhesion decreases linearly with temperature. The uncertainty of the data is ± 8%.

Wu [5] predicted that the temperature coefficient of surface energy ($d\gamma/dT$) of polymers should be about 0.05 mJ/m^2, which is smaller than that of small-molecule liquids, which is about 0.1 mJ/m^2. Since ($d\gamma/dT$) is the surface entropy, the smaller ($d\gamma/dT$) for a polymer is attributed to conformational restrictions of long-chain molecules. The slightly higher temperature coefficient of PVNDC and PVNODC, in comparison with the predicted values for polymers, might be due to the mobility of the side chains. Our measurements have provided the surface energies of each of the release coatings and each of the PSA-LNs. Therefore, we are in position to investigate the interfacial energy between them after we measure the work of adhesion between them.

The Interfacial Energy and Intrinsic Work of Adhesion between PSAs and Release Coatings: Acrylic Acid Effect

Fig. 6(a) and (b) show the results of contact mechanics measurements of adhesion between PVNDC/PSA-LN-NoAA and PVNDC/PSA-LN-10AA at room temperature, respectively. PVNDC/PSA-LN-NoAA

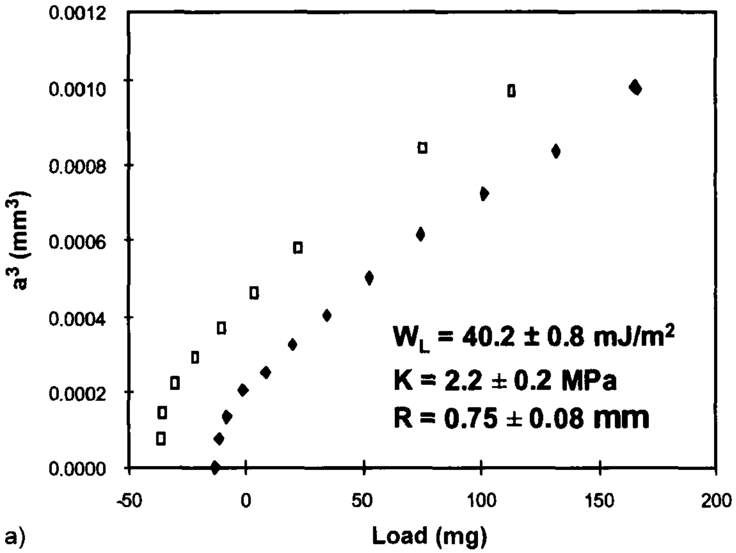


FIGURE 6 JKR curves for interfacial adhesion between PVNDC and PSA-LNs at room temperature. Both step loading (◆) and step unloading (□) were used. (a) PSA-LN-NoAA (b) PSA-LN-10AA.

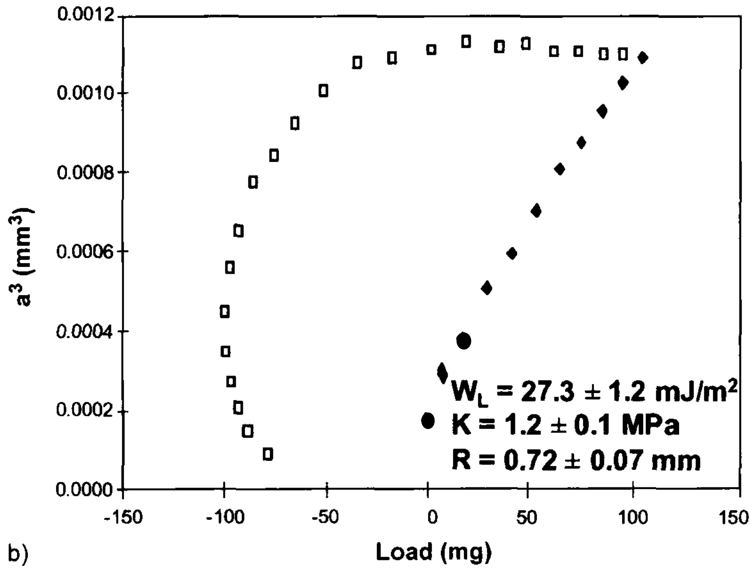


FIGURE 6 (Continued).

contact shows higher intrinsic work of adhesion and less hysteretic behavior than PVNDC/PSA-LN-10AA. The lower intrinsic work of adhesion between PVNDC and PSA-LN-10AA suggests that the addition of acrylic acid enhances the inherent incompatibility between PVNDC and PSA-LN-10AA. However, the higher adhesion hysteresis likely results from interfacial restructuring of PVNDC while in contact with PSA-LN-10AA. The acid-base interaction between the acrylic acid groups in PSA-LN-10AA and the basic urethane and acetate groups in PVNDC provide a bigger driving force for interfacial rearrangement than the case of PSA-LN-NoAA.

The intrinsic work of adhesion and interfacial energy between PSAs and release coatings at room temperature are tabulated in Tables 3 and 4. The intrinsic work of adhesion is obtained from the loading curves of the JKR measurements. The interfacial energy is calculated

TABLE 3 The self-adhesion and surface energy of PSAs and release coatings

Samples	*PSA-LN-NoAA*	*PSA-LN-10AA*	*PVNDC*	*PVNODC*
Self-Adhesion (mJ/m^2)	55.1 ± 1.5	63.0 ± 5.0	40.4 ± 1.2	38.3 ± 2.2
Surface Energy (mJ/m^2)	27.6 ± 0.8	31.5 ± 2.5	20.2 ± 0.6	19.7 ± 1.1

TABLE 4 The work of adhesion and interfacial energy between PSAs and release coatings

Work of adhesion (mJ/m^2)	PSA-LN-NoAA	PSA-LN-10AA
PVNDC	40.2 ± 0.8	27.3 ± 1.2
PVNODC	39.7 ± 1.0	34.2 ± 1.4
Interfacial Energy (mJ/m^2)	PSA-LN-NoAA	PSA-LN-10AA
PVNDC	7.6 ± 0.8	24.3 ± 2.5
PVNODC	7.6 ± 1.1	17.0 ± 2.5

using Eq. (9). Quite similar interfacial energies exist between PSA-LN-NoAA and the two different release coatings. Relatively higher interfacial energy exists between release coatings and PSA-10AA than PSA-NoAA. The surface energy of PSA-LN-10AA cannot be directly measured using the JKR method at room temperature [16, 17]. We estimate γ from measurements at 75°C using $d\gamma/dt$. This leads to a greater uncertainty in the interfacial energy between PSA-LN-10AA and release coatings. However, it is clear that the polymers composing the PSA and release coating are thermodynamically incompatible, as suggested by the high interfacial energy. The presence of acrylic acid seems to provide an inherent incompatibility between PSAs and release coatings due to the significant polarity difference.

Rate Effect on the Work of Adhesion between PSA-LNs and Polycarbamate Release Coatings and Threshold Adhesion Energy

The adhesion energy can be plotted *versus* crack speed, v, where

$$v = \frac{da}{dt} \qquad (9)$$

and a is the radius of the contact between the cylinders in the JKR measurement. As compared in Fig. 7, there is a higher threshold adhesion energy and lower critical crack speed for PVNDC/PSA-LN-10AA than for PVNDC/PSA-LN-NoAA. For the case of contact between PSA-LN-10AA and PVNDC, the critical crack speed is close to 20 nm/s. A much higher value of 200 nm/s is observed for the case of contact between PSA-LN-NoAA and PVNDC.

The rate effect might be related to the restructuring processes occurring at the interface instead of to the bulk viscoelastic behavior

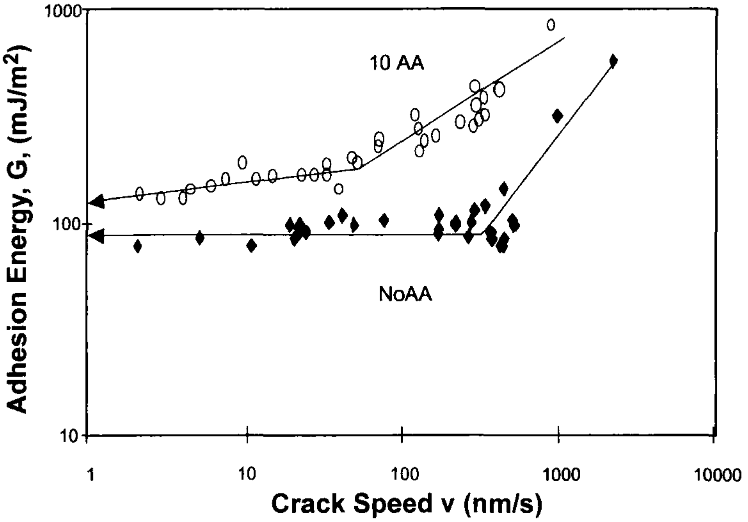


FIGURE 7 The comparison of the rate effect between PVNDC-PSA-LNs with (○) and without (◆) acrylic acid. The unloading rate is 5 nm/s. The uncertainty of the data is ± 10%.

[18, 19]. This hypothesis can be tested by running experiments at elevated temperatures. Since temperature has a dramatic effect on the self-adhesion behavior of release coatings and PSA-LNs, it appeared to be of interest to investigate how temperature affects the interfacial behavior between PSA-LNs and release coatings.

Temperature Effect on Interfacial Adhesion between PSAs and Release Coatings

As shown in Fig. 8, the intrinsic work of adhesion decreases linearly with temperature for PVNDC/PSA-LN-NoAA and PVNDC/PSA-LN-10AA. This result is reasonable due to the linear dependence of both surface energy and interfacial energy on temperature. With the addition of acrylic acid, the work of adhesion between PVNDC and PSA-LNs is decreased. The temperature dependence is also smaller. It is very interesting to note that although acrylic acid increases the self-adhesion energy of PSAs [16, 17], it actually decreases the intrinsic work of adhesion between PSAs and release coatings.

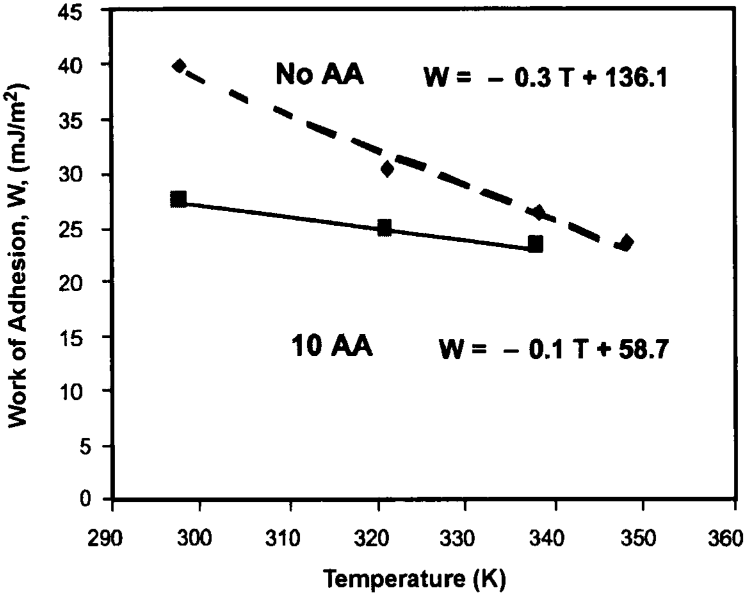


FIGURE 8 Comparison between the temperature effect on work of adhesion between PVNDC and PSA-LNs with (■) and without (◆) acrylic acid. The linear fit of the data suggests that work of adhesion decrease linearly with temperature. The uncertainty of the data is ± 8%.

While the intrinsic work of adhesion decreases with temperature, adhesion hysteresis increases with temperature up to 65°C, as shown in Fig. 9. This can be explained by the increased ease of interfacial restructuring with temperature. Temperature affects not only intrinsic work of adhesion and adhesion hysteresis, but it also changes the rate dependence of the adhesion energy. As shown in Fig. 10, the threshold adhesion energy is much higher at 65°C than that at 25°C. This behavior is contrary to what time-temperature superposition would predict, which supports our hypothesis that interfacial restructuring is dominant rather than viscoelasticity.

Our results on the temperature effect on work of adhesion and surface energy of release coatings and PSA-LNs have shown clearly that the decrease of work of adhesion with temperature is mainly due to the decrease of surface energy with temperature. The temperature coefficient of interfacial tension between polymers is typically about $-0.01\,\mathrm{mJ/m^2}$, much smaller than that of surface energy.

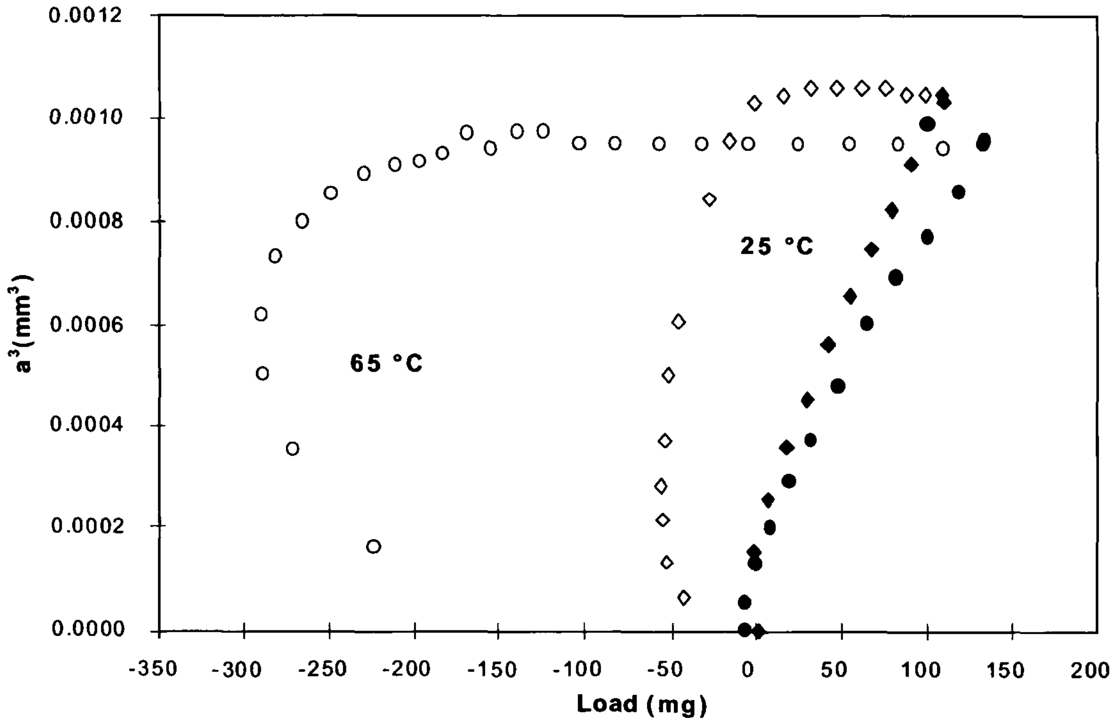


FIGURE 9 Comparison between the JKR plots for PSA-LN-10AA in contact with PVNDC at 25°C and 65°C. The unloading rate is 5 nm/s. Loading 25°C (◆), Unloading 25°C (◊), Loading 65°C (•), Unloading 65°C (○). The uncertainty of the data is ± 8%.

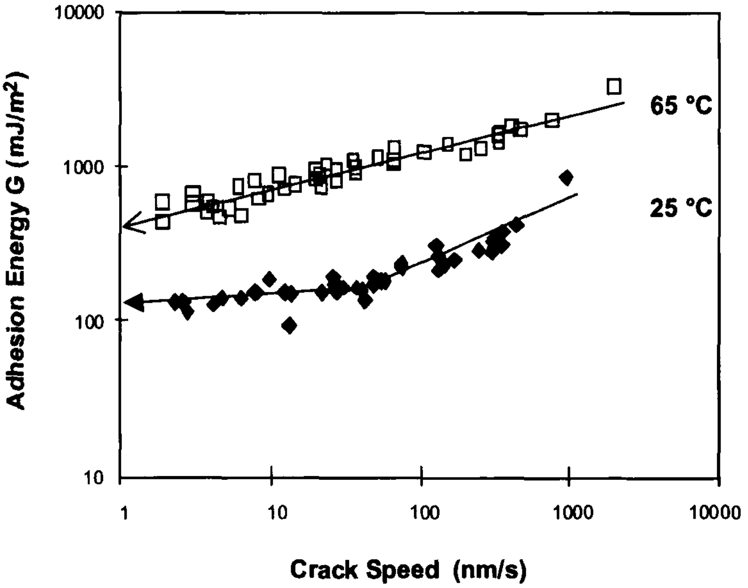


FIGURE 10 Rate effect on adhesion energy for the contact between PSA-LN-10AA and PVNDC at two different temperatures of 25°C (◆) and 65°C (□). The uncertainty of the data is ± 8%.

This temperature dependence is for polymer melts. There are not enough available data for solid polymer contact, due to the difficulty in determining surface and interfacial energies of solids [6].

Dwell Time Effect on Adhesion Energy and Adhesion Hysteresis

By maintaining a constant fast rate of approach and retraction but varying the contact time at a predetermined displacement, we were able to assess the effect of increasing contact time on the adhesion energy and hysteresis. The adhesion energy is obtained from the pull-off force using Eq. (6). The pull-off force increased with time in the case of PSA-LN-10AA. There is a small dwell time effect and much more stable adhesion/release if there is no acrylic acid in the PSA-LNs. This agrees well with the hypothesis that adhesion hysteresis is due to surface restructuring which, in turn, results from acid-base interactions.

As shown in Fig. 11, the effective adhesion energy is higher between PVNDC and PSA-LN-10AA than that between PVNODC and

PSA-LN-10AA. Similar time dependence exists for both PVNDC and PVNODC when in contact with PSA-LN-10AA at 65°C. At room temperature, PVNODC shows much more stable interfacial adhesion with PSA-LN-10AA. The dependence of adhesion energy on contact time follows a 0.1 power law, which has been observed for a number of systems [20, 21]. This is attributed to slow molecular rearrangements at the interface.

The difference in aging behavior for the two different poly(vinyl N-alkyl carbamates) studied here can be attributed to differences in the degree of interfacial restructuring as a function of time and temperature. The degree of interfacial restructuring is related to the segmental mobility and the driving force seems to be acid-base interactions, in this case. The difference in segmental mobility of the two release coatings can be attributed, in larger measure, to the lack of crystalline side chain

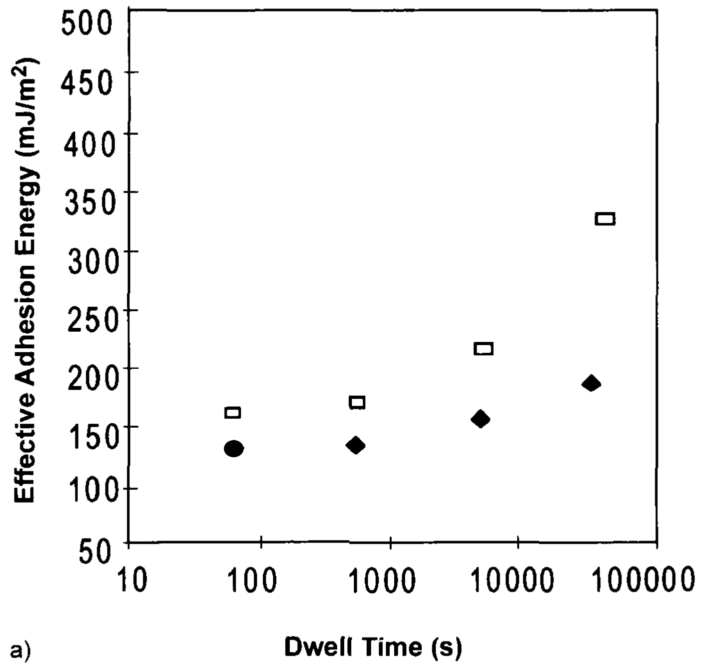


FIGURE 11 Dwell time effect on effective adhesion energy between PSA (10AA) and release coatings over five decades of dwell time range. Effective adhesion energy is obtained from the pull-off force using Eq. (5) at both 25°C (◆) and 65°C (□). (a) PVNODC in contact with PSA-LN-10AA. (b) PVNDC in contact with PSA-LN-10AA. The uncertainty of the data is around ± 10%.

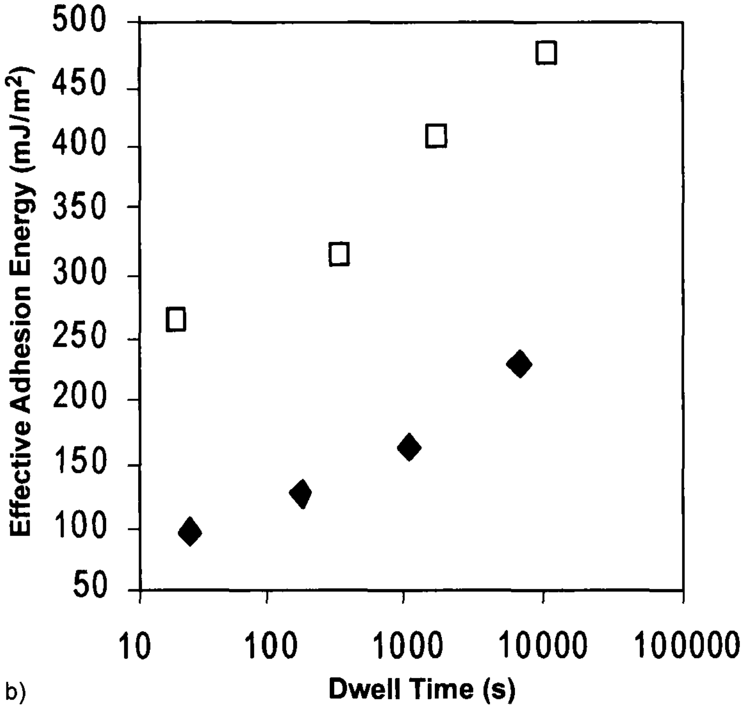


FIGURE 11 (Continued).

packing in the case of decyl side chains. In addition, surface analysis showed that there is a thinner hydrocarbon overlayer and a higher concentration of urethane and vinyl acetate groups, in the near-surface region of the poly(vinyl N-decyl carbamate) [2]. In PVNDC, these are available for acid-base interactions with the AA-containing acrylate PSA. The increased segmental mobility, and the higher degree of acid-base interactions with the PSA, lead to the larger increase in adhesion observed for the poly(vinyl N-decyl carbamate) coatings. The combination of these factors leads to the poorer ability of the PVNDC coating to maintain the initially low adhesion with acrylate PSAs.

Peel Adhesion

Figure 12 shows a comparison between peel measurements of the PSAT-10AA from PVNDC-coated glass and from "clean" glass itself

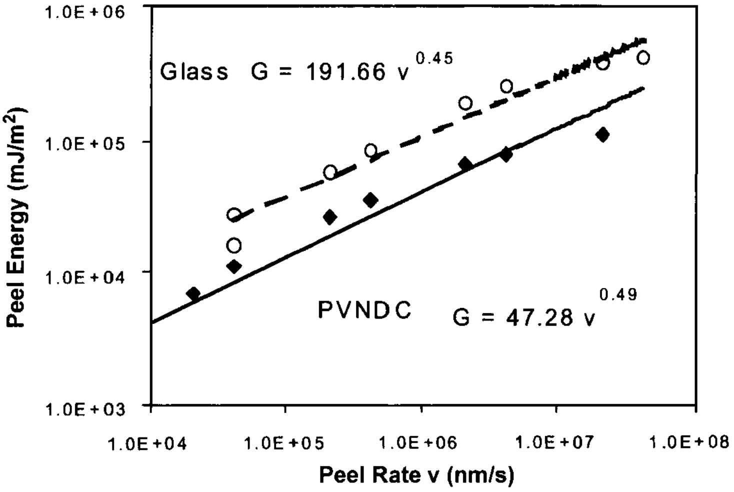


FIGURE 12 Peel energy is plotted *versus* peel rate for PSATs peeled from PVNDC-coated glass (◆) and glass (○) itself. The reduction of peel energy is observed by applying PVNDC as release coating. The uncertainty of the data is around ± 10%.

using a ninety-degree peel fixture. Apparent adhesive failure occurs for both cases at all the crosshead speeds tested. The peel energy is plotted as a function of crack speed. We make the assumption that crosshead speed equals crack propagation speed in this measurement. The strength of adhesion is characterized by the work of detachment, G, per unit area of growth of the cleavage plane, where G is obtained directly from the peel force, P, per unit width of the test strip [22]. The peel results clearly show that the release coating reduces the peel adhesion. PVNODC-coated on glass has an even more dramatic reduction of peel adhesion with PSAT-10AA.

DISCUSSION

Acrylic Acid Effect on Work of Adhesion between PSA-LNs and Polycarbamates Release Coatings

Copolymerization of acrylic acid into a PSA-LN or PSAT decreases the work of adhesion with release coatings as well as the temperature coefficients of surface energy. However, the presence of AA in a

PSA-LN increases the adhesion energy as measured in unloading. Addition of acrylic acid to a PSA-LN increases the interfacial energy with release coatings but it also increases the threshold adhesion energy. The presence of AA in a PSA-LN also provides increasing adhesion energy as a function of contact time. All these facts support the hypothesis that acid-base interactions act as a driving force for the interfacial restructuring between PSAs and poly(vinyl N-alkyl carbamate) release coatings.

This explanation has already been proposed by Kinning [2]. Adhesion build-up can be attributed, in large part, to a restructuring of the PSA-LN/poly(vinyl N-alkyl carbamate) interface. We have shown data to support his proposition. Specifically, if the segmental mobility within the poly(vinyl N-alkyl carbamate) coating is sufficient, and energetically favorable specific chemical interactions can occur between the PSA and the poly(vinyl N-alkyl carbamate), segmental rearrangements near the interface are expected. This restructuring leads to stronger attractive forces at the interface and higher adhesion. In the case of an acrylate PSA containing an acidic comonomer, increase in the degree of acid-base interaction between the acidic comonomer and the basic urethane and vinyl acetate groups in the poly(vinyl N-alkyl carbamate) would be expected to increase the adhesion between the PSA and the poly(vinyl N-alkyl carbamates). Our data agree well with his conclusions.

Since acrylic acid is commonly polymerized into acrylic PSA systems, a stable interfacial structure between the release coating and the PSA is very important for tape performance, especially after storage. A recommendation for resolving the storage problem is the use of longer alkyl side chains. A purely van der Waals surface of fast relaxation time is desirable in order to achieve low release force [18].

Relationship between Intrinsic Adhesion Energy and Peel Adhesion

An attempt was made to correlate contact mechanics measurements with more traditional peel strength measurements. The contact mechanics results are plotted on a graph along with the peel measurements in Fig. 13. We make a potentially dubious assumption that

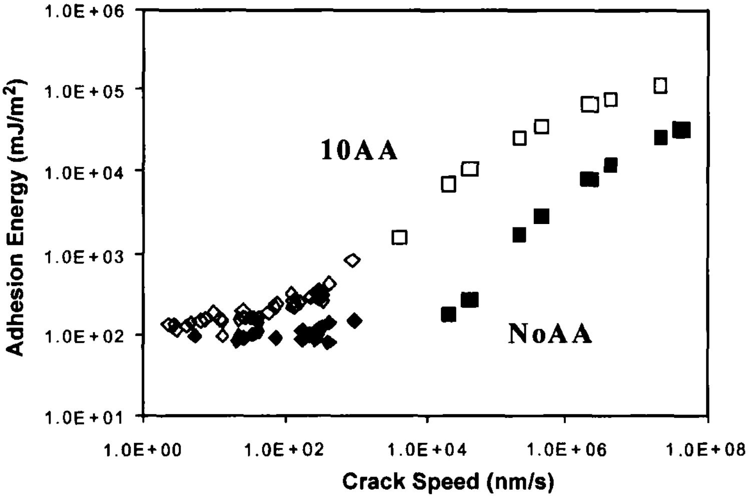


FIGURE 13 The peel energy and the JKR measurements for the contact between PSATs and release coating PVNDC. NoAA-JKR (◆), 10AA-JKR (◊), NoAA-peel (■), 10AA-peel (□). The uncertainty of the data is around ± 10%.

the micro-mechanics occurring at the peel front are the same as for a crack propagating in the elastic JKR measurement. Indeed, no account is made regarding the stiffness of the backing material in the PSAT. Despite these rather substantial omissions, the connection between the JKR results and the traditional peel measurements is striking. The rate dependence is very similar in both the JKR results and peel tests with a power law of 0.5. Inherently, these results mean that the mechanism of crack propagation in the contact mechanics tests is mirrored in the 90° peel test. This result was also found in similar measurements between PSA-LNs and PSATs [16, 17].

The difference in the data between NoAA and 10AA is the increase of threshold adhesion energy and the decrease of the critical crack speed. At rates lower than the critical crack speeds, there is little or no rate dependence for the adhesion energy. This is the threshold adhesion energy, by definition. The threshold adhesion energy, G_0, is about two to three times higher than the work of adhesion between PVNDC and PSA-LNs. This is undoubtedly due to the restructuring of the interface during contact. Above the critical crack speed, the rate dependence falls into a regime having a power law of $0.5 \sim 0.6$ for both JKR tests and peel tests. Maugis and Barquins [10] showed that the peel energy grew empirically as a power law with the crack velocity to the power 0.6 for the peeling of a polyurethane from a glass surface. These values agree fairly well with the theoretical prediction that the rate dependence of adhesion energy for viscoelastic materials should follow a 0.5 power law dependence [23]. Relatively high interfacial energy and low work of adhesion between release coatings and PSAs correlates well with the low peel adhesion.

CONCLUSIONS

Polycarbamate release coatings are poorly wetted by acrylic PSAs due to their lower surface energy. The low surface energy results from a surface dominated by methyl groups. A high interfacial energy and low work of adhesion leads to low peel adhesion, thus, "release". A purely van der Waals surface of fast relaxation time is desirable in order to achieve extremely low peel force [18].

The surface energy of the poly(vinyl N-alkyl carbamates) decreases with temperature. When in contact with acrylic PSA-LNs, the work of adhesion also decreases with temperature. However, the adhesion energy, measured in unloading, increases with the presence of acrylic acid in the PSA-LN and also increases with shorter alkyl side chains in the release coating. This effect is most likely due to interfacial restructuring while in contact, driven by acid-base interactions. The presence of AA in the PSA-LN seems to "repel" the non-polar, primarily hydrocarbon surface of the release coating, especially for the ordered PVNODC surface. However, under conditions of long contact time or higher temperature, the basic carbamate groups are able to rearrange themselves to form complexes with the acid groups in the PSA. The data in this paper and that by Kinning [2] indicate that the alkyl chain length necessary to screen the attraction between polar groups is between 10 and 16 methylene links. The results obtained in this work mirror earlier work in which the poor storage stability of acrylic acid containing PSATs on poly(vinyl N-alkyl carbamate) release coatings was ascribed to interfacial restructuring [2]. Our measurements provide more detailed insight into the phenomenon because of our ability to measure directly the surface energy and interfacial energy between solid polymers.

The result of contact mechanics-based measurements of adhesion energy as a function of crack propagation rate was compared with macroscopic peel strength measurements. Excellent correlation was obtained between these seemingly disparate measurements. Our results provide insight into the connectivity between interfacial interactions and macroscopic measurements of practical adhesion.

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