Unified Theory and Guidelines on Adhesion

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SYNOPSIS

A new approach was proposed to consolidate the many adhesion theories into one coherent concept. The maximum attractive force between two sets of molecules (adhesion strength) is derived from the Lennard–Jones potential function and calculated with measured bond length and bond energy. It leads to two criteria for strong adhesion: intimate molecular contact of closer than 9 Å (necessary condition), and maximum attractive force with minimum potential energy (sufficient condition). The criteria conform to the key elements of most prior adhesion theories. Seven prior adhesion theories and their relevance to these two criteria were briefly reviewed/discussed. In order to draw up a set of guidelines on adhesion and supplement the missing pieces of information, 21 model polymers of varied functionality were synthesized to study (1) the effect of polar groups on adhesion and (2) the effect of polymer conformations on adhesion. The results indicate that polar groups are more effective in polymer backbone than in side chains for promoting adhesion. The presence of both hydrogen donors and acceptors in the same backbone maximizes adhesion. True (active) solvents enhance adhesion, cosolvents (latent solvents) boost adhesion by inducing favorable conformation of polymers in solution, but thinners (diluents) reduce adhesion. The set of guidelines covered the effects of functional groups, solvent blends, pigment loadings, adhesion promotion, and adhesion loss.

INTRODUCTION

A great deal of research has been done and many volumes have been written on adhesion.[1-8] However, the present status of adhesion theory is confusing. At least seven adhesion theories are currently in use. Each theory has its merits, but none is universally applicable. Three factors contributed to this situation: First, each theory deals with only part of the problem; second, similar ideas are presented in different languages depending on the expertise of the author; and, finally, each theory emphasizes its own insight and tends to expel others. With regard to recent advances in research tools for surface analysis, and demands for high performance coatings/adhesives in the automotive, aerospace, and microelectronics industries,[7,8] probably the time is ripe to consider a consolidated theory of adhesion. Ideally, a consolidated theory of adhesion should be able to: (1) explain the origin of attractive forces, i.e., why

things adhere, (2) suit all cases of adhesion such as polymer to metal/oxide (protective coatings, adhesives), polymer to polymer (basecoat/clearcoat, coating plastics), metal to metal (soldering), cement to steel (concrete), etc., (3) encompass all existing adhesion theories, (4) accommodate experimental facts, (5) reveal ways leading to strong adhesion, and (6) interpret the loci of adhesion failures. A consolidated theory of adhesion is proposed here to partially fill these demands. This is possible mainly due to the large number of prior studies. A matching set of guidelines on adhesion is compiled from prior work and supplemented by this study. Certainly, a lot more work is necessary to substantiate or modify the consolidated concept of adhesion.

ADHESION THEORY

The objectives of this study have been to clarify the status of adhesion theory and to shorten the gap between theory and practice by tying together all prior insights in a coherent concept, and by generating a set of guidelines on adhesion for field appli-

cations. The electronic attraction between molecules is the thread of logic used to approach these objectives. The details are discussed below.

Maximum Attractive Force

Theoreticians attempt to solve the Schrödinger equation using perturbation methods, and then calculate the potential energy between molecules which predicts bond strength. But the calculations are extremely tedious even for small molecules and infeasible for polymers.[9] Nowadays, the bond lengths have been accurately measured by X-ray diffraction analysis and the bond energies by calorimetry. Instead of starting from quantum theory to predict bond strength, why not reverse the order by starting from known bond length and bond energy to compute the realistic bond strength, i.e., maximum attractive force? A scheme to pursue this new approach is presented here.

When two molecules approach each other, their interactions can be expressed by a potential energy function in terms of their distance of separation. Quite a few potential energy functions were adopted in quantum mechanics. The most commonly used one is the Lennard–Jones function [eq. (1)], which is valid for neutral molecules such as polymers, metals, and oxides[10,11]:

$$E = \frac{A}{X^{12}} - \frac{B}{X^6} \tag{1}$$

where E = potential energy, X = distance of separation between molecules, and A, B = constants.

The positive term is short range repulsive energy; the negative term is long range attractive energy. The repulsive inverse power may range from 9 to 15,[12] which slightly changes the steepness of the slope. The exponential repulsive functions (Buckingham and Morse) may represent the repulsive term better, but the improvement over the inverse 12th power function is less than 2%.[10] The attractive inverse power could be 1, 2, 3, or 7 in special cases such as Coulomb or retarded attractions.[12] The inverse sixth power attractive function is adequate for the discussion of attraction/bonding between neutral molecules.

According to eq. (1), the overall attractive force (F) between molecules is given by

$$F = -\frac{dE}{dX} = \frac{12A}{X^{13}} - \frac{6B}{X^7} \tag{2}$$

and

$$\frac{d^2E}{dX^2} = \frac{156A}{X^{14}} - \frac{42B}{X^8} \tag{3}$$

The minimum potential energy (E_0) occurs at X_0 when $dE/dX = F = 0$, i.e., the attractive force equals the repulsive force, the net force is zero. The maximum attractive force (F_m) occurs at X_m when $d^2E/dX^2 = 0$. The zero potential energy, $E = 0$, occurs at X_e, which is the off limit of further penetration of electron clouds between molecules. We have

$$X_0 = (2A/B)^{1/6} = \text{bond length} \tag{4}$$

$$E_0 = -B^2/4A = \text{bond energy} \tag{5}$$

$$A = -E_0 X_0^{12} = \text{repulsive constant} \tag{6}$$

$$B = -2E_0 X_0^6 = \text{attractive constant} \tag{7}$$

$$X_m = 1.11 X_0 = \text{apex point} \tag{8}$$

$$F_m = -2.69 E_0 / X_0$$
$$= \text{maximum attractive force} \tag{9}$$

$$X_e = 0.89 X_0 = \text{off limit} \tag{10}$$

$$E_e = 0 = \text{energy equilibrium} \tag{11}$$

$$E = E_0 \left[2 \left(\frac{X_0}{X} \right)^6 - \left(\frac{X_0}{X} \right)^{12} \right] \tag{12}$$

Equation (8) indicates that the maximum attractive force and the minimum potential energy occur in close proximity (11% shift between X_0 and X_m). The fact that the maximum attractive force and the minimum potential energy do not fall on the same point sets off harmonic vibrations, which are the origins of infrared spectra. Equation (9) can be used to calculate the adhesion strength (F_m) from known bond length (X_0) and bond energy (E_0). The adhesion strength of common bonds are uniformly listed in Table I, which reveals that the O — H single bond is stronger than the C = C double bond.

From eq. (12), $E = 0.008 E_0$ (less than 1% E_0) at $X = 2.5 X_0$. For the faintest bonding force in Table I, the critical distance of separation between molecules $X_c = 2.5 \times 3.6 = 9.0$ Å. Beyond 9 Å, the electronic interactions between molecules decrease rapidly to nearly zero. Closer than 9 Å, the molecular contact begins, that is, the penetration of electron clouds, overlapping of molecular orbitals, or mathematically substantial exchange integrals.[13,14]

The above deduction can be summarized in the

Table I Maximum Attractive Force of Chemical Bonds

Bond	Bond Length X_0 (Å)	Bond Energy E_0 (kcal/mol)	Bond Force[a] F_m (dyn/bond $\times 10^{-4}$)
C≡N	1.16	213	34.3
C≡C	1.20	200	31.2
C=O	1.23	179	27.2
O—H	0.96	111	21.6
C=C	1.34	146	20.4
C—H	1.07	99	17.3
N—H	1.01	93	17.2
C—F	1.36	116	16.0
O—Cr	1.57	102	12.2
C—O	1.43	86	11.2
O—Si	1.50	88	11.0
C—C	1.54	83	10.1
C—N	1.47	73	9.28
C—Cl	1.77	81	8.56
N—O	1.24	53	8.00
C—S	1.81	65	6.72
C—Si	1.94	69	6.65
N—N	1.12	39	6.51
C—P	1.87	63	6.30
S—S	2.04	54	4.95
O—O	1.48	35	4.42
Hydrogen bond	2.70	6	0.415
Van der Waals	3.60	2	0.010

[a] The bond force was calculated by eq. (9). It indicates the overall bond strength. Note that the O — H single bond is stronger than the C = C double bond.

following statement: Strong adhesion between materials is governed by two criteria: Intimate molecular contact of closer than 9 Å (necessary condition), and maximum attractive force with minimum potential energy (sufficient condition). Under these conditions the two sets of molecules experience the strongest bonding force (maximum attraction) yet remain the most stable state (lowest energy). This statement conforms to the key elements of most prior theories, *vide infra*, and hence may constitute a consolidated theory of adhesion, a dichotomy theory. The key elements of the seven prior theories and their relevance to the criteria are briefly summarized below. More details are discussed in the section on Merging of Prior Theories.

• **Intimate Molecular Contact:**

Adsorption theory:	Surface energy and rule of spreading/wetting.
Diffusion theory:	Physical contact, compatibility, and permeation.
Interlocking theory:	Flow, wicking, interpenetration, and cohesion.

Weak boundary theory:	Lack of intimate molecule contact.

• **Maximum Attractive Force:**

Chemical bonding theory:	Origin of intermolecular attractive forces.
Acid–base theory:	Hydrogen bonding force is the key of adhesion.
Electrostatic theory:	Electronic attractive forces.
Weak boundary theory:	Defects and lack of covalent/hydrogen bondings.

The reverse treatment offers a few advantages over the traditional treatment: (1) The nature of molecular contact is quantitatively defined; (2) the bond strength is defined with one parameter (maximum attractive force, such as lb/in.^{2}) instead of two parameters (bond length and bond energy); (3) the mathematical barrier of quantum mechanics, such as Hamiltonian operators, differential equations, and matrices, is bypassed without sacrificing its concept; (4) the criteria combine the central

thoughts of most prior theories; and (5) the consolidated concept can be used to interpret/rationalize the ensuing guidelines on adhesion.

Adhesion of Polymers

Attractive forces exist between any molecules when their distance of separation is closer than 9 Å. The attractive forces are usually insufficient for strong bonding when the molecules are small, but the attractive forces become spectacular when the molecules are large. Consequently, all binders/adhesives are made of macromolecules. The adhesion strength of polymers to wood, metal, ceramics, and plastics can be assessed by the afore-derived criteria:

Intimate Molecular Contact

Heat, pressure, solvents, surfactants and surface treatments have been used to promote intimate molecular contact. Solvents are routinely used in organic coatings/adhesives to carry polymers and spread on substrates. This practice is usually without problem for high energy surfaces (metals/oxides, 500–10,000 ergs/cm^2), but not so easy for low energy surfaces (plastics/paraffins, less than 200 ergs/cm^2), because, in the later case, an increase in total surface energy is involved.[15,16] Of course, all systems favor the lowest energy state available.

For low energy surfaces, the rule of spreading has been prescribed by the adsorption theory that spreading/wetting (intimate molecular contact) will occur when the critical surface tension of the solid is higher than the surface tension of the liquid. The critical surface tension of solid surfaces can be measured by the Zisman plot.[17] The measured critical surface tension of all plastics (18–50 dyn/cm) are well below the surface tension of water (72.8 dyn/cm); therefore, all plastic surfaces are hydrophobic.[18]

Maximum Attractive Force

The adhesion of polymers involves various types of chemical bondings. Typical attractive forces often encountered in organic coatings/adhesives are illustrated in Figure 1, where:

- The covalent bond O — Cr between polyester and chromate pretreated metals:

$$X_0 = 1.57 \text{ Å} \quad \text{(known bond length)} \quad (4)$$

$$E_0 = 102 \text{ kcal/mol (known bond energy)} \quad (5)$$

$$A = 1.59 \times 10^{-105} \text{ erg cm}^{12} \quad (6)$$
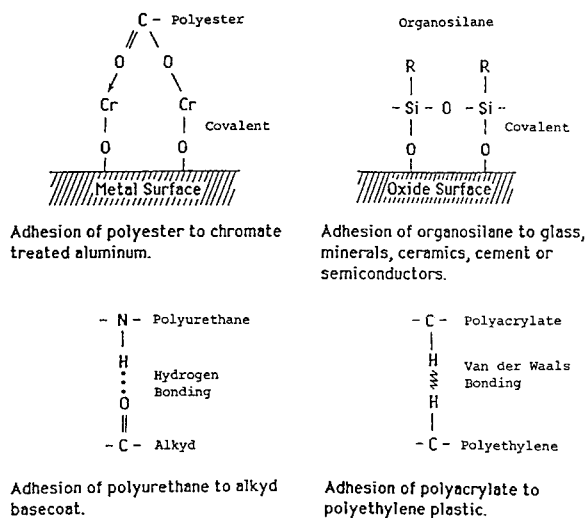
Figure 1 Chemical bondings frequently encountered in coatings.

$$B = 2.12 \times 10^{-58} \text{ erg cm}^6 \quad (7)$$

$$X_m = 1.74 \text{ Å} \quad (8)$$

$$F_m = -2.69, E_0/X_0$$

$$= 12.2 \times 10^{-4} \text{ dyn/bond} \quad (9)$$

$$X_e = 1.40 \text{ Å} \quad (10)$$

Note that 1 kcal/mol/Å = 6.94×10^{-6} dyn/bond.

- The covalent bond O — Si between organosilane and fiberglass:

$$X_0 = 1.50 \text{ Å}$$

$$E_0 = 88 \text{ kcal/mol}$$

$$F_m = 11.0 \times 10^{-4} \text{ dyn/bond}$$

- The hydrogen bond between polyurethane clearcoat and alkyd basecoat:

$$X_0 = 2.7 \text{ Å}$$

$$E_0 = 6 \text{ kcal/mol}$$

$$F_m = 4.15 \times 10^{-5} \text{ dyn/bond}$$

- The van der Waals bond between polyacrylate and polyethylene plastics:

$$X_0 = 3.6 \text{ Å}$$
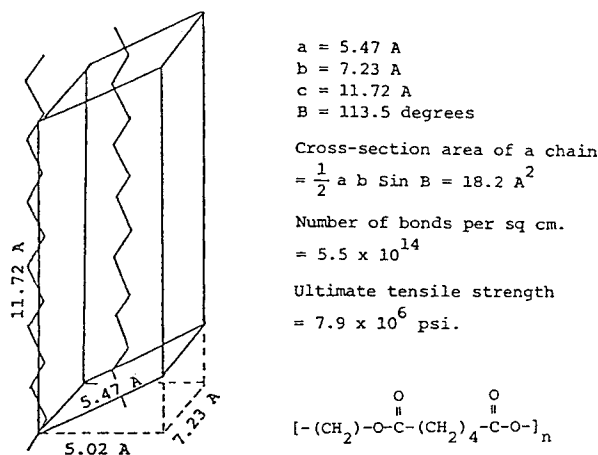
$$E_0 = 2 \text{ kcal/mol}$$

$$F_m = 1.04 \times 10^{-6} \text{ dyn/bond}$$

Covalent bonds are formed from chemical reactions between polymer and substrate, which are rather rare in conventional practice. Van der Waals attractions are always present. Consequently, hydrogen bondings are the only force technologists can put to work for the required adhesion.

The best achievable adhesion strength of a polymer is the cohesion strength of the polymer itself. Cohesion is a special case of adhesion where the two sets of molecules are identical. Equation (9) can also be used to estimate the cohesion strength of polymers. The cross-section area taken by a single polymer chain ranges 15–30 Å^2 (Fig. 2), based on X-ray diffraction data.[19,20] Referring to the bond forces in Table I, the tensile strength of polyethylene adipate fiber ranges between 7.9×10^6 psi (based on C — C bonds) and 7.9×10^3 psi (based on end-to-end van der Waals bonds). The measured tensile strength is in-between (1.3×10^4 psi) due to numerous flaws and hydrogen bondings. Polymer fibers/films are highly oriented; hence their tensile/shear strengths are remarkably anisotropic.

EXPERIMENTAL

In order to draw up a set of guidelines on adhesion and supplement the missing pieces of information, 21 model polymers of varied functionality were syn-

a = 5.47 A
b = 7.23 A
c = 11.72 A
B = 113.5 degrees

Cross-section area of a chain

$= \frac{1}{2} \text{ a b Sin B} = 18.2 \text{ A}^2$

Number of bonds per sq cm.

$= 5.5 \times 10^{14}$

Ultimate tensile strength

$= 7.9 \times 10^6 \text{ psi.}$

$[-(CH_2)-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-]_n$

Figure 2   Polyethylene adipate chains in a monoclinic unit cell determined by X-ray diffraction.
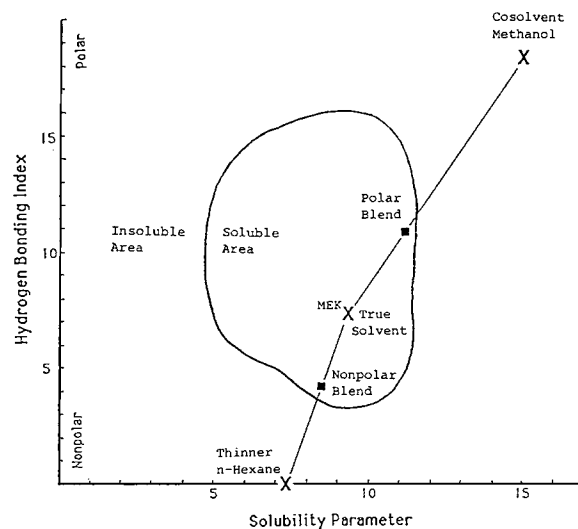
Figure 3   Solubility map and solvent blends.

thesized to study (1) the effect of polar groups on adhesion and (2) the effect of polymer conformations on adhesion. The model polymers are acrylics, epoxies, or urethanes which have been widely used in organic coatings because of their low permeability to air/water hence impeding corrosions. Nine of them, six urethanes and three epoxies, were insoluble; therefore, only 12 polymers were included in the experiments.

Techniques and Procedures

Polymer Characterization

The glass transition (T_g) points were measured with the DuPont thermal analyzer 1090 in DSC mode. The molecular weights were determined by use of the Perkin-Elmer LC Series-10 in GPC mode. Polymer solubility was checked by placing 0.5 g solid polymer into 9.5 g solvent, standing overnight with occasional shaking (ASTM-D 3132). Eleven solvents of varied solubility parameters were chosen to trace the solubility maps.

The polymer conformation in solution may affect its adhesion performance. In polar solvents, the polar groups of the polymer are protruding, but, in nonpolar solvents, the polar groups are buried. The effect of polymer conformation on adhesion were studied by using three solvent systems for each polymer as shown in Figure 3. The polar/nonpolar blends were made in such a way that an excess of a few drops of the nonsolvent would change the polymer solution from clear to cloudy.

Adhesion Performance

The contact angles of sessile drops were measured with a Rame-Hart telegoniometer. Films of about 1–1.5 mil dry thickness were made from polymer solutions of 20% by weight. No additives nor cross-linkers were added. The films dry essentially by solvent evaporation: brief flash off then bake (180°F/30 min). The polymer conformation, i.e, extended/coiled chains and exposed/buried polar groups, was studied by measuring the hydrodynamic volume of the dissolved molecules. An Ubbelohde capillary viscometer in a 25°C thermostatted bath was set up to determine the intrinsic viscosity from which the hydrodynamic volume was calculated according to the Flory theory.[21] The adhesion strength was measured by the Pull-off Test (ISO-4624 and ASTM-D4541, Elcometer or Instron) and occasionally re-checked by the Cross-hatch Tape Test (ASTM-D3359, simple Gardner Cutter).

Results and Comments

Polymer Characteristics and Spreading

The polymer compositions, molecular weights, and glass transition points are listed in Table II. Since the drying temperature was above the T_g's, the maximum intrinsic mobility should be developed. All molecular weights are in regular range, under 300,000.[22] The molecular weights of soluble poly-urethanes are on the low side. Polymers for conven-tional coatings must be soluble. The solubility of polymers in various solvents are presented in Table III. The data under CS_2 and xylene indicate that the solubility parameter alone cannot predict compatibility. The hydrogen bond index and dipole moment are also important parameters. Figure 3 shows that nonsolvents hexane and methanol were used to change the conformation for hydrodynamic volume measurements.

The surface tension of common solvents for coatings are below 30 dyn/cm, such as hexane = 18.4, metanol = 22.6, MEK = 24.6, and xylene = 28.9 dyn/cm. The critical surface tension of polyethylene is 31 dyn/cm (a reference point). That of fluorocarbons and silicones are lower. The critical surface tensions of all other commercial plastics such as SMC, nylon, LOMOD, etc., are higher due to the presence of N, O, Cl, or rings in the molecules.[17] Therefore, the rule of spreading/wetting was satisfied, and no wetting problem was encountered.

Effect of Polar Groups on Adhesion

According to the maximum attractive forces in Table I, the ratios of bond forces between covalent, hydrogen, and van der Waals bondings are 1000/40/1. The 1000/1 ratio would be the best, but covalent bondings are accessible only under unique conditions. Although the 40/1 ratio is the second best, hydrogen bondings are the most practical and should be the workhorse for adhesion. Numerous adhesion tests were run. The key data reflecting the effect of

Table II Characteristics of Polymers[a]

Polymer Composition	T_g (°C)		Mol Wt × 10⁻³		
	Onset	Inflection	M_n	M_w	P_d
MMA/BA	14	35	38.8	84.5	2.2
MMA/BA/DMAEMA	16	41	16.2	45.0	2.8
MMA/BA/glycidyl methacrylate	19	38	66.8	279.0	4.2
MMA/BA/hydroxyethyl acrylate	20	45	37.8	122.9	3.2
MMA/BA/acrylic acid	22	43	54.8	193.2	3.5
MMA/BA/styrene	34	55	36.0	63.0	1.8
MMA/BA/NMEMA	19	45	35.1	109.2	3.1
MMA/BA/vinyl pyrrolidone	45	69	45.6	117.0	2.5
MMA/BA/DMAPMA	29	62	17.2	51.0	3.0
Desmodur/bisphenol-A	41	84	4.4	9.1	2.1
Desmodur/1,6-hexanediol	49	86	14.3	31.2	2.2
Desmodur/CHDM	29	72	14.1	24.3	1.7

[a] MMA = methyl methacrylate, BA = butyl acrylate, DMAEMA = dimethylaminoethyl methacrylate, NMEMA = 2-N-morpholinoethyl methacrylate, DMAPMA = dimethylaminopropyl methacrylamide, CHDM = 1,4-cyclohexanedimethanol.

Table III   Solubility of Polymers[a]

Polymers	Hex	CyH	MAK	BAc	Xyl	Chf	MEK	CS$_2$	Acet	DMSO	MeOH
						Solvents					
Solubility parameter	7.3	8.2	8.5	8.5	8.8	9.3	9.3	10.0	10.0	12.9	14.5
Hydrogen bond index	0	0	7.7	8.8	4.5	1.5	7.7	0	9.7	7.7	18.7
Dipole moment	0	0	2.7	1.9	0.4	1.2	2.7	0	2.9	4.0	1.7
MMA/BA plus											
Straight	X	X	O	O	O	O	O	X	O	O	X
DMAEMA	X	X	O	O	O	O	O	X	O	—	O
GMA	X	X	O	O	O	O	O	X	O	O	X
HEA	X	X	O	O	X	O	O	X	O	O	X
Acrylic acid	X	X	O	O	X	O	O	X	O	O	X
Styrene	X	X	O	O	O	O	O	O	O	X	X
NMEMA	X	X	O	O	O	O	O	X	O	X	X
Vinyl Pyrr	X	X	—	—	O	O	—	X	—	O	X
DMAPMA	X	X	—	—	O	O	—	X	—	O	O
Desmodur plus											
Bisphenol-A	X	X	X	X	X	O	—	X	—	O	X
Hexanediol	X	X	X	X	X	O	X	X	X	—	X
CHDM	X	X	X	X	X	O	X	X	X	X	X

X = insoluble, O = soluble, — = cloudy. All polymer solutions are 5% by weight. Hex = n-hexane, BAc = butyl acetate, MEK = methylethyl ketone, CyH = cyclohexane, Xyl = xylene, Acet = acetone, MAK = methyl amyl ketone, Chf = chloroform, DMSO = dimethyl sulfoxide.

polar groups on adhesion strength are condensed in Table IV. The two-component (2K) systems are commercial products. All others are experimental systems without optimization.

The CONH and epoxy groups in the polymer backbone gave higher adhesion than the pendant

Table IV   Effect of Polar Groups on Adhesion

Polymer System	SMC Plastic (psi)	LOMOD Plastic (psi)	Bonderite Steel[a] (psi)
Different backbones			
Urethane, 2K	690	600	> 700
Epoxy, 2K	420	380	> 420
Urethane	300	300	> 540
Acrylic	350	260	> 350
Different side chains			
MMA/BA	120	110	> 350
MMA/BA + NR$_2$	350	260	> 350
MMA/BA + OH	250	150	> 350
MMA/BA + COOH	140	160	> 350
MMA/BA + C$_6$H$_5$	80	170	> 350
MMA/BA + epoxy	80	150	> 350
MMA/BA + $\rangle$N—	50	50	> 350

[a] Ruptures took place at film/glue or glue/dolly, but not film/steel interfaces, due to the strong adhesion between polymer and Bonderite.

NR$_2$ (CONH$_2$) and epoxy groups. Different pendant groups on the same backbone (MMA/BA) imposed only secondary effect on adhesion. The data seem to indicate that polar groups in backbone are more effective than those in side chains. Not all nitrogen-containing groups promoted adhesion, depending on their ability to form hydrogen bonds with the substrate. Note that the $\rangle$N— in Table IV has no hydrogen for bonding. Crosslinking two-component (2K) systems exhibited fast dry, firm adhesion, and superb durability due to their excellent molecular contact and possible covalent bonding through residual reactive groups.

Commercial plastics contain ester/carboxyl, ether/hydroxyl, epoxy/phenyl, or amine/amide/imide groups which are potential bonding sites. In order to effect hydrogen bondings, the presence of both hydrogen donors (—OH, $\rangle$NH, —CH, —SH) and acceptors ($\rangle$C=O, —NR$_3$, —OH, —NO$_2$, —CN, —CCl$_3$, $\rangle$C=S) in the same backbone may maximize adhesion. Inter/intra bondings could be controlled by properly spacing these groups.

Effect of Polymer Conformations on Adhesion

Solvent blends are routinely used in coatings. Usually only one component in the blend is true (active) solvent. Other components under the names of cosolvent (latent solvent) or thinner (diluent) are nonsolvent. The cosolvent/thinner can be either polar like alcohols or nonpolar like hydrocarbons. In either case, the polymer molecules in solution will be more or less coiled.

When both the solvent and polymer have a similar solubility parameter and hydrogen bond index, the solvent is a true solvent for the polymer. All data in Table V indicate that true solvents enhance adhesion because of larger hydrodynamic volume and better mobility.[23] Alcohol cosolvent, if in the right amount, induces synergetic effect and boosts adhesion because of protruding polar groups. Hydrocarbon thinners tend to bury the polar groups and tighten up the polymer coils, and hence degrade adhesion. The maximum amount of nonsolvent was used in this study as shown in Figure 3 to reveal its effect on conformation/adhesion.

Adhesion Tests

The Pull-off Test is an international standard (ISO) method. The Cross-hatch Tape Test is practiced widely in the coatings industry. Both were used in the present study. No correlation was found between

Table V Effect of Polymer Conformations on Adhesion

Polymer	M_n ($\times 10^{-3}$)	Solvent[a] Composition (wt %)	Intrinsic Viscosity (dL/g)	Hydrodynamic Volume ($\times 10^{-18}$ mL)	Adhesion[b] Strength (psi)
MMA/BA/HEA	37.8	MEK	0.435	5.87	380
		80 MEK/20 hexane	0.420	5.67	300
		20 MEK/80 MeOH	0.273	3.69	380
MMA/BA/DMAEMA	16.2	MEK	0.310	1.79	350
		50 MEK/50 hexane	0.225	1.30	50
		MeOH	0.188	1.09	180
MMA/BA/Styrene	36.0	MEK	0.260	3.34	300
		50 MEK/50 hexane	0.237	3.05	280
		60 MEK/40 MeOH	0.224	2.88	250
MMA/BA/DMAPMA	17.2	Toluene	0.220	1.35	120
		90 Tol/10 heptane	0.248	1.52	100
		MeOH	0.276	1.70	50
MMA/BA/NMEMA	35.1	MEK	0.330	4.14	100
		80 MEK/20 hexane	0.301	3.77	10
		30 MEK/70 MeOH	0.215	2.69	20
MMA/BA/vinyl pyrr.	45.6	Toluene	0.390	6.35	50
		90 Tol/10 heptane	0.394	6.42	10
		30 Tol/70 butanol	0.500	8.14	30
Desmodur/bisphenol-A	4.4	Chloroform	0.245	0.39	300
		90 Chf/10 hexane	0.110	0.17	10
		60 Chf/40 MeOH	0.174	0.27	40
Desmodur/1,6-hexanediol	14.3	Chloroform	0.480	2.45	220
		90 Chf/10 hexane	0.445	2.27	60
		60 Chf/40 MeOH	0.448	2.29	100
Desmodur/CHDM	14.1	Chloroform	0.404	2.03	220
		90 Chf/10 hexane	0.430	2.17	50
		60 Chf/40 MeOH	0.358	1.80	100

[a] Three solvent systems (true, polar, and nonpolar blends) were used for each polymer (Fig. 3). All films for adhesion tests were made from polymer solutions with 20% solids by weight.

[b] Adhesion data from pull-off tests of clear film on plastics. 100 psi or lower indicates poor adhesion.

the results of these tests. Superficially, the Pull-off Test measures tensile strength, and the Cross-hatch Tape Test estimates shear strength. But in reality, the induced stresses in both tests are likely non-uniform and superimposed. Most observed loci of failures were not interfacial except cases of poor adhesion (less than 100 psi). When the Pull-off Tests ran above 300 psi, cohesive failure of SMC often took place due to the weak bonding between the SMC (polyester) and its imbedded fiberglass.

Adhesion of polymer to pretreated steel is much stronger than its adhesion to bare aluminum (the dolly in the Pull-off Test). Therefore, the rupture in the Pull-off Test takes place most likely in the film/glue, glue/aluminum interfaces, or mixed mode, but hardly in the film/steel interface as shown in Table IV.

The adhesion of urethane to both steel and aluminum was excellent. In one incidence, when the Bonderite steel and the aluminum dolly were joined with a black urethane paint, cohesive failure of urethane itself took place. Since both the separated surfaces were black, the evidence was clear-cut.

Solids never rupture as a rigid body. Viscoelastic effects, surface structures, and fracture mechanics are mixed in an intricate manner, such that no ideal adhesion tests exist. Consequently, the value of adhesion strength obtained by different test methods may not be directly comparable.[24,25] Internal consistency of test data is what we can expect.

APPLICATIONS

The consolidated theory serves two purposes: to tie prior insights together such that the adhesion theories become unified and to interpret the guidelines on adhesion which were scattered and never put together due to the lack of a coherent/unified adhesion theory.

Merging of Prior Theories

The prior theories of adhesion overlap to certain degrees. None of them are really incompatible with others. The seven prior theories are briefly reviewed below with comments on how they mesh with the consolidated theory.[26-28]

Adsorption Theory[29-31]

The adsorption theory starts from surface tension equilibrium and arrives at the rule of spreading/adsorption of liquids. It predicts adhesion strength from thermodynamic work of adhesion, and stresses that the intrinsic adhesion arising from van der Waals forces alone may lead to strong adhesion. Its extension beyond liquid/solid adsorption to solid/solid adhesion is less convincing. Adhesion involves the boundary region of finite thickness. Obviously the boundary is not really a two-dimensional surface. The rule of spreading/wetting from the adsorption theory is adopted in this study for assessing the necessary condition of intimate molecular contact.

Chemical Bonding Theory[22,32]

The molecular orbital theory considers the origin of attractive forces between molecules. Adhesion involves all types of chemical bondings: covalent, hydrogen, van der Waals, metallic, and ionic. Only the first three types are operative in organic coatings. Soldering involves metallic bondings; ion implantation/plating in the electronics industry may involve ionic bondings. The chemical bonding theory does not particularly recognize the prerequisite of intimate molecular contact for strong adhesion. It uses two parameters, bond energy and bond length, to characterize bond strength, while only one parameter, bond force (F_m), is necessary to rank bond strength. The reverse treatment of intermolecular attractions avoided the mathematical barrier of quantum mechanics and simplified the chemical bonding theory.

Electrostatic Theory[33]

The electrostatic theory claims that the attractive forces are the electrostatic effects at the interface. It postulates that all adhesion phenomena are charge transfer across the interface giving rise to electric double layers. The evidence was the well-known darkroom demonstration of electrical discharges when adhesive tapes are stripped rapidly from glass. The condenser discharge energy was correlated with the measured work of adhesion. It explains the adhesion of fine particles to surfaces such as Xerography.[34] Further development led to the DLVO theory popular in colloid science.[12] The DLVO theory contains too many parameters which are difficult to measure; hence it is not practical for industrial applications. Furthermore, the DLVO theory draws a lot of information from the chemical bonding theory which is stressed and simplified here.

Acid–Base Theory[35,36]

The acid–base theory applies the Bronsted acid–base concept to predict the relative magnitude of hydro-

gen bonding between polymers and oxide surfaces in the presence of moisture. The acid–base strength of an organic compound is judged by its pK value. The acid–base strength of an oxide surface is measured by its isoelectric point from the zeta potential experiment using aqueous suspension of powdered oxides. A low isoelectric point such as $SiO_2 = 2$ indicates acidic surface where amino materials should adhere well. A high isoelectric point such as MgO $= 12$ indicates a basic surface where carboxylic materials should adhere well. In general, optimum adhesion should be obtained when there is a substantial difference between pK and isoelectric point. The "acid–base force" is almost a synonym of the hydrogen bonding force, which is one of the intermolecular forces emphasized in the consolidated theory.

Mechanical Interlock Theory[37-39]

The lock-key idea explains intuitively the adhesion of polymers to porous substrates (wood, paper, etc.). It is also a major factor for the strong adhesion of organic coatings to pretreated metals, and metal platings to pretreated plastics (metallization). Mechanical interlocking reinforces adhesion with cohesion; hence it is resistant to hydrolytic and thermal degradation. Penetration of polymer into pores forming interlocks is the macroscopic view. Microscopically, the adhesion between polymer and the wall of the pores still involves intermolecular forces. The discussion of intermolecular attractive forces is valid for both adhesion and cohesion.

Diffusion Theory[40-42]

The diffusion theory asserts that adhesion is due to intermolecular diffusion and entanglements across the interface. It is particularly useful for understanding the adhesion of polymer to polymer, especially when both polymers are thermodynamically compatible and above their glass transition points. In concludes that dissimilar polymers are less adherent than similar polymers. Since diffusion is a dynamic process, it may take some time to develop the expected adhesion strength due to diffusion kinetics. Diffusion theory overlaps the interlocking theory. Mechanisms of diffusing, wicking, anchoring, and adhering certainly involve intermolecular attractive forces.

Weak Boundary Theory[43-45]

It represents the mechanical engineers' view of adhesion. Rupture always takes place at the weakest link. The weak spots may be inherent flaws such as bubbles, voids, crevices, or microcracks in the interface region. The weak spots may also be created during service due to stress/corrosion triggered by the permeated gas/water/ions. It is useful to interpret the locus of adhesion failure, and explain the big difference between ultimate and practical adhesion strength. However, it does not consider why things adhere. The weak spots are defects where neither molecular contact nor chemical bonding exists. The weak boundary theory is a theory of debonding rather than bonding or adhesion.
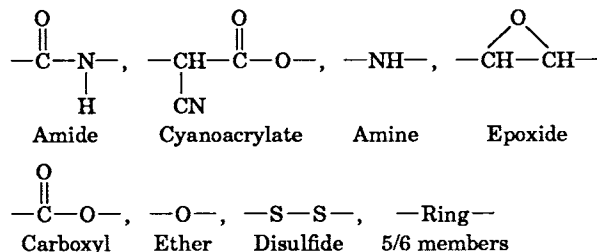
Guidelines of Adhesion

A set of practical guidelines on adhesion is condensed from the adhesion theory, this study, and prior work. These generalized conclusions may help the practitioners to get a perspective view without wading through voluminous literature. The complex behavior of polymers certainly defy simple rules. Only the general trends were sought.
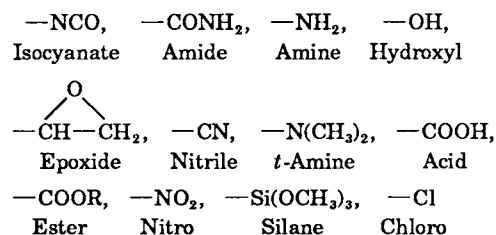
Effect of Functional Groups on Adhesion

The adhesion strength between coatings and substrates comes mainly from van der Waals forces, but substantially reinforced through hydrogen bondings and covalent bondings. Almost all polymers for coatings contain polar groups. As little as 0.1–1.0 mol % of functional groups can drastically increase the adhesion strength.[4] Although the effectiveness of functional groups is quite specific with regard to the surface of the substrate, experimental data of this study appear to indicate that polar groups are more effective in the backbone than in side chains. Different pendant groups on the same backbone impart lesser effects. Hydrogen donors and acceptors in the same backbone may maximize adhesion. Popular functional groups and the polarity of common materials arranged approximately in order of decreasing tendency for hydrogen bonding are compiled in Table VI. Note that poly(vinyl chloride) is nonpolar, poly(vinyl acetate), medium polar, but poly(vinyl alcohol), highly polar. The mobility and spacing of the polar groups are crucial for their ability to reach matching sites. Large molecules have higher cohesive strength but lower mobility. Except 2K systems, a polymer molecule of $M_w = 100{,}000$– $300{,}000$, with a small number of long branches, is probably a starting point before optimization.[22] An excessive number of short branches adversely affect both spreading and adhesion.[46]

Table VI Polar Groups and Polarity of Materials

- **Polar groups in backbone**

Amide	Cyanoacrylate	Amine	Epoxide

| Carboxyl | Ether | Disulfide | 5/6 members |

- **Polar groups in branches/ends**

—NCO,   —CONH$_2$,   —NH$_2$,   —OH,
Isocyanate   Amide   Amine   Hydroxyl

—CH—CH$_2$,   —CN,   —N(CH$_3$)$_2$,   —COOH,
Epoxide   Nitrile t-Amine   Acid

—COOR,   —NO$_2$,   —Si(OCH$_3$)$_3$,   —Cl
Ester   Nitro   Silane   Chloro

- **Polarity of materials**

Highly polar:	poly(vinyl alcohol), polyether, polyurethane, polyurea, polyamide, polyester, melamine, cellulosic, protein, starch, fabric, and sodium silicate
Medium polar:	acrylics, poly(vinyl acetate), polyvinylbutyral, epoxy, acrylonitrile, polysulfide, silicone, and metal oxides
Nonpolar:	fluorocarbons, hydrocarbons, chlorocarbons, natural rubbers, and metals

Effect of Solvents on Adhesion

The conformation of the polymer molecules in solution depends upon the compatibility between polymer and solvent. Extended molecules have better mobility to reach bonding sites on the substrate. It also favors diffusion and entanglements. Experimental data of this study clearly indicate that true (active) solvents always promote adhesion. Alcohol cosolvents (latent solvents) help exposing polar groups by changing the polymer conformation, thereupon realizing a synergetic effect and boosting adhesion. Hydrocarbon thinners (diluents) tighten up the polymer coil and bury its polar groups, and thus reduce adhesion. Note that the cosolvents and thinners are usually nonsolvent.

Effect of Pigments on Adhesion

As a rule of thumb, pigments/fillers in polymer solution/emulsion increase its viscosity when wet, in-crease its cohesive strength when dry, and increase its adhesion when below CPVC (critical pigment volume concentration). A high PVC (less amount of polymer) gives high adhesion; a low PVC (higher amount of polymer) gives high cohesive strength.[2,5] The types of pigments make some difference but do not override the above trend. The acid–base theory provides a convenient tool for matching polymers to pigments for good adhesion.

Promotion of Molecular Contact

Heat, pressure, solvent, surfactant, flame, plasma, corona discharge, radiation energy, catalyst, and chemical treatments are among the industrial techniques to promote adhesion.[1,4,8] The first four improve molecular contact (necessary condition) between the two sets of molecules. The last six create new bonding sites (sufficient condition) on the substrate. Heating polymer above its T_g increases its adhesion. Pressure speeds up flow and eliminates air pockets. True solvents always enhance adhesion. Surfactants may reduce water resistance, and hence should be used sparingly.

DeBruyne's rule of adhesion[47] states that strong joints can never be made to polar adherents with nonpolar adhesives, or to nonpolar adherents with polar adhesives. This is usually true because of the hydrophobic nature of nonpolar adhesives toward moisture-covered polar adherents, and the high surface tension of polar adhesives toward the low critical surface tension of the nonpolar adherents. Intimate molecular contact is hampered in both cases.

Promotion of Bonding Forces

Among the three types of bonding forces, van der Waals forces are always present and contribute the major attractive force in coatings/adhesives. Hydrogen and covalent bondings are far superior in terms of durability, especially in the presence of water. Even a small number of them can substantially reinforce adhesion strength. For coatings applications, 300 psi is good adhesion, but for construction adhesives 500 psi is about the lower limit. Two-part crosslinking systems promise fast-dry, firm adhesion, and superb durability due to the presence of residual reactive groups for covalent bondings.

For nonpolar substrates such as hydrocarbons, fluorocarbons, and chlorocarbons, surface treatments[48] are necessary to impart polar groups which raise their surface tension and create bonding sites. With good wetting, rough surface shows better adhesion because it has interlocking cavities, large

contact area, and redistributed (randomized, averaged, hence not maximum) stress.

Causes of Adhesion Loss

Some coatings/joints fail too soon. The likely causes of adhesion failures are: inadequate surface preparation (contaminated, or nonpolar surfaces), lack of intimate molecular contact (poor spreading/wetting), structural defects (air bubbles, voids, crevices, and other flaws), rigid molecular structure (not enough mobility for alignment to bonding sites), inefficient distribution of polar groups (on side chain or uneven spacing), internal stress/strain (too thick, high shrinkage, odd thermal expansion), corrosion in harsh environments (heat, cold, water, salt, radiations, and fumes), etc. These causes should be kept in mind when formulating coatings.

Adhesion in Harsh Environments

Coatings/adhesives for harsh environments must be specially designed to achieve adhesion. According to the current research trend,[7] polymers of fused/joined/connected rings such as polyimides, polybenzimidazoles, and polyquinoxalines are suitable for high temperature (up to 1000°F) applications. Cyanosilicones and fluoroelastomers can stand low temperatures (down to −100°F). Polyphenyl-*as*-triazines, fluorine-modified polyimides, and chelating agents have good water resistance. Alodining and anodizing pretreatments can endure salt water.

CONCLUSIONS

The consolidated theory of adhesion integrates *seven* diverse theories into a coherent concept. Thermodynamically, spreading of a liquid on a solid will occur if the surface (free) energy of the system is thereby reduced. To ensure intimate molecular contact, the rule of spreading/wetting is adopted from the *adsorption* theory. The driving force of adhesion is the electronic interactions between molecules. When the maximum attractive force is near the minimum potential energy, *chemical bondings* are established. Covalent bonds need special design. Van der Waals bonds are ubiquitous. Only hydrogen bonds are practical for adhesion promotion.

Various chemical elements or groups have different electron drawing power, i.e, electronegativity, which is the source of attractive forces for adhesion. The *electrostatic* force, the *acid–base* force, and the intermolecular force are similar concepts in different terms. The best achievable adhesion of the polymer is equal to the cohesion strength of the polymer itself. *Diffusion*, entanglement, and *interlocking* of polymers across the boundary reinforce the adhesion strength up to their cohesion strength. Adhesion/cohesion are intermolecular hetero/homo attractions, respectively.

Adhesion rupture always takes place at the weakest link. The formation of a *weak boundary* is due to the following mishaps: No molecular contact (crevices, flaws), inadequate molecular contact (poor spreading/wetting), or weak intermolecular attraction (lack of covalent/hydrogen bondings). These conditions may exist originally or develop during service.

The consolidated theory capitalizes on the insights of prior theories. The set of guidelines on adhesion attempts to put the practical aspects of polymer adhesion in a nutshell. Adhesion is a complex and evasive field beyond the reach of any single study. The model polymers and the experiments in this study have only a very limited scope. Further work is in progress to resolve some of the uncertainties. Future advances could make the adhesion theory more quantitative and closer to engineering.

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