

## CHAPTER IV

### THEORY

#### 4.1 CONTACT BETWEEN THE INTERFACE

##### 4.1.1 Surface Tension

Surface tension is the representative of the intermolecular force between their molecules. The shape of liquid in atmospheric is sphere, but when the liquid contact with solid or other liquid, some certain angle will be developed. This angle will be verified in the next section. There are many forces that can be classified according to the initiation of the bonds. London forces are the force that initiated from the circulation of the electron within the molecule. This molecular forces are the characteristic of every substance. Dispersion forces or London forces are the weakest intermolecular forces. Dipole or induced dipole are the other molecular forces that stronger than London force. It is happen by the orientation of permanent electron dipole. These intermolecular attraction usually happen between dipole molecules. Hydrogen forces are the strongest force between molecules. These forces happen because the oxygen atom attract the electron from hydrogen atom that attach with oxygen. These neglected hydrogen atoms will react strongly with other molecules which have free electron atoms. The conclusion of some of the attraction between molecule are in table 4.1.

Table 4.1 Types of physical attractive forces and typical bond energies

Type	Bond energy(kJ/mol)
Permanent dipole-dipole interaction:	
Hydrogen bonds involving fluorine	Up to 40
Hydrogen bonds excluding fluorine	10-25
Other dipole-dipole (excluding hydrogen) bonds	4-20
Dipole-induced dipole	Less than 2
Dispersion (London) forces	0.08-40

Table 4.2 Roughness factors,  $r_f$ , for various aluminium surfaces

Solid surface	$r_f$
Smooth glass plate (reference)	1.0
Anodized aluminium	1.47
Sealed anodized aluminium	1.08
Phosphated aluminium	1.01

#### 4.1.2 Wetting Equilibria

When three phases contact together, air, liquid, and solid, the angle between liquid and gas will form. the situation will be varied depend on the type of the phases. The composition, the roughness, the type of the phases effect the angle. If the angle equal 0, all liquid will be spread through out the solid. If the angle equal 90, the liquid will form the fence all around the contact area. The diagram of the three phases will be shown in figure 4.1.

The energy that related the angle between the three phases is called the surface free energy. Actually there will be two angles between three phases but solid hardly changes the interfaces so the angle will be between liquid-vapor . The surface free energies will have three kinds. The first kind is the solid-liquid surface free energy with the 0 angle ( $\cos(0) = 1$ ). The second kind is the liquid- gas surface free energy with the  $\theta$  angle or the total energy can be written as  $\gamma_{lv} \cos(\theta)$ . The last surface free energy is the solid gas liquid free energy which have 0 angle. The balance of the three equations can be written as follows,

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos(\theta)$$

Some author relates the surface free energy between solid and vapor with the surface free energy of the solid in vacuo,  $\gamma_s$  which is the function of the equilibrium spreading pressure or the equivalent vapor that absorbed when the solid is initially vacuum. However the interpretation of the equation will be the same. The wetting surface of the solid depend on the equilibrium of this equation. If the surface free energy is negative, the wetting can be occurred. If we call the different

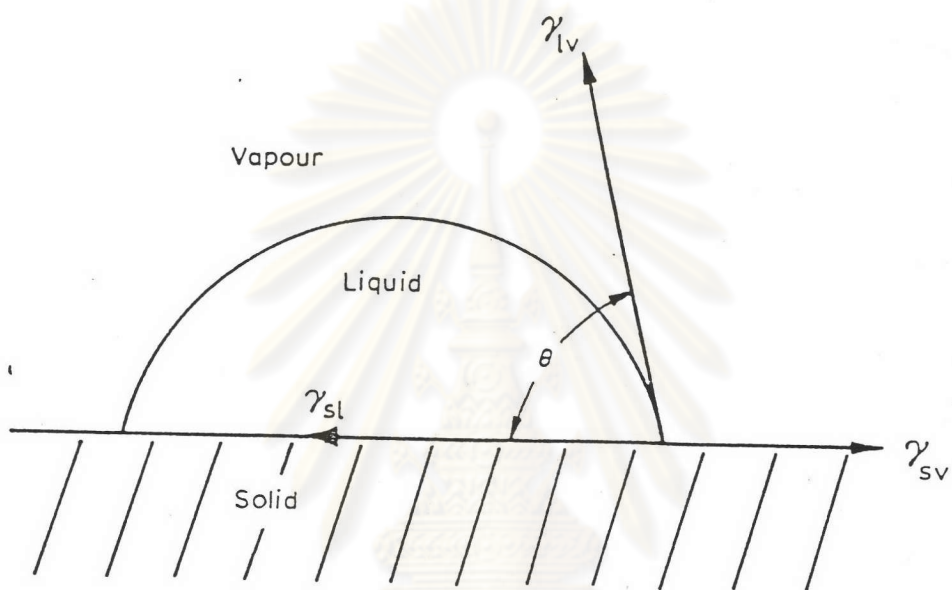


Figure 4.1 A liquid drop resting at equilibrium on a solid surface

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free energy of surface free energy as  $S$ , the negativity of  $S$  will cause the solid to be wetted.

$$S \leq \gamma_{sv} - \gamma_{sl} - \gamma_{lv}$$

The equilibrium spreading coefficient  $S$  will show the spontaneous spreading of liquid onto the solid surface. However  $S$  is the thermodynamics value. It will tell the last situation from the first situation, but it will not tell the kinetics of the spreading. Some situation can be happen thermodynamically but it will not happen in the real situations. If we add  $\cos(\theta)$ , this equation may be more realistic.

The contact angle between liquid-vapor or vapor-liquid can be measured by using a tangent line from the three points of contacts to the two points of contacts. These may be through the image from the microscope and photography. Sessile-drop liquid drop is the special name for the liquid-vapor contact and captive-bubble drop is the special name for the vapor-liquid. However many variables effect the angle. So there are many methods to describe and measure the suitable angle. Some of these methods are shown in the figure 4.2.

Surface roughness has the profound effects on the angle. However the effects are not be in the same way when the surface roughness increased. The most simple equation that can explain the effects of surface roughness in smooth surface range are as below.

$$\cos(\theta_f) = r_f \cos(\theta_s)$$

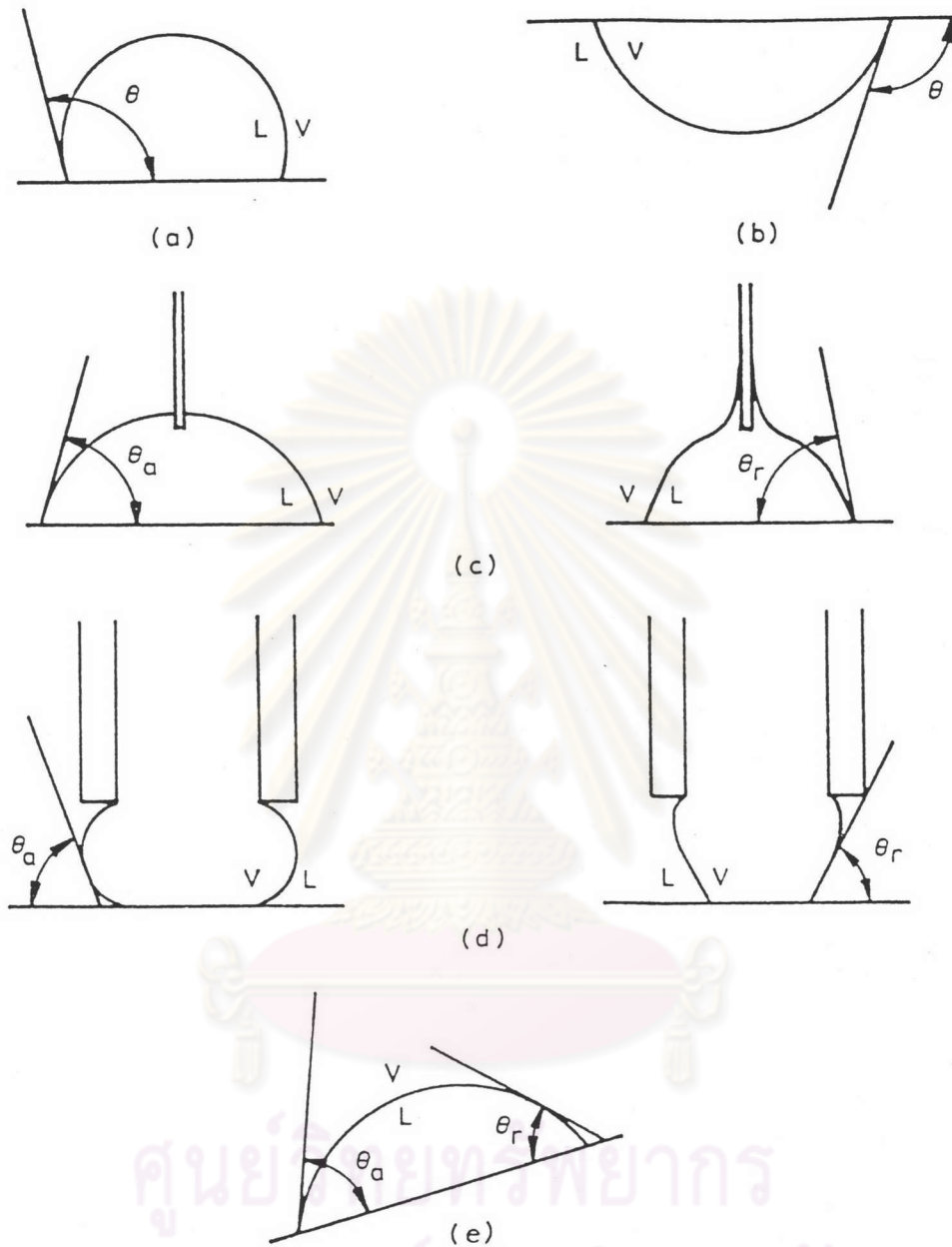


Figure 4.2 Drop and bubble configurations for measurement of equilibrium, advancing and receding contact angles. (a) Equilibrium sessile drop, (b) equilibrium pendant bubble, (c) advancing and receding drop, (d) advancing and receding bubble, (e) drop on the titled plate. L = liquid, V = vapor

The subscript  $f$  is standed for surface roughness. This cosine can be replace the calculation from the wetting of the surface. In the table 4.2, the roughness of the different treatment of aluminum will be shown to emphasize the effects of the roughness. In the next chapter some surface and interfacial free energies will be briefly explained.

#### 4.1.3 Surface and interfacial free energies

The surface can be divided into two types, Low surface energy and High surface energy. Usually the high surface energy allows all liquid to spread through all the surface, so there are no problems when adhesive have to spread thoroughly. Mostly the high energy surface are all metal surfaces. The problem of surface energy of high surface energy usually happen at high temperature. So, in this manuscript, the high energy surface problems will be omitted. The low energy surfaces usually are the polymer which we will concern in details in this chapter.

The most impossible discovery is by Zisman et.al.. They discovered that if we plot  $\gamma_{lv}$  vs.  $\cos(\theta)$ , we will obtain the straight line. This discovery implied that it will be the critical surface energy between polymer and the liquid. Some of this discovery can be shown in the figure 4.3.

Many scientists try to relate this discovery to the old definition of the surface free energy that have already be developed before. One method starts from Good-Girifalco approach and the other come from additivity of components. the Good-Girifago method start from the definition of the interaction between molecules as below,

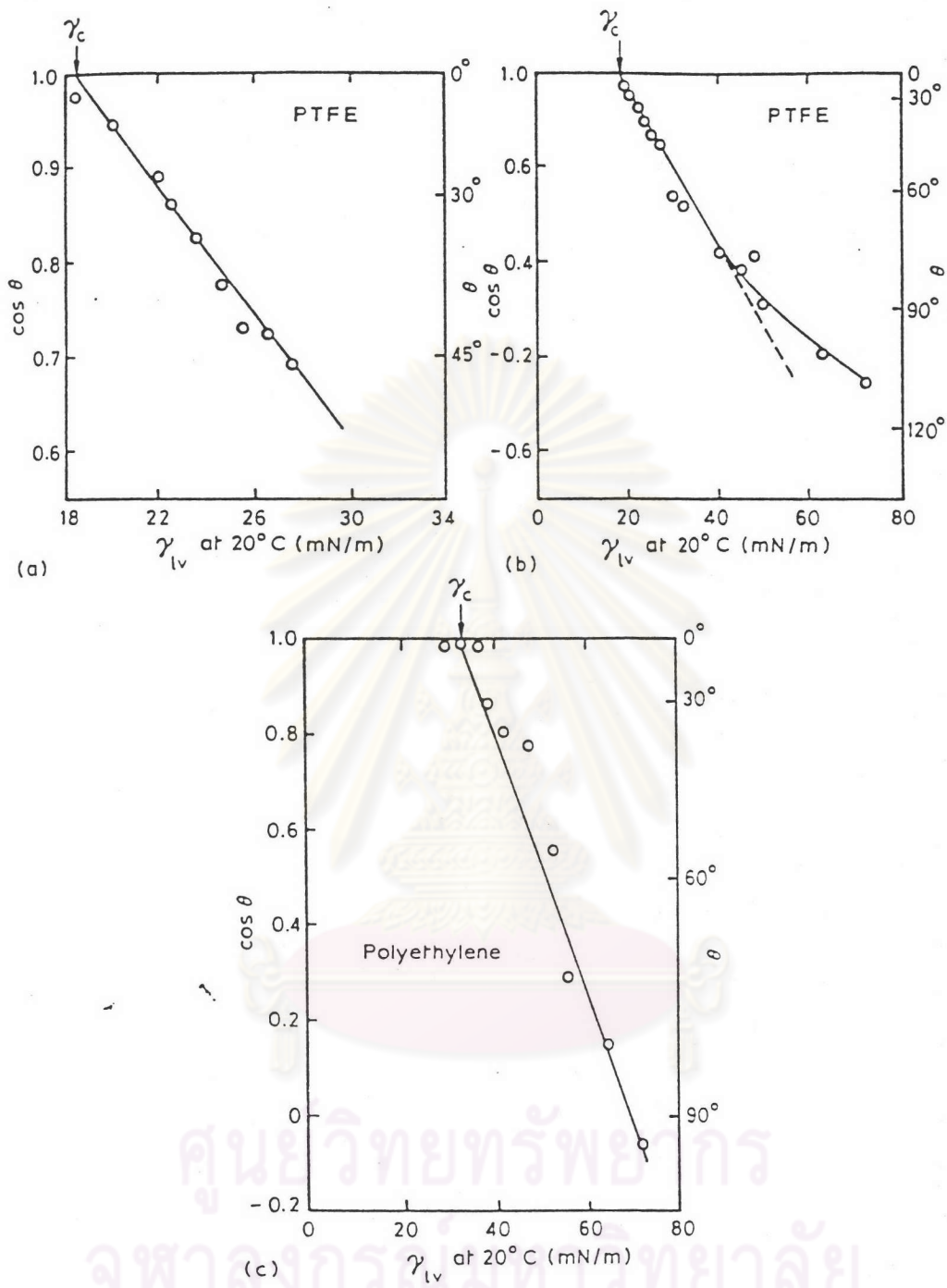


Figure 4.3 Zisman plots for various low-energy polymeric surfaces. (a) Polytetrafluoroethylene (PTFE) with n-alkanes as the liquid series, (b) PTFE with a wide range of liquids, (c) polyethylene with the liquid series commonly used by Zisman.



$$\Phi = \frac{A_{ab}}{(A_{aa} A_{bb})^{1/2}} = 1$$

The A stands for the interaction between molecules as the subscript such as  $A_{aa}$  is the intermolecular forces between species. However the  $\Phi$  can not be more than one in the normal intermolecular forces. When the  $\Phi$  is interpreted in term of surface free energy, there will be as follows,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2\Phi(\gamma_a \gamma_b)^{1/2}$$

From this equation , the angle and all the surface free energy can be related. If we set the angle to be zero and the vacuo surface free energy will become as below,

$$\gamma_c = \Phi^2 \gamma_s$$

The additivity of components modified further from Good-Girifalco approach by adding the dispersion and a polar component in the surface free energy. This can be shown as below,

$$\gamma_a = \gamma_a^D + \gamma_a^P$$

The combination of the equation for the contact between different phases are as ,

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^D \gamma_b^D)^{1/2} - 2(\gamma_a^P \gamma_b^P)^{1/2}$$

Among these difficult theory some conclusions can be summarized. Firstly It can be summarized that if the  $\gamma_c$  of the adhesive is much lower than the substrate. Secondly the adhesive will spread out if the unbalanced in surface free energy of the three phases occurred. If the surface free energy will be negative, the adhesive will flow cover all the surface. However, as mention before, Huntsberger added the surface roughness term that contain all the angle to the equilibrium spreading coefficient(S) equation. This enable us to predict the more accurate values.

#### 4.1.4 Kinetics of wetting

Motion is the important word for kinetics of wetting . However thermodynamics will tell that the change can be happened or not, but kinetics will tell that how fast is the change to occur. There are many gradient in kinetics of wetting. The viscosity, the thermal, the contamination or the surface roughness are the samples of the gradient of the kinetics of the wetting. The sample is the dynamic contact angles which initially is the angle when forced two substrate together. This angle will be different between substances. We can calculate this angle by the equation follows,

$$\tan(\theta_d) = m \left( \frac{\eta v_s}{\gamma_{lv}} \right)^n$$

From this equation,  $m$  and  $n$  is the constant. The  $\eta$  is the viscosity. In the next page the simulation of the dynamic contact angle will be plotted with viscosity will be shown in figure 4.4.

The roughness of the surface have the profound effects on the kinetics of wetting. In the case of the angle below 90 degrees, the roughness will speed up the kinetics up to 50%. However not only the roughness will speed the kinetics, but also can delay the kinetics such as in the case of zinc phosphate. It is very hard to study the effect of the roughness because there are many kinds of roughness. Nevertheless de Bruyne have modeled the depth of the roughness that are the cylindrical pores which the equation can be shown as below,

$$l_p = l \left( 1 - \frac{p_a r_o}{2\gamma_{lv} \cos(\theta) + p_a r_o} \right)$$

From this equation,  $P_a$  is the atmospheric pressure, the  $r_o$  is the diameter of the cylindrical size. With this calculation, if  $r_o$  is small the penetration  $l_p$  will be greater. This shows the spreading of the adhesive will be faster. However if the angle of the  $r_o$  is not equal to 90 degree the hindrance effects will occur as can be shown in the figure 4.5. Packham further modified this equation to use with the quick setting adhesive which can be seen as ,

$$l_p \left( \frac{dl_p}{dt} \right) = \frac{r_o^2 p_r}{8\eta}$$

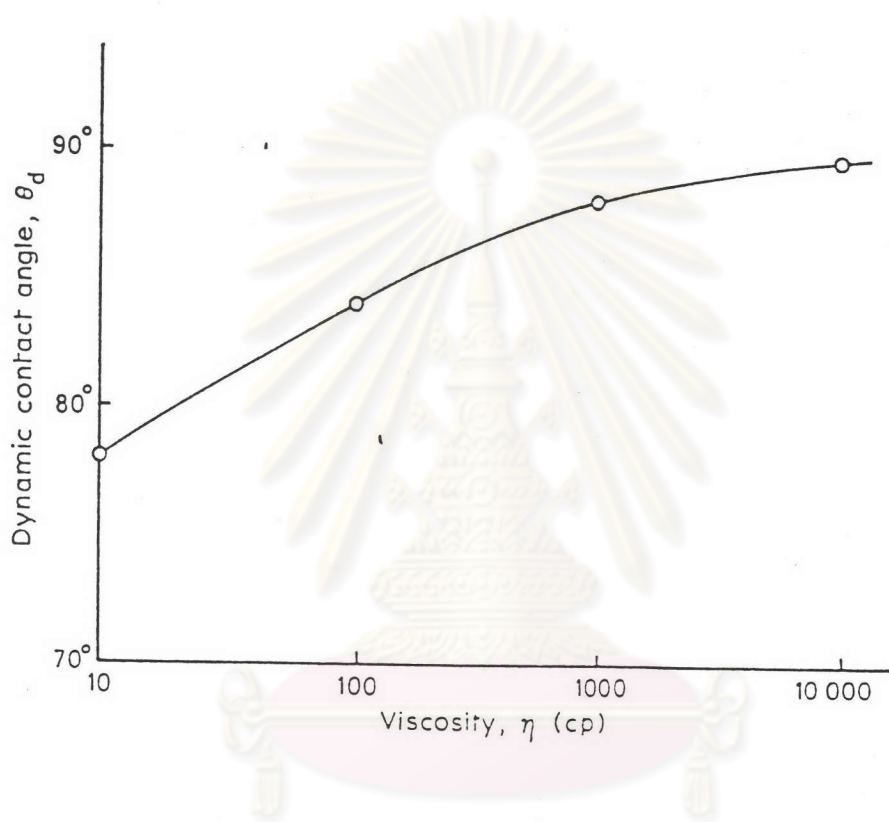


Figure 4.4 Dynamic contact angle,  $\theta_d$ , versus the liquid viscosity,  $\eta$

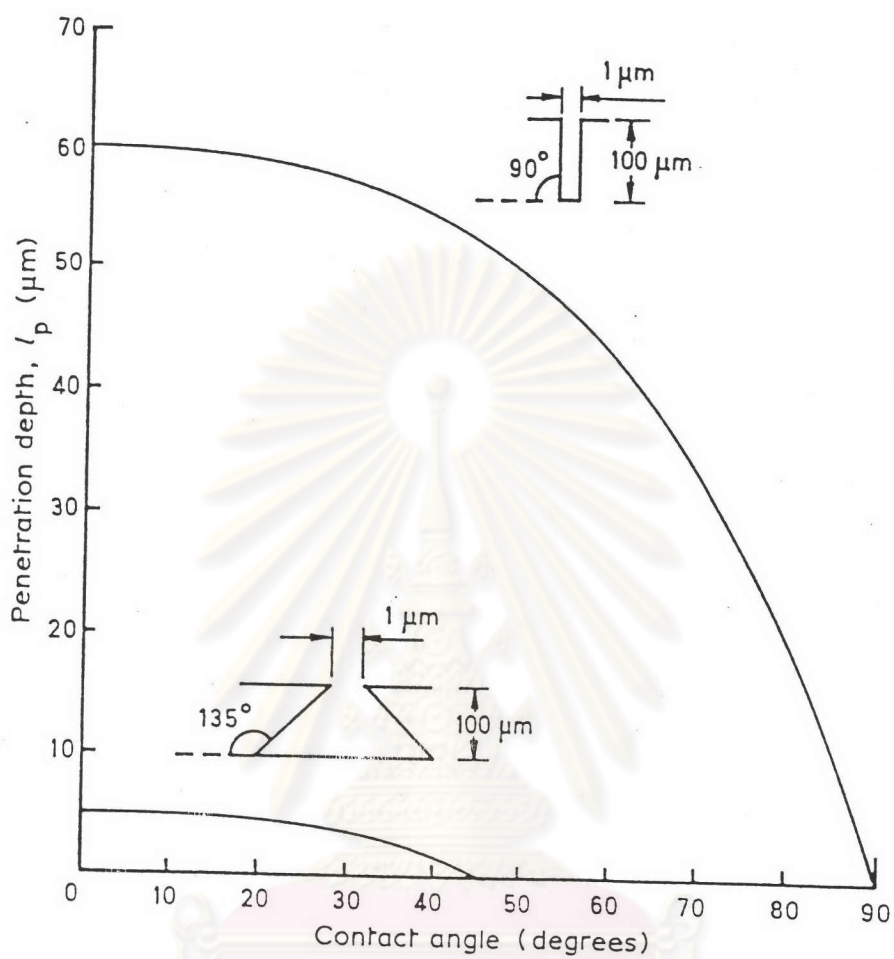


Figure 4.5 Comparison of the penetration of a liquid into cylindrical and 'ink-bottle' pits

The  $P_r$  is instead of  $P_o$  as the equation above. It is because the pressure of the applied adhesive might be higher than the normal pressure. But if the  $P_r$  is substituted by the capillary pressure, this equation can be integrated to be the equation below,

$$l_p^2 = \frac{r_o \gamma_{lv} \cos(\theta)}{2\eta} t$$

From this equation, it can be shown that the kinetics of wetting will be increased by the square of  $r_o$  and  $\cos(\theta)$  and will be reduced if the viscosity of the adhesive is higher. The adhesive air also has the influence on the kinetics. It will speed up the kinetics when it is increased.

#### 4.1.5 The bonding operation

Not only the adhesive is entrapped between the two substrate, but also the air and the humidity. As we can see in the previous section that  $l_p$  is the penetration length which is smaller than real length so some air will trap in the surface roughness. In ordinary joint, this air trap is not so crucial, but in the hot joint operation this air trap will expand and agglomerate to deteriorate the strength of the joint. The correction methods are to vacuum the joints. There are reported that vacuum joints have 30% more strength than the unvacuum joints.

Humidity has more profound effects than the air trap especially when the surface has high surface free energy such as metal or metal oxide. The humidity or

in other word liquid water can be spread cover the substance surface before applying the adhesive. More over the humidity will effect the dipole and polar surface free energy. This effects call the wettability envelopes which can be shown in the figure 4.6. The storage of the treated substrates before applying the adhesive are important. The humidity can be controlled by many method included increasing the temperature.

## 4.2 MECHANISM OF ADHESION

Adhesives bind two substrates together by many forces. In this section , some of the forces will be explained and verified. The main four forces are,

1. Mechanical Interlocking
- 2 Diffusion theory
3. Electronic theory
4. Adsorption theory

These sum of forces bind adhesive with substrate 1, adhesive to adhesive and adhesive with substrate 2. This chains of forces link two substrate together.

### 4.2.1 Mechanical Interlocking

The principle of the mechanical interlocking is very simple. The adhesive failed to interlock key holes that distributed all around the surface. However , these situation can happened harder than adhesive that fall down to capillary hole. This situation can be represented by the figure 4.7. There have been the measurements that can conclude the important of the mechanical interlocking by writing the equation,

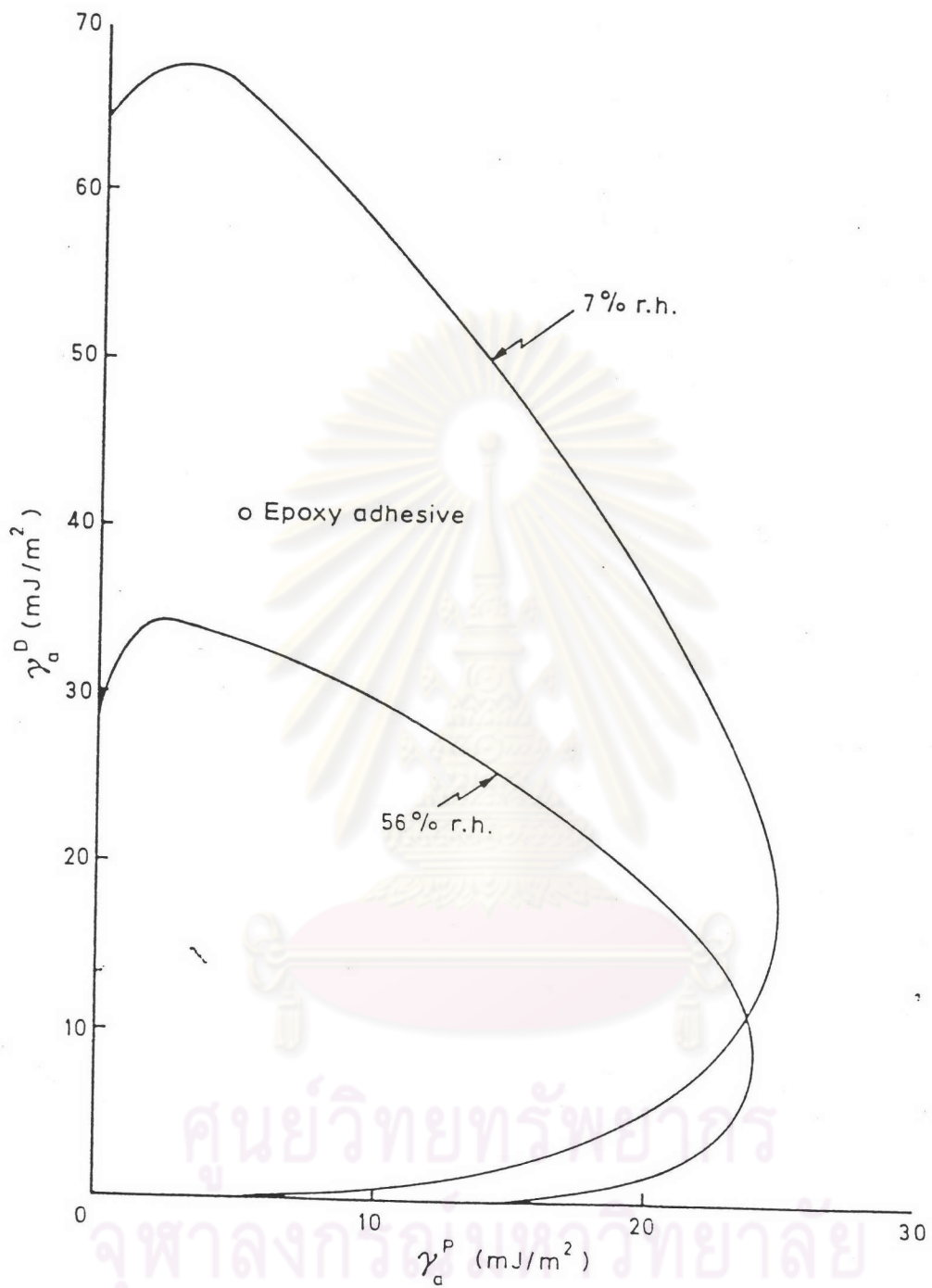


Figure 4.6 Wettability envelopes for abraded mild steel surfaces at various humidities



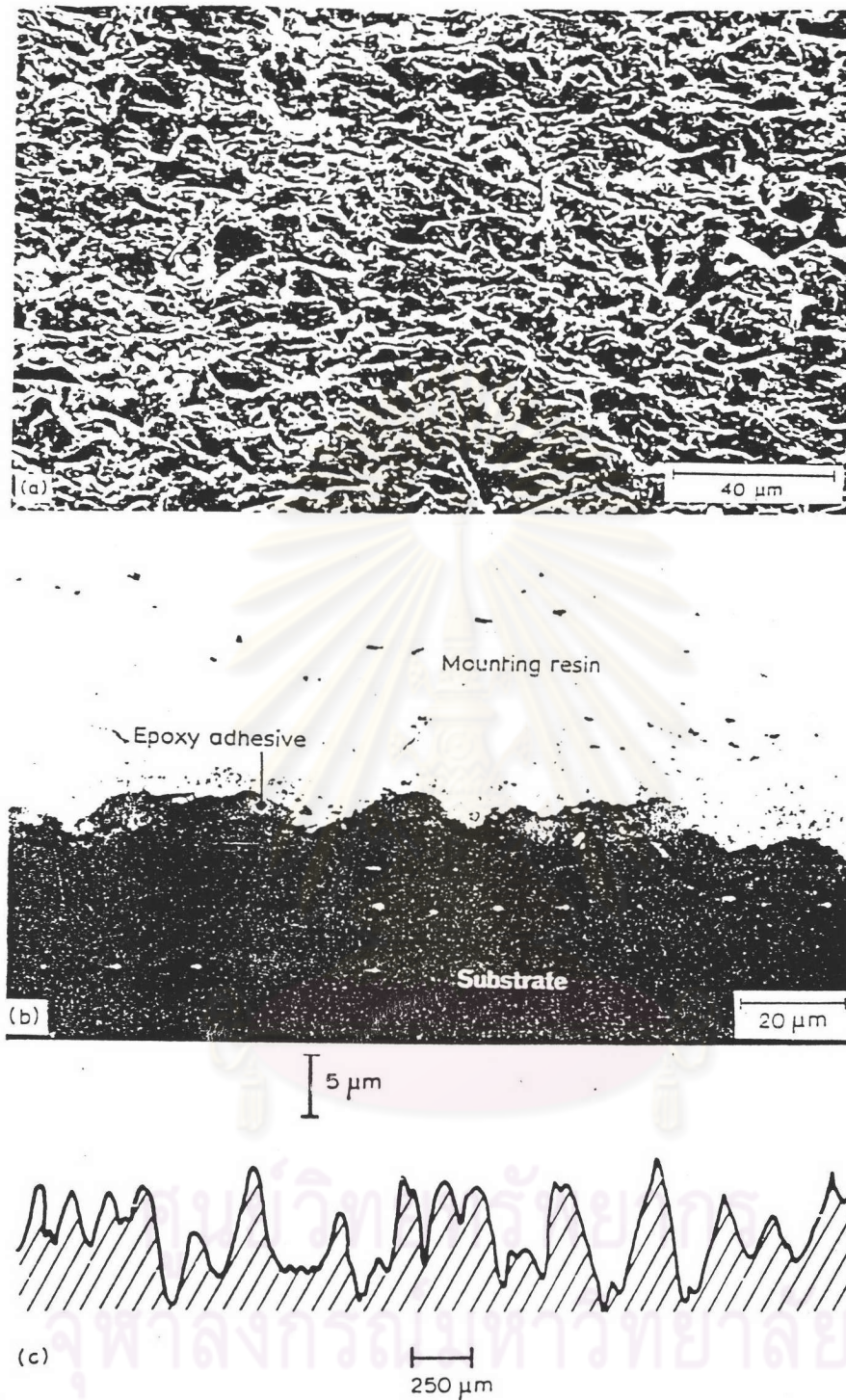


Figure 4.7 (a) Scanning electron micrograph of an abraded mild steel surface. (b) Optical micrograph of a section cut normal to an epoxy/abraded steel interface. (c) Talysurf profilometer trace for an abraded steel surface.

Optimum joint strength = Constant \*

Mechanical interlocking \*

Interfacial chemical component

and one numerical experiment result

Constant	0.23
Mechanical interlocking	2.9
Interfacial chemical component	5.9

From these experiment, the mechanical interlocking is half of the interfacial chemical component bond. The interfacial chemical component bond can be get rid but it is hardly to get rid of the mechanical interlocking.

There are two types of the mechanical interlocking substrates, mechanical and chemical interlocking substrates. The mechanical interlocking substrate come from rubbing or scratch the interface to get rid of unwanted material such as oil and releasing agents. As we said in the last section, the strength of the joint will increase 5 to 30 % . It can distribute the force that come to the joint by create the plastics deformation in the adhesive.

The rest of the treated surface of the mechanical interlocking called chemical interlocking substrates. There are many ways to treat the surface such as flame, electroform, chemical etching. There are some important papers about treating the surface of electroformed copper. The form of the surface will effect the strength of the joint. The strength of the joint increase when the rugosity are

increase. The rugosity will distribute the force and introduce the plastic deformation at the joint. That is why the strength of the joint is better remarkably.

#### 4.2.2 Diffusion Theory

This force is the force that bind the adhesive itself together. This force comprise of Van der Waal force which is very weak, but because of the high molecular weight, the total force between molecule is enough to hold the polymers. This force come from the word “like dissolve like”. The molecules which are the same will dissolve the same molecule. However this rule depend on the thermodynamic theory. The indicator which relate the possibility to dissolve is called Solubility factor ( $\delta$ ). If the solubility factor of the two substances are equal, it mean that these two substances may mix together thermodynamically. If the solubility factor of the two substances are far apart, those two substances can not be mix together thermodynamically. For example, polyethylene can not blend with the polypylene which have the same composition carbon and hydrogen. This is because the solubility of polypropylene is slightly different than the polyethylene. These situation happened because the extra CH<sub>3</sub> groups of polypropylene.

The modeling interfacial diffusion can be start from the equation of motion and further interpreted every terms before integrate numerically or analytically. The diffusion equation of motion can be explained as follows,

$$dw = -D_f dt \left( \frac{dc}{dx} \right)$$

Vasenin first assumed that as the diffusing species interdiffused into the surface regions during the time of contact  $t_c$ , the reduction in the value of the diffusion constant with time would be of the form

$$D_f = D_d t_c^{-\beta}$$

$D_d$  is a constant which characterizes the mobility of the macromolecules and  $\beta$  is a constant which determines the rapidity of change of the coefficient of diffusion,  $D_f$  with time and is of the order of 0.5 in value. Next he deduced that the depth of penetration,  $l_p$ , could be expressed by,

$$l_p = \left( \frac{(\pi D_d t_c^{0.5})^{0.5}}{k_3} \right)$$

The constant  $k_3$  is a constant which characterizes the stiffness bond length and valency angles along the polymeric molecules. Vasenin introduced the new variable that still gives the rest of the equation to be a constant. This new variable is  $N_c$  which is the number of the molecular chains crossing the phase boundary between the adhesive and substrate.

$$N_c = \left( \frac{2N_A \rho}{M} \right)^{2/3}$$

Finally he introduced this equation into the previous equation and created the new constant  $k_4$ . The new equation for the peel tests can be shown as below,

$$P = k_4 \left( \frac{2N_A \rho}{M} \right)^2 D_d^1 t_c^1$$

The  $P$  is the peel energy and  $t_c$  is the contact time. Vasenin has done the experiments and conclude the data as in the explanation in figure 4.8. These equation can explain the relation between the peel energy and the contact time and also the peel energy and the molecular weight. However he predicted the diffusion coefficient of polymer (polyisobutylene) to be  $10^{-14}$  cm<sup>2</sup>/sec. The experimental measurements show the diffusion coefficient of the polymer molecules are about the same or 1000 times more than this value. Many scientist criticized this theory. One of the weak point of this theory is that it did not include the void that come from the twist bond of polymer molecules. This can be shown in the next page. The others thing about the weak point of this equation is the viscoelastic of polymer which is not included in the definition. There are the new theory developed to explain the movement of polymer at the adhesive - substrate interface.

#### 4.2.3 The electronic theory

The electronic force happened between surfaces that have the different in electronic charge. The magnitude depended significantly on the gap between the

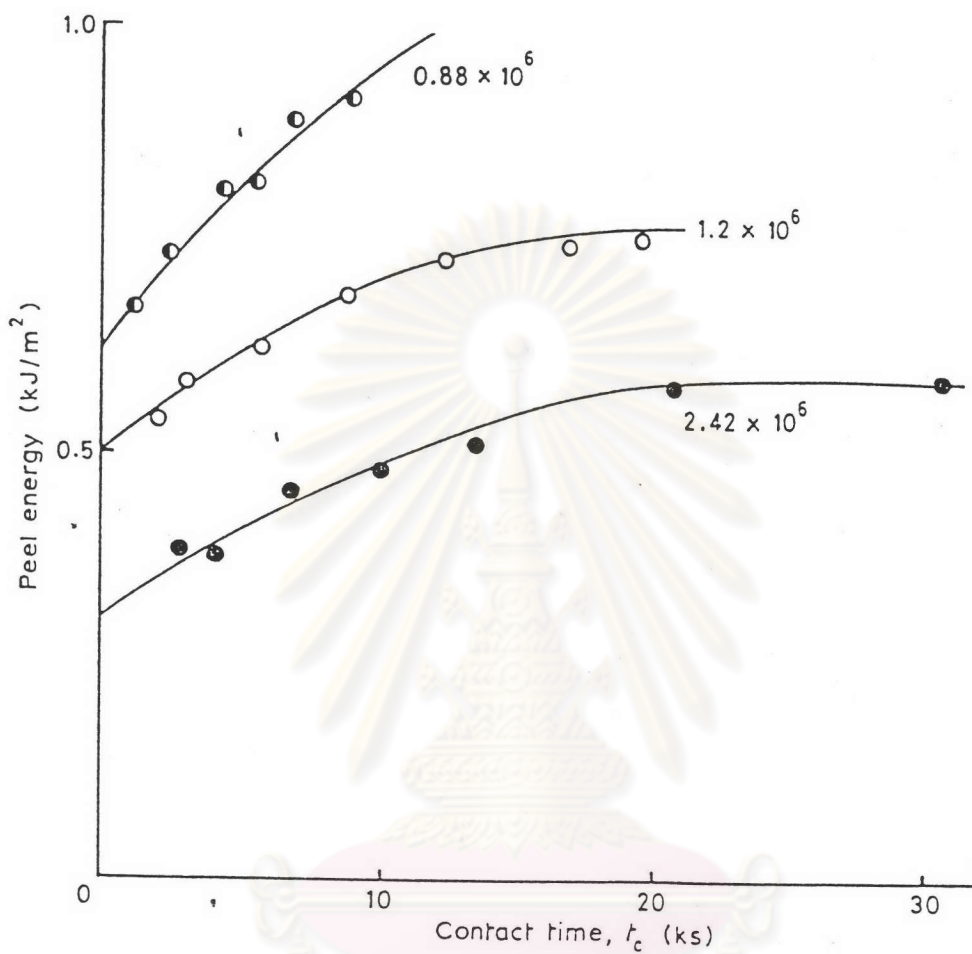


Figure 4.8 Relation between the measured peel energy and contact time for the autohesion of polyisobutylenes of various molecular weights. The points are experimentally determined.

surface. There are some theory and experiment in this field but unclear conclusion is revealed. However when it is no cracking, it is no force in this forms.

#### 4.2.4 Adsorption theory

Adsorption theory is the important theory that explained the significant of the secondary bond. Primary bond is the bond that adhesive bind with adhesive. This bond is already explained in the diffusion theory. Secondary bond is the bond that the adhesive is bond with substrate. This bond is very important and if this bond is strong the strength of the joint will be incredible increased. The bond and the strength of the bond will be shown as in table 4.3.

The strength of the joint depends on both primary and secondary forces and if the joint is free from air trap and other contamination, the strength of the joint will be incredibly high. There are some situation that the strength of the joint mainly come from secondary force. Furukawa et al have used the inelastic electron tunneling (IET) spectroscopy study the hydrogen bond between silane/oxide interface that induce between amino group on the silane and surface hydroxyl groups on the oxide.

In the case of binding polyethylene, the formation of hydrogen bonds has been suggested to be the result of tautomerization according to a series of transformations shown in figure 4.9. This hydrogen bond can be inserted the bond by the water to make the link between the oxygen bond on modified polyethylene and the hydrogen from one molecule water. These work has done by using X-ray photoelectron spectroscopy (XPS). XPS or electron spectroscopy for chemical

Table 4.3 Bond types and typical bond energies

Type	Bond energy (kJ/mol)
Primary bonds	
Ionic	600-1000
Covalent	60-700
Metallic	110-350
Donor-acceptor bonds	
Bronsted acid-base interactions (i.e. up to a primary ionic bond)	Up to 1000
Lewis acid-base interactions	Up to 80
Secondary bonds	
Hydrogen bonds	
Hydrogen bonds involving fluorine	Up to 40
Hydrogen bonds excluding fluorine	10-25
Van der waals bonds	
Permanent dipole-dipole interactions	4-20
Dipole-induced dipole interactions	Less than 2
Dispersion (London) forces	0.08-40



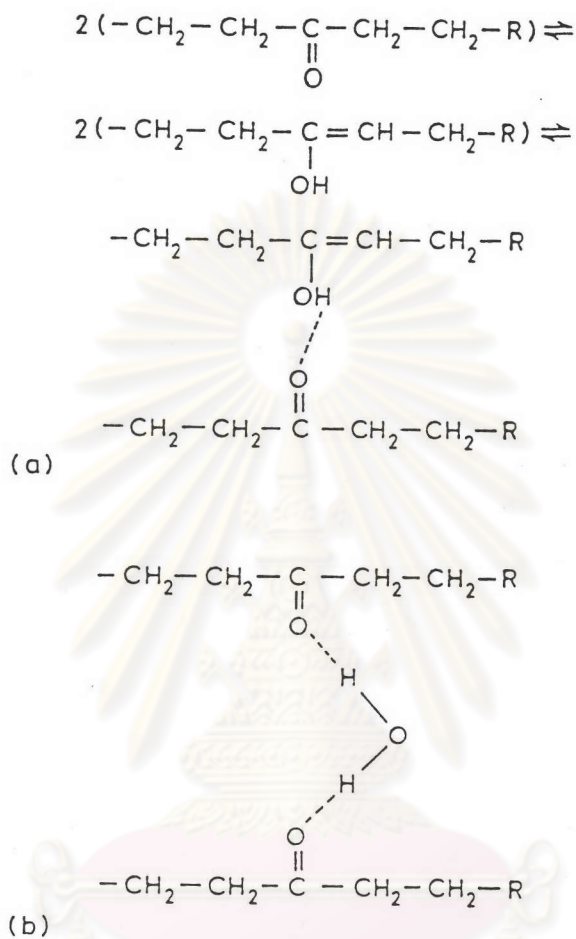


Figure 4.9 Possible hydrogen-bonding mechanisms in the autohesion of oxidized polyethylene. (a) Via tautomerization, (b) via a water molecule.

analysis (ESCA) can provide very good quantitative and qualitative elemental analysis of a surface and reasonably good determination of the chemical bonding. XPS involves the bombardment of the specimen surface with mono-energetic X-ray in ultra high vacuum (<0.00000001 Torr). Eject electrons from the bombard specimen will be recorded and analyzed. The other technique which also useful for studying surface is called AES ( Auger Electron Spectroscopy ). AES will give the better resolution but the sample can be eroded but XPS can analyze the surfaces of insulators readily.

Dupre equation can be explained the adhesion of the adhesive. This equation is similar to the equation of wetting by add/subtract some other terms. This equation can be shown as below,

$$W_A = \gamma_{as} - \gamma_a - \gamma_s = 2\left(\gamma_s^D \gamma_a^D\right)^{1/2} + 2\left(\gamma_s^P \gamma_a^P\right)^{1/2}$$

The reversible work of adhesion shows that the substrate and the adhesive can attach together or not and with how strong of the joint. After the thermodynamics definition of  $W_a$ , Zisman discover the  $\gamma_c$ , the relation between  $\gamma_c$  and the joints strength were published which can be shown as in figure 4.10. There are two energy that relate with the breakage of the adhesive joints. The first energy, called  $G_0$ , relate the energy that use to tear the joint plastically. The others energy, called  $\Psi$ , relate the energy that use to dissipate viscoelasticity. These two energy help to strengthen the joint.

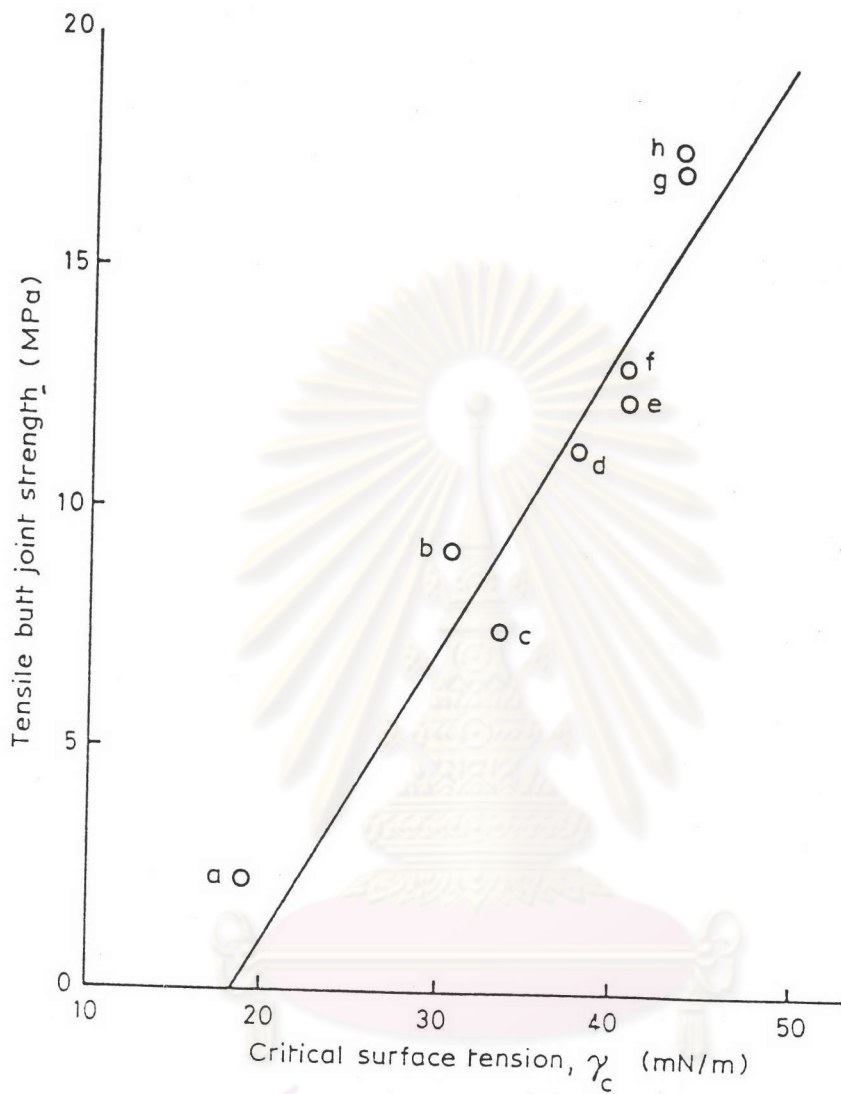


Figure 4.10 Relation between measured joint strength and critical surface tension,  $\gamma_c$ , of the substrate for an epoxy bonding various polymeric substrates. (a) Polytetrafluoroethylene, (b) poly ( vinyl fluoride ), (c) polystyrene, (d) poly(vinyl alcohol), (e) polyvinylidene chloride), (f) poly ( vinyl chloride ), (g) poly ( ethylene terephthalate ) and (h) poly(1,4-cyclohexylene dimethylene terephthalate).

The substrate such as PMMA can be changed the properties with the different silica solvent to become proton donor or receiver such as in figure 4.11. The Donor-acceptor interactions come from the combination of the constant of acid-base and base-acid. This interaction will strongly strengthen the interface and the joint. There are many equation that try to predict the strength of this interaction but all equation still have the weak point.

There are some chemical that can modified the substrates to be suitable with the adhesive. One chemical is polyacrylic acid which will modified the oxide of the metal. The other is the coupling agent which will attach silica with the oxidizing bond. Kinlock et.al. study this phenomenon by using the static secondary ion mass (SIMS). Some pictures will be shown as in figure 4.12. The results from SIMS show the polysiloxane attraction and surprisingly the Fe attraction. In figure 4.13, there will be the sample of the coupling agent that dramatically increase the joint strength. In conclusion, the secondary force, the plastic deformation will increase the joint strength beside the other forces that we have already mention.

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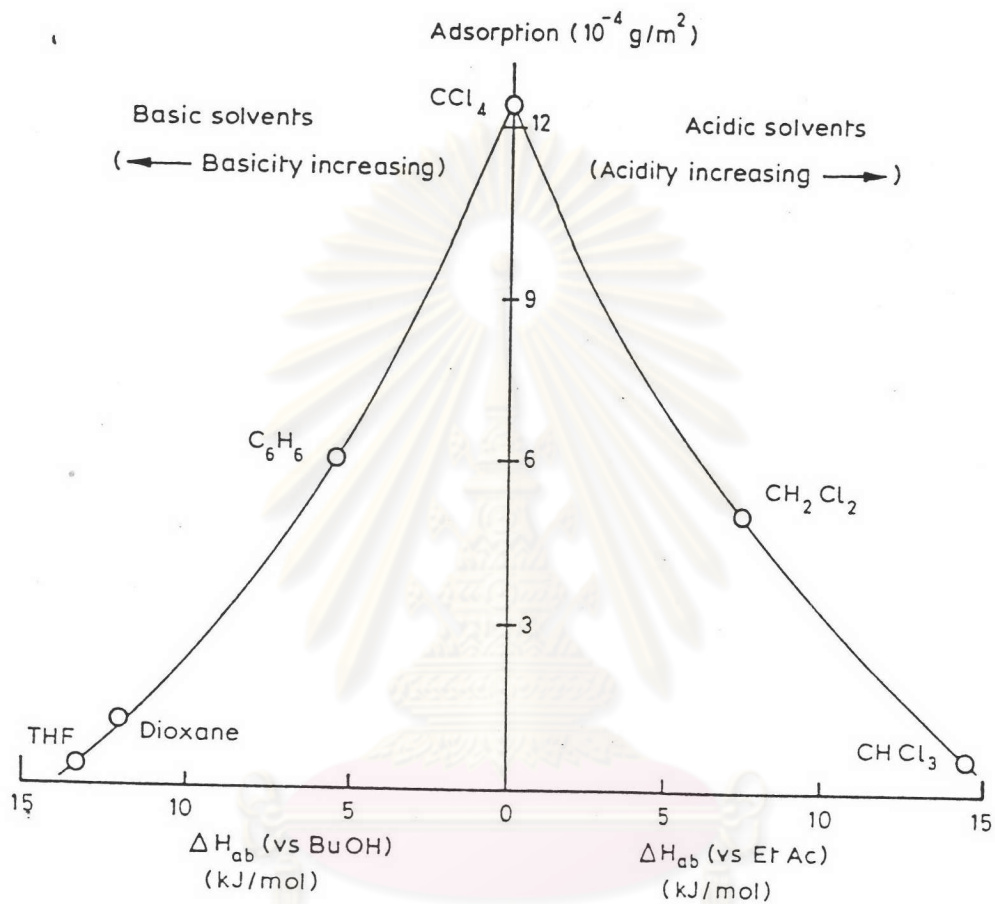


Figure 4.11 Adsorption of poly(methyl methacrylate), a basic polymer, onto the acidic surface of silica from basic, neutral and acidic solvents.

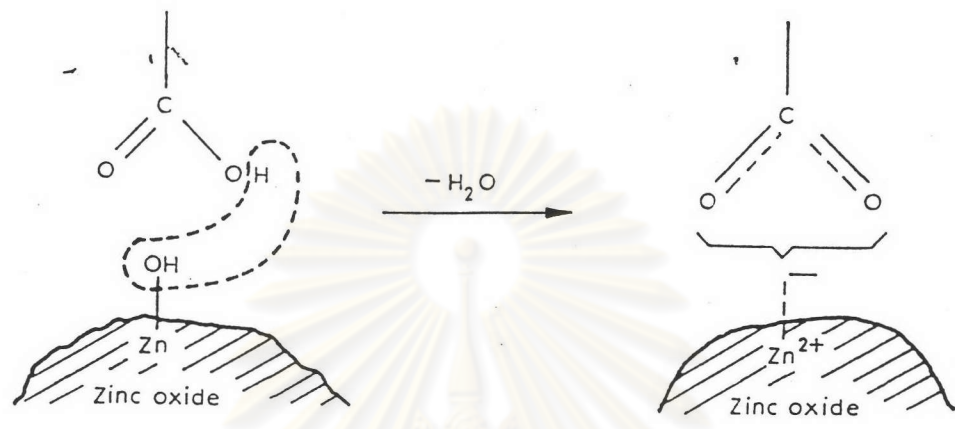


Figure 4.12 Possible reaction scheme for a poly(acrylic acid) bonding to a zinc oxide surface.

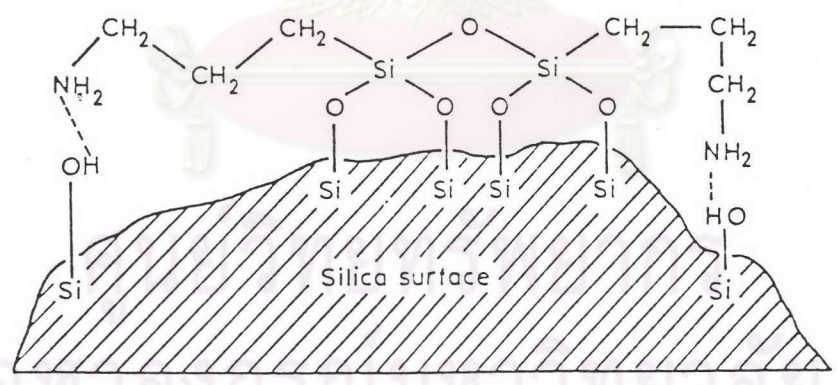


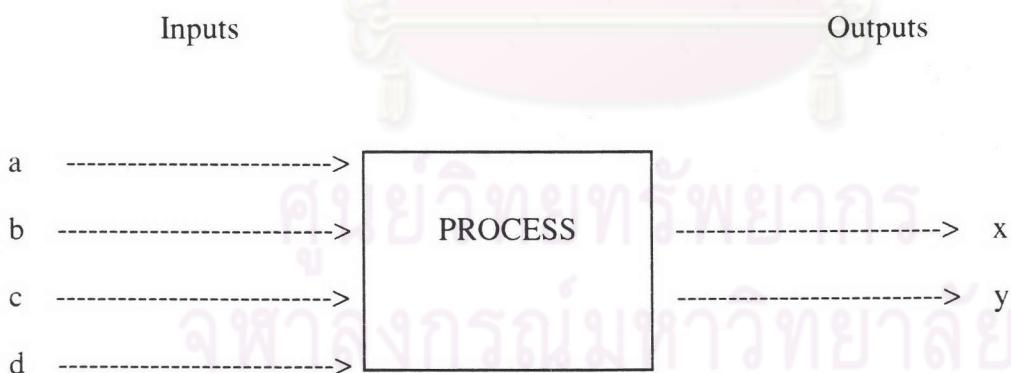
Figure 4.13 The structure and interfacial bonding of  $\gamma$ -aminopropyltriethoxysilane on a silica surface.

### 4.3 EXPERIMENTAL DESIGN

#### 4.3.1 Purpose of EXPERIMENTAL DESIGN

Objective of an experimental design is to obtain the maximum amount of information using a minimum amount of resources. Determine which factors shift the average response, which shift the variability, and which have no effect. Then build empirical models relating the response of interest to the input factors. Find factor setting that optimize the response and minimize the cost and validate the results.

Experimental design is to purposeful change the input (factors) in order to observe corresponding change in the output ( response ).



If a,b,c,d are inputs of the process and x,y are outputs. We can set experimental table as following.

Run	a	b	c	d	x	y	.....	Y	Sy
1									
2									
3									
-									
-									
-									

:

#### 4.1.2 How to set up the design

Factors	Factors	Factors
Number of Levels	2	3
Number of	$2^p$	$3^p$

Number of factor and level are used to specify number of experiment as show in the table above. Factors are the types of raw materials we choose to vary



to identify the results. The levels are quantity of that factor. The more numbers of factors and levels are required the more experiments for testing.

If the experiment is specified to have four factor and two level, then there are 16 batch to be test as in table 4.4.



ศูนย์วิทยทรัพยากร  
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formula	factor A	factor B	factor C	factor D	response Y
1	-	-	-	-	
2	-	-	-	+	
3	-	-	+	-	
4	-	-	+	+	
5	-	+	-	-	
6	-	+	-	+	
7	-	+	+	-	
8	-	+	+	+	
9	+	-	-	-	
10	+	-	-	+	
11	+	-	+	-	
12	+	-	+	+	
13	+	+	-	-	
14	+	+	-	+	
15	+	+	+	-	
16	+	+	+	+	
AVG -					AVG
AVG +					
Delta $\Delta$					
$\bar{Y}$					

AVG = average of response Y , AVG + = average of response Y of higher level

Delta  $\Delta$  = (AVG+)-(AVG-) , AVG- = average of response Y of lower level

$$\bar{Y} = \frac{(AVG) + (\Delta/2)(A) + (\Delta/2)(B) + (\Delta/2)(C) + (\Delta/2)(D)}{1}$$

TABLE 4.4 How to set up the design