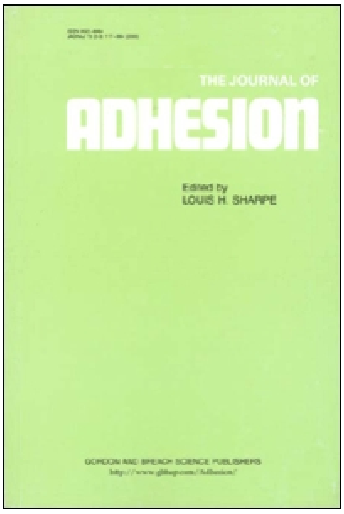

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An Investigation of the Cling of Thin Polymeric Films*

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The results of an investigation into the mechanisms and debonding energy associated with the cling between thin polymeric films and various substrates are presented in this paper. The thermodynamic work of adhesion as well as electrostatic attraction apparently play significant roles in the cling of a film to a substrate. Peel tests are conducted and strain energy release rates are determined which show different debonding energies for the various film-substrate combinations.

Keywords: Cling; polymeric films; adhesion; surface energetics; contact electrification; electrostatics; peel test; energy release rate

1 INTRODUCTION

Thin polymer films often exhibit weak adhesion when brought into contact with other materials. The primary objective of this work is to gain an understanding about the attraction or cling of these flexible polymeric films to rigid substrates. Cling between film and substrate can be analyzed in terms of a global energy balance approach [1], assigning the total debond energy associated with cling to various attractive mechanisms and factors. The attractive mechanisms associated with

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cling have been examined for other adhesive problems; in particular, a number of authors have investigated the role of van der Waals and electrostatic attractive forces [2,3,4]. This study examines the role of thermodynamic and electrostatic forces, energy dissipation due to plastic or viscoelastic deformation of the films, material polarity, material transfer, and surface roughness on the observed cling of thin polymeric films to various substrates.

Three polymer films were investigated in this study: plasticized poly(vinyl chloride), low density polyethylene, and plasticized poly(vinylidene chloride). The films are commercially available and are typically used for food packaging. The substrates examined were Pyrex glass, stainless steel, high and low density polyethylene, and polypropylene. The substrates were chosen to be representative of materials often wrapped with these polymer films.

Experiments were conducted to investigate the roles which the attractive mechanisms and factors play in the overall cling of a film to a substrate. Initially, material properties of the films were determined and surface analyses of the substrates were conducted. Contact angle measurements and peel tests were utilized to determine the thermodynamic contribution to the work of adhesion and the fracture energy associated with the separating film-substrate combinations. Conclusions are presented from the results of these investigations regarding the various adhesive mechanisms and the behavior of the various films.

2 PREVIOUS WORK

In considering the phenomenon of cling between two materials, it is useful to employ the classic conservation of energy principle. The amount of cling between two materials, defined as the amount of energy required to separate the two materials from each other, is quantified by utilizing an energy balance approach to examine how the debonding energy is expended. In addition, the contribution of the various attractive mechanisms to the total cling may also be investigated with this methodology. An energy balance equation for the peeling of a thin polymeric film from a substrate is given by

$$\delta W - \delta U = [W_a + \Psi_e + \Psi_p + \Psi_{ve}]\delta A \qquad (1)$$

where δW is the work input of the system and δU is the stored strain energy. The energy terms expended in the debonding of the film are on the right-hand side of the equation. This energy is associated with the thermodynamic work of adhesion (W_a), electrostatic attractive forces (Ψ_e), and dissipation associated with plastic (Ψ_p) and viscoelastic (Ψ_{ve}) deformation of the film for a differential area, δA.

2.1 Work of Adhesion (W_a)

The work of adhesion is a thermodynamic quantity that describes the work done in bringing together or separating two materials [5]. It is worth noting that van der Waals forces act over distances on the order of 10 nm or less [6]. Although the work associated with peel tests is typically two to three orders of magnitude higher than the thermodynamic work, it is believed that the thermodynamic work of adhesion plays a major role in the total work of separating two materials [3, 7]. Since the total energy required to peel polymer films without an adhesive from substrates is small, the work of adhesion may be an even greater contributor to overall adhesion than is typically found in other material systems.

2.2 Electrostatic Attraction (Ψ_e)

The role of electrostatic attraction in adhesion has been examined for many systems [2, 4, 8, 9, 10, 11]. It was quite obvious in preparing the test specimens for this study that electrostatic attractive and repulsive forces were present. The polymer films traveled across large distances to contact other surfaces due to electrostatic attractive forces which act over distances of more than 2 cm, orders of magnitude greater than the effective range of van der Waals forces. It is necessary to consider both how the electrostatic attractive forces develop and how they contribute to adhesion.

An electric field develops when a difference in net charge exists between two materials due to an imbalance between electrons or ions. The charge distribution associated with two materials will generally contribute towards both the attraction and repulsion of the two surfaces. An electric field which develops as a result of contact electrification will contribute only towards the attraction of the two surfaces since the charges are opposite [12].

Although contact electrification between insulators has not been widely studied, it has been suggested that the process is similar to contact electrification between metals and insulators [13]. When two materials are brought into contact, charge is transferred from one to the other. If the materials are separated, an electric field develops across the separation distance as shown in Figure 1. This electric field produces attractive forces between the materials which decrease as the separation distance increases since the materials are of finite dimension. It should be noted that, unlike metals, identical insulating materials may still transfer charge due to patches of varying charge present on the material surface and asymmetry inherently present when two materials are brought into contact [14].

The thickness of the film may also affect the amount of charge transferred since the charge may penetrate into the polymer. The depth of charge penetration is dependent on the material system and the type of contact. Based on the work of Fabish, Saltsburg and Hair [15], the films studied in this project were all of a thickness greater than charge is capable of penetrating under single contact conditions; therefore, the thickness of each of the various films does not limit the amount of charge transferred.

The electric field between two materials remains until the charge is discharged. This will occur when the charge finds a path to ground. For example, water could condense from the air and create a path to some grounded source. In this work, a path is created through ions in the air produced with an ion generator to neutralize the charge on the films and on the substrates prior to contact. It is also possible for the charge to break down in the air [16] or to be neutralized by electron tunneling [17].

The attractive and repulsive components of an electrostatic charge are observed to act over large distances. Although the breakdown voltage increases as the separation of two plates increases, the magnitude of the electric field is limited by the distance separating the two surfaces and the environment. The maximum sustainable electric field between two plates decreases as the separation distance between the two surfaces increases due to charge breakdown in air [16]. Because of charge breakdown and increased opportunities for dissipation of the charge [2], it is valuable to make a distinction between the effects of electrostatic attraction acting within an electrostatic process zone (located near the crack tip) and acting across the larger separation distances of the post-peel region as shown in Figure 1(c).

2.3 Plastic Deformation (Ψ_p)

It is also possible that the films may be undergoing plastic deformation. Since the films are thin (16–21 μm), it is extremely difficult to observe permanent deformation. A ramification of this in the energy balance approach is that a portion of the energy measured in debonding the film from the substrate could actually be dissipated in plastic deformation. This energy would have to be accounted for in the experimentally-measured strain energy release rate.

The dissipative component due to plastic deformation during peel tests has been primarily studied for 90° and 180° constant angle tests, assuming elastic-perfectly plastic film behavior [18, 19, 20, 21]. Making use of a non-dimensionalized peel force, η, defined by Kim and Kim [19], the following relation from Thouless and Jensen [20] is rewritten as

$$\eta = \frac{P^2}{\sigma_y^2 t^2}(3\sin^2\theta - \cos^2\theta) + \frac{P}{t}\left[\frac{6E}{\sigma_y^2}(1-\cos\theta) + \frac{2}{\sigma_y}|\cos\theta|\right] \tag{2}$$

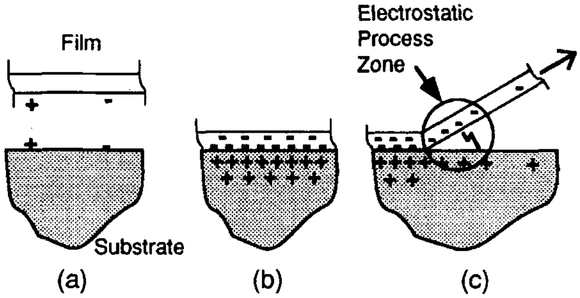

FIGURE 1 Electrostatic charge before contact of film to substrate (a), during contact (b), and during debonding (c).

where P refers to the load per unit width, σ_y is the yield strength of the film, t is the film thickness, E is the elastic modulus of the film, and θ is the peel angle. The non-dimensionalized peel force, η, is less than or equal to one when the film remains elastic and is greater than one when plastic deformation occurs.

2.4 Viscoelastic Effects (Ψ_{ve})

It is theoretically possible to attribute a portion of the debond energy to viscoelastic dissipation if a relationship between peel rate and measured strain energy release rate can be determined. Typically, this phenomenon is due to the time dependency associated with the disentangling of long polymer chains. In peel systems, the viscoelastic behavior of the film affects both the bending of the film as it debonds from the substrate and the stretching of the film in the post-peel region.

2.5 Factors Influencing Cling

In addition to the above mechanisms which contribute to adhesion, a number of factors also play a role in cling by influencing the attractive mechanisms. Both the role of surface roughness and the effect of material transfer have been considered in this work. A correlation between adhesion and the polarity of the various material systems is also suggested. Assessing the contributions of these factors to cling is difficult because they often influence more than one attractive mechanism.

Roughness may be thought of on a variety of scales. In this work, roughness was analyzed over areas of 400 μm^2. Although roughness may also play a role on larger scales, where differences in film rigidity may be significant, this aspect was not considered. When considering a perfectly smooth material, the contact area would equal the total measured area of the contacting materials. Unlike the case for liquids, increasing roughness decreases the contact area since the solid films are unable to conform to the variations in surface topography. Therefore, the energy required to debond a film is modified by the actual area of contact.

Increasing roughness, which leads to decreases in contact area, impacts the thermodynamic forces which are highly dependent on separation distance. Also, since liquids are used in the contact angle experiments which predict the role of thermodynamic forces in cling, the contact angle results must be carefully considered since the films and substrates are solids and contact between the two is not intimate. Roughness also influences electrostatic charging since the electrostatic charge is due primarily to contact electrification when the charge on the films and the substrates is neutralized before contact.

The effect of material transfer between film and substrate was also considered. This transfer results from bringing the two materials into contact. Earlier studies showed material transfer occurring between metal-polymer and polymer-polymer systems [22]. It was shown that the amount of material typically transferred exceeded that necessary to cause the observed contact charging by several orders of magnitude. Subsequent material contact was shown to produce minimal material transfer, although it did produce similar contact charging results. Therefore, it has been suggested that material transfer may only play a secondary role in contact charging [14]. Material transfer may potentially influence the work associated with van der Waals attraction.

The final factor to be considered in the cling of thin polymeric films is the effect of material polarity. The degree of polarity is expressed in terms of the polar contribution to the solubility parameter of each polymer, which is dependent on the side-groups of the polymer backbone as well as the plasticizer added to the film. This factor may influence the degree to which charge is transferred to the polymer during contact and retained by the polymer during separation. The material polarity is expected to impact the contribution to cling resulting from electrostatic attraction as well as the contribution resulting from thermodynamic forces.

3 EXPERIMENTAL PROCEDURES

Three polymeric films, three polymeric substrates, and two other substrates were considered in these experiments. All are commercially available and widely used. The films studied were polyethylene (PE film), plasticized poly(vinyl chloride) (PVC film), and plasticized poly(vinylidene chloride) (PVDC film). The three polymer substrates selected were low density polyethylene (LDPE), high density polyethylene (HDPE), and polypropylene (PP). A stainless steel and a Pyrex glass substrate were also included in the experimental system. To analyze the role of surface roughness, three HDPE substrates with varying roughness were utilized.

3.1 Surface Energetics and Material Properties

The contribution of the thermodynamic work of adhesion to cling was investigated by using contact angle measurements to analyze surface free energies of the various films and substrates. The contact angle of a 5μL droplet of three probe liquids (water, bromo-napthalene and formamide) was measured with a goniometer. With knowledge of the surface free energies of the probe liquids, the Young-Dupré equation

$$W_a = \gamma_{lv}(1 + \cos\varphi) \tag{3}$$

was used to determine the work of adhesion, W_a, for each liquid-solid combination, where γ_{lv} refers to the surface free energy at the liquid-vapor interface and φ is the measured contact angle. The spreading pressure is assumed to be negligible. The geometric mean equation

$$W_a = 2[(\gamma_{lv}^d \gamma_s^d)^{1/2} + (\gamma_{lv}^p \gamma_s^p)^{1/2}] \tag{4}$$

was used to determine the dispersive and polar components of the surface energy, where the superscripts d and p refer to dispersive and polar, while the subscript s refers to the solid surface. This is done by rearranging the geometric mean equation into the following form

$$\frac{W_a}{2(\gamma_{lv}^d)^{1/2}} = (\gamma_s^d)^{1/2} + (\gamma_s^p)^{1/2}\left(\frac{\gamma_{lv}^p}{\gamma_{lv}^d}\right)^{1/2} \tag{5}$$

and plotting the left-hand side of Eq. (5) as a function of $(\gamma_{lv}^p \gamma_{lv}^d)^{1/2}$. The data points show a linear relationship and the slope of the line is taken as the square root of the polar component of the solid surface free energy and the intercept as the square root of the dispersive component of the surface free energy [23].

The resulting values of the dispersive and polar components of the surface free energy were combined in the following manner to determine the surface free energy of the material

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{6}$$

The total thermodynamic work of adhesion, W_a, between two materials is then given by the geometric mean (Eq. (4)) using the surface free energy values of the film and substrate. It is important to consider that liquid probes were used in determining surface free energies experimentally while, in the final system, two solids were placed into contact. Therefore, while liquids have the ability to come into intimate contact with the solid surface, in cases of solid-solid contact, surface roughness plays a critical role in the final contribution of thermodynamic forces to adhesion. The actual thermodynamic work of adhesion is then expected to be less than the predicted value, especially for increasing surface roughness.

The stress-strain behavior of the films was investigated by testing ASTM D-3588 uniaxial dogbone specimens at ambient temperatures. The loading rate was 25 mm per minute. Each film was tested a minimum of three times in the machine and transverse directions using a Minimat miniature test frame.

3.2 Peel Testing

A measure of the cling associated with a particular film-substrate combination is the energy required to debond the film from the substrate. From the results of the peel tests, the debonding energy is expressed in terms of a critical strain energy release rate, G_c, which is defined as [21]

$$G_c = \frac{dU_{\text{ext}}}{bda} - \frac{dU_s}{bda} - \frac{dU_d}{bda} - \frac{dU_k}{bda} \tag{7}$$

where U_{ext} is the external work done, U_s is the strain energy, U_d is the dissipated energy, U_k is the kinetic energy, and bda is the fracture area created when the film debonds a length da for a width b. By assuming the strain energy, the dissipated energy, and the kinetic energy to be negligible, it is possible to rewrite Eq. (7) as

$$G_c = P(1 - \cos\theta) \tag{8}$$

where P is the load per unit width and θ is the angle at which peel occurs [24]. This equation is valid when the material behaves in a linear elastic manner, the substrate is rigid, and the geometry of the region around the crack tip does not change as the film peels. In determining a critical strain energy release rate, both constant angle and constant load experiments were conducted. For the former, a critical debonding load was measured; for the latter, a critical angle at debond was measured.

A constant 90° angle peel testing platform was constructed to be used in an Instron material testing machine as shown schematically in Figure 2(a). These tests were performed under ambient laboratory conditions (60 percent relative humidity and 20°C) at rates which ranged from 0.1 mm/min to 500 mm/min. The load required to cause debonding of the film was used in calculating G_c.

A variable angle peel test was also developed for this study, as shown in Figure 2(b). A 4 g mass was attached to the base of the film when the film and substrate were completely vertical (this corresponds to a constant load of 39.4 mN). By using a stirrer motor attached to a series of worm gears, the substrate and film were rotated at an angular rate of 0.7° per second until debonding occurred. The angle at which

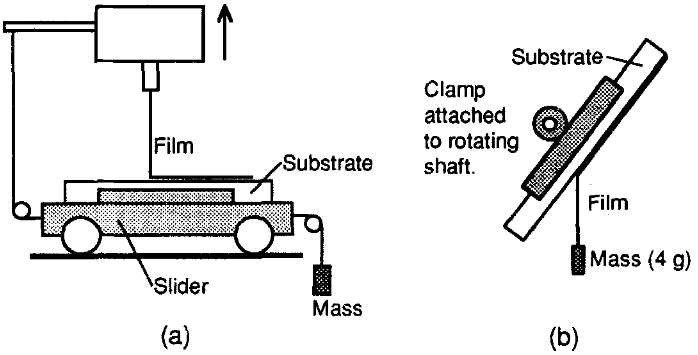

FIGURE 2 Configurations of the constant 90° angle peel test (a) and the variable angle peel test (b).

failure occurred was used in determining G_c. The variable angle peel test is compact and the experiments were conducted in a temperature and humidity controlled chamber, normally at 25 percent relative humidity and 30°C. Tests were conducted at up to 60 percent relative humidity and showed no difference in measured debonding energies.

Before each peel test, the substrates (50 mm wide and 150 mm long) were cleaned with methanol and passed over a volume static eliminator (Chapman VSE 3000) to remove any residual electric charge. The static eliminator produces a balanced mixture of positive and negative ions so that the substrate isolated from ground will not accumulate any net potential greater than 0 ± 5 volts. The film was likewise passed over the static eliminator before it was applied to the substrate. Any air bubbles in the interface were smoothed out before the load was applied in both test procedures by lightly rubbing the film.

As quickly as possible after the film had debonded from the substrate (within 1–3 seconds) a hand-held electrostatic field meter (Monroe Electronics Stat-Arc Model 255) was used to measure the surface charge density on both the film and the substrate. The residual charge measurement gives an indication about the electric field created between two surfaces as a result of contact electrification, although some charge may well have already dissipated or discharged after debonding occurred. Therefore, the residual charge may be much different from the charge induced by contact electrification.

It is critical to be able to compare strain energy release rates determined for the various tests where peel angles range from less than 20° to greater than 100°. To ensure that the mode mix between mode I and mode II fracture remains nearly identical, the phase angle (Ψ), defined as

$$\Psi = \tan^{-1}\left[\frac{\sqrt{\sin^2\theta + 2(1-\cos\theta)/\varepsilon_\infty} + \tan\omega\cos\theta}{-\tan\omega\sqrt{\sin^2\theta + 2(1-\cos\theta)/\varepsilon_\infty} + \cos\theta}\right] \tag{9}$$

was determined for each test, where θ is the peel angle, ω is the angular quantity defined by Suo and Hutchinson [25], and ε_∞ is the applied strain

$$\varepsilon_\infty = \frac{P}{Et} \tag{10}$$

For this work, ε_{∞} was approximately equal to zero. The phase angle is a function of the load, the material properties of both the film and the substrate, the film thickness, and the peel angle. Over the range of peel tests conducted, the phase angle varied between $-34°$ and $-38°$. Since this variation is small, it is acceptable to make comparisons between the experimentally-determined strain energy release rates for the different film-substrate systems.

3.3 Investigating Electrostatic Attraction

To investigate the effect of electrostatic attractive forces acting over the post-peel region, three peel tests were conducted with varying peel angles and bond widths. Varying the bond width was done to highlight the edge effects associated with long-range forces. From fundamental physics, the attraction due to an electric field between two infinite surfaces is independent of the separation distance of those surfaces. Since this is not the case for finite surfaces, changing the surface area is expected to change the attraction between the two surfaces. Different peel angles lead to different separation distances between the substrate and the film as the film is peeling. Therefore, changing the peel angle is also expected to change the attraction between the surfaces. Finally, the free-hanging end of the film that had already debonded during the variable angle peel test was also observed to see if any curvature toward the substrate occurred, an indication of significant long-range attractive forces. As will be mentioned later, no such effects were observed.

To analyse charge transfer, the residual charge on both the film and the substrate was measured after debonding. Since the charge was normally removed before the materials were brought into contact, the remaining charge was due primarily to contact electrification but was mitigated during the peel process. The sensitivity limit on the electrostatic field meter is 10 V/in. The amount of charge transferred was categorized into three general ranges: low charge transfer (less than 0.5 kV/in), intermediate charge transfer (2–5 kV/in), and significant charge transfer (in excess of 5 kV/in). Two peel tests were conducted with films which were not neutralized before contact with the substrate. This procedure gives insight into the difference between the charge due to contact electrification (which produces attractive forces) and the charge inherently present on the film (which produces both attractive and repulsive forces).

3.4 Surface Roughness and Material Transfer

Surface roughness was analyzed with an atomic force microscope (Digital Instruments NanoScope III Scanning Probe Microscope) and the topology of sections of the surface area (20 μm by 20 μm) were recorded. The standard deviation of the vertical deflection of the surface with respect to a center plane was calculated to establish a hierarchy of surface roughness for each of the substrates. All of the surfaces were used as received, with the exception of the roughened HDPE, which was milled.

To investigate the occurrence of material transfer, X-ray photoelectron spectroscopy (XPS) was utilized to make chemical surface characterization measurements. Experiments were conducted by placing and rubbing the films over both low and high energy substrates. By analyzing the spectra for the individual elements on clean and rubbed surfaces, it is possible to determine the amount and type of material transferred.

4 EXPERIMENTAL RESULTS

The results from the experiments investigating the factors influencing cling are presented first so that their influence in surface energy studies and peel tests will be better understood. The surface roughness experiments show that the glass, stainless steel, LDPE and HDPE-smooth substrates are the smoothest of the materials. The PP substrate is somewhat rougher and the HDPE-intermediate even rougher still. The HDPE-rough substrate is the roughest of all the materials. The standard deviation values, R_q, for the various substrates are shown in Table I.

Material transfer results obtained from XPS analysis shows that a significant change in the surface oxygen content occurs on the polymeric substrates after rubbing with the PVC films. It was also observed that the PVC films showed an extremely small transfer of hydrocarbon material to the high surface energy substrates.

TABLE I Summary of surface roughness results

Substrate	R_q *(nm)*
Glass	23
Steel	28
LDPE	34
HDPE-smooth	36
PP	51
HDPE-intermediate	52
HDPE-rough	130

An estimate of material polarity was used to rank the polymeric films and substrates by predicting the polar component of the solubility parameter based on the polymer component group contributions [26]. The estimates of polarity for the various polymers suggest that the LDPE, HDPE and PP substrates show no contribution from a polar component to the solubility parameter. Therefore, these polymer substrates were classified as exhibiting low polarity. This result was identical for the PE film. Due to the chlorine content of the PVC and PVDC polymer chains and because of the added plasticizer in these materials, these two films exhibited a high degree of polarity.

The results from the contact angle experiments determining the contribution of the thermodynamic work of adhesion to cling are presented in Tables II and III. Contact angle experiments were conducted four times on each material. Table II shows the data from the contact angle measurements for the polar and dispersive components of the surface free energy of the polymer substrates and films as well as the surface free energy values of the three probe liquids [7]. Although experiments were conducted for each of the film-substrate combinations, the work of adhesion values were found to be nearly identical for the three films for each of the film-substrate combinations. Therefore, the W_a values are shown in Table III for each of the substrates.

The tensile test results for the PVC and PE films show initial elastic regions followed by large plastic regions, with ultimate failure at strains greater than 100 percent, as shown in Figure 3. The PVDC films exhibited more brittle behavior, fracturing at less than 20 percent strain. By comparing the stress-strain curves obtained from both machine and transverse directions, the residual orientation present in the films from processing was apparent only in the plastic region of stress-strain behavior for the PE film. A summary of the elastic moduli and

TABLE II Experimentally-determined values of surface free energy for each material

	Material	$\gamma (mJ/m^2)$	γ^d (mJ/m^2)	γ^p (mJ/m^2)
Substrates	LDPE	38.0	35.1	2.9
	PP	38.9	34.7	4.2
	HDPE-smooth	35.4	35.1	0.3
	HDPE-intermediate	37.8	37.0	0.8
	HDPE-rough	38.8	35.8	3.0
Films	PVC	48.6	42.7	5.9
	PE	49.9	40.8	9.1
	PVDC	48.3	44.5	3.8
Liquids	Water	(72.2)	(22.0)	(50.2)
	Formamide	(58.3)	(32.3)	(26.0)
	Bromo-Napthalene	(44.6)	(44.6)	(0.0)

TABLE III Experimentally determined thermodynamic work of adhesion values for each substrate-film combination. Since the value of W_a was approximately independent of the film material for each case, the results are shown in terms of the substrate material only

Substrate	W_a (mJ/m^2)
LDPE	87
PP	88
HDPE-smooth	80
HDPE-intermediate	84
HDPE-rough	87
glass	180[†]
steel	250[†]

[†] The work of adhesion values for the glass and steel are approximate estimates and an organic layer was assumed to be present after cleaning with methanol.

yield strengths for each of the three films along with an average film thickness are presented in Table IV. Because of the thickness of the films, it is quite difficult to observe permanent deformation of the films, indicative of plastic behavior. With the results shown in Table IV, the non-dimensionalized peel force (Eq. (2)) was calculated for each of the test systems. The results from this analysis suggest that plastic behavior may be associated with the variable angle peeling of the PVC film from the LDPE substrates.

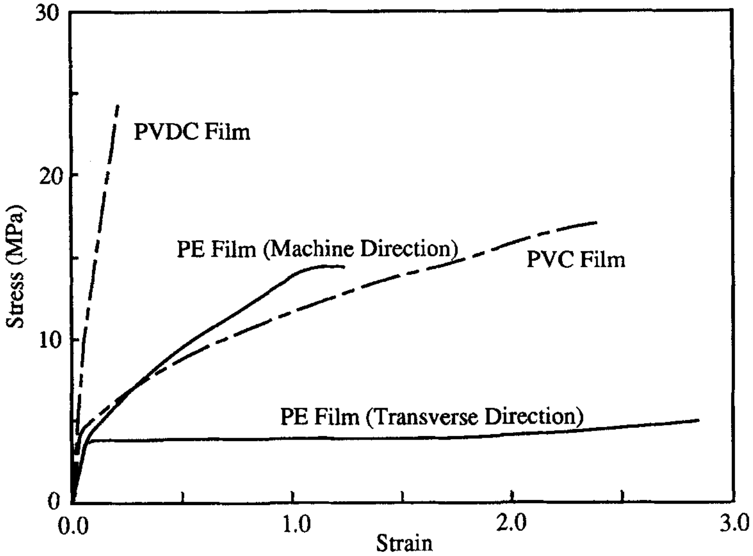

FIGURE 3 Stress-strain curves of PVC, PE (machine and transverse directions), and PVDC films. There was no distinction in the machine and transverse directions for the PVC and PVDC films.

TABLE IV Material properties and thickness of polymeric films

Films	*Elastic Modulus (MPa)*	*Yield Strength (MPa)*	*Thickness (μm)*
PVC	120	4.6	19
PE	80	3.5	16
PVDC	210	9.0	21

As was previously discussed, the amount of charge present on the film and substrate was measured after each test. In all cases where intermediate to significant charge transfer occurred, the film retained a negative charge while the substrate had a lower positive charge. Charge transfer involving PE films was always classified as low. Due to the limited sensitivity of the equipment, it was often difficult even to measure a surface charge density in these cases. The PVDC films most often showed intermediate charge transfer and occasional significant charge transfer. The PVC films showed both intermediate and significant charge transfer. There was no correlation between substrate material and charge transfer, other than that the steel substrate displayed very low charge density. This is due to the conductive nature of the material.

The results from the peel tests for the various film-substrate systems shown Figures 4 and 5 are given in terms of the critical strain energy release rate, G_c, with units of mJ/m^2. The error bars shown represent standard error. The results shown in Figure 4 show the values of G_c for each of the three films on the five substrates determined from the variable angle peel test. The substrates are shown in order of roughness, from smoothest to roughest. (The HDPE substrate used here is the smoothest of the three HDPE substrates).

The effect of varying surface roughness is shown in Figure 5. The values are shown for G_c for the three films debonding from the surfaces of HDPE of various roughness during the variable angle peel test. It should also be noted that the charge transfer dropped significantly for the case of the HDPE-rough substrate.

In the variable angle peel tests, it was not possible to control the rate of peel, but a few observations of rate are warranted. For the rough HDPE substrate and for the steel substrate, the films remained

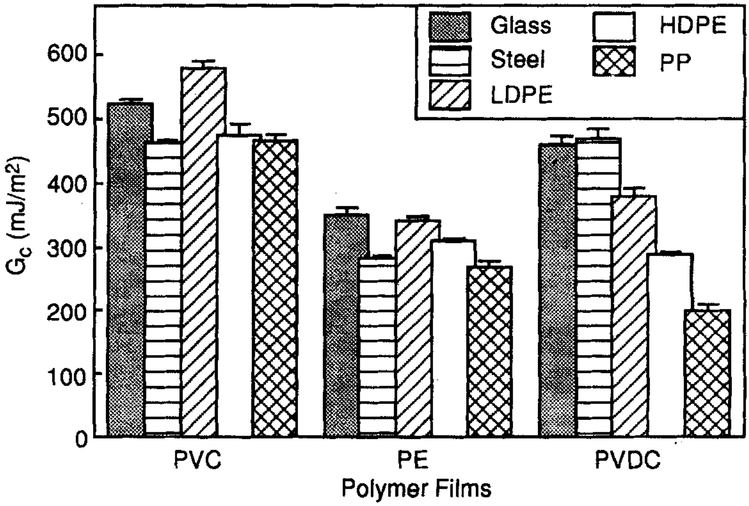

FIGURE 4 Critical strain energy release rates for the various film-substrate combinations.

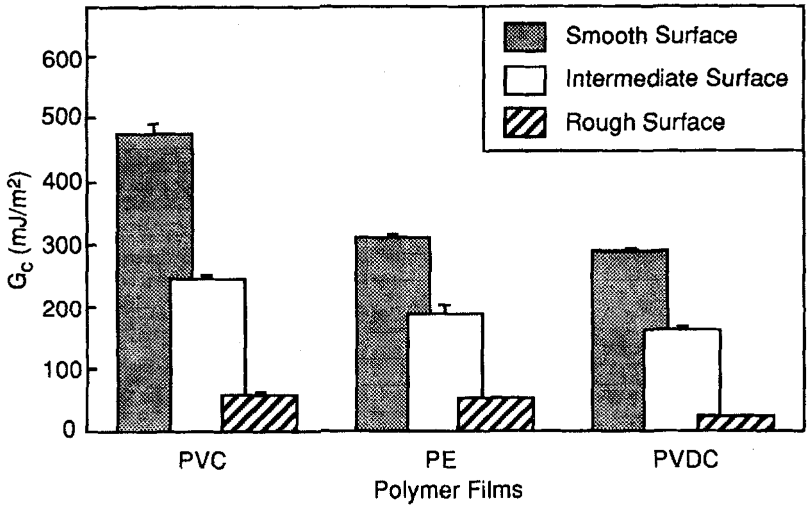

FIGURE 5 Critical strain energy release rates for the various films on the three HDPE surfaces of varying roughness.

attached until the critical angle was reached and debonding progressed very quickly (greater than 50 mm/s). For the other cases, a statistical analysis of peel rate showed no discernible correlation between peel rate and strain energy release rate for any of the cases. For these film-substrate systems, it was typical for peel rates to vary between 1 mm/s and 20 mm/s.

The tests conducted to highlight the effects of long-range electrostatic attractive forces showed no difference in the measured strain energy release rates. Although substrate widths were varied (between 50 and 100 mm) and peel angle was varied (65°, 90°, and 104°) no changes in debonding energy were observed. In conjunction with the observation of the free-hanging end of the film, it is possible to conclude that long-range attractive forces do not play an observable role in the cling of these films to these substrates and that the measured cling is due solely to short-range attractive forces, including short-range electrostatic attractive forces.

Tests were also conducted with PVC film and smooth and rough HDPE substrates by not removing the charge present on the film before contact. For the case of the smooth substrate, there was no observable difference in debonding energy when comparing the results with the case where the charge on the film was neutralized. The film, with its inherent charge, placed on the roughened substrate showed an approximately 50 percent drop in debonding energy when compared with the neutralized film case. This is due to the mixed attractive and repulsive charge present on the film and the decreased opportunity for contact charging resulting from the roughened surface.

The results from the 90° peel tests conducted to study rate effects on measured G_c are shown in Figure 6. These results have only been obtained for the three films attached to the HDPE-smooth substrate. The figure shows data points of peel rate *versus* measured critical strain energy release rate for the three polymer films. The error bars represent plus and minus one standard deviation of the experimental results (three to ten tests were conducted for each film and rate combination).

5 DISCUSSION

The greatest variation in strain energy release rates caused by changing substrates was due simply to increasing surface roughness. Even though the roughest substrate appears smooth to the naked eye, the impact of minor surface variations cannot be overstated. This is most likely a result of the importance that surface roughness has on multiple mechanisms affecting cling. Although the contact angle measurements demonstrated little change in W_a for increasing roughness from smooth to rough HDPE, the peel tests showed an average decrease in G_c of approximately 90 percent from smooth to rough HDPE substrates. Due to imperfect wetting, reduced contributions from both van der Waals attractive forces and contact electrification are expected.

An exact understanding of the contribution to cling from thermodynamic forces is difficult since surface roughness leads to major discrepancies between the predicted work of adhesion from contact angle studies and the actual debonding energy as measured by peel tests. In fact, the predicted work of adhesion resulting from surface energy studies is greater than the measured total work of adhesion for the various films attached to the rough HDPE substrates. In order to limit the effect of surface roughness in this conclusion, the studies involving the four smoothest substrates are considered (LDPE, smooth HDPE, glass, and steel). By considering the predicted work of adhesion values determined from contact angle studies as maximum limits on the contribution to cling due to van der Waals forces, it is possible to attribute the remaining debonding energy to a combination of electrostatic attraction and plastic and viscoelastic dissipation. Table V shows the approximate contribution to cling due to these other mechanisms as a percentage of the total debonding energy for the polar films (PVC and PVDC) films, the non-polar film (PE), and the four smoothest substrates.

Since varying the peel angle and the substrate width of a number of tests involving the PVC film-HDPE substrate system had no noticeable effect on debonding energy, long-range attractive forces are believed to have no influence on cling. As was mentioned previously, plastic dissipation may only play a role in debonding the PVC film from the LDPE substrate. Therefore, electrostatic attractive forces acting within the process zone and viscoelastic dissipation play a significant role in the adhesion process. From Table V, this combined contribution to cling between the various substrates and the polar films (PVC and PVDC) is similar for each of the substrates and higher than the contribution from the non-polar film (PE) for the glass and steel substrates.

It is also interesting to note that, although the PVC and PVDC films show relatively similar contributions to cling due to electrostatic attraction and viscoelastic effects, the PVC and PE films exhibit similar patterns of behavior when comparing the experimentally-determined strain energy release rates. The values of G_c for the PVC and PE films for each

TABLE V Approximate percentage of contribution to cling due to a combination of electrostatic attraction and plastic and viscoelastic dissipation

Substrates	*Polar Films (PVC and PVDC)*	*Non-Polar Film (PE)*
Polymer (LDPE, HDPE)	~80%	~75%
Pyrex Glass	~65%	~50%
Steel	~45%	~10%

of the various substrates are all within 100 mJ/m^2 of one another. The G_c values for the PVDC film range approximately between 200–500 mJ/m^2.

In addition to information from Ref. 14, all of the films have been observed to cause sparking when the film has been repeatedly applied to glass substrates. Electrical breakdown was also evident by hearing static from an AM radio during peel. Therefore, although each of the polymers has the potential to carry significant charge, it is possible that the approximately 50 percent higher values of G_c associated with PVC when compared with PE may be attributed to increased charge transfer during contact, increased charge retention during peel, and/or the highly polar nature of PVC.

The three films also show rate dependency for measured G_c. As is shown in Figure 6, higher peel rates are associated with higher values of G_c, which is typical for many bonded systems. Since the data are shown on log-log scales, the magnitude of the range of debond rates and G_c is quite large, suggesting that time dependency may play a major role. Possible sources of time dependency include the viscoelastic behavior of the film and the potential for time-dependent electrostatic discharge. Additional work must be done before suggesting

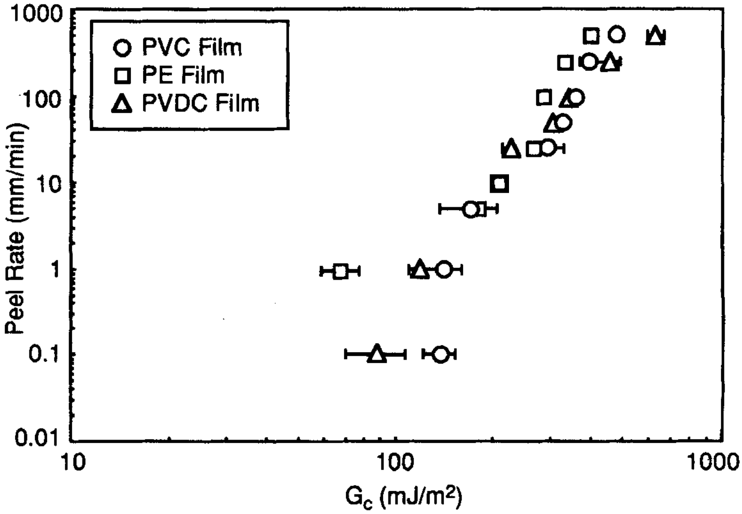

FIGURE 6 Pell rate *versus* G_c for the three films attached to the HDPE-smooth substrate.

more definite conclusions about the source of time-dependent effects, whether viscoelastic or electrostatic, on the system.

6 SUMMARY

Experimentally-determined values of energy associated with the work of adhesion, through contact angle tests, and the total debonding energy, through peel tests, were conducted. Surface roughness was a dominant factor influencing cling between film and substrate, due primarily to its impact on both wetting and contact electrification. Under the test conditions of this study, the poly(vinyl chloride) film exhibited superior cling to the substrates studied. In addition to the work of adhesion, both electrostatic and viscoelastic mechanisms play some role in the cling of these polymeric films to the various substrates. Since the calculated work of adhesion values was primarily dependent on the substrate material and not on the film, the superior cling of the poly(vinyl chloride) film is likely due to the effects of electrostatic attraction and/or the viscoelastic behavior of the film.

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References

[1] Farris, R. J. and Goldfarb, J. L., *J. Adh. Sci. Technol.* **7**(8), 853–868 (1993).
[2] Lee, S., Jensen, L. C., Langford, S. C. and Dickinson, J. T., *J. Adh. Sci. Technol.* **9**(1), 1–26 (1995).
[3] Mangipudi, V., Tirrell, M. and Pocius, A. V., *J. Adh. Sci. Technol.* **8**(11), 1251–1270 (1994).
[4] VanHarrach, H. G. and Chapman, B. N., *Thin Solid Films* **13**, 157–161 (1972).
[5] Israelachvili, J. N., *J. Vac. Sci. Technol. A* **10**(5), 2961–2967 (1991).
[6] Israelachvili, J. N., *Intermolecular and Surface Forces* (Academic Press, London, 1985).
[7] Andrews, E. H. and Kinloch, A. J., *Proc. R. Soc. Lond. A* **332**, 385–399 (1973).
[8] Dickinson, J. T., Jensen, L. C., Lee, S., Scudiero, L. and Langford, S. C., *J. Adh. Sci. Technol.* **8**(11), 1285–1309 (1994).
[9] Scudiero, L., Dickinson, J. T., Jensen, L. C. and Langford, S. C., *J. Adh. Sci. Technol.* **9**(1), 27–45 (1995).

[10] Roberts, A. D., *J. Phys. D: Appl. Phys.* **10**, 1801–1819 (1977).

[11] Horn, R. G. and Smith, D. T., *Science* **256**, 362–364 (1992).

[12] Hays, D. A., in *Fundamentals of Adhesion,* Lee, L. H., Ed. (Plenum Press, New York, 1991).

[13] Duke, C. B. and Fabish, T. J., *J. Appl. Phys.* **49**(1), 315–321 (1978).

[14] Lowell, J. and Rose-Innes, A. C., *Advances in Physics* **29**(6), 947–1023 (1980).

[15] Fabish, T. J., Saltsburg, H. M. and Hair, M. L., *J. Appl. Physics* **47**, 940–948 (1976).

[16] Cobine, J. D., *Gaseous Conductors* (McGraw-Hill Book Company, New York, 1941).

[17] Stokes, H. T., *Solid State Physics* (Allyn & Bacon, Newton, MA, 1987).

[18] Gent, A. N. and Hamed, G. R., *J. Appl. Polymer Sci.* **21**, 2817–2831 (1977).

[19] Kim, K. S. and Kim, J., *J. Eng. Mat. Technol.* **110**, 266–273 (1988).

[20] Thouless, M. D. and Jensen, H. M., *J. Adhesion* **38**, 185–197 (1992).

[21] Williams, J. G., *J. Adhesion* **41**, 225–239 (1993).

[22] Salaneck, W. R., Paton, A. and Clark, D. T., *J. Appl. Physics* **47**(1), 144–147 (1976).

[23] Berger, E. J., *J. Adh. Sci. Technol.* **4**(5), 373–391 (1990).

[24] Anderson, G. P., Bennett, S. J. and DeVries, K. L., *Analysis and Testing of Adhesive Bonds* (Academic Press, New York, 1977).

[25] Suo, Z. and Hutchinson, J. W., *Int. J. Fracture* **43**, 1–18 (1990).

[26] VanKrevelen, D. W., *Properties of Polymers: Their Estimation and Correlation with Chemical Structures* (Elsevier Scientific Publishing Company, Amsterdam, 1976).