AN INVESTIGATION OF ADHESION MECHANISMS

by

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ABSTRACT

Various peel tests and zeta potential measurements were performed on untreated and modified polyethylene/butyl rubber adhesive systems to investigate the basic mechanisms of adhesion. The polyethylene was modified through various treatments such as glow discharge, doping, and quasi-chemical treatment.

The results showed that peel strength and zeta potential both varied from one polyethylene to another. In addition, the experimental work has shown that the various theories of adhesion in the literature can neither account for the increase in peel strength of untreated polyethylene as a function of bonding temperature nor for the increase due to the modifications. However, it does suggest that electron interaction may explain the results from the zeta potential measurements.

Conclusions drawn from the results of the experimental work include the vital role of electron interaction underlying the mechanism of adhesion. To promote adhesion, the surfaces of the bonding materials must be such that the surface charges are similar in both sign and magnitude.

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NOMENCLATURE

A	area
A_1, B_1	arbitrary constants
B_k	magnetic force vector
D	diffusion coefficient
D_j	electric derived vector
D_o	characteristic material diffusion constant
E	Young's modulus
E_a	applied potential
E_j	electric force vector
E_A	activation energy
EM	electrophoretic mobility
F	force
$F\ (\sigma_1, \sigma_2, \sigma_3)$	function of principal stresses
G	shear modulus
G_F	Gibbs free energy
G_F^m	Gibbs free energy of mixing
G_F^{system}	Gibbs free energy of a system
H_k	magnetic derived vector
H^m	enthalpy of mixing
K	stress intensity factor
K_c	critical stress intensity factor
P	pressure
R	gas constant

S	entropy
S^m	entropy of mixing
T	temperature
U	total energy
V	volume
W	work
W_{AD}	work of adhesion
c	concentration
d	distance between condenser plates
e	strain
$\dot{e}$	strain rate
e_{1c}, e_{2c}	critical strains
e_o	charge
k	Boltzmann's constant
k_1	reaction rate
ℓ	length of crack
m	mass
n	amount of species
n_-, n_+	number of ions
q	heat
t	time
v_1	velocity
x	coordinate axis
z	valence of ions
γ	surface energy

γ_c	critical surface energy
γ_l	surface energy of liquid
γ_{ls}	surface energy of liquid-solid interface
γ_s	surface energy of solid
γ_F	fracture surface energy
γ^d	dispersion component of the surface energy
γ^{dd}	dipole-dipole component of the surface energy (polar) component
γ^{di}	dipole-induced dipole component of the surface energy (polar) component
γ^h	hydrogen component of the surface energy (polar) component
γ^p	polar component of the surface energy
ε	dielectric constant
ε_1	stored energy
ζ	zeta potential
η	viscosity
η_o	characteristic material viscosity
θ	contact angle
μ	chemical potential
ρ	charge density
σ	stress
$\sigma_1, \sigma_2, \sigma_3$	principal stresses
$\sigma_{tensile}$	uniaxial tensile stress
σ_A	applied stress

σ_0	surface charge density
τ_{oct}	octahedral shear stress
ψ	potential
ψ_0	surface potential

I. INTRODUCTION

Adhesion, the bonding at an interface of two different materials, which is the subject matter of this thesis, has been known and utilized since early man. For thousands of years, natural adhesives such as animal, fish, and blood glues were used to hold materials together. There is considerable archeological evidence, derived from burial artifacts, that pitches and other natural resins were utilized by early man to fasten arrows and spearheads to shafts. The Egyptians apparently understood the general phenomenon as demonstrated in the veneers applied to burial coffins.

Today, there are many synthetic polymeric adhesives which have greatly improved the adhesive joint strength over that of early, natural adhesives. These adhesives can be divided into two major groupings - structural and nonstructural. Structural adhesives are used for holding materials together and resisting high loads. Examples of these include thermosetting adhesives such as epoxies, polyesters, and polyurethane. Nonstructural adhesives are not required to support substantial loads but merely hold materials in place. Thermoplastic adhesives such as hot-melt adhesives are examples of nonstructural adhesives. Elastomeric-type adhesives such as latex cement belong to the nonstructural group.

Sir Isaac Newton wrote in his Opticks two and one-half centuries ago: "There are agents in nature able to make the particles of joints stick together by very strong attractions and it is the business of experimental philosophy to find them out." It has been only recently that any real progress has been made in understanding the forces operating in adhesion. Since the advent of synthetic polymer systems such as phenolic resins for adhesives, adhesion has become an area of intense scientific study. It has proved to be a catalyst for adhesive development. In the past two decades, much progress has been made in the science of adhesion due to the explosive growth in the production and application of polymers, thus improving the understanding of adhesive requirements. Several important conferences concerning adhesion and the literature indicate a considerable advancement in the sophistication of the approaches to adhesion. The study of adhesion encompasses a large number of disciplines such as chemistry and physics of surfaces, mechanics, etc.

Adhesion or nonadhesion is important in several areas such as friction and wear, fabrication of laminates and composites, application of paints and other type of coatings, development of biocompatible materials, and production of adhesive tapes of all varieties. The study of adhesives is also included with adhesion because materials, which will not normally adhere to each other, may do so with a proper adhesive. Although there are many areas where adhesion and adhesives are important, there still exists a mystery as to why materials do or do not adhere to each other. This has lead to the various theories of adhesion found in the literature.

The purpose of this research was to investigate the adhesion mechanisms and develop a fundamental understanding of adhesion to establish the proper conditions required for adhesion or nonadhesion as one desires. Since the research was performed in cooperation with the Kendall Company in Lexington, Massachusetts, the work was done with the Kendall adhesive tape (#980-20 IMEK) and its components. Specifically, the experimental work involved improvement of adhesion between the polyethylene backing and butyl rubber adhesive by various surface treatments. However, the approach and results are of general nature.

This thesis will present the background of the problem, basic mechanisms and theories of adhesion, suggestion for a more basic mechanism of adhesion, and experimental work and results that verify the suggestion.

II. BACKGROUND

The interest in adhesion was generated as part of the work in progress, for the Kendall Company, to develop a new process for the production of adhesive tape. It was done as part of the MIT-Industry Polymer Processing Program. The following is a brief background of the project leading to that interest.

The conventional method of producing adhesive tape is by the calendering process. Calendering is a continuous sheet forming process, from molten polymers, between two or more cylinders. The method presently used by the Kendall Company for the production of adhesive tape* consists of three calender rolls arranged vertically as shown in Fig. 1. The polymer backing sheet is formed from molten polyethylene, which is fed between the bottom and middle rolls. Before the polyethylene cools down, the preheated adhesive and polyethylene sheets are fed between the middle and top rolls to form a bonded tape. The finished product is then cooled and wound on a take-up roll.

The calendering process has several important advantageous features in the production of adhesive tape. The process provides a mechanism for sheet formation of the molten polymer and adhesive. It also permits adhesion of the formed sheets under pressure and at a relatively high temperature. In addition, the process induces uniaxial orientation to the polyethylene sheet thus incorporating high strength to the adhesive tape in the calendered direction. There are several disadvantages of the calendering process, however. The capital investment is very high. Cracking of the rolls, which occurs occasionally, can halt or limit production. Although cal-

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*J.F. Morris, The Kendall Company, "Method of Making Fused Film Laminates," U.S. Patent No. 2,879,547, March 31, 1959.

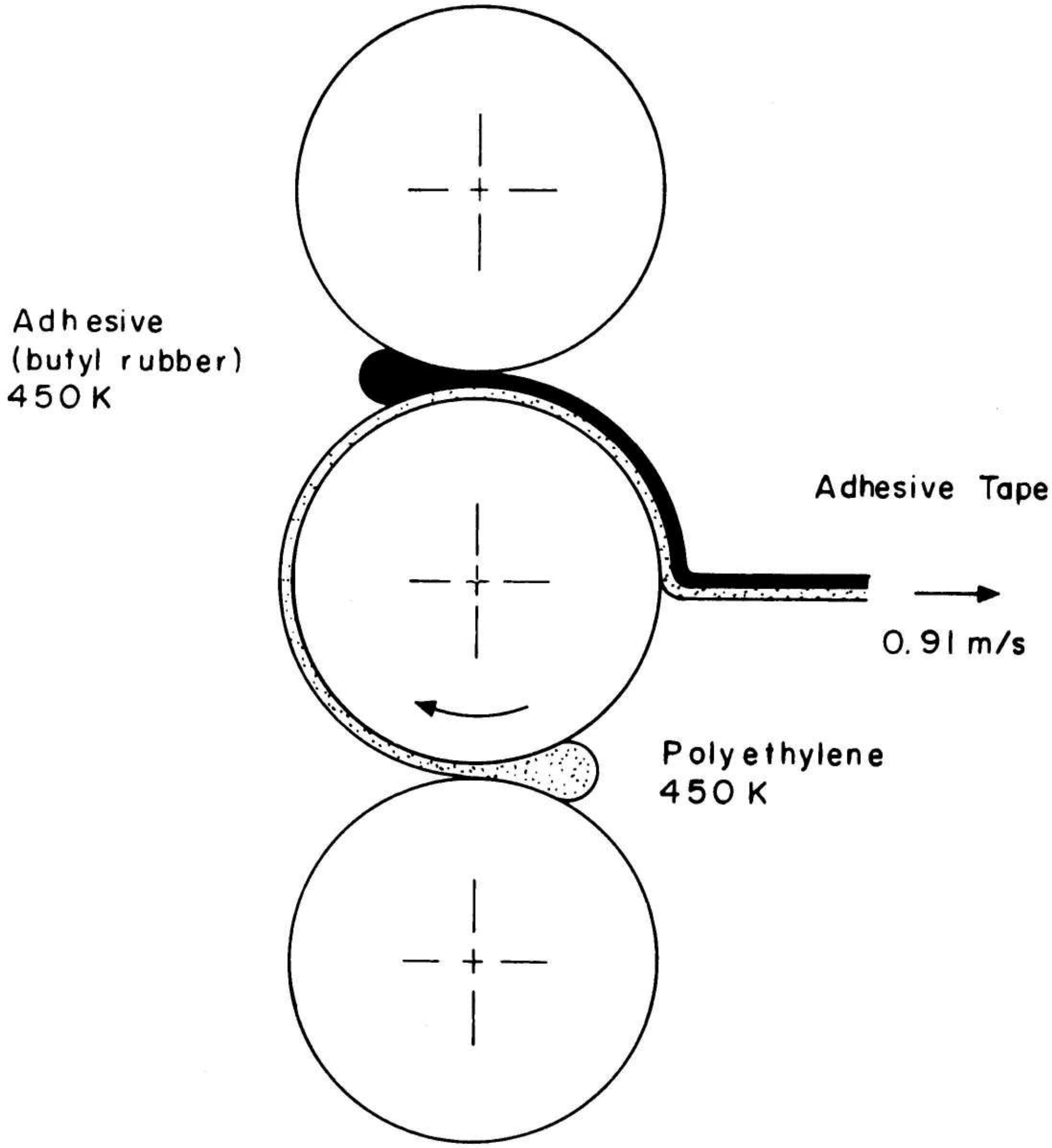

Fig. 1. Schematic diagram of calendering.

endering is a compact process for making adhesive tape, it is difficult to control the dimensions, orientation, bond strength, etc., of the tape independently.

The overall objective of the work was to investigate the feasibility of an alternative method of producing adhesive tape, which will have all the advantages of the calendering process and eliminate the disadvantages. The basis of developing an alternative method was to design an economical processing system that would isolate each processing step of the calendering process so that each individual step could be controlled independently.

The new processing scheme is shown in Fig. 2. The basic scheme was to make the adhesive tape from extruded polyethylene and adhesive. Orientation would be imparted to the polymer film after extrusion to increase the tensile strength. Some treatment on the oriented polyethylene film may be required to produce a strong adhesive joint. After the treatment of the polyethylene, bonding of the polyethylene and extruded adhesive would follow.

A preliminary investigation and literature search yielded the following results. The polyethylene and adhesive can be easily extruded as demonstrated in the Kendall Company's calendering process in which both are fed in by extruders. In addition, the polyethylene and adhesive could be extruded into sheets, with sheeting dies, without much difficulty. Orientation of the polyethylene film could be achieved by stretching it, after crystallization, at a temperature below the melting point. This stretching can be accomplished by pulling the extruded film at a slightly higher speed than the rate of extrusion. Several types of treatments for polyethylene were found for improvement in adhesion and mechanical strength. These include chemical and electrical type of treatments. The bonding of the polyethylene and adhesive sheets was temperature limited since the adhesive bond would have to be made at

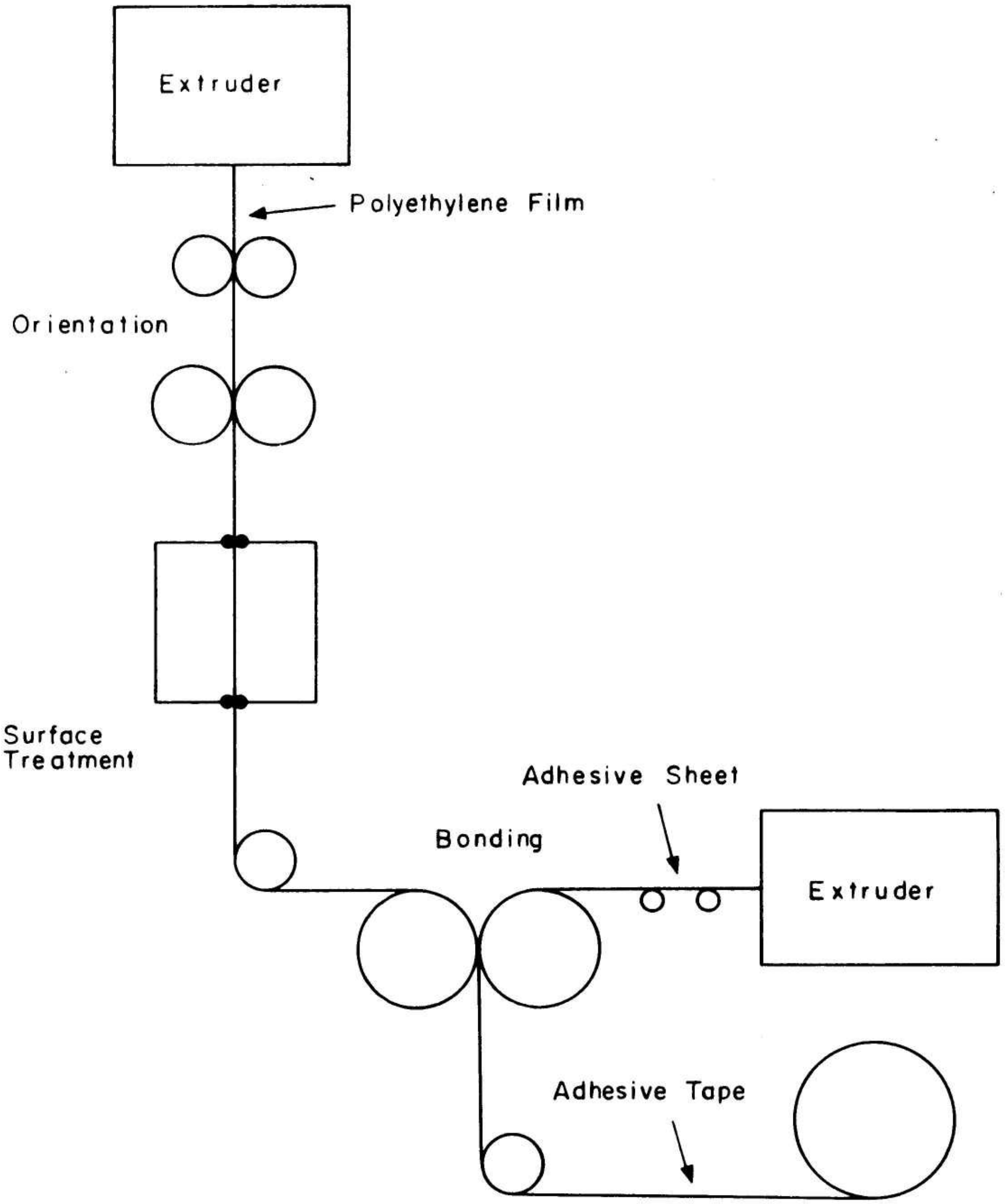

Fig. 2. Schematic diagram of the new processing scheme for making adhesive tape.

a low temperature to prevent any loss of orientation. Raising the surface temperature without bulk heating such as by radiation heating of both polyethylene and adhesive, or by dielectric heating of the adhesive were possible alternatives. However, the cost of such processes was estimated to be prohibitively high.

Based upon the above evidence, development of an alternative processing method to produce adhesive tape is feasible. However, the problem lies in forming a good adhesive bond between the polyethylene and adhesive at temperatures below the melting point of polyethylene without any loss of orientation. This warranted a closer look into the mechanism of adhesion, which is the subject of this thesis.

III. LITERATURE SURVEY

A. Introduction

A knowledge of the existing adhesion theories can assist in understanding the basic requirements for adhesion, although the literature indicates that the actual mechanism is not yet very well understood. The following is a brief overall view of the various adhesion theories. It is in no manner a comprehensive review since the topic of adhesion has been studied and written about very extensively over the recent years. For a more in depth review, the reader is referred to the original papers listed in the references.

There exist several competing theories of adhesion which attempt to account for the mechanism of adhesive bonding. These include the adsorption theory, the chemical theory, the diffusion theory, the electrostatic theory, the mechanical theory, the mechanical deformation theory, and the weak boundary layer theory. Each theory is generally suitable for a specific set of materials, and bonding and testing conditions as will be seen later.

The various theories of adhesion may be separated into two distinct groups - those theories concerned with bond formation and those advanced to describe the destruction of the bond. Each group contains several theories and each theory emphasizes certain mechanisms more than others. In general, for adhesion to occur, certain conditions must be met. Intimate contact between the bonding materials is required. Establishment of many contact points is important in developing a good bond since often the real contact area is much less than the apparent area. At these contact points, atomic or molecular attraction between the materials must take place. This constitutes the bond formation process. The bond formed may fail in two ways. One way is to have failure at the interface because of too few strong contact points. If the contact points do form strong links across the interface and when they are many, the remaining way for failure is for it to occur in one of the bonding materials. This emphasizes the bond destruction process. Adhesion theories which describe the bond formation process include the adsorption, diffusion, and chemical theories. The theories involved with the destruction of a bond are the mechanical deformation, weak boundary layer, electrostatic, and mechanical theories.

In this section, each theory will be reviewed in some detail and any experimental evidence that supports the theory is also presented.

B. Theories of Bond Formation

1. Adsorption theory

The adsorption theory states that intimate contact between adhesive and adherend allows permanent bonding to occur through the forces of molecular attraction. The process of forming an intimate contact between the adhesive and adherend is known as wetting.

The initial work in studying wetting was done with a liquid - solid interface. The thermodynamics of the liquid-solid interface is based on Young's concept[1] of the contact angle. From equilibrium considerations, the surface energy of the solid, γ_s, is related to the surface energy of the liquid, γ_l, the surface energy of the liquid-solid interface, γ_{ls}, and the contact angle, θ, at the liquid-solid boundary by Young's equation. If the solid is insoluble in the liquid,

$$\gamma_s = \gamma_{ls} + \gamma_l \cos\theta \qquad (1)$$

For the given model, the work of adhesion, W_{AD}, that is the work required to form a unit area of liquid-solid interface, is

$$W_{AD} = \gamma_s + \gamma_l - \gamma_{ls} \tag{2}$$

Substituting Eqn. (1) into Eqn. (2), we obtain

$$W_{AD} = \gamma_l \quad (1 + \cos\theta) \tag{3}$$

The above equation is simply the thermodynamic expression of the fact that the reversible work of separating the liquid and solid phases must be equal to the change in the free energy of the system. Eqn. (3) also demonstrates that the contact angle is determined by the relative strengths of the adhesion of the liquid to solid, and to itself which is 2 γ_l. If the contact angle is zero, $W_{AD} = 2\ \gamma_l$, so that the liquid attracts the solid as much as itself. The angle will also be zero if the liquid attracts the solid more than itself. A contact angle of 90° shows the liquid-solid attraction is one-half of the liquid-liquid attraction. When the angle is 180°, no adhesion between the liquid and solid is indicated. As there is always some adhesion, angles of 180° are not realized.

Zisman's extensive studies[2] of contact angles and wetting led him to the conclusion that the surface of a solid has a "critical surface energy," γ_c. This is the surface energy that divides the liquids forming zero contact angle on the solid from those forming contact angles greater than zero. If a liquid has a surface energy lower than γ_c, then adhesion is very likely to occur. A more detailed theoretical justification of Zisman's conclusion was given by Good and Girifalco[3,4] by considering the intermolecular forces across the interface.

Fowkes' phenomenological approach[5] identified a "dispersion component" of surface energy due to the London dispersion forces acting between neighboring atoms or molecules. He proposed that the surface energies are a measure of the attractive forces between surface layers and liquid phase, and that such forces and their contribution to the free energy are additive. Thus the surface energy can be resolved into nonpolar (dispersion) and polar components, γ^d and γ^p respectively, e.g.,

$$\gamma^p = \gamma^d + \gamma^p \tag{4}$$

This equation shows that even though two different materials can have the same surface energy, they may not behave in a similar manner when in contact with another because the dispersion and polar components may be different. Generally, the molecular attraction due to dispersion forces are weaker than the dipole forces.

Recently the theory of various dipole interaction across an interface has been proposed by many including Kaelble[6] to define, more closely, the polar component of surface energy. These interactions include dipole-dipole, dipole-induced dipole, and hydrogen bonding. Thus, the polar component, $\gamma\gamma^p$, may be broken into dipole-dipole, γ^{dd}, dipole-induced dipole, γ^{di}, and hydrogen bonding, γ^h, fractions, e.g.,

$$\gamma^p = \gamma^{dd} + \gamma^{di} + \gamma^h \tag{5}$$

Eqn. (5) emphasizes the same line of thought as Eqn. (4) that although the polar component may be the same the behavior may not be.

Several people including Anand, et al,[7-11] believe that the establishment of intimate (atomic) contact between the two surfaces is the primary requirement of bonding. The time dependent phenomenon of adhesive bonding can be accounted for by the time taken for viscoelastic solids to deform and form intimate contact. They made use of the deformation theory of elastic, viscous, and viscoelastic materials developed by Alfrey and Gurnee.[12] For a simple Voigt model, the stress required to deform the solid is given as

$$\sigma = 2Ge(t) + 2\eta\dot{e}(t) \tag{6}$$

where σ is the shear stress, G is the shear modulus, e (t) is the strain as a function of time, η is the viscosity, and $\dot{e}$ (t) is the strain rate as a function of time. Anand, et al, also suggested

$$\eta = \eta_o \exp(E_A/kT) \tag{7}$$

where η_o is the material characteristic viscosity, E_A is the activation energy, k is Boltzmann's constant, and T is the absolute temperature. The above equations suggest the ways the mechanical properties, G and η, the strain, and the strain rate may be affected by the bonding parameters-presssure, time, and temperature. The above line of thought is known as the contact theory of adhesion. After intimate contact is achieved between the adhesive and adherend through wetting, the intermolecular forces come into play. The bonds formed may be represented by dipole-dipole bonds, dipole-induced dipole bonds, and hydrogen bonds as stated earlier.

From the evidence presented, several predictions can be made about adhesion through the adsorption theory. Eqn. (3) demonstrates that a low contact angle will improve adhesion. Eqns. (4) and (5) show the role of the various components of surface energy in Eqn. (3) may affect the bonding behavior such as poor adhesion with nonpolar component. High pressure and temperature, and long times of bonding will yield a strong adhesive joint according to Eqns. (6) and (7).

In spite of the broad acceptance of the adsorption theory of adhesion, there exist several limitations. As shown by Deryaguin and Krotova,[13] the peeling work of an adhesive bond can reach as high as 10^{11}-10^{13} N/m^2 but the work required to overcome molecular forces does not exceed 10^9-10^{10} N/m^2. Thus the real work of adhesion is several orders of magnitudes higher than that predicted from molecular forces. They have also shown that adhesion depends upon the peeling rate of the adhesive bond, as will be seen later, whereas the work to separate the bond due to the molecular forces do not depend on the separation rate of the molecules. The adsorption theory cannot account for the adhesion of nonpolar polymers such as polyisobutylene and natural rubber which do adhere well. While it is time that good joints are made at high pressure and temperature, and long time, in some cases, Eqn. (6) does not spell out explicitly the exact mechanism of bonding and hence is not universally valid. The fact that materials like polyamides (nylon), polytetrafluorethylene (PTFE), and polyethylene do not yield good joints with common adhesives, even when they are applied in liquid form, is well known.

2. Diffusion theory

The diffusion theory proposed by Voyutskii[14] is based on mutual diffusion of atoms and molecules at the interface. This concept arises primarily from the observation that adhesion of similar materials (autohesion) generally increases with time and temperature used for bonding the materials together.

Fick's first law is used to describe the basic diffusion process which is given as

$$dm = - D \frac{dc}{dx} dt \qquad (8)$$

where dm is the amount of substance diffusing in the x-direction across a unit area in time dt with a concentration gradient of dc/dx and D is the diffusion coefficient. The diffusion coefficient is temperature dependent and may be written as

$$D = D_o \exp \left\{ -E_A/kT \right\} \qquad (9)$$

where D_o is the material characteristic diffusion constant, E_A is the activation energy, k is Boltzmann's constant, and T is the absolute temperature. These equations exhibit the effect of time and temperature of bond formation on the peel strength as the result of a diffusion bond mechanism.

Wake[15] derived a relation between the adhesion and the force required to separate the diffused molecules. By setting the force equal to the momentum of the molecule at a given rate of extraction times the frequency of impact of the number of molecular groups involved, it is possible to predict how the force increases with time of diffusion. It is given as

$$F = A_1(t)^{1/4} + C_1 \qquad (10)$$

where F is the force, t is the time, and A_1 and C_1 are constants. This relation shows the force to break a bond, formed by diffusion, should increase as the one-fourth power of time.

Basically, this theory predicts, through Eqns. (8)-(10), that a good adhesive joint will occur when the amount of material diffusing increases with longer times and higher temperatures of bonding, and that the amount of force required to separate the joint is a one-fourth power of time.

In the Western world, the diffusion theory is not yet regarded as highly as the adsorption theory. One reason lies in the fact that a high adhesion strength is achieved in very short times with the low diffusion coefficients for typical polymers. High bond strength of dissimilar materials, where mutual solubility and diffusion would be limited, such as metal/polymer systems, also contradict the basis of this theory.

3. Chemical theory

The chemical theory requires the adhering materials to undergo a chemical reaction with each other to form primary valence bonds at the interface. These reaction rates are temperature dependent as shown by the following Arrhenius equation,

$$\frac{d\ln k_1}{dT} = \frac{E_A}{RT^2} \qquad (11)$$

where E_A represents the energy of activation per gram mole, k_1 is the reaction rate, which is concentration dependent, at an absolute temperature T, and R is the gas constant. For bonding to occur, the chemical reaction, whose rate is time and temperature dependent, must occur appreciably within the bond formation time at the given temperature. The creation of primary bonds strengthens the interface so that interfacial failures do not occur. This theory predicts that bonding will occur with high temperature and concentration of reacting materials.

The chemical theory of adhesion is not widely accepted because, while it may be true that chemical reaction does sometimes occur at the interface, there is no proof that such a reaction contributes to the mechanical strength of an adhesive bond. Many people believe secondary bonds, which occurs more often, are more responsible for adhesion instead of the primary bonds which results from the chemical reactions.

C. Theories of Bond Destruction

1. Mechanical Deformation Theory

The mechanical deformation theory or the rheological theory states, whatever the cause of interfacial adhesion, the strength of the bond is determined by the mechanical or rheological properties of materials and by the local stress. The basis of this theory is on the belief that the bond strength is not determined by the interfacial forces because clean failure at the interface is an uncommon occurence. Failure is generally cohesive in the adhesive or adherend, or both, or in some boundary layer. In addition, the strength of an adhesive joint is also governed by the type of joint, the separation mode and rate, and the temperature and environment of testing.

In general, adhesive joints involve sharp corners and voids between adjacent materials which act as stress concentrators, particularly after a crack or imperfection nucleates at such a location. In a typical case consisting of two adherends and a third interlayer material as the bonding adhesive, there are several potential locations of failure, a cohesive failure in any of the three materials, or an adhesive failure at either of the two interfaces. The mode of failure under different conditions and the reasons for the failures are found in the mechanical properties of the materials rather than in the physical chemistry of the surface. The analysis of bond destruction involves determining the location of the weakest link in the joint and the magnitude of stress which is required to cause failure. There are two basic points of view in assessing bond destruction, depending upon whether the joint failure is cohesive or adhesive.

In the first case, failure occurs in the bulk of one of the materials of the adhesive joint. The failure criterion is based on the octahedrial shear stress, τ_{oct}, containing all three principal stress, σ_i, and defined as

$$\tau_{oct} = \frac{1}{(2)^{1/2}} \left[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right]^{1/2} \tag{12}$$

Assuming the criterion applies, one predicts failure whenever the above combination of principal stresses at any point of the material exceeds τ_{oct}. The critical value of τ_{oct} is obtained by applying the criterion to the failure of a simple uniaxial tensile specimen having stresses $\sigma_1 = \sigma_{tensile}$ and $\sigma_2 = \sigma_3 = 0$. Thus

$$\left[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right]^{1/2} > \left[2\sigma^2_{tensile} \right]^{1/2} \tag{13}$$

or in the more general case,

$$F(\sigma_1, \sigma_2, \sigma_3) > \sigma_{tensile} \qquad (14)$$

The octahedral stress criterion is best used for smoothly varying stress fields with no exaggerated stress concentrations present and for materials having a uniform distribution of reasonably small micro-flaws. The mechanics of the above failure can be summarized into a model and its resulting equation presented by Hata.[16] He proposed a three element model where the surface force is represented by a spring and the mechanical behavior of the adhesive by a Voigt model. The resulting equation describing the stress field is

$$\sigma = e_1 G_1 = e_2 G_2 + \eta \dot{e}_2 \qquad (15)$$

where σ is the stress, e is the strain, G is the shear modulus, η is the viscosity, $\dot{e}$ is the strain rate, and the subscripts 1 and 2 refer to the adherend and adhesive respectively. Interfacial failure would occur when

$$\sigma = e_{1c} G_1 \qquad (16)$$

and cohesive failure when

$$\sigma = e_{2c} G_2 + \eta (\dot{e}_2)_{e_2 = e_{2c}} \qquad (17)$$

where the subscript c indicates a critical value. The above equations demonstrate the two different ways of failure. The evidence presented above indicates that a good adhesive joint may be obtained in several ways. According to Eqn. (15) the joint strength will increase with higher viscosity, i.e., lower temperatures of testing, and faster strain rates of testing. Eqns. (16) and (17) predict cohesive failure will occur if the materials selected are such that the critical strain of the interface is greater than of the bulk of the materials.

In the second case, i.e., when the failure occurs at the interface (adhesive failure), the failure criterion is based on fracture mechanics. The foundation of all present day theories of fracture of materials is the Griffith crack model.[17] The Griffith model, adopted from the work of Inglis,[18] states that the strength of the material is considered proportional to the energy required to propagate a crack, flaw or otherwise a stress concentrator in the material under an imposed stress field. The condition for crack growth and therefore separation of the material is

$$\frac{\partial}{\partial \ell} (4 \gamma_F - \varepsilon_I) > 0 \qquad (18)$$

where ℓ is the crack length, γ_F is the fracture surface energy, and $-\varepsilon_I$ is the stored energy $\pi^2 \sigma_A \ell^2/E$ where σ_A is the applied stress and E is Young's modulus. The final form of the critical applied stress was determined as

$$\sigma = \left(\frac{2E\gamma_c}{\pi \ell} \right)^{1/2} \qquad (19)$$

where γ_c is the critical surface energy. In an advance of the Griffith approach, Irwin,[19, 20] derived the Griffith type formulation based on a critical stress criterion. He observed that the stress field in the vicinity of the crack tip could be defined by a single stress intensity factor, K, proportional to the stress concentration parameter. When the stress intensity factor reaches a critical value, K_c, the crack will propagate. Since an adhesive joint can be modeled as a solid with high stress concentration factors, the above analysis apply to adhesive joints.

What distinguishes these two cases is material properties, in particular, the viscoelasticity. In ductile materials, where crack propagation is not a major factor, the octahedral stress criterion is best suitable. Crack propagation is important in glassy solids. Thus the limitations of the Griffith formulation lies in the fact it applies to brittle materials. Application to ductile materials will give erroneous results.

The basic flaw of the first case is that most adhesive joints possess very high stress concentration at corners or along bond lines due to geometric conditions, and usually contain substantially larger than average internal flaws. Thus the flaw distribution becomes denser and/or of longer size than expected and decreases the maximum permissible allowable stress. The second case does not apply to ductile materials where crack propagation is limited. In general, the mechanical deformation theory does not account for adhesion per se. It does not state why adhesion does or does not occur but offers some explanation why adhesive joints fail. Many people believe this theory accounts for bond failure which is not necessarily the same as bond formation. Thus this theory is lightly regarded by many.

2. Weak boundary layer theory

Bikerman[21] has suggested the weak boundary layer theory which claims that when bond failure seems to be at the interface, usually a cohesive break of a weak boundary layer is occuring. Weak boundary layers result from the adhesive, adherend, or environment. They occur in the adhesive or adherend if an impurity concentrates near the surface and form a weak attachment to the substrate. The bonding environment, generally air, causes a weak boundary layer of adsorbed gases such as oxygen to prevent wetting by the adhesive and thus lower bond strength. Two examples of these effects are polyethylene and metal oxides. Polyethylene has a weak, low molecular weight constituent that is evenly distributed throughout the polymer. This weak boundary layer is present at the interface and contributes to low peel strength when polyethylene is used as part of an adhesive joint. Some metallic oxides are weakly attached to their base metals. Failure of adhesive joints made with these materials occurs cohesively within the oxide.

The weak boundary layer theory criticism follows the same line of thought as those for the mechanical deformation theory. It accounts for adhesive joint failure and not for the mechanism of adhesion. In addition, Kaelble[6,22] has presented experimental evidence which indicates this theory is not totally valid. The evidence includes peel strength tests where a discontinuous change of adhesive strength due to the failure mode transformation from cohesive to interfacial when the rate of peeling was varied. It would be difficult to assume that two bonds of weak boundary layers exists to account for the discontinuity.

3. Electrostatic theory

The electrostatic theory formulates the electrically charged layer created at the interface of each material will provide a coulombic attraction necessary for adhesive bonding. This Russian theory, proposed by Deryaguin,[23] treats the adhesive-adherend system as a capacitor which is charged due to the contact of two different substances. The strength of the bond is presumed due to the electrostatic forces which resist separation resulting from the existence of an electrical double layer. Indication that electric phenomena occurs in the peeling of bonded polymer specimens is given by the following: electrization of surfaces formed, presence of the electrical discharge and electronic emission in some cases, and decrease of adhesion upon irradiation.

The electrostatic theory, like the diffusion theory, is not widely accepted. In this theory, the adhesive-adherend system is treated as a capacitor where the charge is stored on the surface of each of the bonding material. This implies adhesion should not occur when conductors are used since the charge is free to travel and not required to stay at the surface. It is well known that some conductors do adhere well. The theory also predicts electrical discharges should occur each time an adhesive is peeled from an adherend since the "capacitor" is being discharged; this phenomenon does not take place each time and occurs only occasionally. This theory cannot also account for the high adhesion between similar materials where the charge on the surfaces are the same and the forces are repulsive instead of attractive.

4. Mechanical theory

The mechanical theory states that when an adhesive permeates the surface of the adherend and hooks with it, bonding will occur due to mechanical interference. This theory is based on the high bond strengths of porous materials and of roughen material surfaces.

The basic flaw of the mechanical theory of adhesion is the good adhesion between smooth materials where mechanical anchoring is limited. While adhesive strength can be improved by surface roughening, etc., it has been shown that mechanical effects are not always of great importance. It may be due to the change in both physical and chemical properties of the surface.

D. Summary

Each of the various adhesion theories contain points which are valid for different materials, and bonding and testing conditions. It also has serious limitations which prevent its use as a fundamental theory of adhesion. These discrepancies in the theories present a problem in explaining the basic mechanisms of adhesion.

IV. STATEMENT OF THE PROBLEM

A. Introduction

As shown in the literature survey, some of the flaws existing in the various adhesion theories prevent any one theory from explaining the fundamental mechanism of adhesion. The following is an attempt to put the various theories of adhesion in proper perspective so the problem may be more easily identified.

B. Basis of Bond Formation

Understanding the process of bond formation enables a better in depth grasping of adhesion. It presents a clearer and unified picture of the apparent confusion and diversity in this area.

The process of bond formation between two given materials may be considered thermodynamically. In this process, bodies of materials A and B with surfaces A' and B' respectively are placed in contact to give a single body with an interface layer A'B'. From the first law of thermodynamics for any infinitesimal process

$$dU = \delta q + \delta W \qquad (20)$$

where U is the total energy, q is the heat, and W is the work. The second law states,

$$\delta q = T\,dS \qquad (21)$$

where T is the temperature and S is the entropy. In general, work done on the system may be expressed as the sum of mechanical, chemical, electrical, and magnetic terms, i.e.,

$$\delta W = -PdV + \gamma\, d A + \sum_i \mu_i\, dn_i + \frac{1}{4\pi} \sum_j E_j dD_j + \frac{1}{4\pi} \sum_k B_k\, dH_k \tag{22}$$

where P is the pressure, V is the volume, γ is the surface energy, A is the area, μ_i is the chemical potential, n_i is the amount of species, E_j is the electric force vector, D_j is the electric derived vector, B_k is the magnetic force vector, and H_k is the magnetic derived vector. Substituting Eqns. (21) and (22) into Eqn. (20) yields

$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i\, dn_i + \frac{1}{4\pi} \sum_j E_j\, dD_j + \frac{1}{4\pi} \sum_k B_k\, dH_k \tag{23}$$

The above equation may be integrated to yield

$$U = TS - PV + \gamma A + \sum_i \mu_i\, n_i + \frac{1}{4\pi} \sum_j E_j\, D_j + \frac{1}{4\pi} \sum_k B_k\, H_k \tag{24}$$

when subjected to Gibbs-Duhem relation,

$$SdT - VdP + Ad\gamma + \sum_i n_i \, d\mu_i + \frac{1}{4\pi} \sum_j D_j \, dE_j + \qquad (25)$$

$$\frac{1}{4\pi} \sum_k H_k \, dB_k = 0$$

Eqn. (23) gives the dependence of energy in a set of independent variables S, V, A, n, D, and H. Another set of independent variables may be obtained by defining a new thermodynamic function, Gibbs free energy as

$$G_F = U + PV - TS \qquad (26)$$

The change of free energy for a surface of an interface is obtained from combining Eqns. (26) and (24) together to yield

$$\Delta G_F = \Delta\gamma A + \Delta \sum_i \mu_i \, n_i + \frac{1}{4\pi} \Delta \sum_j E_j \, D_j + \qquad (27)$$

$$\frac{1}{4\pi} \Delta \sum_k B_k \, H_k$$

To satisfy the thermodynamic requirement, reduction of the free energy of the system, i.e., of the adhesive and adherend

$$\Delta G_F^{system} = \Sigma \, \Delta \, \gamma \, A + \Sigma \, \Delta \sum_i \mu_i \, n_i + \frac{1}{4\pi} \Sigma \, \Delta \sum_j E_j \, D_j + \qquad (28)$$

$$\frac{1}{4\pi} \Sigma \, \Delta \sum_k B_k \, H_k$$

where the summations account for the phases in the system, is a necessary condition for the process of adhesion. This thermodynamic condition implies

$$\Delta G_F^{system} < 0 \tag{29}$$

This condition can be achieved in several ways. The reduction of G_F^{system} can be due to a simultaneous reduction in various energy terms or it could also be due to a substantial decrease in any one term which will outweigh any increase in the other terms. Thus,

$$\begin{aligned} &(a) \quad \Sigma \Delta \gamma A < 0 \\ &(b) \quad \Sigma \Delta \sum_i \mu_i n_i < 0 \\ &(c) \quad \frac{1}{4\pi} \Sigma \Delta \sum_j E_j D_j < 0 \\ &(d) \quad \frac{1}{4\pi} \Sigma \Delta \sum_k B_k H_k < 0 \end{aligned} \tag{30}$$

represent the condition when $\Sigma\Delta\gamma A$, $\Sigma\Delta\sum_i\mu_i n_i$ etc., alone dominates the other terms. Condition (a) accounts for the adsorption theory. It shows that a change in the surface energy of the system will decrease the free energy. Condition (b) accounts for the diffusion and chemical theories of adhesion. The amount change of the present species in the system through the process of diffusion, and the variation in the chemical potential and the number of species from a chemical reaction both satisfy the thermodynamic requirement for bond formation. Condition (c) accounts for the change of free energy due to the electrical nature of the material whereas condition (d) accounts for the magnetic nature.

Thus, the thermodynamic argument gives the reason for the existence of several theories of bonding in the literature. Each theory of adhesion accounts for the reduction in the free energy due to only one term of Eqn. (28). Then it goes on to describe the details of the kinetics of the mechanism. For example, adsorption and diffusion theories describe how the free energy is minimized, as required by conditions (a) and (b) respectively, by spreading and mass diffusion.

However, the thermodynamic approach is not sufficient to understand adhesion. The limitations of pure thermodynamic approach were suggested by Eley[24] and several others. In addition to thermodynamics the kinetics of the process determines if the bonding will occur within specified conditions when the thermodynamic condition is met. Thermodynamics makes no comment on this important fact. In addition, the thermodynamics in the adsorption theory are valid only for liquid or adsorbed gaseous films since there is an approximate equivalence between net work expended in creating a new surface and the free energy gained. However, it is not valid for solids which undergo appreciable plastic flow. Similarly, thermodynamics does not shed any light on the rate of diffusion or chemical reaction. As the result, it is always necessary to construct some ad hoc model and theories to describe the kinetics.

C. Basis of Bond Destruction

The basis of the theories of bond destruction can also be evaluated in terms of thermodynamics also. In bond destruction, the mechanical terms of the free energy equation is emphasized more than in the previous argument for bond formation. Initially, the belief was that the energy required to fracture was the energy of the new surfaces created as a result of fracture. Ideally, this is equivalent to the cohesive energy of the material and the surface energy, according to this argument, is one-half of the cohesive energy. The fracture strength is the strength of a single bond times the number of bonds per area. Various experimental evidence, however, have shown the stress required is much lower than anticipated and the energy to fracture does not correlate well with the surface energy of the materials. This lead Griffith[17] to propose cracks or flaws exist in the material. He suggested that the mechanical stress required was proportional to the energy needed to propagate a crack as given in Eqn. (19). This energy approach is an application of thermodynamics to bond destruction and accounts for the fact how fracture strength could be lower than the cohesive strength by several orders of magnitudes. However, this approach could not explain the total difference between the realized and expected values of strength because the fracture strength does not correlate very well with the surface energy of the materials. It fails to describe adequately failure of ductile materials where extensive plastic and viscous deformations make the process irreversible. Irwin[19, 20] extended the Griffith concept, in an attempt to account for the difference, by converting the energy criterion of fracture to stress criterion. In this way it is possible to account for the plastic and viscous nature of the materials. Thus, although the mechanical deformation, weak boundary layer, and mechanical theories rely on the mechanical terms in the free energy, an estimation of the bond strength, however, involves Irwin's fracture mechanics approach. Similarly, although the electrostatic theory considers electrical terms only, again a realistic estimate of the strength can only be made by using the fracture mechanics analysis. Thus, the problem is one of the analysis of stresses at the cracks and corners of adhesive joints taking into consideration the properties of the materials that constitute the joint.

D. Approach

The present macroscopic theories of bond formation only give a limited picture of adhesion and the failure criteria of bond destruction provide no insight as to the causes of adhesion. Thus, the approach to the adhesion problem appears to be the combination of a microscopic view of bond formation and macroscopic view of bond destruction. The approach consists of developing an understanding as to what occurs on the microscopic level in bond formation and then testing this knowledge with bond destruction tests with constant parameters.

The basis of the microscopic approach is that there must be some electron interaction between the two bonding materials.* This idea results from the fact that electrons at the surface of each material are stable at an energy level different from the bulk material. This condition arises from the change of the electron structure due to the formation of the surface. Bonding will not occur even if the materials are in intimate contact because each surface is at a different state of minimum energy. For bonding to occur, the present electron situation at the surface must be disturbed. Various means such as thermal, chemical, mechanical, and irradiation can disturb the electron state. In fact, the various theories of adhesion already discussed can be accounted for by some electron activity, e.g., adsorption - electron arrangement determining whether the surface is polar or nonpolar, diffusion - ionic affinity determining solubility and the amount of diffusion, chemical-reactions involving sharing or losing of electrons. Thus, it seems the necessary and sufficient condition for adhesive bonding is electron interaction. Therefore, it was decided to attempt to correlate adhesion to electron interaction in this study.

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*Suggested by N.P. Suh in "A Contribution on Adhesive Bonding," unpublished paper, Department of Mechanical Engineering, M.I.T., Cambridge, Massachusetts, October 2, 1975.

The experimental tests used to determine the nature of bonding surfaces and the electron interaction were through the surface charge obtained from the zeta potential measurements. To clearly illustrate this point, it is convenient to consider the definition of the zeta potential. The following is a brief description on the concept of the zeta potential and how it can be related to electron interaction via surface charge. A concise description of the definition of the zeta potential, the measurement of electrokinetic parameters and the calculation of the zeta potential values from these parameters are given in the appendix.

In a system consisting of finely divided particles (colloids) in aqueous suspension, the zeta potential, ζ, may be defined as the potential of the plane of shear between the fixed layer (Stern layer) of liquid adjacent to the particle and the liquid constituting the bulk solution. The particle typically has a net electronegative charge surrounded by stationary positive charges. These in turn are surrounded by a diffuse layer of positive and negative ions. For most natural colloids suspended in distilled or tap water, the zeta potential is negative. The above definition is used widely by most people in discussion of electrokinetic theory. The zeta potential is related to the surface potential, ψ_0, and to the surface charge density, σ_0, in several possible ways. The latter relation is discussed more fully in the appendix. Changes in the zeta potential will only reflect changes in the surface potential provided the ionic strength remains constant and there is no specific adsorption other than by potential determining ions, i.e., only potential determining and in different ions are present. Measurement of the zeta potential may be determined by electroosmosis, streaming potential, and electrophoresis. As stated earlier, the appendix contains a general description of the measurement methods with a heavier emphasis on electrophoresis - the measurement technique used in the experimental work.

The electron structure at the surface of the polyethylene was changed by a variety of treatments. They include glow discharge treatment in different gases, doping with fillers, quasi-chemical treatments, etc.

The peel strength tests, a method of determining the relative resistance of adhesive bonds, were used as an indication of adhesive strength. There are some limitations of this test however. This destructive test involves both interfacial and bulk mechanisms. The interfacial strength has two components - an equilibrium surface force which accounts for the peel strength at low velocities and a viscous peeling force which depends on the peeling rate. If the peel strength tests are run at a constant and high velocity, magnification of the viscous peeling force occurs. In addition, interfacial and bulk effects are hard to distinguish from each other because there is always some bulk deformation even in the case of interfacial failure.

In view of the above complications, peel tests were always conducted at room temperature and at constant peel velocities. Further, tests were also conducted to check whether the bulk properties of the polyethylene changed with treatments. No differences in properties were noted. Thus, it is presumed that peel strengths reported in this work reflect the bond strength of the joint, at least qualitively.

V. EXPERIMENTAL MATERIALS AND PROCEDURES

A. Materials

The polyethylene and adhesive used in the experimental work were acquired through the courtesy of the Kendall Company. As mentioned earlier, these materials are the components of Kendall's adhesive tape.

The polyethylene was a mixture of low and high density polyethylene with a slight amount of carbon black. It is used as the backing of the adhesive tape. The carbon black filled polyethylene was in the form of extruded and calendered films, 3.0×10^{-4} m thick. The polyethylene was also available without the carbon black in the form of calendered film 3.0×10^{-4} m thick. The low and high density polyethylenes used to make the above films were also available in the form of pellets.

The adhesive was a mixture of virgin and reclaimed butyl rubber with clay filler, tackifier, and several other minor components. It was in the form of a 3.0×10^{-4} m thick film with a 3.0×10^{-4} m thick polyethylene backing. The adhesive was also supplied in blend form.

B. Procedures

1. Surface modification

The polyethylene was modified so as to induce a different surface charge by three different methods - by using a glow discharge treatment on the polyethylene, by doping the polyethylene with various fillers, and by a quasi-chemical treatment on the polyethylene. Each method modified the surface charge uniquely from each other. The logic and procedure used in each of the modifications of the polyethylene were as follows:

a. glow discharge treatment

The method used to modify the polyethylene was a slightly altered version of Schonhorn's glow discharge treatment[25] called Crosslinking by Activated Species of INert Gases (CASING). It is a surface treatment in which the surface is bombarded by activated species of an inert gas produced by an electrodeless discharge at low pressures and high frequencies. Schonhorn has shown that there is a substantial increase in adhesive bond strength when a polymer is treated by the CASING process. In the present work, organic and other non-inert gases were also used in addition to the inert gases.

The apparatus used for the glow discharge treatment is shown in Fig. 3. Its design is similar to glow discharge equipment found in the literature.[25-27] The glow discharge was achieved by an inductively coupled radio-frequency (RF) coil (10 turns of copper tubing 3.2×10^{-4} m OD) with an inductance of 6.6 microhenries. The plasma was produced a 100 watt Hallicrafters RF oscillator connected to a Drake linear amplifier to increase the power output to 3.0×10^{3} watts. An Ultimate Transmatch matching transformer was used to optimize the match between the RF power supply and the inductive load. The standing wave ratio (SWR), the ratio of maximum current to minimum current along the 50 ohm transmission line, was measured by a Port-A-Lab 500 SWR meter to determine the mismatch between the power supply and the load. The current in the line was measured by a Simpson RF ampere meter, and the voltage across the RF discharge coil and the frequency were measured by a Tektronix cathode-ray oscilloscope. The discharge vessel consisted of a Pyrex tube (5.0×10^{-2} m OD, 4.7×10^{-2} m ID, 3.1×10^{-1} m long) sealed at each end by two-piece vacuum aluminum flanges. It was evacuated with a mechan-

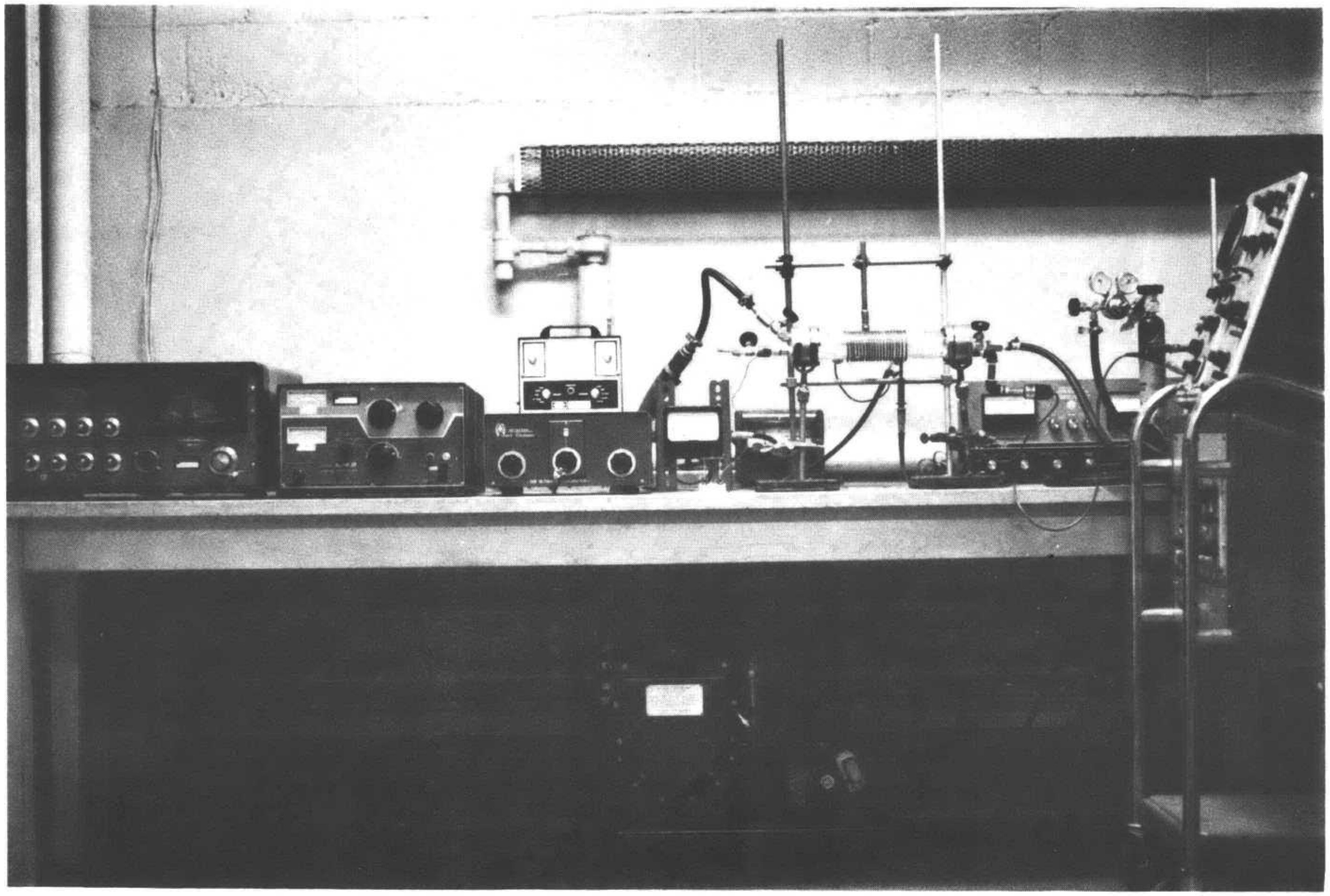

Fig. 3. Glow discharge apparatus.

ical pump and the pressure monitored by a NRC 701 Thermocouple Vacuum Gauge. The gas flow rate into the vessel was controlled through a needle valve from a regulated gas cylinder. The temperature in the vessel was measured by a copper-constantan thermocouple.

The procedure used in the treatment was as follows. Up to five strips of polyethylene film (1.02×10^{-1} m long, 2.54×10^{-2} m wide) were placed longitudinally on the inner wall of the discharge vessel and held in place with double stick tape applied to both ends of each strip. The vessel was evacuated with a mechanical pump to a pressure of 3.33×10^{4} Pa. A continuous flow of gas was allowed into the vessel and controlled with the needle valve such that the pressure of the vessel was maintained at 1.33×10^{5} Pa. After steady state has been achieved, the vacuum gauge was turned off to prevent any damage to it during the glow discharge. The temperature of the vessel was then taken and recorded. The plasma was produced by slowly increasing and tuning the output of the RF oscillator at a frequency of 14×10^{6} Hz for maximum power of 100 watts through the linear amplifier, transmatch, and SWR meter. It was often necessary to ionize the gas initially at a slightly higher power level than the desired 100 watts before the power was reduced to the proper level. The discharge was maintained for 1.0×10^{3} seconds. At the end of this time period, the RF oscillator and linear amplifier were turned off, and the temperature of the gas in the vessel was recorded again. The temperature rise was no more than 5.0 K. The vacuum pump and gas valves were shut off and air was admitted into the vessel. The polyethylene strips were then removed and stored at room conditions until the joints were made.

b. doping

Doping the polyethylene with various fillers to induce a different surface charge was based on the results of a paper presented by Taylor, et al[28] on polyurethane - carbon black system. They made samples of Goodyear polyester polyurethane filled with acetylene carbon black to various degrees from 0.0 to 31.9 percent. Zeta potential measurements were made and the results showed that the percentage of carbon black changed the zeta potential from various degrees of negative values to the positive values at the higher concentrations of carbon black around 28.0 percent. It was believed that the high concentration of the "positive" carbon atom drew the electrons from the surface of the polyurethane and made the surface appear positive. Thus the idea was to place fillers in the polyethylene such that the electrons would be pulled away from the surface. The transition elements could be used as fillers since these elements have empty d-orbitals and would tend to attract electrons. The various fillers used were each added into the polyethylene by a solvent method. The polyethylene was melted in toulene and the filler was then added. The solvent was drawn out of the polyethylene in a vacuum oven at a temperature of 353 K for twelve hours. A filled polyethylene remained after cooling to room temperature.

c. quasi-chemical treatment

To achieve a positive surface charge, a quasi-chemical treatment was performed on the polyethylene. This treatment was based on the results of a paper by Falb, Leininger, and Crowley.[29]* The treatment consisted of adsorption of a quaternary ammonium salt to the surface. Quaternary ammonium salts containing a single long chain alkyl are sometimes easily displaced. However, two or more long chain alkyl groups are water insoluble and are not easily displaced from the

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*After private communication with Dr. R.I. Leininger, another paper by Ericksson, Gilbery, and Lagergren[30] was also suggested as a reference to the quasi-chemical treatment.

surface. A boiling solution of the quaternary ammonium salt in a 1:1 toulene-petroleum ether mixture was applied to the polyethylene. Afterwards, the polyethylene was placed in an oven at 353 K for one hour to drive off the excess toulene-petroleum ether. During the above process, the chloride is dissociated and washed away from the nitrogen thus leaving a positive charge.

2. Bond specimen preparation and testing

The adhesion between two materials was determined by peel strength tests performed on bonded specimens consisting of the given materials. The peel strength tests were T-peel tests which primarily determined the relative peel resistance of the adhesive bond between adhesives and adherends by means of pulling apart a T-type specimen.

a. specimen preparation

The T-peel specimen was prepared by forming a 1.02×10^{-1} m long, 2.54×10^{-2} m wide bonded laminated strip of adhesive and the various polyethylenes to be tested. Kendall adhesive tape (1.52×10^{-1} m long, 2.54×10^{-2} m wide) was used as two-thirds of the laminate to provide a 3.0×10^{-4}m layer of adhesive and also a 3.0×10^{-4} m backing to grip the adhesive layer. The final third of the laminate was a 3.0×10^{-4} m layer of polyethylene strip (1.52×10^{-2} m long, 2.54×10^{-2} m wide) which was bonded to 1.02×10^{-1} m of the adhesive of the laminate. The rest of the exposed adhesive was covered by a piece of Kendall adhesive tape to prevent any adhesion between the remaining 5.08×10^{-2} m strip of the adhesive and the polyethylene, and allow the specimen to be gripped without difficulty.

The laminate was bonded together at various temperatures (295-453 K) with different applied pressures (1.72×10^{4} - 2.14×10^{6} N/m^{2}) for several times (1.0 -4.32×10^{4} seconds) to ensure contact between the adhesive and the polyethylene.

The specimens were heated in an oven, and pressed together between two aluminum blocks (1.02×10^{-1} m long, 2.54×10^{-2} m wide) in the compression mode of an Universal Hydraulic Testing Machine with Tate-Emery Indicator. The T-peel specimens were then tested within twenty-four hours.

b. peel tests

The T-peel specimens were pulled apart on an Instron Universal Testing Instrument at a crosshead speed of 4.23×10^{-4} m/s. The peeling force required to separate the adhesive and adherend was recorded. The average T-peel strength in N/m width for each specimen was logged. In addition, the type of failure, that is, cohesive failure within the adhesive or adherend, adhesion to the adherend, or combination thereof, for each individual specimen was recorded. All the peel tests were done at room temperature.

3. Zeta potential

a. specimen preparation

Specimens for the zeta potential measurements were fine particles (colloids) approximately 40×10^{-6} m in size of the modified polyethylene and adhesive in an electrolyte solution. The solution used was a 40:60 percent mixture of methanol and water because the particles stay suspended in this solution. The particles were ground, in liquid nitrogen, to the desired size with a Wiley cutting mill. The polyethylene specimens were prepared by modifying the polymer, either before or after grinding depending on the type of alteration used, and then placing the particles into the methanol-water solution. The adhesive specimens were ground and placed into the solution. The above specimens were handled with and stored in non-metallic equipment to avoid any change in the surface charge due to the presence of conductors. They were stored at room condition until testing.

b. measurements

The zeta potential was measured with a ZETA-METER.* At the time of testing, the electrophoresis cell was filled with the suspension under study. The temperature of the suspension was recorded. A potential of 65 volts was then applied to determine the standard conductance of the suspension to establish whether the solution was within the desired range of electrolyte concentration. With an objective lens that gave a small depth of focus, the microscope was focused on the front wall of the cell at mid-depth as mentioned in the appendix. A potential (150-300 volts) was applied by increasing the DC voltage slowly from zero to the desired voltage in ten to fifteen seconds to prevent any significant overturn. The time for a particle to move a known distance on the "tracking line" was recorded. At least ten particles were followed for each sample. The results were then recorded as an average electrophoretic mobility, the particle velocity under a given applied electric field, and converted to the zeta potential by the mobility and zeta potential given in the appendix. In addition to that relation, the results were also obtained from the instruction manual of the ZETA-METER which contained charts for zeta potential determinations based on the relation.

4. Other tests

a. tensile

Tensile tests were performed on various polyethylene films (1.02×10^{-1} m long, 2.54×10^{-2} m wide, 3.0×10^{-4} m thick) with an Instron Universal Testing Instrument. The crosshead speed used was 4.23×10^{-4} m/s. The force applied and elongation of the polymer were recorded simultaneously. These tests were performed

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*Instrumentation developed and built by the ZETA-METER, Inc., New York, New York.

at room temperature.

b. stress relaxation

Stress relaxation tests for the polyethylene were also done on the Instron. Polyethylene tensile test specimens were elongated such that the initial stress was 4.14×10^4 N/m. The force decay for this constraint was measured as a function of time at room temperature. The stress relaxation behavior for the adhesive was obtained by stretching a piece of adhesive (6.35×10^{-3} m^2, 3.81×10^{-2} m long) 100 percent and clamping down the ends - one end to a force transducer. The output of the transducer was fed to a Sanborn recorder which recorded the decaying force as a function of time at room temperature.

c. viscosity

The viscosity tests for the polyethylene and adhesive were done with a Monsanto Automatic Capillary Rheometer. Initially, the barrel of the rheometer was heated to the desired temperture (293-493 K). The test materials were then loaded into the barrel. A force is then applied, via a gas piston-driven ram, to extrude a given volume of material through an orifice. The time was recorded for this extrusion process. A shear rate of 4.5 second^{-1} was maintained through the manipulation of the extruding force. The Automatic Capillary Rheometer measured the flow characteristic of the test materials four times per sample loaded into the barrel. The viscosity was calculated by a formula, in the Monsanto instruction manual, that included the force of the ram, orifice radius and length, volume of material extruded, and extrusion time.

d. crosslinking determination

The amount of crosslinking in the polyethylene after glow discharge treatment was determined as follows. Pieces of ethylene and ethane treated polyethylene were initially weighed on a Mettler balance to an accuracy of +/- 1.0×10^{-6} Kg and then placed in boiling toulene. The uncrosslinked material dissolved, leaving the crosslinked material. The remaining polyethylene was extracted from the hot toulene, dried in an oven at 353 K for twenty-four hours, and then weighed. The weight change ratio was recorded.

VI. RESULTS

Several experiments have been conducted on the basis of the theoretical considerations given in a previous chapter. Physical properties of the polyethylene and adhesive, and results of the peel tests, zeta potential measurements, and other tests are given in this chapter.

Results of the tensile tests performed on the various polyethylene films are illustrated in Fig. 4. The extruded film shows no orientation preference whereas the calendered film shows a preference in the longitudinal direction as shown, for example, by the higher yield strength. The elastic range of the nonoriented films appears to be 10×10^6 N/m^2 and while it is 27.5×10^6 N/m^2 for the calendered film. The calendered film in the longitudinal direction was found to extend with a diffuse neck whereas the extruded film and the calendered film in the tranverse direction exhibited extensive local necking and cold drawing. As the tests were terminated after an extension of 120 percent, it is not possible to quote the actual fracture strain; it is expected to be much larger than 120 percent.

Figs. 5 and 6 show the viscoelastic behavior of the polyethylene and adhesive at room temperature. The former figure shows the stress ratio, the ratio of the stress at a given time to the initial stress for a given fixed strain, as a function of time. The relaxation times were obtained from Fig. 5, by assuming the materials to be Maxwell solids, as 2.5×10^4 seconds for the polyethylene and 2.0×10^1 seconds for the adhesive. Most of the peel tests lasted for durations of the order of 6.0×10^1 seconds. It may be assumed, therefore, that the polyethylene was essentially elastic for testing conditions used in this work, whereas the adhesive is viscoelastic.

To investigate the viscous behavior of the materials, viscosity was determined

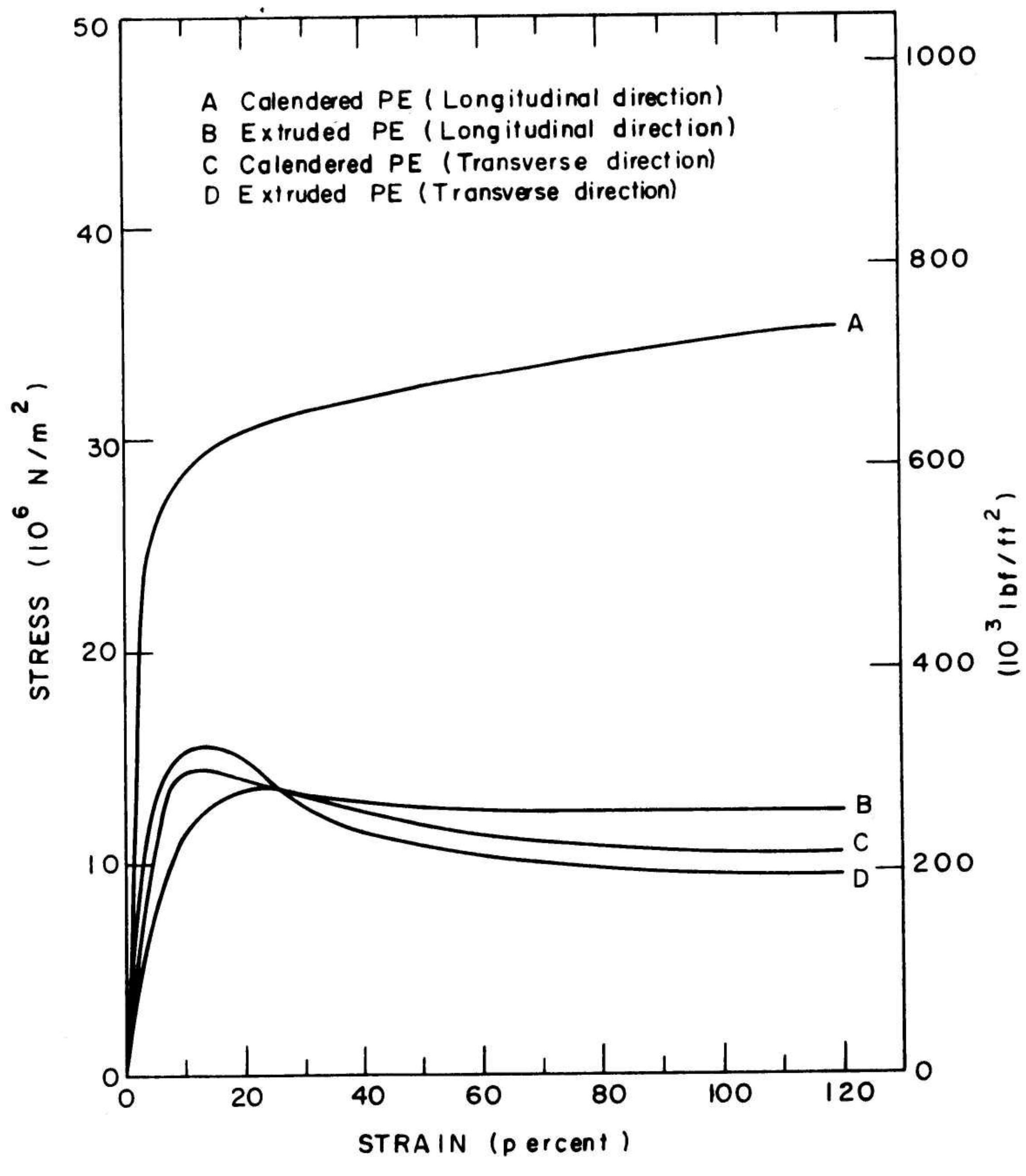

Fig. 4. Stress-strain plot of various polyethylene films. The temperature was 290 K and the crosshead speed was 4.23×10^{-4} m/s.

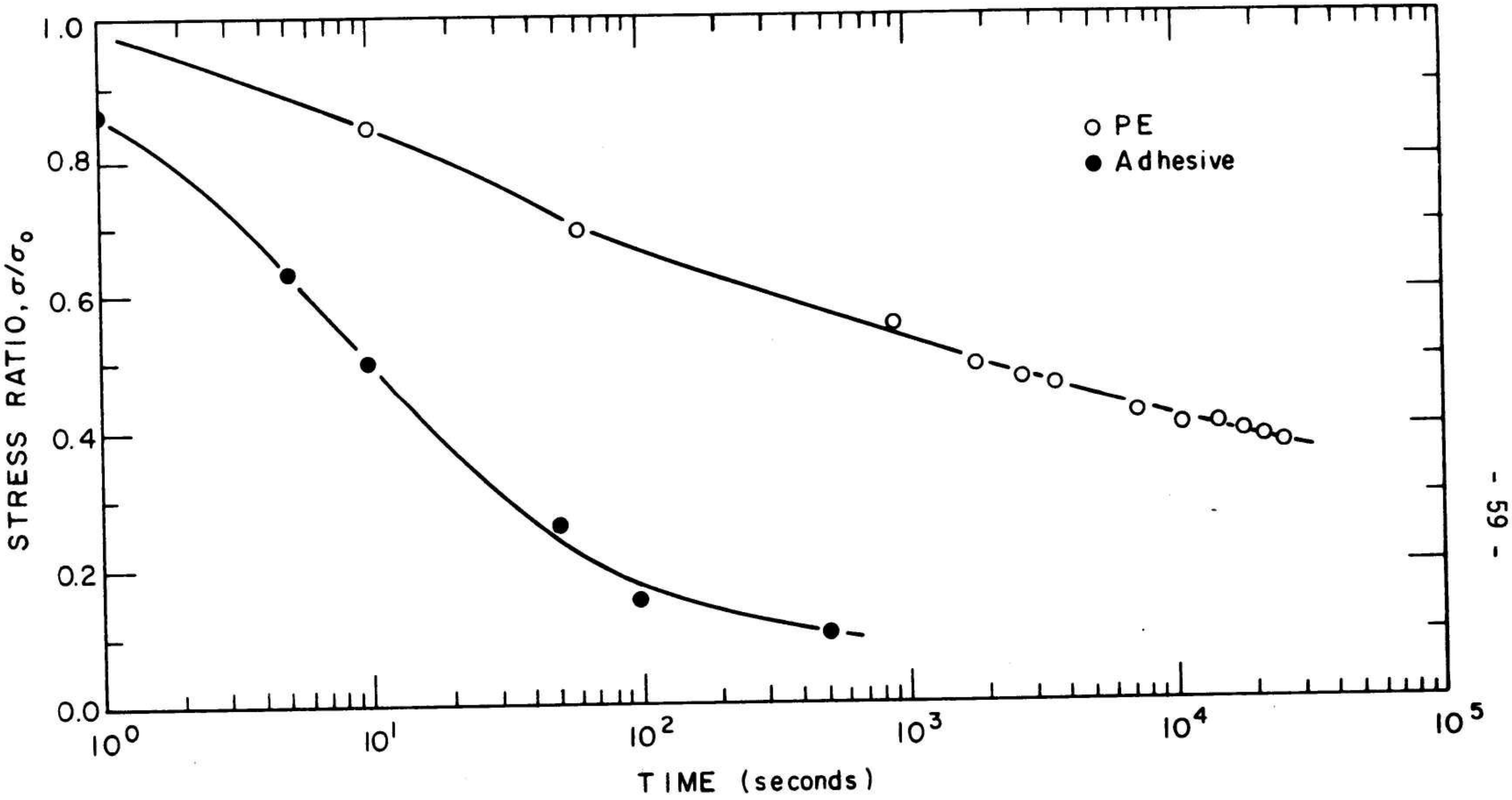

Fig. 5. Stress relaxation behavior of the polyethylene and adhesive. The initial stress, σ_o, was 4.14×10^4 N/m^2 for the polyethylene and 1.14×10^4 N/m^2 for the adhesive. The temperature was 296 K.

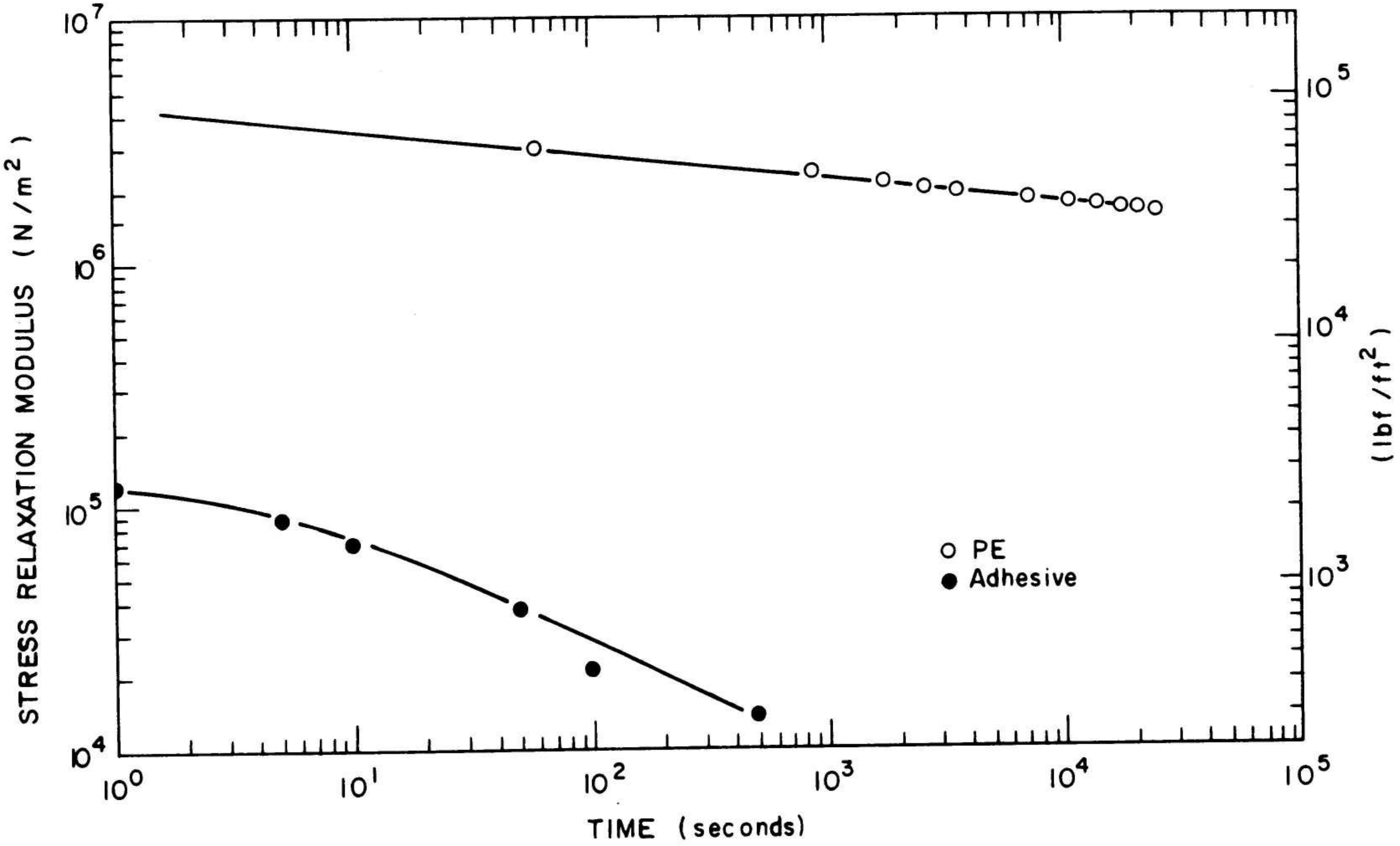

Fig. 6. Stress relaxation properties of the polyethylene and adhesive. Data from Fig. 5 are used in determining the stress relaxation modulus.

as a function of temperature. Fig. 7 shows the general trend that the polyethylene undergoes a drastic transition at approximately 375 K and the adhesive shows a slight hint of such a transition below the room temperature. Further, the viscosity of the adhesive is always lower than that of the polyethylene over the given temperature range. It should be noted that the room temperature viscosity value for polyethylene was calculated and not measured from a capillary rheometer as done with the other values.

The peel strength data for different bond pressures and times on untreated polyethylene at room temperature are given in Table I. There appears to be no major deviation between the peel strengths of the specimens bonded under these various conditions.

To study the effect of the various modifications to the polyethylene on adhesion, bond specimens of polyethylene with various treatments were made at room temperature. The results of the peel tests are shown in Table 2. In general, the peel strengths were higher for the modified polyethylenes than that of the untreated polyethylene. All specimens failed in an adhesive mode. The peel strengths for adhesive/adhesive specimens were also determined and found to be 2.31×10^3 N/m. However, these specimens failed in a cohesive mode.

The effect of temperature on the peel strength was investigated by bonding specimens of a few selected modified polyethylenes along with the untreated polyethylene at various temperatures. These results are given in Fig. 8. The untreated polyethylene exhibits a sharp transition in peel strength at a temperature near 375-410 K. (The melting point of polyethylene is approximately 383-393 K.) The glow discharge treated polyethylenes, helium and ethylene, show the same increasing monotonic function; the helium treated polyethylene showing a higher peel strength

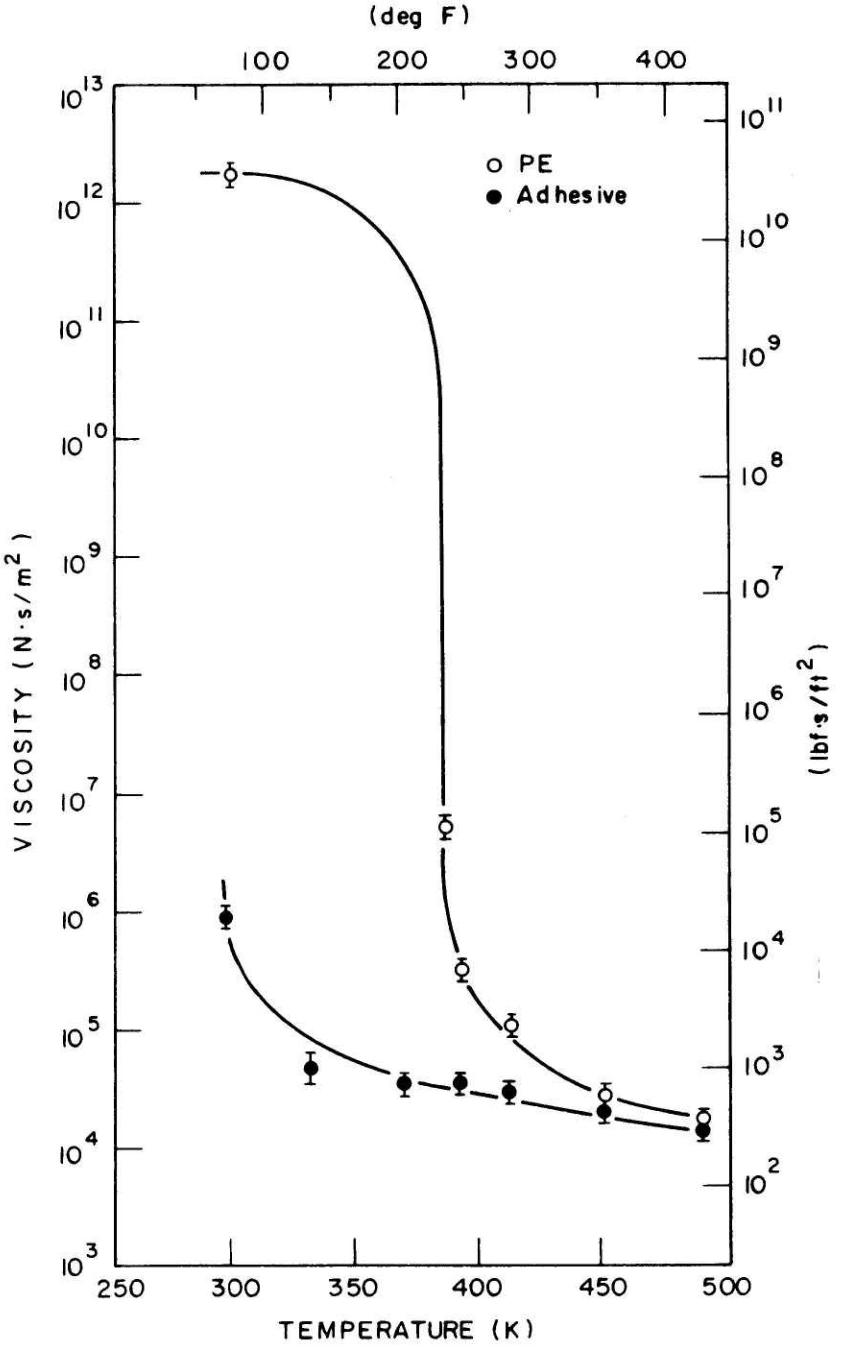

Fig. 7. Viscosity of the polyethylene and adhesive as a function of temperature. The shear rate was 4.5 seconds^{-1}.

Table 1

Peel Strength Data for Untreated Polyethylene for Various Bonding Conditions

Pressure (N/m^2)	Time (seconds)	Peel Strength* (N/m)	Std. Dev.
1.72×10^4	10^0	2.77×10^2	31.5
1.72×10^4	10^1	3.68×10^2	24.5
1.38×10^4	10^4	3.41×10^2	19.3
2.14×10^6	4.32×10^4	3.85×10^2	12.3

*Measured at a crosshead speed of 4.23×10^{-4} m/s and at room temperature for five specimens.

Table 2

Peel Strength Data for Untreated and Modified Polyethylene

Bond Specimen*	Peel Strength** (N/m)	Std. Dev.
Untreated PE	2.77×10^2	3.15×10^1
Glow Discharge Treated*** PE		
Ethylene	4.48×10^2	4.55×10^1
Ethane	6.48×10^2	7.01×10^1
CO_2	7.25×10^2	1.14×10^2
Nitrogen	7.53×10^2	6.13×10^1
NH_3	8.27×10^2	1.42×10^2
Helium	1.03×10^3	4.38×10^1
Doped PE		
LDPE/Aluminum	3.22×10^2	8.80×10^0
LDPE/Carbon Black	5.32×10^2	4.35×10^1
Quasi-Chemically Treated PE		
Witco Emcol E607	1.04×10^2	1.93×10^2
Ashland Variquat K-300	4.64×10^2	8.58×10^1

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* Bond specimens formed at a pressure of 1.72×10^4 N/m^2.

** Same peel test conditions as in Table 1.

*** Treatment was at a frequency of 14×10^6 Hz, a pressure of 1.33×10^5 N/m^2, and a power of 100 watts for 1.0×10^3 seconds.

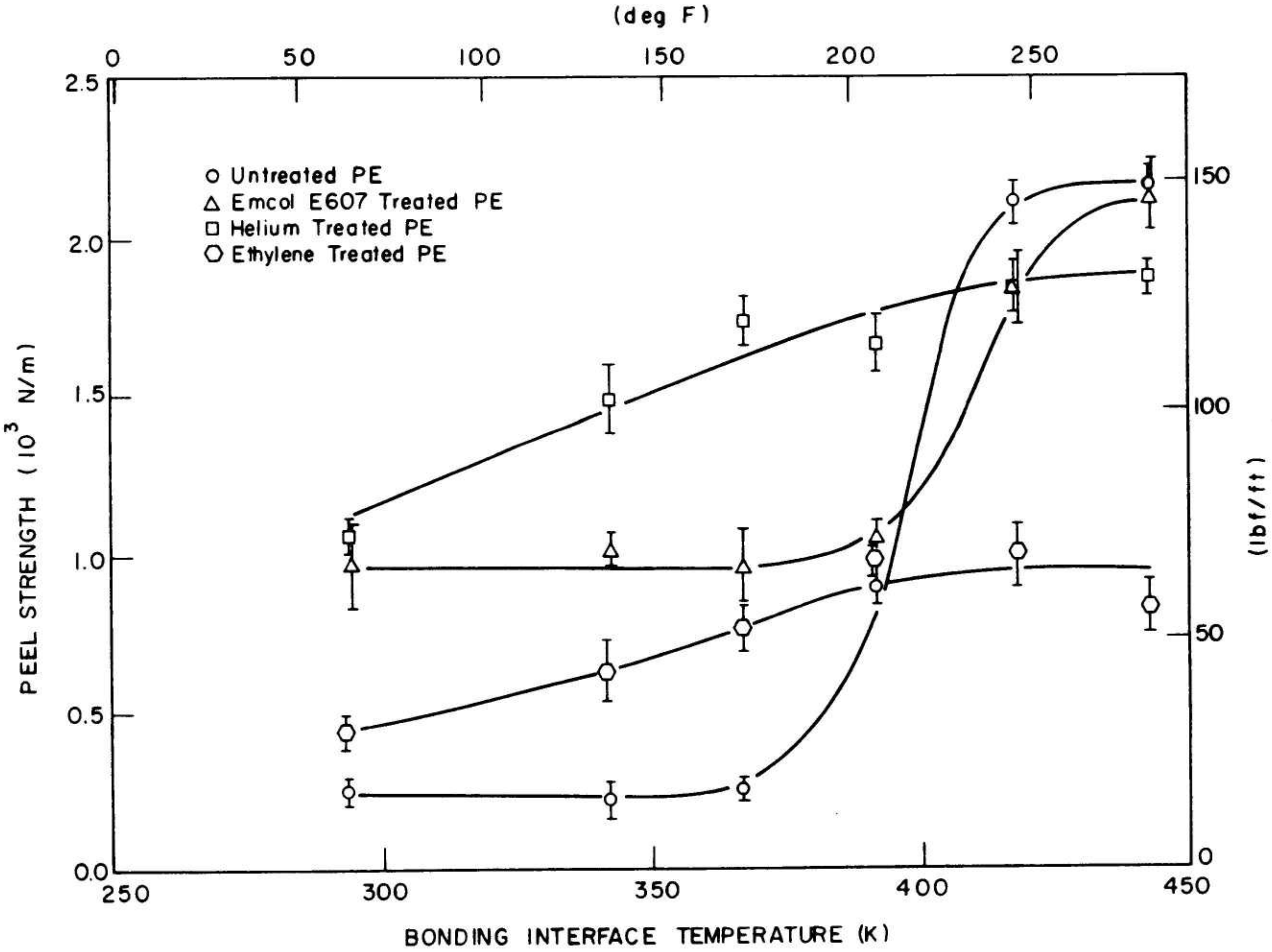

Fig. 8. Effect of the bonding interface temperature on peel strength for various polyethylenes. Same peel test conditions as in Table I.

and eventually leveling off near the same high peel strength as the untreated polyethylene. The quasi-chemically treated polyethylene (Witco Emcol E607) showed a similar trend to that of untreated polyethylene but its room temperature peel strength was higher than the untreated polyethylene. (The decomposition temperature of the chemical is roughly 393 K.) All failures were adhesive in nature except for the untreated polyethylene at 418K and 443 K, and Emcol E607 treated polyethylene at 443 K which were cohesive failures.

To investigate the role of diffusion as a mechanism responsible for the increase of peel strength, peel tests were performed on untreated polyethylene bonded for various times at 443 K, a temperature above the melting point of polyethylene. The results, plotted in Fig. 9, show that the peel strength was independent of time. A comparison with Fig. 8 shows that the peel strength is independent of temperature also above the melting point of polyethylene.

To determine whether crosslinking of the polyethylene occurs with glow discharge treatments, tests were performed on ethylene and ethane treated polyethylene. As shown in Table 3, it appears that crosslinking does occur with the glow discharge treatment. The ethylene seems to crosslink the polyethylene more than the ethane.

For the purpose of studying the surface alteration as the result of the modifications done on the polyethylene, zeta potential measurements were taken of the materials used in the room temperature peel tests. The correlation between the peel strength and zeta potential is shown in Fig. 10. There is a bell-shaped relation with the peak near -3×10^{-3} volts. The zeta potential of the adhesive, the common component of each bond specimen, was determined to be -9.6×10^{-3} volts.

The effect of the electrolyte concentration on the zeta potential and surface

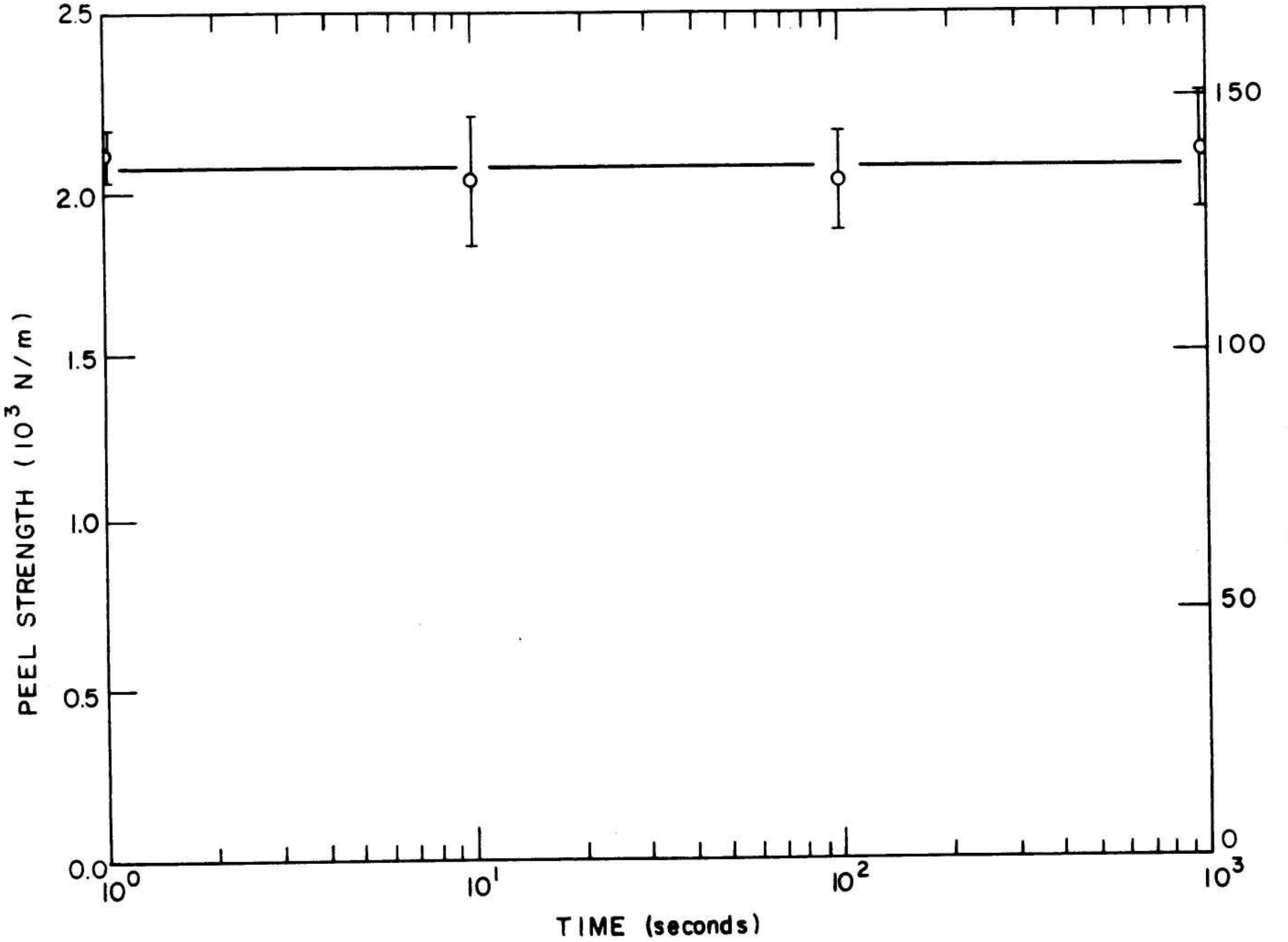

Fig. 9. Peel strength as a function of time at an elevated temperature (443 K). Same peel test conditions as in Table I.

Table 3

Effect of Glow Discharge Treatment on the Crosslinking of Polyethylene

Gas	Percent of Crosslinking
Ethylene	65.7
Ethane	26.6

*Same glow discharge treatment conditions as in Table 2.

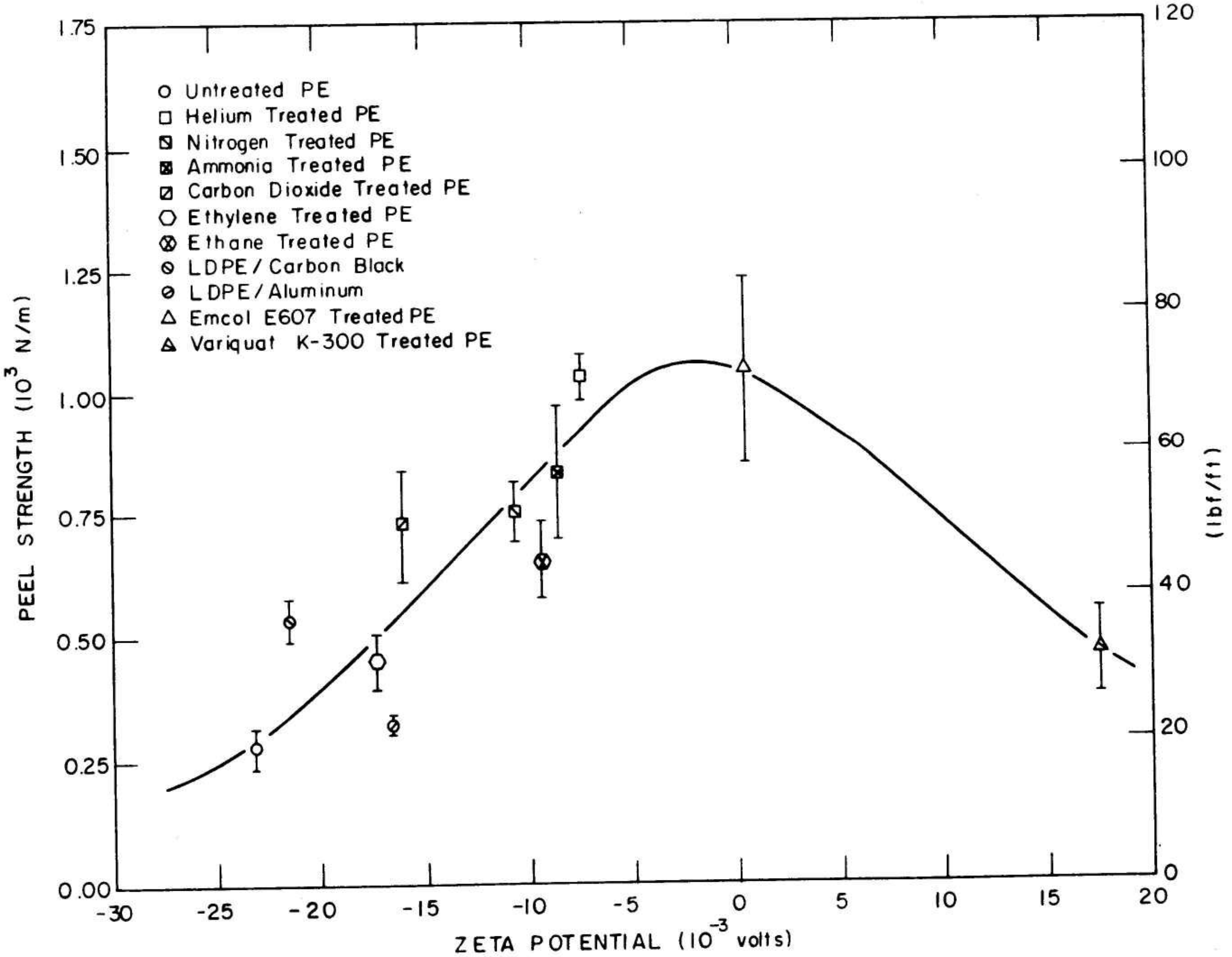

Fig. 10. Peel strength versus zeta potential. Same peel test and glow discharge treatment conditions as in Table 1 and Table 2 respectively. The electrolyte solution was 40:60 percent methanol-water at room temperature.

charge density are shown in Figs. 11 and 12 respectively. The zeta potential versus concentration plot, Fig. 11, is typical of those electrolyte solutions which do not reverse the sign of the surface charge when the concentration is varied. Fig. 12 shows the calculated surface charge density to be an increasing function of the concentration of the electrolyte. It appears to be approaching a horizontal asymptote. These two figures show that the zeta potential is a relative number.

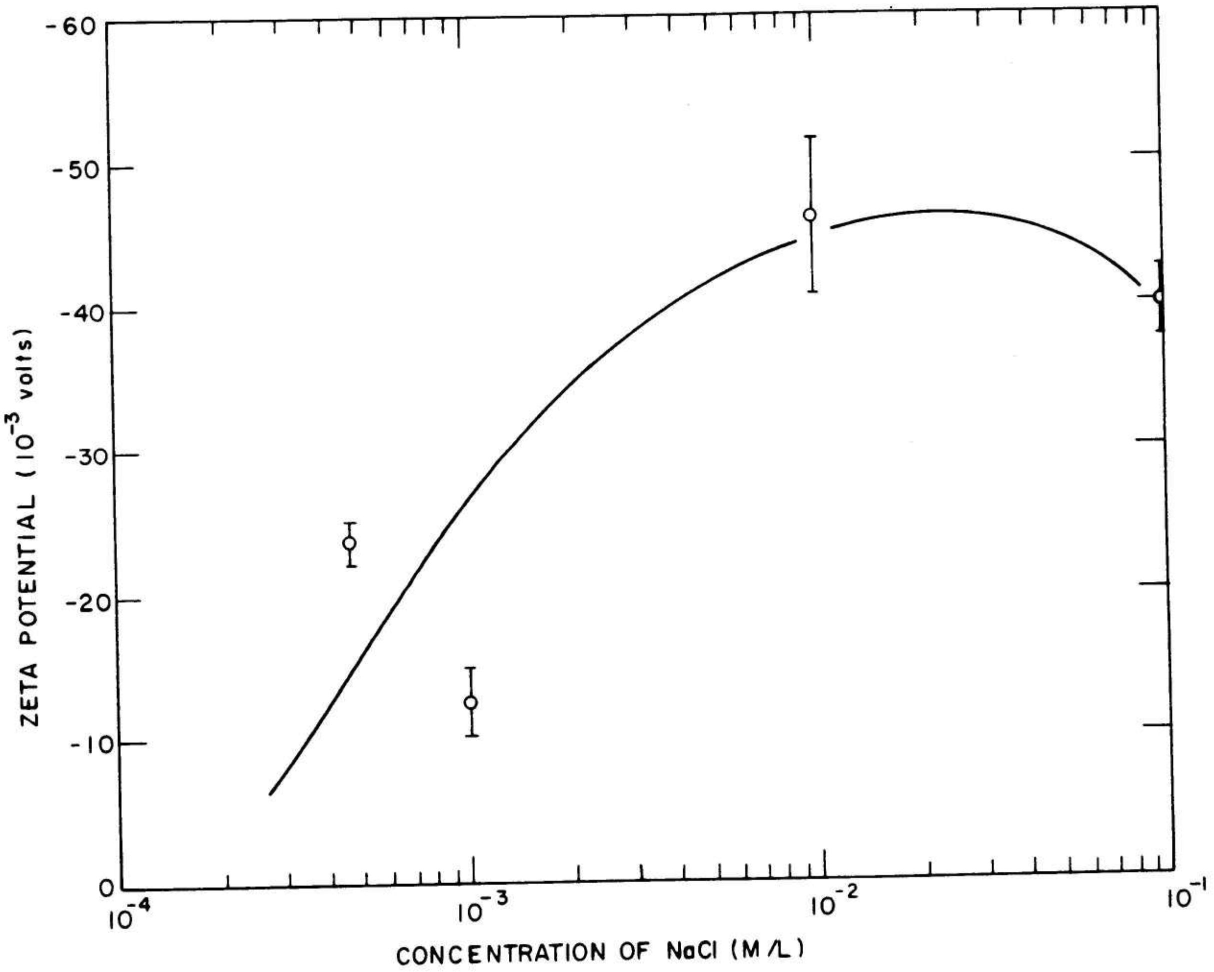

Fig. 11. Effect of electrolyte concentration on zeta potential. The temperature was 296 K.

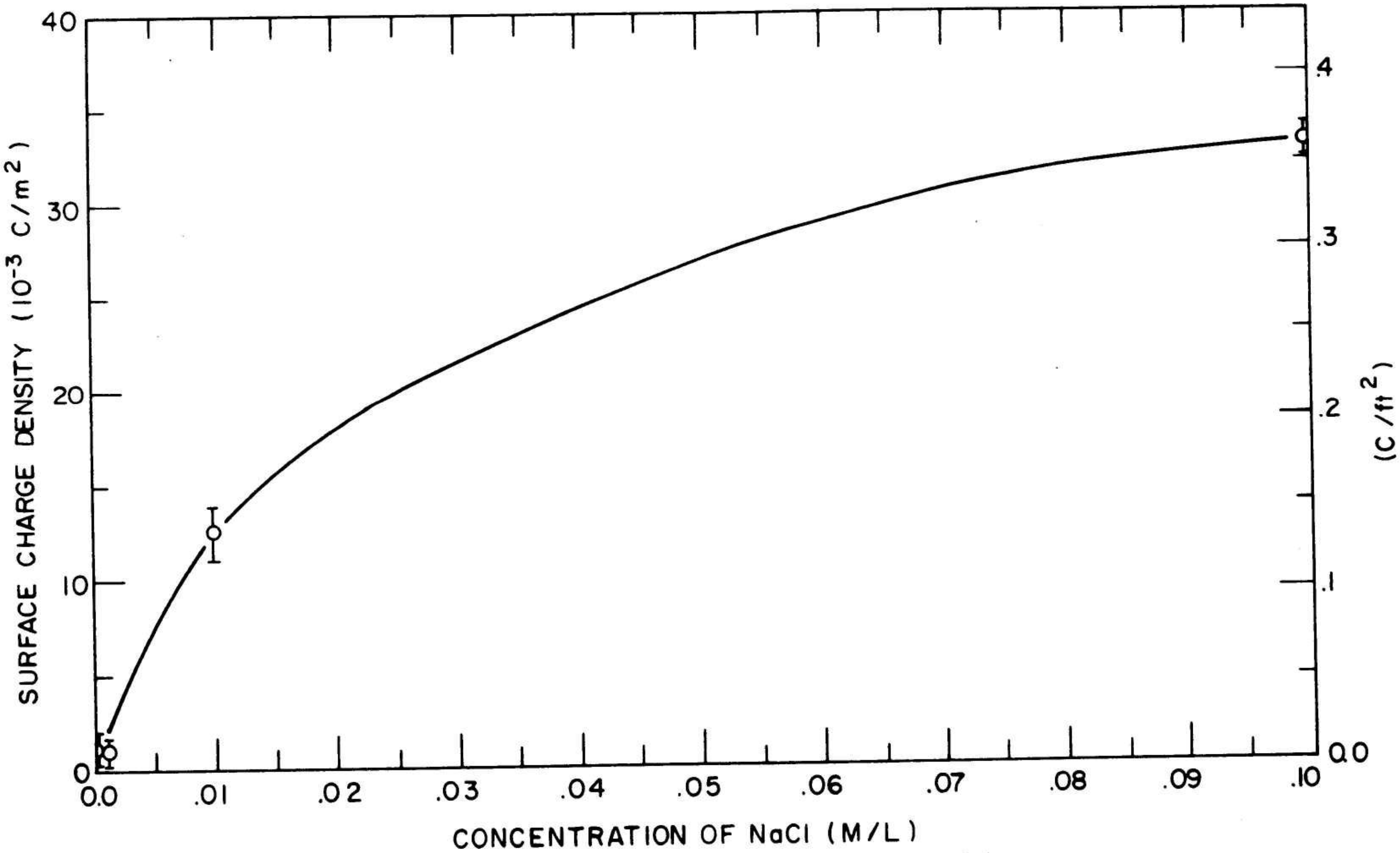

Fig. 12. Variation of surface charge density as a function of solution concentration. Data of Fig. 11 were used to calculate the surface charge density from Eqn. (A-11).

VII. DISCUSSION

A. Introduction

The following is a discussion on the results obtained through the experimental work. Discrepancies between the existing theories of adhesion and the results of both untreated and modified polyethylenes are brought forth. In addition, the possible role of electron interaction in adhesion, on the basis of the results, is suggested.

B. Untreated Polyethylene

The evidence, based on this thesis, when compared with existing theories in the literature, shows the shortcomings of the various theories for the untreated polyethylene results. Each theory will be considered in light of the experimental results obtained.

Although the rise in the peel strength as a function of bonding temperature appears to be in accordance with the adsorption theory apparently, a closer examination of the results show that indeed it is not the case. This is because the adsorption theory can not account for the sharp inflection in the peel strength in Fig. 8. The viscosities over the given temperature range 300-500 K, illustrated in Fig. 7, demonstrate this point. Even though the viscosity of the adhesive falls by two orders of magnitude in that temperature range, which may explain for increasing peel strength, the peel strength, however, does not increase by the same amount as it should according to the contact theory.[7-11] The viscosity of the polyethylene does show an inflection at its melting point (383-393 K), but the viscosity of the adhesive is below that of the polyethylene at all temperatures. Thus, contact between the adhesive and polyethylene is controlled at all temperatures by viscous properties of the adhesive.

In addition, the surface energy approach[1-6] can not explain the inflection either. As mentioned earlier, the work of adhesion is given by Eqn. (2). Wu[31] has shown the variation of the surface energy of polyethylene as a function of temperature as illustrated in Fig. 13. It can be seen that the surface energy exhibits a linear decay with increasing temperatures. The same trend can be expected for the adhesive and interfacial surface energies. Thus the work of adhesion does not exhibit the inflection and the surface energy arguments can not explain the sharp increase in the peel strength at the melting point of polyethylene. The inflection of the peel strength may be associated in some other manner with the melting point of polyethylene.

According to the diffusion theory,[14] the force required to separate an adhesive joint should be related to the time needed to form the bond. As mentioned previously, Wake[15] showed the force should vary as the one-fourth power of time. The results of Table 2 and Fig. 9 show that the peel strength is independent of bonding time both at room temperature and at 443 K.

Also, the solubility of the adhesive into the polyethylene or vise versa indicates if diffusion will occur across the interface. From a thermodynamic viewpoint, for a solution to form, the free energy of mixing must be negative. The equation

$$\Delta G_F^m = \Delta H^m - T \Delta S^m \qquad (31)$$

defines the free energy of mixing G_F^m where H^m is the enthalpy of mixing, T is the temperature, and S^m is the entropy of mixing. For typical polymers and elastomers,

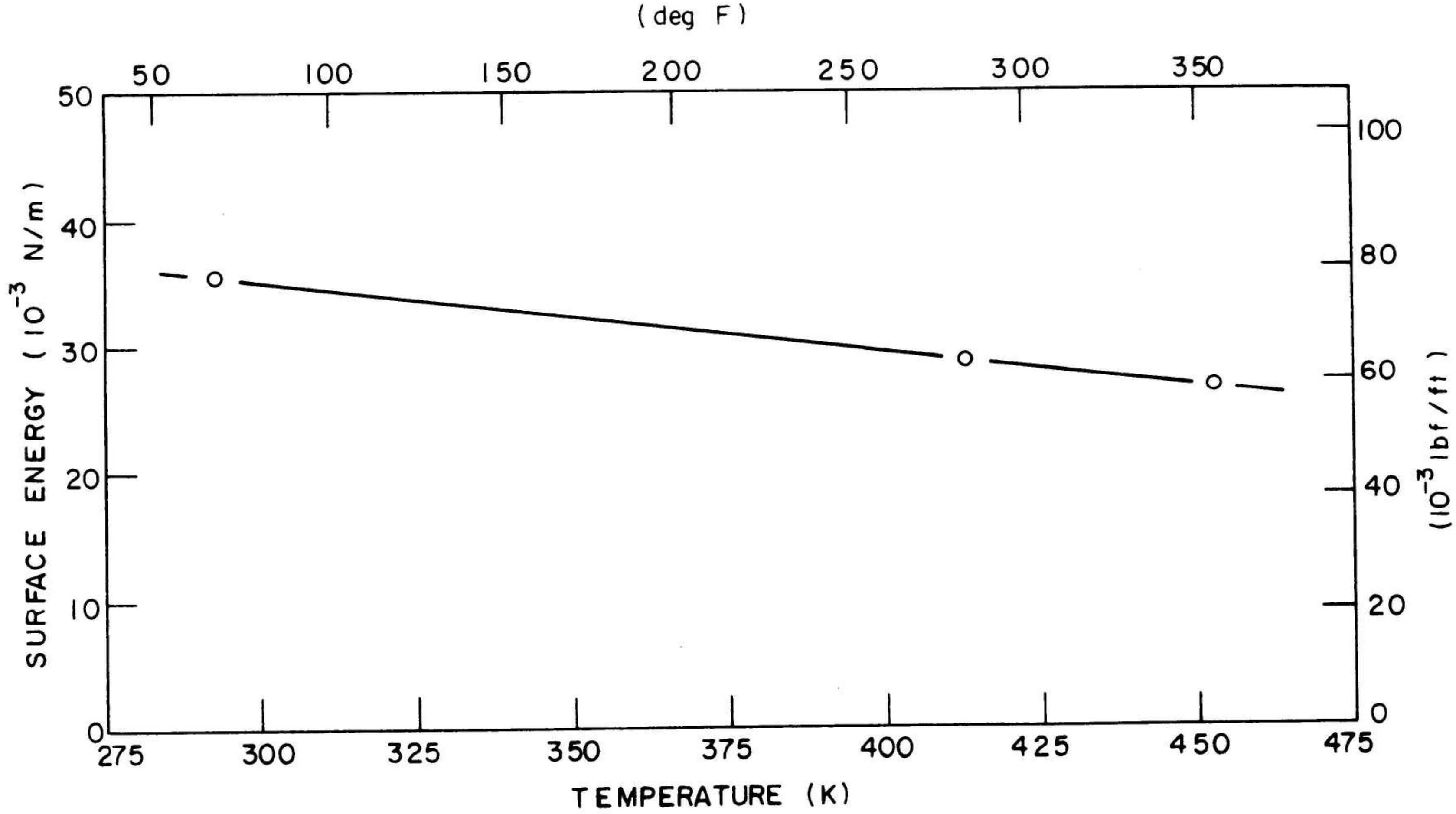

Fig. 13. Surface energy of polyethylene as a function of temperature. (From Reference 31.)

the entropy of mixing is small because the long chained molecules tend to be less mobile and limit the number of positions it can occupy. For nonpolar molecules and in the absence of hydrogen bonding, the enthalpy of mixing is positive.[32] Both quantities tend to remain constant or slightly increase with higher temperatures. Thus to meet the thermodynamic requirement, a high temperature is required but the minimum temperature needed is often above the degradation temperature.

Further evidence of the lack of diffusion across the polyethylene/adhesive interface is demonstrated by delamination of the adhesive from the polyethylene backing in the Kendall adhesive tape at temperatures below 263 K. "Clean" interfacial failures occur at these low temperatures.

The chemical theory is not applicable in describing the inflection in Fig. 8 either because no primary bond mechanisms are present at the interface. For a nonpolar system, the only mechanism permitting covalent bond formation is generating free radicals from intitiators and/or producing saturated bonds from double or triple bonds. Since neither initiators nor unsaturated bonds exist in the polyethylene/butyl rubber system, it can be assumed that no primary bonding occurs at low or high temperatures. The arguments about the low temperature delamination of the Kendall tape are also valid for this case.

The mechanical deformation theory[16-20] can not be checked with the results because the T-peel test parameters were held constant. Since the geometry of the bonded specimen and the testing parameters, i.e., separation rate, temperature, and environment, did not vary, no comparisons can be made in determining whether the mechanical deformation theory can explain the peel strength results. However, as the properties of polyethylene and adhesive did not change appreciably during the bonding process, this theory cannot account for the change of peel strength.

In fact, the materials would tend to degrade at the high temperatures and cause peel strength to decrease instead of increasing. In any case, this theory relies on good adhesive strength because cohesive failure is impossible unless the interface is stronger than the bulk.

According to the weak boundary layer theory,[21] elimination of the weak layer at high temperatures by diffusion of the weak surface material into the bulk and/or by mechanical removal of the weak material could account for the increase in the peel strength. The disappearance of the layer raises the joint strength to that of the material strength thus forcing cohesive failure to occur. This is what appears to happen at high temperatures above the melting point.

The polyethylene and adhesive are both nonpolar materials thus making it difficult to assume that the electrostatic theory applies. The theory[23] cannot explain the change of peel strength from the variation of temperature except through the change of the dielectric constant of the testing environment, usually air, between the two materials. The dielectric constant may change with temperature, however. As the testing temperature was held constant at room temperature for all peel tests, this theory cannot account for the peel strength transition.

The mechanical theory approach does not include temperature effects thus it can not explain the results of the untreated polyethylene behavior in Fig. 8.

C. Modified Polyethylene

The increase of the peel strength of the various modified polyethylenes over that of the untreated polyethylene can not be totally explained again, by the various theories. The arguments of the diffusion, mechanical deformation, and electrostatic theories remain the same as those for the untreated polyethylene. The remaining theories seem to explain the increase in the peel strength but each of these theories cannot justify the results of each of the polyethylene modifications. At least one modification is unexplainable in each theory. The following discussion demonstrates these points.

The diffusion, mechanical deformation, and electrostatic arguments for untreated polyethylene apply to the modified case also. The diffusion and electrostatic theories are based on the bulk properties of the materials whereas the various modifications done on the polyethylene produce only surface effects. Thus they cannot account for the increase of peel strength above that of the untreated polyethylene at the lower temperatures let alone at the higher temperatures. The T-peel test parameters are constant as used with the untreated polyethylene thus making the mechanical deformation theory invalid in this given case.

According to the adsorption theory, a change of the surface energy in the polyethylene could have occured with the glow discharge treatment which may explain the increase of peel strength. However, Schonhorn[33] has shown the surface energy (3.5×10^{-3} N/m) of his treated polyethylenes did not change. Thus, as far as this theory is concerned, the peel strength at room temperature should have remained the same instead of increasing.

Free radicals may be generated in the glow discharge to allow primary bonds to form. This permits the chemical theory to predict an increase of peel strength. However, this does not occur for the quasi-chemical treatments where only entanglement of the hydrocarbon chain occurs nor for the doped polyethylene where a macroscopic mixing occurs. It is generally believed that crosslinking is achieved and not the generation of free radicals in the glow discharge treatment as observed by ATR spectroscopy.[33]

The weak boundary layer states that the glow discharge eliminates the weak boundary layer by crosslinking the weak surface material. Therefore, the peel strength will increase. The results of Table 3 show that the ethylene glow discharge crosslinks the polyethylene more than the ethane glow discharge but yet its peel strength is less than that of the ethane. The other modifications cannot strengthen or eliminate the weak layer.

According to the mechanical theory, the surface roughness may have changed slightly due to the activated species bombardments in the glow discharge. This will increase the peel strength but not as a function of temperature. The roughness does not change for the quasi-chemical and doped modifications but yet the peel strength increases. It appears unlikely that the peel strength increases because the surface roughness change.

The results of the modified polyethylenes in Fig. 8 show the effects of the surface treatments on peel strength as a function of temperature. The helium treated results have the same trend as found in the literature.[33] In general, it can be seen that at the temperatures below the melting point of polyethylene, the treatments show a relative improvement of the peel strength although adhesive failure occurs. As the temperature is increased, the helium and Emcol E607 peel strengths and failures approach the peel strength and cohesive failure of the untreated polyethylene at the higher temperature range 400-450 K whereas the ethylene does not. In fact, it appears that treatments can increase peel strength but not beyond the strength level for cohesive failure since all the failures were adhesive except for the untreated polyethylene at 418 K and 443 K, and Emcol E607 treated polyethylene at 443 K. To achieve cohesive failure, high temperatures are required. This is what occurs in the Kendall calendering process where a temperature of 450 K is reached.

Thus, it seems modifications are good for moderate improvements in peel strength of adhesive failure at temperatures below the melting point of polyethylene. However, they can not improve the peel strength greater than the peel strength of untreated polyethylene, at high bonding temperatures, resulting from cohesive failure. It seems that since the untreated polyethylene peel strengths are higher at temperatures above 400 K, any modifications appear to decrease the untreated polyethylene peel strength at these temperatures.

D. The Role of Electron Interaction in Adhesion

The above discussion has shown that the various theories of adhesion cannot explain the peel strength results obtained from the experimental work. However, the results involving the zeta potential measurements show the underlying role of electron interaction in adhesion. This belief is justified as follows.

Since the zeta potential is an indirect measure of the surface charge, the results of Fig. 10 show the peel strength variation with the surface charge of various polyethylenes. It appears that the surface charge of the untreated polyethylene has been altered in some manner for the modifications made. The alteration in surface charge seems to increase the peel strength but not by the same amount. The manner in which the peel strength varies as a function of surface charge provides a basis for a hypothesis as to what may occur in adhesion. The peel strength is a bell-shaped function of the zeta potential with the peak near the zeta potential of the adhesive at -9.6×10^{-3} volts. This behavior indicates that the zeta potential and the surface charge of the materials being bonded together should be the same for good bonding. This idea is similar to that presented by Wu.[31] He states that the polarities of the bonding materials should be exactly the same to achieve "optimum" wetting. Intuitively it seems that the surface charges should be opposite of each other; but it appears that this factor is minor in comparison to the compatability of the materials because of the charge similarity of the bonding surfaces. Therefore, for conditions where adhesion is undesirable, the zeta potential and the surface charge should be as diverse as possible. The change of the electron configuration from that of the untreated polyethylene appears to explain the peel strength increases of 1.2 - 4.0 times that of the untreated polyethylene.

The results of Fig. 8 can also be justified with the above argument. The increase of the peel strength with temperature is the result of thermal activation which disturbs the electron states at the surface. The inflection in the untreated polyethylene curve is from the change of electron state, perhaps due to phase change of the polyethylene at the melting point. The peel strength results of Fig. 9, where the temperature is constant and above the melting point of polyethylene, should be independent of time, in the absence of diffusion, since the electron disturbance is a function of temperature only. A similar argument also applies to the peel strengths of Table 1.

The results of Figs. 11 and 12 do demonstrate that the zeta potential depends on the electrolyte, concentration of potential determining ions, etc., and so does not give an absolute value for the surface charge for the different polyethylenes. It does give a relative hierachy, however. The curves are such that for the given concentration range, 0.0-0.1 M/L, the sign of the zeta potential and the surface charge do not reverse such as in the case of positive polyvalent ion electrolytes. Thus, the hierachy established in the results will not vary either because of slight concentration variations, shape, size, and distribution of particles, etc. The surface charge calculated from the data of Fig. 11 and with Eqn. (A-11), and plotted in Fig.

12, show the charge is approaching an asymtote at 35 x 10^{-3} C/m^2. This is probably because the surface becomes saturated with ions and cannot interact with remaining ions in the electrolyte. It appears that an absolute surface charge measurement may be obtained at the corresponding concentration level; however, when the electrolyte is varied, this saturation level and the concentration at which it occurs also change.[34] In fact, the zeta potential-concentration behavior may also vary such that the sign of the zeta potential reverses. Thus, only relative measurements can be made for a given electrolyte and concentration. This fact does not negate the results obtained since the zeta potential does show there is some surface charge change which is necessary for electron interaction.

The various surface charges obtained in the polyethylenes are the result of the change of surface electronic states. The change occurs because of some disturbance of these states as the result of the different modifications. It appears these changes decay very slowly in time as indicated by the time (approximately 9.0 x 10^2 seconds) between treating the polyethylene and forming the bond specimen.

The role of electronic states have been found in classical works Keesom,[35] Debye,[36] and London[37] on non-ideal gas systems. Extrapolations to solids have been made. However, the conditions for bonding must be understood by an approach that deals with the role of intermolecular forces across solid surfaces. Several people, Kirkwood and Buff,[38] Ninham and Parsegian,[39] Langbein,[40] and Lifshitz[41] have stressed the importance of the role of intermolecular forces in adhesion. The results of this thesis relate to that approach by indicating the importance of electron interaction with molecular forces in adhesion.

VIII. CONCLUSIONS

The effect of the various polyethylene modifications to enhance adhesion was systematically studied. The following conclusions can be drawn from that study.

1. Although intimate contact is necessary for good bonding, it cannot explain why adhesion does not take place at low temperatures even when there is intimate contact.
2. Good bonding can be obtained even when there is no interdiffusion of adhesive and adherend.
3. Although the improvement of adhesion of polyethylene, when treated in glow discharge treatment, has been explained in the past on the weak boundary layer hypothesis, it can be explained that such improvement is due to changes in surface electronic states.
4. Electron interaction seems to play a vital role in adhesion. To promote adhesion, the surface of the bonding materials must be such that the surface charges are similar. To prevent adhesion, the surface must be such that the surface charges are dissimilar.
5. For a given pair of bonding materials, the above condition may be achieved by disturbing the surface electron equilibrium by thermal, mechanical, chemical, electrical, and/or irradiation methods.

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APPENDIX

Zeta Potential

This appendix includes descriptions of the definition of the zeta potential, the measurement of electrokinetic parameters, the calculation of the zeta potential values from these parameters, and the relationship between the zeta potential and surface charge density.

A. Definition

From several phenomena observed in colloidal systems, it has been inferred that the dispersed particles carry an electric charge. The charge is developed because one type of charge may dominate the surface. Thus, ions of opposite sign are strongly attrracted to the surface when the particle is suspended in an electrolyte. Since the electrolyte as a whole is electrically neutral, the dispersion medium must contain an equivalent and opposite charge distributed in the bulk. These charges are carried by ions, i.e., by an excess of ions of one sign at the particle surface and an excess of ions of the opposite sign in the solution. Hence, if each particle is considered separately, is surrounded by an electric double layer. The concept of the existence of differently charged layers, or of the electrical double layer, at the solid-liquid boundry was suggested by Helmholtz.[1] He also suggested that an electrical double layer is generally formed at the surface of separation between phases. By making the assumption that the double layer is virtually an electrical condenser with parallel planes a molecular distance apart, Helmholtz was able to treat the subject mathematically. According to his model, the potential gradient at the interface should be sharp, but modern views are in favor of a diffused double layer as proposed by Gouy[2] and supported by others. A more recent view suggested by Stern[3] has shown that neither the sharp nor the diffuse double layer is alone adequate but their essential characteristics could be combined. According to Stern, the double layer can be divided into two parts. The first part consists of approximately a single ion in thickness and remains fixed to the solid surface. In this layer, there is a sharp fall of potential. The second part extends some distance into the liquid phase and is diffuse. In this region, thermal agitation permits the free movement of the ions but the distribution of positive and negative ions are not uniform. The result is a gradual fall of potential into the bulk of the liquid where the charge distribution is uniform. In order that simple mathematical considerations may be applied to the electrokinetic phenomena, it is necessary to assume that the diffuse double layer is equivalent to an electrical condenser with parallel plates d m apart, each carrying a charge e_o per sq. m with the difference of potential between the plates as equal to the zeta potential, ζ. If is the dielectric constant of the medium between the hypothetical plates, then it is know from electrostatics,

$$\zeta = 4 \pi \frac{e_o d}{\varepsilon} \tag{AI}$$

This is the fundamental equation for the quantitative treatment of all types of electrokinetic phenomena.

B. Measurement

There are several types of electrokinetic phenomena but the three basic ones - electroosmosis, streaming potential, and electrophoresis, are used in determining the zeta potential. When small charged particles, suspended in an electrolyte, are held stationary, the liquid will move under the influence of an applied potential gradient because when an external electric field is applied tangentially to a fixed surface, the mobile portion of the diffuse double layer will flow due to the forces acting on the excess ionic charge contained within it. This permits the zeta potential to be calculated with the appropriate formula relating it to the measured flow rate. This phenomenon is known as electroosmosis. If the liquid moves under the influence of an applied pressure gradient instead, the zeta potential can be determined with an appropriate formula by measuring the resulting voltage. This voltage is known as the streaming potential. If the particles are free to move under the influence of the applied potential gradient. This behavior is known as electrophoresis. The resulting velocity of the particles can be measured and converted to the zeta potential. In the experimental work of this thesis, the zeta potential was determined with the electrophoresis method.

The apparatus used in the method of electrophoresis was instrumentation built by the ZETA-METER, Inc., New York, New York. This instrumentation was made available through the courtesy of the Kendall Company. The basic components of the ZETA-METER were a variable DC power supply and timer, a circular electrophoresis cell with a molybdenum anode and a platinum cathode, and a stereoscopic microscope with a multi-scale ocular micrometer and illuminator.

The procedure necessary to use the method of electrophoresis involves measuring the velocity of particles individually. The time for a particle to travel a given distance under an applied potential is recorded and converted to the zeta potential by

$$\zeta = \frac{4\pi\eta v_1}{\varepsilon E_a} \qquad \text{(A2)}$$

where η is the viscosity of the liquid, v_l is the velocity of the particle, ε is the dielectric constant of the liquid, and E_a is the applied potential. It is often convenient to rewrite Eqn. (A2) in terms of electrophoretic mobility (EM) as

$$EM = \frac{v_l}{E_a} \qquad \text{(A3)}$$

Eqn. (A2) may be rewritten into Eqn. (A4)

$$\zeta = EM\frac{4\pi\eta}{\varepsilon} \qquad \text{(A4)}$$

The above equation may be transformed into

$$\zeta = 113{,}000\ \frac{\eta}{\varepsilon}\ EM \qquad \text{(A5)}$$

where ζ is the zeta potential of the suspended particle in 10^{-3} v, η is the viscosity of the liquid in poises, ε is the dielectric constant of the liquid, and EM is the electrophoretic mobility in 10^{-6} m/s per v $/10^{-2}$ m. Caution must be taken in measuring the proper particle velocity. The electrical double layer at the walls of the electrophoresis cell itself imparts a motion to the whole suspension in the cell. The suspension moves rapidly in one direction near the wall, more slowly further away from it, and in the opposite direction at the center of the cell. At some point in the cell, there is no net motion applied to the suspension as the result of the zeta potential of the cell wall-liquid interface. It is at this point that the observed velocity of the particles in the system is equal to the electrophoretic velocity. Calculations have shown that this stationary position is located at a distance 14.8 percent of the diameter from the wall of a cylinderical cell. The velocity of all the particles was measured at this point.

C. Relation between Zeta Potential and Surface Charge Density

The zeta potential may be related to the surface charge density through the theory proposed by Gouy[2] for large particles. In general, by satisfying Poisson's equation, a relationship between the potential, ψ , across the double layer and the average electrical charge density, ρ ,is obtained and given as

$$\nabla \cdot \nabla \psi = -\frac{4\pi\rho}{\varepsilon} \tag{A6}$$

where ε is the dielectric constant of the liquid. For large particles, at a distance x from the surface of an infinite plane of potential, the density of charge in a liquid is simplified to

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi\rho}{\varepsilon} \tag{A7}$$

The electrical charge density is also related to the number of positive and negative ions and thus to the concentration of the electrolyte according to the Boltzmann equation

$$\rho = (n_- z_1 e_o) \exp\left(-z_1 \frac{e_o\psi}{kT}\right) - (n_+ z_2 e_o) \exp\left(z_2 \frac{e_o\psi}{kT}\right) \qquad \text{(A8)}$$

where n is the number of ions, z is the valence of the ions, e_o is the charge, ψ is the potential, k is Boltzmann's constant, and T is the absolute temperature of the liquid. Assuming $n_- = n_+ = n$ and $-z_1 = z_2 = z$, Eqn. (A8) may be transformed into

$$\rho = 2 \sinh\left(z \frac{e_o\psi}{kT}\right) \qquad \text{(A9)}$$

Thus Eqn. (A7) may be written as

$$\frac{d^2\psi}{dx^2} = - \frac{8\pi\rho}{\varepsilon} \sinh\left(z \frac{e_o\psi}{kT}\right) \qquad \text{(A10)}$$

Solving Eqn. (A10) with the boundary conditions

$$x = 0 \qquad \psi = \psi_o = \frac{4\pi\sigma_o}{\varepsilon}$$

where σ_o is the surface charge density

$$x = \infty \qquad \psi = 0$$

yields

$$\sigma_0 = 35{,}300 \ (c)^{1/2} \ \sinh \left(\frac{z\zeta}{50}\right) \tag{A11}$$

where σ_0 is the surface charge density in esu/10^{-2} m^2, c is the concentration in moles/liter, z is the valence of the ions, and ζ is the zeta potential in 10^{-3} volts. The above equation assumes a temperature of 291 K and the dielectric constant to be that of the solution. Thus this is Gouy's equation for large particles relating zeta potential to surface charge density.

References

1. Helmholtz, H., "Studren über elektrische Grenyschichten," Wied. Ann. (in German), 7, 337 (1879).
2. Gouy, G., "Constitution of the Electric Charge at the Surface of an Electrolyte," J. Phys., 9, 457 (1910).
3. Stern, O., "Theory of the Electrolytic Double-layer," Z. Electrochem, 30, 508 (1924).

SUGGESTIONS FOR FUTURE WORK

The results and conclusions drawn from the experimental work indicate several suggestions for future work.

1. A better characterization of the surfaces, microstructural and electronic, is needed in understanding precisely what happens during the process of adhesion.
2. Other methods of treatments, prior or in situ, to bonding to change the electron structure at the surface, by methods such as irradiation by infrared to X-rays, etc., should be investigated.
3. Methods of establishing primary bonding across an interface, by chemical modification of the surface, proper choice of materials, etc., are required to obtain high joint strength and cohesive failure in the adhesive.