CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Theory

2.1.1 Basic principle of adhesion[1]

In ancient times it was found that solids could be made to adhere strongly by wetting each surface to be jointed with a thin layer of liquid which would harden or solidify gradually during contact. Early in this century the selection of adhesives and application techniques was an art depending on the use of glue formulation made from fish and animal products or cements made from inorganic slurries or solutions. The advent of synthetic polymeric adhesives having better and more reproducible propertied has promoted a wider use of adhesives in the past 40 years, has increased the interest in expanding the art, and has converted it into a science. Despite the advanced technology of today, there are many unanswered questions about the principles underlying the mechanism of adhesion, and there still excessive empiricism in current application techniques. Guidance is also needed in the search for adhesives suitable under more extreme conditions.

Adhesion[1] is defined as the state of holding together two surfaces of bodies (called adherents) by interfacial forces such as valence forces, mechanical interlocking and a combination of both.

Of course, in our discussion on adhesives, we will be concerned with these valence forces through which adhesives work. Valence forces, which are responsible for the surface attraction, can either primary valence bonds or secondary valence bonds.

Primary valence bonds are the well-known covalent, coordinate, electrovalent, or metallic bonds, which are formed when atoms or molecules either share or transfer electrons. Their bonding forces range from 10 – 100 kcal/mole. Far more important from the standpoint of adhesives, however, are the weaker secondary bonds known as Van der Waal forces (2-4

cohesion of non-polar liquid molecules, for example. Also, these weak forces can provide good adhesion between two surfaces; however, in order for these forces to act, molecules must be between 3 to 10 $^{\circ}$A. Beyond 10°A, these forces are no longer effective in that they decrease at a rate equal to the sixth power of the intermolecular distance. Even the smoothest of two solid surfaces cannot have enough surface area at intimate contact to achieve any adhesion between the two solids. This is because the apparent smooth surfaces are not at all smooth at the microscopic level as shown below.
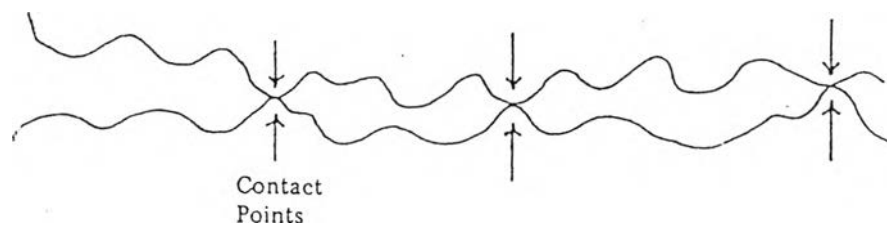
Contact
Points

Figure 2.1 Contact points

This is where the role of the adhesive comes in. Most of adhesives, whether they are hot melts, evaporation types, chemical reactive types, etc, are applied to the adherent in a liquid state. The application as a liquid is necessary in order to sufficiently " wet " the surface of the adherent. This allows the adhesive molecules to get in close proximity to the surface molecules of the adherent in order to establish valence forces. Therefore, it is imperative that the adhesives being applied have sufficiently low viscosity to allow the adherent surface to be wetted properly. If the viscosity of adhesive is too high, then it will not penetrate properly into the surface pores and crevices. This is important in that if gas bubble or voids occur between the glue line and the adherent, stress will be concentrated more in a smaller area, thus weakening the strength of the bond. It is common practice in adhesive technology to clean and roughen the surface of and adherent before the application of the adhesive. This is done not only to remove oxides from a metallic surface, but because a rough surface provides greater joint strength as well as helping to prevent crack propagation along the glue line by isolating air pockets that may have formed from incomplete wetting. The roughness provides " teeth " to the bonded joint. While the adhesive is still a liquid, it displays no cohesive strength to the bond. With cooling, vaporization of the

carrier, or through a polymerization reaction, the adhesive will later become a solid which will then provide the cohesive strength to the bond.

In order for a given adhesive to effectively wet an adherent surface, that adhesive must be compatible with the adherent if a lasting bond is to result. Thermodynamically, for a bond between an adherent and an adhesive to be strong, there must be a resulting decrease in free energy (ΔG) from the combination of adhesive and substrate. In order to words, the ΔG must be negative in the following equation.

$$\Delta G = \Delta H - T \Delta S$$

where
ΔG = Change in free energy

ΔH = Change in heat of mixing

ΔS = Change in entropy

T = Temperature

In general, when an adhesive and adherent meet, entropy is increased (more disorder), so entropy only contributes to the loss of free energy. Therefore, only the heat from mixing (ΔH), can prevent a negative ΔG from resulting. Thus, provided that the heat of mixing is not too great, the adhesive and adherent will combine. This is even more likely at elevated temperature. Another way to look at it, is to say for the adhesive to work, the adhesive attraction between the liquid adhesive and the adherent must be greater than the cohesive forces within the liquid adhesive being applied. The following are examples of a "good " and " bad " adhesive bond.

"Good" Bond

A

Concave Meniscus

"Bad" Bond

B

Convex Meniscus
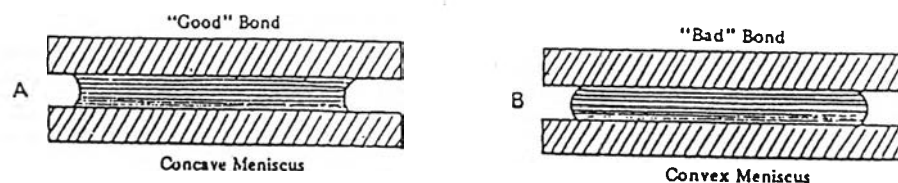
In figure A, the adhesive forces exceed the cohesive forces of the wet adhesive. Therefore, the adhesive spreads over the adherents and "wets" the adherent surface. In figure B, the cohesive forces of the wet adhesive are greater than adhesive forces between the adhesive and adherent. Therefore, in figure B, the adhesive is not compatible to the adherent material.

One method to help determine the compatibility between an adhesive and a given substrate was explored by W. A. Zisman of the Naval Research Laboratory in Washington, D.C. Zisman and his colleagues measured the critical surface tensions (γ_c) of different selected polymer surfaces. This critical surface tension measures the "wettability" of a given solid surface. γ_c gives the maximum surface tension that an adhesive can have. If the adhesive's surface tension exceeds γ_c, it will not be able to wet the surface of the given substrate. Zisman was able to measure γ_c of many surfaces by measuring the changes in contact angles of different selected liquids that were applied to the surface. All these liquids he used for his measurement already had known predetermined surface tensions. Therefore, the critical surface tension could be determined.
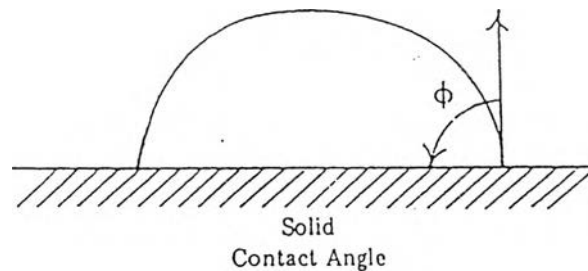

Solid
Contact Angle

Figure 2.2 Solid contact angle

As the contact angle approaches zero, the drop will cover a larger and larger area. When $\phi = 0$, complete spreading of the liquid has occurred across the surfaces. Therefore, ϕ is inversely a measure of wettability.

In general, it can be noted that polymers that are highly polar in molecular structure give relatively high critical surface tensions. For example, nylon 6,6 (a polyamide) has $\gamma_c = 42$ and polyester (polyethylene terephthalate) has a $\gamma_c = 43$. Conversely, the γ_c for silicone rubber is 22 and for Teflon (polytetrafluoroethylene) it is only 18. The difference we see among these polymers is due to differences in the dispersing force component of intermolecular attraction.

Another method of measuring compatibility is by using Hildebrand solubility parameters. This solubility parameter δ is equal to the square root of the cohesive energy density (internal pressure) as shown below.

$$\delta = \sqrt{\Delta E / v}$$

where

ΔE = Change in energy of vaporization

v = Molar volume

The energy of vaporization for low molecular weight liquids is easily measured. Fluorocarbon and hydrocarbon liquids are well known to have lower energy of vaporization values per cc compared to polar liquids of the some molecular weights such as alcohol or water. The energy of vaporization cannot be measured directly for polymers because they are obviously non – volatile. Therefore, indirect methods must be used to measure the solubility parameter δ of polymers. These values can be calculated, but the common method is to simply compare the solubility properties of a given polymer to different selected solvents of known values in order to find the best solubility. A strong positive correlation has been reported between the critical surface tension (γ_c) and the Hildebrand solubility parameter (δ) for a wide range of different selected polymers. Although this correlation is by no means perfect, it does show that both γ_c or δ can be used to help predict the compatibility of an adhesive with a select adherent.

In general, different solids have different specific surface free energies (ergs/cm^2). Solids with strong intermolecular forces, such as carbides, metal oxides, metals, etc, have high-energy surfaces. On the other hand, very low melting organic solids of weak intermolecular forces have low energy surfaces. Glasses and some salts are considered intermediate. Lastly, most all liquids are considered to have low energy surfaces. Therefore, liquids generally will easily spread over the high-energy surface solids. For low energy surfaces such as Teflon, this is not the case. A high-energy surface can also be converted to a low energy surface by the treatment with say polmethylsiloxane (silicone) to form a monomolecular layer across the surface. From this treatment, a liquid that previously would have spread quite readily is repelled instead. This is why silicone is used as a mold release agent in many applications.

So far discussed are those conditions necessary to obtain a good adhesive bond. But there is still one other condition that should be mentioned concerning the nature of the glue line itself. As mentioned earlier, an adhesive is applied in liquid state, but later hardens to provide the necessary cohesive strength to the bond. The adhesive will harden by cooling, if it is a hot melt;

by loss of a volatile carrier, if it is a solvent based or latex adhesive; or by polymerization, if it is a reactive adhesive. All these methods can cause the applied adhesive (glue line) to shrink, because of thermal contraction, loss of carrier mass, or loss of a low molecular weight by-product from polymer condensation reaction. If this shrinkage is not controlled, it can create strains within the glue line, which can result in an adhesive failure. Such methods to control this contraction are as follows.

1. Use fillers in compounding the adhesive to reduce the contraction.

2. Select an adhesive the either does not greatly contract or is somewhat flexible in its hardened state.

3. Try not to make the glue line too thick.

4. If the adherent is impervious, and solvent based adhesive is being applied, allow the greater part of the solvent to be lost after application before joining the two adherents to form the bond.

2.1.2 Functional uses

Before considering the functional uses of various chemicals and polymers used in compounding adhesives, we should first discuss the basic types of adhesives. These types are listed below.

1. Chemically reactive types

2. Evaporation types

3. Hot melt types

4. Pressure sensitive types

The chemically reactive types of adhesives usually involve the polymerization of low molecular weight liquid components upon application to form a polymerized glue line, which will have good cohesive strength. There are two basic types of chemically reactive adhesives. One type consists of those reactive adhesives, which give off a low molecular weight by-product (usually water) during a polymer condensation reaction. Examples of this type are the phenol-formaldehyde and resorcinol-formaldehyde adhesives. The other type of reactive adhesive polymerizes without the formation of a low molecular weight by-product sometimes through addition polymerization. Examples of this type are epoxies, cyanoacrylates, urethanes, and polyesters.

Evaporation type adhesives consist of a polymeric material being carried in a liquid state by a liquid carrier whether it is as a aqueous colloidal dispersion (latex) or as a solution in an organic solvent. Of course after application, the liquid carrier must be lost by evaporation or by diffusion into a porous substrate in order to obtain a solid glue line and good cohesive strength. The organic solution adhesives are faster drying than the latex adhesive; on the other hand, for the glue line to have a good cohesive strength may require a higher molecular weight polymer. Generally, the higher the molecular weight, the higher the solution viscosity. But if the viscosity is become to high, the adhesive may not wet properly. Therefore, there is a limit of say 30% or so in the total solid content of a solution system. A latex adhesive, on the other hand, has an advantage in that it can have a higher total solids content without raising the viscosity to excessively high levels. At levels above about 50% polymer concentration, latex particle agglomeration may occur.

Elastomeric adhesives are commonly used in both solvent solution form and in latex form. One complicating factor in classifying adhesives is that either of these adhesive forms may or may not contain rubber curatives. The rubber curatives are sometimes added to initiate rubber vulcanization and make the glue line stronger than it would be otherwise. Then these two types of elastomer adhesives with certain additions can be classified as both vaporization type and reactive type adhesives. The third type of adhesive is called a hot melt adhesive. It consists of a thermoplastic polymer and usually other additives. The adhesive when applied hot (above melting) to a given substrate, effectively wets the surface; however, on cooling, the molten polymer returns to its solid form providing good cohesive strength to the bond. The advantage to hot melt adhesive types is that they set very quickly after applied.

Lastly, we have the pressure sensitive type adhesives. As you recall, the adhesives we have been discussing were all applied to a substrate in a liquid state in order to "wet" the substrate. Then through various means, that liquid is converted into a solid form. In the case of a pressure sensitive adhesive, this physical transformation does not occur. A pressure sensitive adhesive is, in a way, both in the liquid state (for wetting) and in the solid state (for cohesive strength) at the same time. A pressure sensitive adhesive consists of a viscoelastic material which is fluid enough to wet a surface under a slight applied external pressure, yet cohesive enough to provide some moderate strength in holding the adherents together after external pressure is released. Typically, these pressure sensitive adhesives are based on various elastomers which have been made sticky with the used of resin additives. The applications in providing adhesion

for tape and labels are known. One obvious disadvantage of a pressure sensitive adhesive is its relatively poor cohesive strength compared to other adhesive types. All these adhesives must only be applied when there is adequate ventilation for their use.

2.1.3 Advantages of adhesive bonding

1. Thin film, fiber and small particle that could not be combined as well as at all, by other gum, are readily bonded with adhesive

    -   Glass wood insulation.
    -   Abrasive wheels, sand paper.
    -   Tires reinforce.
    -   Corrugated board.

2. Stresses are distributed over wide areas, making possible lighter and stronger assemblies than could be achieved with mechanical fastening such as airplane wings, foils and fuselages.

3. The strength - to – weight ratio and dimensional stability of anisotropic material can be improved by cross – bonding.

4. The glue line provides electrical insulation in capacitor, printed.

2.1.4 Polymers[19]

The large production capacity for ethylene and vinyl acetate monomers during 1960s and early 1970s made ethylene- vinyl acetate resins with 18-40% of vinyl acetate content (VA) readily available. In fact, with the exception of the period of the oil embargo in 1974-1976, when price escalated rapidly, the polyolefin resins such as low molecular weight polyethylene, ethylene copolymers, and polypropylene resins took on the characteristics of commodity products. Each of these polymers is used intensively in producing hot melt adhesives. The ethylene-vinyl acetates were the most popular because of their superior adhesion to the most substrates and their ease of formulation. Thus, EVA-based hot melt adhesives were developed for a wide variety of end-use applications. Low molecular weight polyethylene resins found their widest use in packaging applications with paper substrates, primarily paperboard cartons and corrugated containers.

Atactic polypropylene (APP) is tacky as produced and is not easily formulated. It is uses essentially as a neat resin or extended with a small amount of wax or a polymer to add hot tack. Atactic polypropylene used to be a byproduct in the production of crystalline polypropylene, but with the development of new, more efficient catalysts, less atactic polypropylene is produced. As a result, at least two companies are now producing APP directly. This means that a greater number of precise products are available; however, pricewise they will have to bear the full cost of production. It is anticipated that atactic polypropylene resins will be developed mainly for specific applications having higher value-added performance.

The properties of polyolefin polymers which make them desirable as the base for the hot melt adhesives are determined largely by two factors: molecular weight and the amount of co-polymer. In the case of ethylene homopolymers an increase in molecular weight provides improvement in some properties; see Table 2.1. Molecular weight is characterized by melt index, (a lower melt index represents an increase in molecular weight).

The potential for variations in polymer properties increases significantly as comonomers are introduced into the polymer. Considerable expertise and experimentation are involved in selecting the proper polymer composition for a specific adhesive application. In fact, most adhesives manufacturers have now developed computerized programs, which will predict an adhesive formulation (polymer grade, tackifier, and extender) to match a specific set of properties. In Table 2.2 the property changes which can be expected by a change in melt index for ethylene vinyl-acetate copolymer are listed. It is following by Table 2.3 showing the effect of vinyl acetate content on polymer properties.

The number of polymer suppliers continues to increase slowly as do the type of polymers. A listing of some of the polymer suppliers is given in Table 2.4. New polymers for hot melt adhesive production are constantly being introduced.

Table 2.1 Effect of melt index on ethylene homopolymer adhesive properties.

High	Improves heat seal strength ⟶	Low
melt	⟵ Improves flexibility	melt
index 500	⟵ Improves low temperature performance	index 2.0
	Improves hot tack ⟶	
	Increases melt viscosity ⟶	

Table 2.2 Effect of EVA copolymer melt index on adhesive performance.

High	Improves heat seal strength ⟶	Low
melt	Improves flexibility ⟶	melt
index 500	⟵ Improves low temperature performance	index 2.0
	Improves hot tack ⟶	
	Improves cohesive strength ⟶	
	⟵ Decreases melt viscosity	
	Decreases open time ⟶	

Table 2.3 Effect of EVA copolymer-vinyl acetate content on adhesives.

Lower vinyl	Increases solubility ⟶	Higher vinyl
acetate content	Improves flexibility ⟶	acetate content
9%	⟵ Higher seal strength	60%
	⟵ Increases blocking resist	
	⟵ Increases paraffin solubility	
	Improves hot tack ⟶	
	Improves adhesion ⟶	
	Improves low temperature performance ⟶	

Table 2.4 Polyolefin polymer suppliers for hot melt adhesive applications.

Polyethylene homopolymers

 Eastman Chemical products

 USI Chemicals Co.

 Union Carbide Corp.

 Exxon Chemicals

Ethylene-vinyl acetate copolymers

 E. I. DuPont de Nemours & Co., Inc.

 USI Chemicals Co.

 Union Carbide Corp.

 Exxon Chemicals

Other olefin copolymers and terpolymers

 Ethylene – ethyl acrylate : UCC. Dow Chemical, DuPont

 Ethylene – acrylic acid: Dow Chemical

 Ethylene – methaacrylic acid: DuPont

 Ethylene – vinyl acetate-mehtacrylic acid: DuPont

2.1.5 Ethylene vinyl acetate (EVA)[1], [15]

This thermoplastic polymer is the most versatile and widely used thermoplastic polymer in hot melt adhesive formulations. This is mainly because of the acetyl functional group which provides good adhesive strength to polar substrates. Also the polymer is relatively inexpensive.
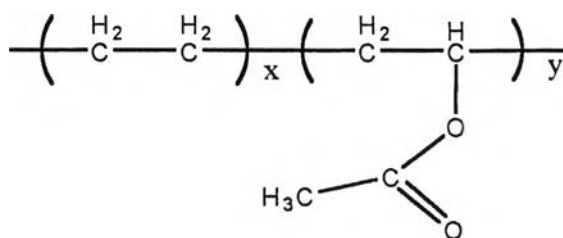

Figure 2.3 Structure of EVA

EVA polymer commercially available vary considerably in percentage of vinyl acetate contents (ranging from below 5 to 50 % incorporation) and average molecular weight. Products that are fabricated EVAS, depending on their VA content, range all the way from thermoplastic to elastomeric materials. The higher the %VA contents, the better will be the adhesion with polar adherents. On the other hand, a low VA content is needed for good adhesion to non-polar substrates such as olefins.

EVAs[16] are mainly recognized for their flexibility and toughness (even at low temperatures), adhesion characteristics, and stress - crack resistance. Compared to LDPE, EVAs are more polar and less crystalline. A lower melt index (higher average molecular weight) for an EVA polymer will generally improve low and high temperature adhesive strengths. These resins are selected for injection and blow molding, and for virtually all extrusion processes, and they are blended and compounded with other materials to produce a variety of adhesives, color concentrates, coating, and textile products.

2.1.5.1 Chemistry and properties of ethylene vinyl acetate copolymers

EVAs are made by the copolymerization of ethylene and vinyl acetate. Most often, this free radical polymerization, initiated by either a peroxide or perester, is done in a conventional stirred autoclave or a high-pressure tubular reactor.

The VA monomer results in basically LDPE like resins with randomly distributed pendant acetoxy groups. VA and ethylene monomers have very similar reactivity ratios; therefore, the pendant acetoxy groups in the resulting copolymer are randomly distributed throughout.

Two main characteristics of EVAs are controlled in the polymerization process: crystallinity and molecular weight.

Unlike with LDPE polymerization, increased density of EVAs does not increasing in a crystallinity. Rather, as VA content increases, they also an increase in density, but a decrease in crystallinity and its related propertied.

Thus, as the VA content increases, clarity improves, and low – temperature flexibility, stress – crack resistance, and impact strength all increase; on the other hand, there is a decrease in softening and sealing temperature, as well as barrier properties. Above 50% VA incorporation, EVAs are totally amorphous.

The acetate side chain brings a polarity to EVAs resins. As polarity increased, there also is an increase in tackiness, adhesion in variety of substrates, and solubility in common solvents, i.e., a shift in chemical resistance.

EVAs are not only differentiated by their VA content, but also by their average molecular weight. Molecular weight is controlled by the addition of chain transfer agents, such as propylene or isobutylene.

As the molecular weight of EVAs increases, so does melt viscosity, heat seal strength, toughness, flexibility, stress – crack resistance, and hot tack strength. EVAs range in melt index from a low of 0.3 gm./10min.to over 1000 gm./10min.

2.1.5.2 Processing

Injection molding, blow molding, and film extrusion of EVAs can be done with standard processing equipment. EVAs with VA levels in the 2 to 10% range are generally used for injection molding (both lower and higher VA grades are also available).

Blow molding grades generally contain less than 5% VA content; and extrusion grades have VA contents of 15 to 30% VA incorporation, EVAs can be extruded into blown and cast film. Because of its excellent adhesion properties, EVAs can be used as an extrusion coating.

The lower melt viscosity and limited thermal stability of EVAs necessitate processing at lower temperature. Above 450 $^{\circ}$F., the acetoxy bonds begin to break and acetic acid is formed.

2.1.5.3 Application

The primary markets for EVAs are packaging, wire, and cable insulation, adhesives, coatings, and compounding, as a carrier resin for colorants.

EVA packaging film, the largest single market (estimated at over 60% of total sales), is used in meat and poultry wrap, cereal/carton liners, stretch film, produce bags, heavy – duty bags, ice bags, and bag – in – box. EVAs with 5 % VA content and less are used in thin films for their moderate toughness and improved clarity.

For tougher film, which require improved impact, low–temperature properties, and stretch performance, copolymers with 6 to 12% VA are used. At 15 to 18%VA incorporation, EVA film is useful as heat – seal layers in coextruded films, and in blends with homopolymers. Also

include in the packaging film category are EVAs for extrusion coating on polyester, cellophane and polypropylene film for cheese wrap, medical film, and other critical application.

Adhesives, carpet bagging, and wax – based coating, the second largest EVA market (about 20%), are made from copolymers, which typically contain 15 to 30% VA. When used for adhesives, EVAS are further modified to provide even greater adhesion.

Wire and cable, and color – compounding constitute the third largest market category (6%). For use in wire and cable insulation, EVAs tend to crosslink more easily and require less crosslinking energy than do homopolymers. For use as color concentrate, EVAs are selected as base resin because they wet out pigment easily. This property also is advantageous for making mineral filled compounds. Molding and extrusion applications, such as injection molded shoes and closures/liners, blow-molded bellows, and extruded hose/tube, are the fourth largest market (5% in 1991) for EVAs.

One of the true advantages of EVA over other thermoplastic polymers is its wide latitude of compatibility for being compounded with tackifying resins, plasticizers, waxes, etc.

2.1.6 Starches [17]

Starch is one of the major components of cereal grains. The major sources of the commercial starches in the whole world are corn and wheat. Other sources of the starch include potatoes, rice and peas. Starch is a mixture of two polysaccharide or repeating 1,4-α-glucopyranosyl unit form: amylose and amylopectin. Amylose and amylopectin are anhydrous D-glucose polymers. Amylose is a straight chain water-dispersible form, molecular weight between one thousand and one million, made up of several hundred glucose units linked by α 1-4 glycosidic linkages. Amylopectin is a branched, less water dispersible polymer of glucose units with α 1-6 glycosidic linkages at the branching points and α 1-4 glycosidic linkage in the linear region commonly used native starch has amylopectin content of about 80-85 %. The molecule weight of amylopectin can run into several millions. Commonly used starches have an amylose content of 25%, although starches containing varying amylose content can also be found for specialty used. Today, starch is used primarily as a food ingredient and in adhesive industry.

The structure of amylose and amylopectin is shown in Figure 3.4(a) and 3.4(b). Starch is not truly thermoplastic as most synthetic polymers. However, it can be melted and made to flow at high temperature under pressure and shear. If the mechanical shear becomes too high then

starch will degrade to form products with low molecular weight. Addition of water or other plasticizer enables starch to flow under milder condition and reduces degradation considerably.

In principle, some of the properties of starch can be significantly improved by blending it with synthetic polymers are immiscible with starch at the molecular level. This thermodynamic incompatibility often leads to poor performance of these blends.
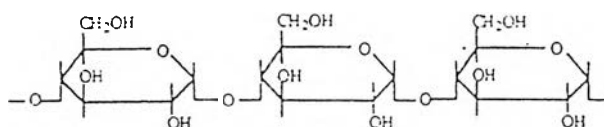

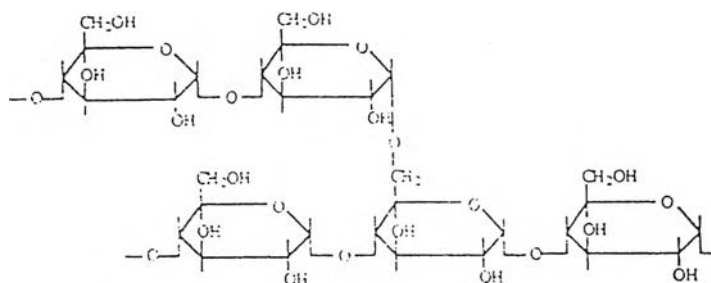
Figure 2.4 (a) Structure of amylose

Figure 2.4 (b) Structure of amylopectin

In order to overcome this drawback, graft copolymerization of vinyl monomer on the starch backbone is used to modify starch.

Corn starch is the most commonly used starch in America; however other countries may be larger consumers of wheat starch, potato starch, rice starch, and tapioca starch in adhesive application. The biggest use for starch adhesives is in paper packaging, wallpaper, etc.

2.1.7 Tackifiers[1]

Tack is the bond strength that is formed immediately when a given material comes in contact with another surface. It has been called "instantaneous adhesive", after which bonding strength may rise to a higher level later in time.

Many elastomers and thermoplastic polymers have very poor inherent tack properties. In order to improve this tack quality, tackifying resins are added to most of these adhesive formulations including evaporation types, pressure sensitive types, and hot melts. Elastomer adhesive formulations almost always require the addition of a tackifying resin to the compound to provide good ultimate adhesion. Many hot melts are greatly dependent on the tackifiers in their formulations in order to work.

The addition of tackifiers can improve performance of polymeric adhesive in several ways. First of all, the proper selection and loading of a given tackifying resin can improve the compatibility of a given polymer to a selected substrate. For example, a non-polar elastomer such as butyl rubber can be made to have a more polar surface through the use of tackifing resins.

Another way that tackifying resins improve adhesion is through improving the wetting power by changing the viscoelastic properties of the polymer so there is more plastic and less elastic behavior. This allows closer contact of polymer to substrate.

Lastly, tackifying resins improve the properties (initial stick) of the adhesive to the substrate, which leads to a strong permanent bond later.

The proper selection of a tackfying resin is critical to the performance of a given adhesive formulation. Above all, the proper selection of a tackifier with the right degree of chemical compatibility with the base polymer is imperative. The variety of different types of resins will be discussed shortly.

Also the selection of the proper molecular weight for the resin (usually determined by softening point) is important. Unlike the tackifing resin used in rubber and plastic compounding, resin used solvent adhesive compound tend to be a lower molecular weight in order to keep the

adhesive solution viscosity low (for better wetting). By using lower molecular weight resin, higher loading of resin can be used in solvent adhesives without adversely raising the viscosity.

With elastomeric solvent based adhesive, they may be critical loading level below which a selected resin does not really improve tack adhesive over those properties already inherent with the base polymer. This critical concentration may be lower for higher molecular weight resins than for lower molecular weight resin of the same type. However, the lower molecular weight resin, while requiring higher concentrations to work, generally impart a higher level of tack improvement than the higher molecular weight resins are capable of displaying. These phenomena are believed to be differences in phase separations.

2.1.7.1 Rosin esters

These substances are abietic acid resin mixtures derived from wood. If the rosins are derived from the naphtha extraction of old pine stumps, these extracts are called "wood rosins". If the rosins are derived from the destructive distillation of turpentine oil, they are called "gum rosins". Finally, if the rosin are obtained from the destructive steam distillation of tall oil (a byproduct paper manufacture), they are called "tall oil rosins".
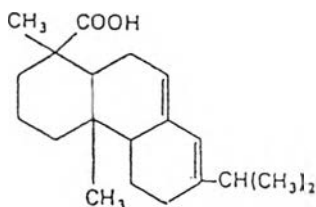

Figure 2.5 Structure of abietic acid

Rosins are one of the earliest materials to be used as tackifier in adhesive applications. In fact, rosins are sometimes referred to as "naval stores" because they use to be used by sailors to make repairs on wooden ships in the eighteen century.

Today, rosins are used as tackifiers in all types of adhesive: however, they have a disadvantage in heat applications such as hot melts where they oxidize easily because their unsaturation. To help solve this problem, they are made available also in hydrogenated forms which display improved thermal stability.

Another class of rosin derivative is the resinate. These rosin products are formed from the reaction of rosin with a metal oxide. Examples of these products are zinc resinate and calcium resinate. These resinates melt at an elevated temperature compared to straight rosins. This enables them to provide better heat resistance in adhesive compounds.

Lastly, ester forms of rosin acids are available which display different solubility properties.

2.1.7.2 Hydrocarbon resins

These resins are generally from the polymerization of olefins from petroleum refining operations. Some hydrocarbons still is obtained from coal tar, but this source is much less common.

Basically, the two main types of hydrocarbon resins are the aromatic resins and aliphatic resins. The aromatic resins are typically the coumarone – indene or polyindene type resin. The aliphatic resins are polymerized mixed olefins, which do not have indene as their central structure.
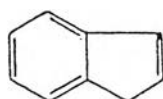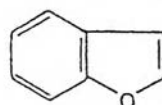
Indene   Coumarone

2.1.7.3 Phenolic resins

These phenol - formaldehyde tackifying resins are different from the thermosetting type phenol-formaldehyde resins already mentioned. These phenol - formaldehyde resin tackifiers are generally non-heat reactive in that these phenolic resins are alkylated at the para position to prevent further crosslinking three-dimensionally.

2.1.7.4 Polyterpenes

These resins are polymerized from beta-pinene obtained from wood. These resins are used extensively in elastomer solvent adhesives, pressure sensitive adhesives, and hot melts. Polyterpene is somewhat resistant to aging effects.
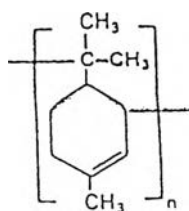

Figure 2.6 Structure of polyterpene

2.1.8 Waxes[18]

Waxes are solid, low melting substances that may be of plant, animal, mineral, or synthetic origin. Waxes are generally slippery, plastic when warn, and, because their molecular weights are rather low, fluid when melted. Waxes[19] are included in hot melt adhesive formulations for several reasons, two of which are to lower cost and to reduce viscosity. Properties affected by the wax content are blocking characteristics, softening point, and open time. The high melting microcrystalline waxes (m. p. 190-195°F) and synthetic waxes (m. p. 210-245 $^\circ$F) are used because they contribute to high temperature properties and greater cohesive strength. The higher melting paraffin waxes

(m. p. 150-160 $^\circ$F), a colorless, translucent wax obtained from petroleum – refining residues, a mixture of mostly saturated, straight – chain hydrocarbons melting between 49 and 63°C, are used extensively in hot melt coating for their barrier, antiblocking and heat seal properties as well as their lower cost.

Waxes are generally included in hot melt adhesive formulations at the 20-30% level, but this concentration may drop in the future. Waxes have become considerably more expensive as refineries choose to lower their production of these products. Also, synthetic waxes produced by

polyethylene producers are being structure to provide similar properties. Furthermore, as the polymer manufactures modify their products to do the complete adhesive job, fewer additives will be required in the adhesive formulation.

2.2 Literature reviews

Jauregui et al.,[2] investigated the dynamic viscoelastic measurements of a series of binary blends of hydroxyethyl ether of starch and ethylene-vinyl acetate copolymer (EVA), which were correlated with the granular arrangement of the starch derivative within the EVA matrix and the adhesion between the two phases, using scanning electron microscopy. The theological properties were similar to those of polymers filled with solid spheres, although they found a minimum in the Newtonian viscosity and a maximum in the elasticity at low starch derivative concentrations, which have been attributed to a change in the density of chain entanglements.

Jeremic et al.,[3] investigated the influence of such low amounts of thermoplastic polymer (TPP) on the processability, mechanical properties and water resistance of thermoplastic starch (TPS). The obtained results showed that TPS blends behaved as pseudoplastic polymers and that even 10 % by weight of EAA or EVA significantly decreased the TPS viscosity, whereas addition of the same amount of CA had no influence on the TPS viscosity. Tensile measurements showed that the relative humidity (RH) had a much larger influence on the tensile properties than the addition of the investigated TPP. Tensile strength and tensile modulus values for TPS and its blends, after conditioning at 45% RH were an order of magnitude larger than the values for the corresponding samples kept at 85% RH, whereas elongation at break values were nearly ten times smaller. Dynamic mechanical analysis of the TPS and its blends was performed using a mechanical spectrometer. The specimens were subjected to dynamic torsion at a constant frequency in the temperature range from 30 to $170^{\circ}C$. The glass transition temperature, determined from the temperature dependence of tan delta, was influenced much more by relative humidity than by the type of TPP used. The swelling of the TPS and the investigate blends was determined gravimetrically. It was found that the TPS/EAA blends had the largest water resistance.

Ramkumar et al.,[4] studied high-shear and transient viscosity of starch and maleated ethylene-vinyl acetate copolymer blends, and resulted that blends with higher starch content blends at the same shear rates. Blends with higher starch content relaxed faster both in stress relaxation tests and in the step-strain experiments. Increasing the temperature increased the relaxation behavior of blends with lower starch content but no appreciable effect on blends with higher starch content was observed. Both blends seem to have time-strain reparability at long duration in the step-strain experiments. Blends with 70% starch did not show significant variation with temperature in the elongation low shear viscosities, and relaxation modulus.

Ramkumar et al.,[5] investigated the stress growth function in shear and viscoelastic properties of blends of corn starch with ethylene-co-vinyl acetate, EVA, and maleic anhydride modified ethylene-co-vinyl acetates (EVAMA), containing 28% and 18% of vinyl acetate with different starch contents. The results showed that the viscosity-composition curve of these blends goes through a maximum. The transition behavior of the blends was studied with dynamic mechanical analysis, the dynamic data indicated that the storage and loss modulus increased with increasing starch content.

Stauffer et al.,[6] prepared the hot melt packaging adhesive compositions consisting essentially of 20 to 50% by weight of an ethylene n-butyl acrylate copolymer containing 25-45 % by weight of n-butyl acrylate and having a melt index of at least 10, 30 to 60 % of an aliphatic or cycloaliphatic hydrocarbon resin or hydrogenated derivative thereof or a hydrogenated aromatic hydrocarbon resin, and 10 to 30 % by weight of a high melting synthetic wax provide adhesives characterized by an excellent balance of high and low temperature performance without sacrifice to mechinability or thermal stability. Furthermore, the adhesive was characterized by a low density and consequently was readily filterable in recycling systems.

Shin et al.,[7] evaluated the influence of wax on the viscoelasticity and adhesion of ethylene vinyl acetate copolymer (EVA)-based hot melt adhesives, resulted that wax was not affected the glass transition temperature of a homogeneous EVA/rosin blend. However, for a heterogeneous EVA/rosin blend, wax addition increasing the EVA-rich phase portion resulting a higher rubbery response. The T-peel fracture energies of EVA/tackifier/wax blends bonded to polypropylene film are controlled by two factors: (1) a weak boundary layer of wax, which had a deleterious effected on bonding, and (2) on the other hand, an increased rubbery response in the stick-slip region, which tends to strengthen joints.

Shin et al.,[8] prepared and investigated the viscoelastic properties and peel adhesion of a series of EVA-based hot melt adhesives containing either a rosin or a hydrocarbon (C5-C9) tackifier. Fracture energies were determined by the use of a T-peel geometry (two polypropylene films bonded with model EVA adhesives). The rosin had only one glass transition temperature, but the C5-C9 resin had two glass transition temperatures, indicated phase separation. The rosin had better compatibility with EVA than the C5-C9 resin. The bond strength of tackified EVA to polypropylene depended not only on compatibility, but also on viscoelastic properties. A higher storage modulus resulted in a higher T-peel strength. Under certain test conditions, glassy C5-C9-rich domains aced as reinforcing filler, resulting in a higher storage modulus. Hence, a C5-C9-tackified EVA adhesive had higher T-peel strength than the one containing rosin.

Boggs et al.,[9] prepared the hot melt adhesives comprising of a blend of at least one modified polyethylene resin, an ethylene vinyl acetate copolymer, a tackifying resin, and an ethylene/propylene rubber. This hot melt adhesive had a novel combination of properties including excellent elevated temperature properties which also provided excellent adhesion to nonporous substrates such a fluorocarbon treated paper which is used as an oil and grease barrier in multiwall bags.

Godfrey et al.,[10] prepared and studied the hot-melt adhesives comprising of a blend of ethylene vinyl acetate copolymer contained 5-25% of vinyl acetate content, a tackifying resin, modified polyethylene and microcrystalline wax . These hot-melt adhesives had a novel combination of properties such as high tensile, low elongation and good bonding properties for adhering polyethylene film to nonwoven substrates such as disposable diapers.

Liedermooy et al.,[11] prepared and studied hot-melt adhesive compositions consisting essentially of 15-45% by weight of at least one ethylene n-butyl acrylate copolymer containing 15-40% by weight of n-butyl acrylate and having a melt index of at least 600; 25-55% of terpene phenolic tackifying resin or a hydrogenated derivative thereof, the resin having a Ring and Ball softening point less than 125°C, 15-40% by weight of a low melting point synthetic Fischer-Tropsch wax; and 0-1.5% of stabilizer. The adhesives were characterized by an excellent balance of high and low temperature performance without sacrifice to machinability or thermal stability.

Aliani et al.,[12] prepared ethylene vinyl acetate copolymers had a melt index of 700-10,000 and containing from 11-40% of vinyl acetate useful in hot melt systems and particularly in formulating low viscosity hot melt adhesives, preferable in binary composition with nature or synthetic tackifiers. The adhesives shown long open times with short setting times, and excellent adhesive properties.

Utpal R. V.and Mrinal B.[13] studied the properties of blends of starch with styrene maleic anhydride copolymers (SMA), ethylene-propylene-g-maleic anhydride copolymer (EPMA), and corresponding nonfunctional polystyrene and ethylene propylene copolymers. The concentration of starch in the blend was varied between 50 and 80% by weight. The torque generated during blending is reported as a function of starch content, mixer speed, and mixing time. Torque increased with increasing starch content for starch /SMA blends; the reverse was true for starch/EPMA blends. The torque was higher for the blends of the anhydride functional polymer compared to the blends of corresponding nonfunctional polymers. Water absorption of the blends increased with an increase in the starch content. Starch/SMA blends made at higher mixer speed or time were more water sensitive. Blends containing EPMA absorbed less water than SMA blends containing the same weight fraction of starch. Tensile strength of blends containing functional group were superior compared to the blends made from nonfunctional polymers. When the starch contents increased from 60 to 70%, the tensile strength remained unchanged for SMA blend but increased for EPMA blend. All samples allowed the growth of microorganisms, which increased with increasing starch content.