"TO VALIDATE THE CURING TIME FOR DIFFERENT

LAMINATE STRUCTURES"

A MAJOR PROJECT REPORT SUBMITTED IN THE PARTIAL

FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF

MASTER OF ENGINEERING IN

POLYMER TECHNOLOGY

IN THE FACULTY OF TECHNOLOGY, UNIVERSITY OF

DELHI, DELHI BY

ANKUR SRIVASTAVA

Under the guidance of Prof. G.L.Verma & Dr. Meenu Sachdeva



Department of Applied Chemistry & Polymer Technology Delhi College of Engineering, Delhi-110042 June2006

CERTIFICATE

This is to certify that the dissertation entitled "**To Revalidate The Curing Time For Different Laminate Structures**" has been submitted by **Ankur Srivastava** as partial fulfillment for the degree of **Master of Engineering** in **Polymer Technology**, Delhi College of Engineering, University of Delhi. This is a record of his own work carried out by him under my supervision & guidance. The matter embodied in this major thesis report hasn't been submitted for the award of any other degree or diploma.

•

Prof. G. L. Verma

Dr. Meenu S. Sachdeva

HEAD, Department of Applied Chemistry & Polymer Technology. Delhi College of Engineering Delhi- 110042 Joint Executive Manager, Flex Industries Limited, (Convering Division),

ACKNOWLEGEMENT

I feel honored in expressing my profound sense of gratitude and indebtedness to

Prof. G. L. Verma, Head Of Department of Applied Chemistry & Polymer Technology, Delhi college of Engineering, Delhi for giving me the opportunity to work on such a practical problem, and Dr. Meenu Sachdeva for her optimism and advice. I am very much thankful to Shri Amitva Ray (President of Converting Division, Flex) for giving me an opportunity to carry out this project work in Flex Industries Limited, Noida, U.P. and staff of Q.A. lab for the materials and methods.

I express my thanks whole heartily to Dr. A. P. Gupta., Dr. R. C. Sharma, Dr. Archana Rani, Mrs. V.K.Smitha, Mr. S.G. Warker.

Finally, I offer special thanks to Dr. Meenu Sachdeva, once again without whom the project would not have existed.

ABSTRACT

Bonding has become an indispensable technique for joining two or more substrates with each other, not only in industry but also in everyday life. Bonding allows the production of laminated materials, facilitates mobility and communications, positively influences the handling of foods, supports health and hygiene and improves the quality of our lives. Depending on the application, an adhesive may have to withstand extremely low temperatures or heat of several hundred degrees, it may have to be highly elastic or extremely stable.

Flexible packaging laminates are being manufactured by printing and laminating the transparent, opaque or metallised films of PET, PP, HDPE, LLDPE, PVC, Paper, Aluminium Foils etc. Various type of adhesives are being used for laminating these films but Polyurethane adhesives are most popular. In flexible packaging, mostly Two Part Polyurethane adhesives are used. Adhesive is mixed with the hardener to ensure the crosslinking and curing and solvent is used as a carrier.

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ABBREVIATIONS

1.	Polyethylene Terephthalate		
2.	Poly Propylene	PP	
3.	Cast Poly Propylene	CPP	
4.	Poly Ethylene	POLY	
5.	Biaxially Oriented Poly Propylene	BOPP	
6	Metallized Film	MET	
7.	Natural or Virgin Polymer	(N)	
8.	Polyurethane	PU	
9.	Tackiness	Tack	
10.	Gram per square metre	GSM	
11.	Phenol Formaldehyde	PF	
12.	Pressure sensitive adhesive	PSA	

OBJECTIVES

A Curing Time is a very important operation in flexible packaging industries. A less or no curing can leads to many problems like low bond strength, and low seal strength, opening of laminate film etc.

The aims of the project are:

- To find out the effect of different solvent based PU adhesive on curing time
- To establish the curing time of different laminate structures
- To find out the effect of thickness of films on the curing time
- To establish the relation between the bond strength and curing time
- To revalidate the curing data with the actual production samples

CHAPTER 1

Packaging is the way goods are wrapped either by the manufacturer or the distributor before being sold or handed over to the final consumer/end user. A good packaging should keep the product clean, should prevent losses, contaminations, chemical and physical damages and must provide identification and instruction.

Packaging can be broadly classified into three categories: Rigid, Semi Rigid and Flexible packaging

1.1 Rigid Plastics:

Rigid Plastics are solid plastic containers of various types including bottles, cans and plastic jars. These products are often products of low value added. Local manufacturers have only emerged in recent years.

Demand for rigid plastics is estimated to be growing at 20% per annum. Many of the local producers are involved in the production of jerry cans and buckets. However, there is increased demand for plastic bottles given the growing number of pharmaceutical and fruit juice processing industries plus the absence of glass bottle manufacture

1.2 Semi rigid Packaging:

They lie in between the rigid and flexible packaging for example toothpaste and cosmetic tubes. Typical applications include part of the packaging process for biscuits, processed foods or fruits. The plastic wrap is also used to package chicken and other meat products. A distinguishing factor of these products is that they are thermo formed rather than injection or blow molded. There exists an opportunity for new investors to take care of the packaging of the growing poultry, food and horticultural industry

1.3 Flexible Packaging:

This covers a wide range of products from simple plastics with a print contact to more elaborate multi-layer plastics with or without print. Presently, both the demand for and supply of this family of products is limited. By its very nature, high value added flexible packaging tends to be associated with the packaging of high value added products. In many applications, flexible packaging has replaced the rigid packages due to their several advantages. These are Light weight

- Excellent barrier and functional properties
- Easy to handle and convenient for retailers and customers
- Provides much more product per a given amount of package
- Tremendous savings in raw material consumption
- Aquire the shape of the product to be packed
- Cost saving in storage and transport due to its length weight and small size

In flexible packaging, various films like PET, BOPP, PAPER, and foils used as a single layered or multilayer with each side printed or non printed. The conversion of a films to a printed or unprinted laminate is called converting process. It goes through following steps-

(a) **Printing Process** : It is the first step, which is used to decorate the product, to give product information, various instructions etc.Printing is done onto almost every film but Polyester films are the most preferred one because of their good ink adhesion characteristics.

(b) Laminating Process : These printed films are then combined with various films to give the products desired properties like mechanical properties, barrier properties, heat sealability etc. This is done with the help of suitable adhesives which is applied to either or both the sides of substrate.

(c) Slitting Process : Flexible packaging materials generally do not have perfectly flat surfaces. In the slitting process, the laminated web is cut to give specific width and defected material is removed from the laminated rolls with the help of sharp blade, before dispatching the material to the pouching.

(d) **Pouching :** The web from the roll is converted to the pouches as per the customer/product requirements. Versatility of various kinds of pouches is enhanced by using different accessories like rope handle, punch handles, spouts ,performed handles, self sticking tape zipper, pilfer proof membrane etc.



Figure 1 : different Examples of Flexible Packaging

In the present work, hand laminates of different polymeric structures like PE/POLY, BOPP/MET BOPP, PET/CPP etc. are prepared with the help of Bar and Coater putting adhesive GSM and type of adhesive to be constant and taking adhesive & hardener ratio to be fixed and put in the oven at 40°C for 4 hours to 48 hours and bond strength is measured at different time intervals and tackiness is observed. When tackiness is vanished, It is cured. The time taken to be curing is noted, it is curing time. Then the results will be compared with the actual production samples. Adhesive used for lab trials was CAC-2511 from Converters Adhesives And Chemicals company because it shows good adhesion properties.

2.1 Polymeric Films:

A plastic material below the 0.25 mm or 0.010 inches in thickness is generally considered a Film, above this thickness is called Sheet. Film thickness is also described in mils, which are equivalent to thousand part of an inch. However the term Micron is widely used term for film thickness.

2.2 Packaging Films :

Films which are used single or with combination of other films are used in packaging the articles, are called Packaging Films. Several polymers have characteristics to behave like a films .Some important polymers are used in flexible packaging are as follows-

2.2.1 Cellulose:

Plain cellulose is glossy, transparent film which is odorless and biodegradable. It is tough, puncture resistant, but tears down easily, non heat seal able and has less gas and moisture barrier properties.

2.2.2 Polyesters:

It is very tough and strong and is normally transparent. Slip additives are added and this makes the film slightly hazy. Water vapour permeability is of the odour as that of LDPE but gas permeability is lower than PVC films. Ink adhesion is very good hence used for printing layer of laminates. It is used for vacuum packaging of cooked meat products, boil in bag packs and for oven roasted meat.

2.2.3 Nylon:

It is tough with high tensile strength, softening point, barrier properties but high moisture permeability. It is used for vacuum packaging of food stuffs and packaging of surgical equipments.

2.2.4 Polypropylene:

It is clear glossy film with a high puncture resistant ,high moisture barrier,but has less tear strength and stiffness. It is available in various forms like bi-axially oriented polypropylene and cast polypropylene(CPP).

2.2.5 Polyethylene:

Polyethlene is classified as follows

a) Low density polyethylene (LDPE):

It is heat sealable inert odour free, shrinks when heated ,good moisture barrier but has high gas permeability, sensitivity to oils and poor odour resistant. It is less expensive than other films and is therefore widely used.

b) Medium density polyethylene(MDPE):

It is used as an alternative to LDPE where greater stiffness and high heat resistance is required.

c) High density polyethylene(HDPE):

It is stronger ,thicker ,less flexible , lower permeability to gas and moisture ,higher softening temperature (121deg C) and therefore can be heat sterilized .It is also waterproof , chemical resistant, high tear strength, high penetration resistance and high seal strength.

d) Linear low density polyethylene(LLDPE):

It is a copolymer fil with high puncture resistance, high ear strength. It provides comparable properties to other olefins even in thinner gauges.

2.2.6 Polystyrene:

Biaxial oriented polystyrene films are used for some packaging which require high water vapour transmission.

2.2.7 Polycarbonate:

It has outstanding combination of high impact strength, high temperature resistance and clarity. Water vapour permeability is higher than that of polyolifins, PVC, useful for boil in bag packs and for skin packaging.

2.2.8 Metallized film:

These films have high water vapour and gas barrier properties. Metallization can be used for improving the water vapour and gas barrier and light barrier properties of BOPP, CPP, BOPET and Nylon etc.

2.2.9 Pearlized BOPP:

It has pleasing pearl like appearance with good heat sealing properties. It has good barrier properties and used for packaging of frozen products e.g. Ice candy etc.

2.2.10 Coextruded films

It is multilayered co extruded film to meet the properties of different polymers in single film. It has high tensile properties, good sealability and barrier properties. It is widely used in oil packaging and lots of other products.

2.2.11 Aluminium foil:

It has high resistance to most of fats, petroleum greases and organic solvents, unaffected by heat and moisture .It has excellent barrier properties against water vapours and gases as well as good esthetic look.

2.3 General Terms(Related To Adhesives)

2.3.1 Adhesion: Adhesion is the process by which two surfaces are held together by interfacial forces (surface attraction) or mechanical interlocking.

2.3.2 Adhesive: An adhesive is a substance which is capable of holding materials together in a useful fashion by means of surface attraction. Surface attraction results from placing a thin layer of adhesive between two objects.

While many substances are capable of holding materials together, not all are useful. Molasses, for example, can be used to hold two pieces of wood together, but the joint can hardly be considered useful. **2.3.3 Bond Line:** The bond line is the space or gap between two substrates which contains the adhesive.

2.3.4 Substrate: A substrate is a material which is held by an adhesive. Substrate is a generic term for the objects that are being bonded.

2.3.5 Surface: The surface of an object is that face of the object that is coated with an adhesive. Surfaces are usually not what they seem. A steel surface, for example, has layers of metal atoms beneath additional substances, which include metal oxides, an oxygen-hydrogen (OH) layer and water. An adhesive is actually applied to this water layer.

2.4 Adhesive Composition

The following terms relate to the composition of an adhesive.

2.4.1 Activators : Activators are chemicals which can be applied directly to a surface or `substrate or mixed with an adhesive to speed up the solidification of the adhesive. Activators are similar to both the curing agents and catalysts

2.4.2 Catalysts : Catalysts, also called accelerators, are chemicals which, when added Accelerators in small amounts, cause adhesives to solidify.

2.4.3 Curing Agents : A curing agent is a chemical which reacts with an adhesive polymer to cause it to solidify. Approximately equal amounts of adhesive resin and curing agent are mixed together to form a solid adhesive. Miscellaneous Some additional components that may be found in an adhesive include

Components pigments, flame retardants, antifoam agents, and tougheners.

2.4.4 Plasticizers: A plasticizer is a chemical added to an adhesive to prevent it from becoming brittle. Many adhesive polymers are very strong, yet brittle enough to crack under impact. Plasticizers are added to soften the adhesive to keep it from becoming too brittle.

2.4.5 Polymers : Polymers are large chemicals composed of repetitive units. Polymers make up the largest portion of an adhesive.

2.4.6 Solvents: Solvents are liquids used to dissolve or suspend adhesives. Solvents are added to an adhesive formulation to make them fluid, allowing the adhesive to be spread or sprayed on a surface more easily. After the adhesive has been applied, the solvent evaporates during cure. Solvents are also used as thinners for some types of adhesives.

2.4.7 Tackifiers A tackifier is a chemical which is added to an adhesive to make it "stickier". The tackifier holds the substrates together while curing is taking place. Not all adhesives contain tackifiers.

2.5 Adhesive Characteristics:

The following terms deal with the application and usable life of adhesives.

2.5.1 Cure : When an adhesive cures, it is converted from a liquid to a solid state.

The curing process may be accomplished by cooling, loss of solvents, or internal chemical reaction. Curing generally implies some type of physical or chemical change in the adhesive, while hardening or melting is reversible. Green Strength The green strength is a measure of the ability of the adhesive to support a load during the green time.

2.5.2 Green Time : Green time is the time between application and solidification of the (Open Time) adhesive. During the green time, it is still possible to position parts.

2.5.3 Fixturing time : (the amount of time before bonded parts can be handled)

is often somewhat longer than green time. Kickover is the sudden increase in viscosity which accompanies the curing of an adhesive. Once an adhesive "kicks over", it is almost in its solid state and can no longer be easily spread.

2.5.4 Pot Life: The pot life of an adhesive is the length of time it remains usable for mixing . Pot life is usually an important factor only with adhesives that are mixed together and begin curing almost immediately.

2.5.5 Rheology: Rheology is the ability of a material to flow and deform. Adhesives with good rheology flow easily and break cleanly at the end of a bead.

2.5.6 Shelf Life: Shelf life is the usable storage time of a material. Most adhesives have a shelf life of 6 to 12 months. The shelf life of an adhesive may be increased by refrigeration, and is usually shortened by exposure to heat.

2.5.7 Viscosity : Viscosity is the resistance to flow or degree of thickening of a fluid. Some adhesives flow very easily, whereas other types of adhesives are so thick they hardly flow at all. Water and thick putties represent the extremes of viscosity.

2.5.8 Wetting : Wetting is intimate contact of a liquid and a surface. Good wetting is only possible if there is good attraction between the surface and the liquid. Proper wetting of a mating surface is essential for good bonding.

2.6 History Of Adhesive:

The first adhesives were gums and other plant resins. Archaeologists have found 6000-year-old ceramic vessels that had broken and been repaired using plant resin. Most early adhesives were animal glues made by rendering animal products such as the Native American use of buffalo hooves. Native Americans in what is now the eastern United States used a mixture of spruce gum and fat as adhesives and as caulk to waterproof seams in their birchbark canoes. During the times of Babylonia, tar-like glue was used for gluing statues. Also, Egypt was one of the most prominent users of adhesives. The Egyptians used animal glues to adhere tombs, furniture, ivory, and papyrus. Also, the Mongols used adhesives to make their short bows. In Europe in the Middle Ages, egg whites were used to decorate parchments with gold leaves. In the 1700s, the first glue factory was founded in Holland, which manufactured hide glue. Later, in the 1750s, the British introduced fish glue. As the modernization continued, new patents were issued by using rubber, bones, starch, fish, and casein. Modern adhesives have improved flexibility, toughness, curing rate, temperature and chemical resistance.

Adhesives are not the only materials that must stick or adhere . Adhesion is essential for printing inks, sealants, paints and other surface coatings, and at interfaces in composite materials such as steel or textile fibers in rubber tyres and glass- or carbon-fibers in plastics. Mother nature uses

adhesion rather than mechanical fasteners (nuts and bolts, nails, staples, etc.) in constructing plants and animals, and some animals are masters at the exploitation of adhesion.

A disadvantage of adhesives as a means of joining is that they are generally weakened by water and its vapour. Also, their service temperature ranges are less than for metal fasteners (nuts, bolts, welds, staples, etc.), being limited by their glass transition temperature and chemical degradation. Advantages include their ability to join dissimilar materials and thin sheet materials, the spreading of load over a wider area, the aesthetic and aerodynamic exteriors of joints, and application by machine or robot.



Figure 2 Classification Of Adhesives on chemical basis

The Classification of adhesives can be done by several ways, some of them from practical point of views are as follows: -

3.1 Clssification Of Adhesive On Application basis

According to the application(in which form adhesive applied to the substrate)adhesive can be classified as follows:

3.1.1 Natural Adhesives:

(a) Starch and dextrin

These materials are derived from cereals or roots such as corn, wheat, tapioca, sogo, etc. The basic constituent is polysaccharide which on hydrolysis yields long chain glucose units. Variations can occur with the use of different food materials and with changes in hydrolysis methods.

The main use for these adhesives is the paper industry where they are used in multiwall bags, corrugated paper etc. Dextrin which is dry roasted starch is used in remoistenable adhesives.

(b) Gelatine (animal, fish, vegetable glues)

There is a wide range of products included in this overall category. Generally they are all proteins which are derived from the hydrolysis of either collagen or soya flour, or by separating casein from skim milk.

• Animal glues from bones and hides are used in gummed tape, textiles and the paper industry such as book-binding and case making.

• Fish glues manufactured from skins have been used in rubber gasket to steel bonding, paper to steel etc.

- Caseirs from skim milk are used mainly in wood to wood bonds.
- Soya bean glues are used in paper backs.
- Blood glues are mainly used in veneering and plywood.

(c) Asphalt and Bitumin

These high fractions of crude oil are more used as sealers rather than adhesives except in the bonding of coarse grade papers to produce waterproof building papers.

(d) Natural rubber

Rubber is derived as a latex from the rubber tree (*Hevea brasiliensis*). The raw latex is collected and concentrated and either sold as a latex or coagulated and sold as solid for solvent dissolution. Adhesives made from natural rubber, which is essentially polyisoprene, are very tacky and are used in pressure sensitive applications or where long bond times and tack are required such as tapes, ceramic tile adhesives, flooring adhesives etc.

(e) Resins, Shellac

Natural resins have been used as adhesives. Shellac is used in bonding mica splittings to form micaboard and used to be used in abrasives. Gum arabic is used in remoistenable adhesives. Copal gums are used in spirit soluble lino cements.

3.1.2 Drying adhesives :

These adhesives are a mixture of ingredients (typically polymers) dissolved in a solvent. Glues and rubber cements are members of the drying adhesive family. As the solvent evaporates, the adhesive hardens. Depending on the chemical composition of the adhesive, they will adhere to different materials to greater or lesser degrees. These adhesives are typically weak and are used for household applications. Some intended for small children are now made non-toxic.



Figure 3 glue gun, an example of a hot adhesive

3.1.3 Hot adhesives (thermoplastic adhesives)

They also known as "hot melt" adhesives, these adhesives are thermoplastics; they are applied hot and simply allowed to harden as they cool. These adhesives have become popular for crafts because of their ease of use and the wide range of common materials to which they can adhere. A glue gun, pictured right, is one method of applying a hot adhesive. The glue gun melts the solid adhesive and then allows the liquid to pass through the "barrel" of the gun onto the material where it solidifies.

3.1.4 Reactive adhesives:

Reactive adhesives are generally thermosetting plastics. Epoxy resins are the most common example of this kind of adhesive. Reactive adhesives generally come in two separate containers. The two ingredients of the adhesive must be mixed in certain proportions immediately before application. Generally one ingredient is a monomer, or resin, and the second is a reaction initialiser. When the two are mixed together, a polymerisation reaction occurs which solidifies the adhesive.

Reaction adhesives may also react with the surface of the materials to be stuck together. This process is called bonding, in which the adhesive forms chemical bonds with the material, and is distinct from sticking, the action of common glues.

A special case of this kind of adhesive is cyanoacrylate (more commonly known by the brand name "super glue") which reacts with trace moisture on the surfaces being bonded and therefore does not need any mixing before application.

Reactive adhesives are very strong and are used for high-stress applications such as attaching wings to aircraft. Because the strength of a reactive adhesive is a result of chemical bonding with the surface material, reactive adhesives are applied in thin films. Reactive adhesives are less effective when there is a secondary goal of filling gaps between the surfaces..

Such adhesives are frequently used to prevent loosening of bolts and screws in rapidly moving assemblies, such as automobile engines. They are largely responsible for the quieter running modern car engines.

3.1.5 Pressure sensitive adhesives

In order to form a permanent bond, structural adhesives harden via processes such as evaporation of solvent or water (white glue), reaction with radiation (dental adhesives), chemical reaction (two part epoxy), or cooling (hot melt), as described above. In contrast, pressure sensitive adhesives (PSAs) form a bond simply by the application of light pressure to marry the adhesive with the adherend. Pressure sensitive adhesives are designed with a balance between flow and resistance to flow. The bond forms because the adhesive is soft enough to flow, or wet, the adherend. The bond has strength because the adhesive is hard enough to resist flow when stress is applied to the bond. Once the adheisve and the adherend are in close proximity, there are also molecular interactions such as val der Waals forces involved in the bond. These contribute significantly to the ultimate bond strength.

Pressure sensitive adhesives (PSAs) are designed for either permanent or removable applications. Examples of permanent applications include safety labels for power equipment, automotive interior trim assemply, and sound/vibration damping films. Some high performance permanent PSAs exhibit high adhesion values and can support kilograms of weight per square centimeter of contact area, even at elevated temperature. Permanent PSAs may be initially removable (for example to recover mislabeled goods) and build adhesion to a permanent bond after several hours or days.

Removable adhesives are designed to form a temporary bond, and ideally can be removed after months or years without leaving residue on the adherend. Removable adhesives are used in applications such as surface protection films, masking tapes, bookmark and note papers, price marking labels, promotional graphics materials, and for skin contact (wound care dressings, EKG electrodes, athletic tape, analgesic and transdermal drug patches, etc.). Some removable adhesives are designed to repeatedly stick and unstick. They have low adhesion and generally can not support much weight.

Pressure sensitive adhesives are manufactured with either a liquid carrier or in 100% solid form. Articles are made from liquid PSAs by coating the adhesive and drying off the solvent or water carrier. They may be further heated to initate a crosslinking reaction and increase molecular weight. 100% solid PSAs may be low viscosity polymers that are coated and then reacted with radiation to increase molecular weight and form the adhesive; or they may be high viscosity materials that are heated to reduce viscosity enough to allow coating, and then cooled to their final form

3.2 Adhesive Classification On Structural Basis:

All Adhesives contain a binder, which provides toughness and cohesive strength. The chemical make up of this binder gives the most important properties of the adhesives like bond strength and tackiness etc.

Structural or Performance Adhesives are load-bearing adhesives. That is, they add strength to the products being bonded. Structural adhesives are used to build products as varied as office

furniture, boats, and automobiles. There are approximately ten adhesive families commonly referred to as structural adhesives:

Acrylic, Anaerobic, Cyanoacrylate, Epoxy, Hot Melt, Methacrylate, Phenolic, Polyurethane, Solvent Cement and Tapes. The seven most commonly used are:

- Acrylic
- Anaerobic
- Cyanoacrylate
- Epoxy
- Hot Melt
- Methacrylate
- Polyurethane

3.2.1 Acrylic Adhesives:

Acrylic Adhesives have formulations that tolerate dirtier and less prepared surfaces generally associated with metals. They challenge epoxies in shear strength, and offer flexible bonds with good peel and impact resistance. Acrylics are two-part adhesives, the resin is applied to one surface and an accelerator or primer to the other. The two parts can be pre-applied and later mated. Once mated, handling strength is typically achieved

in a few minutes. Curing can be completed at room temperature. Newer formulations of acrylics are now available in mix-in formulations. Anaerobic Adhesives are one of the most easily applied structural adhesives. Because the curing mechanism is triggered by deprivation of oxygen (hence the name "anaerobic", or "without air"), anaerobic adhesives will not cure prematurely. These adhesives are based on acrylic polyester resins and are produced in viscosities ranging from thin liquids to viscous thixotropic pastes. Although they have high cohesive strength, they have low adhesive strength and are not suited to permeable materials. Anaerobics do not fill gaps well and may require primers. They are generally used as thread fasteners (i.e. Henkel Omnifit).

3.2.2 Cyanoacrylate Adhesives (Crazy Glue' or Super Glue'):

Cyanoacrylate Adhesives are also easily applied and offer extremely fast cure rates. Cyanoacrylates are relatively low viscosity fluids based on acrylic monomers and, when placed between closely fitting surfaces, some will cure to a strong joint in two to three seconds. Cyanoacrylates' ability to bond plastics and rubbers to themselves or to other substrates are their biggest advantage. On the other hand, cyanoacrylate adhesives exhibit poor impact resistance, are vulnerable to moisture and solvents, and are suitable only for bonding small areas. In addition, they do not fill gaps well, require precise mating of bonded surfaces, and are relatively expensive. They also have poor solvent and water resistance.

3.2.3 Epoxy Adhesives:

Epoxy Adhesive have been available longer than any other engineering adhesive and are the most widely used structural adhesive. Epoxy adhesives are thermosetting resins which solidify by polymerization and, once set, will soften but not melt on heating. Two-part resin/hardener systems will solidify on mixing (sometimes accelerated by heat), while one-part materials require heat to initiate the reaction of a latent catalyst. Epoxies offer very high shear strengths, and can be modified to meet a wide variety of bonding needs. Generally, epoxy bonds are rigid; they fill gaps well with little shrinkage.

3.2.4 Hotmelts:

Hot Melts are various polymers can be used as hotmelts. In a heated state the polymers are liquid, and can hence be processed, but on cooling they solidify. Hotmelts used by industry can be in the form of blocks, rods, granulate, powder and film at room temperature. They are applied to the substrate surface as a melt. The adhesive is applied by rolling or spraying and joining is carried out immediately after application or after reheating the solidified layer. Alternatively the solid adhesive can be laid on the substrate as a film or net and then hot-pressed. In general the joining step requires the application of pressure. A feature of hotmelts is that on cooling they very rapidly build up their internal strength. A natural hotmelt familiar to everyone is beeswax which bees use as a building material Bond strengths between 15 and 35 MPa can be achieved with industrial hotmelts. They do however have a tendency to undergo creep when subjected to continuous stress or high temperatures. On the plus side, these adhesives can be used to create thermally detachable and also redetachable bonded joints due to their thermoplastic structure. The bonded joint must however not be heated up to its melting temperature range because the adhesive loses strength at considerably lower temperatures in the so-called "softening region".

The processing temperature can be varied within a certain range and depends on the desired viscosity of the adhesive for the particular application. The viscosity of the melt determines the application properties of the adhesive. In general a low viscosity facilitates wetting. Hotmelts are used in industry for a wide range of applications. The packaging industry (manufacture of packaging from paper, cardboard and sheet metal) is one of the major users. Hotmelts are also used in the printing industry for bonding the spines of books, in the textile industry for bonding appliqué and in the shoe-making industry for bonding for example shoe soles. The wood processing industry uses hotmelts for veneer surrounds and edging. The car manufacturing industry employs hotmelts for a host of applications including bonding insulating and cushioning materials, bonding headlight covers into metal frames and for wheel covers. The electronics industry also uses hotmelts, for example for bonding coil windings and coil ends

3.2.5 Methacrylate :

Methacrylate Adhesives provide a unique balance of high tensile, shear, and peel strengths with the maximum resistance to shock, stress, and impact across a wide temperature range. Methacrylates can generally be used without surface preparation when joining plastics or metals. They are two-component reactive materials based on methyl methacrylate monomer that, when mixed together, have a controlled cure speed based on the appropriate application process. Methacrylates are tolerant to off-ratio mixing and remain strong and durable under severe environmental conditions. They resist water and solvents to form an impenetrable bond.

3.2.6 Polyurethane Adhesives:

Polyurethane Adhesives are named after the polymer type formed on completion of the reaction. The adhesives are usually two-component, one side is always isocyanate based, the other formulated from one of several co reactants often amines or glycols. They are known for toughness and flexibility even at low temperatures. They have fairly good shear strength and excellent water and humidity resistance.

3.3 Adhesive Classification On Component Basis

a)One Component Adhesive

These are available in one component solution, hot melt or emulsion form and applied directly to the substrate to make bond.

b)Two Component Adhesive

These are available in two separate components in the form of solution or emulsion.Pre mixing of these two components is required before applying to the substrate.They have good performance but their pot life is very less.

3.4 Chemically curing adhesives

The different types of chemically curing adhesives (reactive adhesives) are described below. They are classified into three groups depending on the basic nature of the reactions involved In order to ensure that the adhesive only actually cures in the bonded joint, the manufacturers have had to develop a processing technique which enables the chemical reaction that forms the solid adhesive to be blocked or suppressed for a sufficient period of time to allow the adhesive to get to its final intended place, namely the bonded joint. The exact processing technique depends on the curing mechanism of the various adhesives: Adhesives which after mixing with their reaction partners spontaneously react, i.e. at room temperature, are sold as 2-component (2-C) adhesives. They are present as "resin" and "hardener" in separate containers and are hence physically apart. They are only mixed together to form the adhesive a short time before application. With singlecomponent adhesives (1-C), the adhesive components are premixed in their final proportions. They are however chemically blocked: As long as they are not subjected to the specific conditions which activate the hardener they will not bond. They acquire either high temperature or substances or media (light, humidity) from the surroundings to initiate the curing mechanism. The containers in which this type of adhesive are transported and stored must be carefully chosen to prevent any undesired reactions.

Chemically curing adhesives

Description	Curing mechanism	Base raw materials	Areas of application
Cyanoacrylates	Polymerisation	Cyanoacrylates	Bonding small components, bonding all types of glass, fabric adhesive, spray-on bandage
Methyl methacrylates		Methyl methacrylates	Bonding plastics in the car and rail vehicle manufacturing industries
Anaerobically curing adhesives		Diacrylates of diols	Engines, electric motors, securing screws, shaft-cam connections
Radiation curing adhesives		Epoxy acrylates, polyester acrylates	Bonding glass and transparent plastics, dental technology
Phenol-formaldehyde resins		Phenols, formaldehyde	Wood materials, bonding brake and clutch linings, structural bonding of aluminium in aircraft manufacture
Silicones	Polycondensation	Polyorganosiloxanes	Seals, car manufacturing, electrical engineering; special applications in aeronautics and aerospace technology
Polyimides		Aromatic tetracarboxylic acid anhydrides and aromatic diamines	Bonding metals in aeronautics and aerospace technology
Epoxy resin adhesives		Oligomeric diepoxides and polyamines or polyamidoamines	Structural adhesive in car and aircraft manufacture, vehicle bodywork construction, electronics, bonding fibre-reinforced plastics, repair work
Polyurethanes	Polyaddition	Di-functional and sometimes tri-functional isocyanates, polyols	Vehicle bodywork construction, bonding materials with very different load and temperature expansion properties, bonding panes of glass in car manufacture

Figure 4: Chemically Curing Adhesives

3.4.1 Polymerisation adhesives

(a) Cyanoacrylates (superglues)

In everyday parlance, cyano acrylates are termed "superglues". This term describes very clearly the dominant feature of this class of adhesives. Within a few seconds, hand-tight bonds can be

realized with these adhesives. Their final strength is however only reached after several hours. From a chemical point of view superglues are 1-C reactive adhesives based on cyano acrylates. The special structure of cyano acrylates also explains the high speed at which the curing reaction starts .The cyano and ester groups exert a strong electrophilic effect that promotes attack by nucleophilic substances, e.g. amines, and stabilises the resulting carbanion. Hydroxide ions, resulting from the dissociation of water, or amines, which are present in primers, can attack and initiate an anionic polymerization reaction. The curing of this type of adhesive can be triggered by either a humidity of between 50 and 70%, by moisture present on the substrate surfaces or by contact with basic surfaces. However, if acid is added or acid surfaces are present, the necessary concentration of nucleophilic hydroxide ions is so much reduced that the curing of the superglues is slowed down. Strong acids cause protonation of the carbanion and result in immediate termination of the chain reaction. Although weak acids can also cause termination, their nucleophilic conjugated bases can initiate new polymerisation reactions. In a neutral or basic medium the reaction runs until all monomer molecules have been used up. The behavior of cyanoacrylates to water is however ambivalent: Although they require water to cure, too high humidity can cause detachment of the bond. The reaction mechanism involved here is thought to be base catalysed hydrolysis of the cyanoacrylate polymer. Formaldehyde can indeed be detected as the reaction product of the hydrolysis. Also giving credence to the postulated mechanism is the increase of the reaction rate by two orders of magnitude when the pH is increased from 7 to 8, from which it can be concluded that the reaction is initiated by hydroxide ions. Besides their relatively high strength, other typical properties of superglues are their brittleness, low flexibility and being thermoplastics they only possess limited resistance to heat. In addition, non-cured superglues are usually very thin liquids, meaning that only gap widths of

ca. 0.1 mm can be bridged using this class of adhesives. For wider gaps there is an additional problem, related to the curing mechanism of cyanoacrylates. When higher adhesive film thicknesses are used, the required moisture does not penetrate far enough into the bonded joint, so causing the polymerization to terminate. The result is an adhesive that cannot fully cure. The areas of application of superglues are very diverse. Superglues are suitable for bonding many combinations of materials and are in general used for bonding small components. Superglues are popular for bonding all types of glass. On highly alkaline glass there is however the risk of shock curing. Stress in the adhesive film can reduce the strength of the bond. The same effect can be

caused by high humidity (> 80%). In addition to many applications in optics, microelectronics and vehicle technology, there will in the future be a growing and extremely diverse spectrum of applications for special superglues in the area of medical technology, e.g. as a textile adhesive and for spray-on bandages.

(b) Methyl methacrylates (MMA) :

Methyl methacrylates are reactive adhesives based on methyl methacrylate (methacrylic methyl ester). A hardener, di benzoyl peroxide (typically added as a radical-former and N, N- dimethylp- toluidine (typically added as an accelerator) are also present. The curing of the reactive system comprising MMA monomers, radical-former (3 to 5%) and accelerator occurs via a radical chain polymerization mechanism. If the fraction of hardener is greater than 5%, the strength of the adhesive slightly decreases. If the fraction of hardener is lower than 3%, the curing time increases considerably but this is accompanied by only a slight increase in the bond strength. With MMA adhesives, lap shear strengths (before aging) up to greater than 30 MPa can be achieved and in many cases strengths of over 5 MPa are attained after just 5 minutes. At room temperature the final strength is reached after ca. 12 to 24 hours. Increasing the curing temperature accelerates the process but the final strength is adversely affected. MMA adhesives cure as thermoplastics. They can withstand temperatures between -50°C and ca. 100°C, and even up to 180°C for short periods. They possess good bonding properties to many different plastic surfaces and are relatively insensitive to surfaces that contain a certain amount of oil/grease. Depending on the viscosity of the adhesive, this type of adhesive can be used to bridge larger gap widths. The elasticity and flexibility of the cured adhesive can be adjusted within certain limits. An interesting feature is the differing processing conditions used for MMA adhesives. Besides the techniques normally used for 2-C adhesives (adhesive application using

twin cartridges, processing by direct addition of the hardener), with MMA adhesives the different components can each be applied separately to one of the substrates. The actual curing reaction then only takes place in the bonded joint after bringing the substrates together. This so avoids having to mix difficult mixing ratios (for example, resin: hardener 100:3) and prevents a very short pot life having to be closely complied with in an industrial production which would clearly give rise to problems. MMA adhesives are used for bonding plastics to each other and for

bonding metals to plastics. Classic applications for this type of adhesive are in the car manufacturing industry and in the rail vehicle manufacturing industry.

3.4.2 Adhesives that cure via polycondensation :

(a) Phenol-formaldehyde resins

Phenol-formaldehyde adhesives (usually called phenolic resins for short) cure at temperatures between 100 and 140°C depending on the composition of the adhesive. The mechanism of these reactive adhesives involves a reaction between formaldehyde and phenol under alkaline conditions to form an addition product: a so-called resol .This reaction has already reached completion in the ready-to-use adhesive. This resol is cured in the bonded joint, liberating water to form a thermoset (condensation reaction) .As the curing process requires temperatures above 100°C, the liberated water is present in gaseous form. In order to avoid foaming, phenolic resins are cured under contact pressures of up to 0.8 MPa. Pure phenolic resins are very brittle and sensitive to contain additives to increase the elasticity, e.g. synthetic rubber. Modified phenolic resin adhesives generally give high bond stability and bonds with good mechanical properties. Phenolic resins have very good adhesion and long-term stability on oxidatively

etched aluminium surfaces. They also have good temperature stability up to ca. 250°C. In

addition to using phenol as the starting monomer for the condensation reaction with formaldehyde, phenol derivatives, e.g. resorcinol (m-dihydroxybenzene) are also employed in adhesives. Resorcinol-formaldehyde resins have a higher degree of crosslinking than other phenolic resin adhesives and due to this have greater resistance to water and weathering effects. They are mostly used for wood structures that have to be resistant to water and weathering (boat adhesives). In general phenolic resins are preferred when the adhesive film is exposed to high temperatures. A classic application is the bonding of brake and clutch linings. Other typical application areas for this type of adhesive are in aircraft manufacture ,for the structural bonding of aluminium and in the furniture-making industry. From a quantitative point of view, the biggest use of phenolic resins is for bonding wood in the furniture making industry.



Figure 5: Curing of PF resin

(b) Polyurethanes:

Just as for the epoxy resin adhesives, users can choose between different reactive polyurethane systems. Polyurethane adhesives (PUR) are available as cold curing 2-C systems, hot curing 1-C systems and moisture curing 1-C systems (where a poly condensation reaction takes place as the first part of the curing process and the addition reaction takes place in a second step), and reactive 1-C PUR hot melts (for which there is second crosslinking stage induced by moisture, heat or a combination of both). These systems can cure to form elastomers or thermosets. The degree of crosslinking and hence the bond strength are determined by the various raw materials in the adhesives.

In the **2-C systems,** the curing process is initiated by bringing together and mixing the resin (polyglycols or PUR prepolymer with terminal OH groups) and hardener (modified isocyanate). At room temperature the curing can take from a few hours up to several days. This process can however be accelerated by heating and this also increases the strength of the bond. After curing, the adhesive film of 2-C systems ranges from tough and hard to rubber-like and flexible depending on the raw materials used.

Hot curing 1-C systems consist of PUR prepolymers with terminal hydroxyl groups and chemically blocked isocyanate hardeners. The isocyanate groups are capped with phenol and form phenyl carbamine acid ester groups. The temperature required for cleavage can be decreased by employing suitable catalysts. For example, for a dimeric TDI prepolymer (Desmodur TT) there is cleavage at 120°C but this is reduced to room temperature when a phosphine catalyst is used. Hot curing 1-C systems require a temperature of 100 to 200°C to cure, with the duration varying from a few minutes to several hours depending on the actual temperature employed. Bonds formed using PUR adhesives are generally tough and hard and of high strength, but still elastic. The heat employed for curing 1-C PUR adhesives liberates isocyanate compounds from the system, some of which can be a health hazard. Hence suitable ventilation is required.

The moisture curing 1-C systems are viscous adhesives that consist of non-volatile PUR prepolymers having isocyanate end-groups. These systems require moisture to trigger the curing reaction. A portion of the isocyanate groups on the prepolymer are converted to amino groups. A small quantity of carbon dioxide is released but this has no effect on the bonding process. The amine groups then react with the remaining isocyanate groups and so cure the adhesive system. This reaction can take place in a temperature range from 5 to 40°C, with a relative humidity of 40 to 70% being required. There are also so-called booster systems commercially available that function using a moisture containing gel. These accelerate the curing and the curing is now independent of the level of the air humidity. With 1-C systems, the moisture dependent curing of the adhesive film (that is based on the formation of urea linkages) takes place from outside to inside at a rate of a few millimetres per day. When processing adhesives, the so-called "skinning" time" must be heeded, namely the time after which the adhesive solidifies on its surface (forms a "skin") and wetting of the second substrate is no longer possible. Once this has occurred, adhesive interactions can no longer occur. In its cured state the adhesive is elastic and flexible and this is why moisture curing 1-C PUR systems are used where materials with widely differing elongation under loads and differing temperature expansion behavior have to be joined. An example is the bonding of glass-fibre reinforced plastics (GFP) to steel, and aluminum wall and floor plates to steel supports. Figure 44 shows a high-speed ferry in which the polycarbonate windowpanes were bonded to the aluminum ship structure using these adhesives.



Figure 6: Isocyanates as hardener

3.5 Other Curing Technique:

3.5.1 Radiation Curing:

Radiation cured coatings have replaced many conventional low solids, solvent borne coatings, and radiation curing, or "radcure" technology has become an established and important commercial process.

Radiation curing uses electron beam (EB), ultraviolet (UV) light, or visible light to polymerize a reactive and usually solvent-free coating material.
Although the final properties of radiation cured coatings are often superior to other systems, the reason for their popular growth has been primarily due to improvements in productivity and environmental emission considerations. However, radiation cured coatings are having a difficult time emerging from their early status as a niche product. This is mainly due to the high materials cost and capital investment required for radiation cured product lines. However, radiation cured coatings are often justified on a "total" cost basis when considering energy bills, reduced waste, labor cost, production time, factory space availability and transportation costs.

The primary applications for radiation cured polymers include inks, adhesives, and coatings where coatings are by far the largest segment. Some of the more important coating applications are found in every day products such as hardwood flooring, metal and wood furniture, electrical wire and cable, release papers, beverage cans, magazine covers, packaging, leather finishes and computer magnetic media

3.5.2 Benefits/ Limits Of Radiation Curing:

UV/EB radecure technology is a proven technology used worldwide for a broad range of applications. Its success is due to three main benefits:

1. The UV/EB technology allows to improve productivity: the curing mechanism, when exposed to UV or EB radiation, is a lot faster than drying times involved with conventional solvent or water-based coatings. So the product is immediately ready for testing and shipment. Moreover the rapid cure speed allows one continuous process instead a multi-step process including intermediate drying.

2. It is also an environmentally-friendly technology without any VOC emissions and no flammability. And the energy consumption of the process is lower.

3. UV/EB coatings can be used for heat-sensitive substrates (wood, plastics...).

Even with the above mentioned advantages, radiation curing technology presents also limits:

1.Certain formulations are chemically limited by oxygen inhibition or by end use instability when exposed to sunlight.

- 2. Some raw materials are skin irritants until they are fully cured
- 3. Complex geometries, thick or opaque coatings face problems to be cured.

3.5.3 APPLICATIONS:

- Full-bond strength achieved immediately upon cure.
- One component systems.
- Adhesive remains unchanged until cured.
- No viscosity adjustments.
- Shelf-life at least six months.
- 100% reactive systems offer near zero VOCs.
- Potential for application at room temperature.
- Easy clean up.
- Potential for very low misting.
- Compatible with multiple ink systems including water-base, solvent-base, and UV/EB-curable inks.
- No isocyanates.
- No aromatic amines.

3.5.4 Crosslinking Mechanism:

Radiation is used to crosslink (Figure 1) or cure unsaturated organic resins into durable coatings having excellent physical properties with high chemical and temperature resistance. Radiation curing technology involves at least four considerations:

- Type of radiation source
- Organic polymer to be irradiated,
- Mechanisms of physical and chemical interaction,

• Final properties associated with the cured product.

Radiation curing coatings react through unsaturated sites on oligomers and monomers. These active sites (double bonds) are capable of reacting to form larger and crosslinked polymers. Then, three dimensional network structures are obtained.





When the UV or EB radiation dose increases, the molecular weight increases as well, resulting for the coating properties in:

- A decrease of tack,
- An increase in cohesive strength,
- An increase in temperature and chemical resistance.

The exact curing window for a product must be determined for every formulation and for each thickness. For many radiation curing coatings, the processing window is narrow, making it easy to under-cure or over-cure the coating.

The main sources of energy for curing coatings by radiation are electron beam (EB) and ultraviolet light (UV). Both provide instantaneous curing of coatings that polymerize from a liquid to a solid when irradiated.

3.5.5 Electron Beam Curing:

Electron beam curing mechanisms are similar to the UV-free radical mechanism. However, the electrons are accelerated to a much higher energy state, and the electron itself has sufficient energy to initiate polymerization. The impact of these electrons is high enough to break chemical bonds and to generate ions. The ions then transform themselves into free radicals, which then initiate polymerization. Thus, the EB mechanism requires no photo initiator. There is also greater penetration of the radiation (greater depth of cure) with less interference from pigmentation.

3.6 Adhesives for packaging materials:

An extremely high proportion of all industrial products are sold in packaging – either due to stability requirements for storage and transport or for aesthetic reasons. Although normal envelopes and paper bags consist of just a single layer of material, most packaging materials used nowadays are in fact different materials laminated together .By laminating cardboard with paper, in particular high gloss paper, it is possible to put product information on the cardboard and give the product a commercially alluring appearance. Adhesives based on starch, dextrin and glutin, and also polyvinyl acetate dispersions, are used for this purpose. Important requirements on overprinted packaging materials, in particular the various types of packaging materials used for foods, are their strength, stability to heat and impermeability to moisture, oxygen and aromas. These properties along with desired appearance can usually only be obtained by combining different materials. Laminated films can be manufactured from polyester (PETP, PBTP), polyamides, polyethylene, polypropylene, cellophane, paper, polyvinyl chloride, polyvinylidene fluoride, polyimides, aluminium and a few other materials. Metallic foils are also often used. Solvent-containing adhesives based on polyurethane are used for laminating films; the most

recent developments in this area however involve solventfree systems, so-called high-solid products and adhesives based on aqueous polyurethane dispersions. For application using automatic packaging machinery, high requirements are put on the constancy of the adhesive properties, especially with regards to its viscosity stability. Dispersion adhesives and hotmelts are used to seal packaging (e.g. folding cartons, packets).

CHAPTER4

THEORIES OF ADHESION

Several theories of adhesion exist which are based on surface-chemical phenomena. It is generally considered that there is no generalized, unified theory of adhesion since the phenomenon is known to exist between a great diversity of material types. In some special cases, either pure adsorption, or electrical or diffusion attractive forces are found at an adhesive-bound interface. More frequently, one finds adhesion to be a synergistic combination of all of these driving, attractive forces. This is especially true in the case of practically all adhesive bonding situations.

Four mechanisms or theories of Adhesion

- 1. Mechanical Interlocking
- 2. Diffusion Theory
- 3. Adsorption and Surface Reaction
- 4. Electrostatic

4.1. Mechanical Interlocking

1) Applicable in situations where the adherends are impermeable to the adhesive.

- 2) Surface of adherend is usually rough.
- 3) Interphase may exhibit a "lock and key" effect .
- 4) Rubber tire repair kit is a good example.
- 5) Rough surface increases area of physical contact.

Demonstration of surface roughness on adhesion for a copper surface bonded with epoxy adhesive Pore penetration by adhesives is dependent on the radius of the Pore.

Pakham's calculation of distance microporous surface	penetrated by molten Polystyrene into a
Pore Radius (micrometers)	Distance penetrated into "x" (micrometers)
1000	220
10	22
1	7
0.1	2.2
0.01	0.7

4.2. Diffusion Theory :

1) Based on the solubility of one material into another.

2) Interphase instead of an interface (Figure 6.3).

3) No stress concentration in the interphase because no

discontinuity exists in the physical properties.

4) Use cohesive energy density to interpret diffusion bonding.

Cohesive Energy Density (C.E.D.)

$$C.E.D. = \frac{E_{coh}}{V}$$

Ecoh is the amount of energy necessary to separate molecules to an infinite distance. V is the molar volume

Solubility Parameter

$$\boldsymbol{\delta} = \sqrt{\frac{E_{coh}}{V}}$$

For good adhesion solubility criteria of adhesive and adherand should have similar solubility parameter.

Solvent Welding

1) methylene chloride - PMMA

2) PVC + plasticizer in THF and toluene - PVC

Block Copolymers at Interfaces

PMMA and PS are not soluble in one another

Block copolymers with varying length of the two blocks were annealed and the level of adhesion increased with the increase of molecular weight of the blocks at any thickness of the block copolymer Adhesion was controlled by the entanglement molecular mweight (Me) of the block on each side of the interface. When Me is exceeded for both sides of the interface and bonding is improved the *aerial chain density* (S) has been achieved. Physics of the separation process are governed by a phenomenon called *chain pull-out*.

4.3 Adsorption theory

In adsorption theory the attractive forces between materials is interpreted in terms of the chemisorbed and physisorbed atomic and molecular species that exist at an interface. Essentially this theory regards adhesion as one particular property of a phase interface wherein polar molecules or groupings will be orientated in an ordered way. The forces are initially involved in this mechanism are the Van der Waals' forces - the orientation, induction and dispersion effects. If a molecule, which is large enough to contain a polar group and a non-polar part as separate and distinct entities, approaches an interface at which the dielectic constant changes it will orientate itself. It will move so that its non-polar part will be in the medium of lower dielectic constant and its polar part in the medium of high dielectic constant. This is the process that takes place in adsorption and must really take place if an adsorption theory is valid.

4.4 Chemical Bonding Theory:

The Chemical bonding theory of adhesion invokes the formation of covalent, ionic or hydrogen bonds across the interface. There is some evidence that covalent bonds are formed with silane coupling agents, and it is possible that adhesives containing isocyanate groups react with active hydrogen atoms, such as hydroxyl groups, if wood or

paper are the substrates. In these two examples, Si—O bonds (strength 369 kJ mol__) and C—O bonds (351 kJ mol__) would be formed. Another possibility is the reaction of an epoxideadhesive with a surface containing amine groups (see Chapter 4) to give C—N bonds (291 kJ mol__). The potential energy of two ions of charge

$$E_{\rm pp} = \frac{-2\mu_1^2 \mu_2^2}{3kT(4\pi\epsilon_0)^2 r^6}$$

Where μ_1 , μ_2 are the dipole moments, \mathcal{E}_0 is the permittivity of the vacuum and k is the Boltzmann constant and T is the absolute temperature

4.5 Electrostatic Theory:

Electrostatic forces occur between atoms or molecules which bear a charge.

- + + Repulsive
- - Repulsive

+ - Attractive

Electrostatic adhesion is used extensively in the coatings industry.

Polymer particles are negatively charged and the piece to be coated is positively charged or grounded. This is based on the phenomenon of a electrical double layer formed at the junction of two materials. At any boundary an electrical double layer is produced and the consequent coulombic attraction might account for the adhesion and resistance to separation.

4.6 Criteria for obtaining a good adhesive bond:

For a material to perform as an adhesive it must have four main requirements:

• It must "wet" the surfaces - that is it must flow out over the surfaces that are being bonded, displacing all air and other contaminates that are present.

• It must adhere to the surfaces - That is after flowing over the whole surface area it must start to adhere and stay in position and become "tacky".

• It must develop strength - The material must now change its structure to become strong or nontacky but still adherent.

• It must remain stable - The material must remain unaffected by age, environmental conditions and other factors as long as the bond is required.

The basic definition of an adhesive as used by the Adhesive Sealant Council in America is

A material used for bonding that exhibits flow at the time of application

CHAPTER 5

POLYURETHANE ADHESIVES

A polyurethane is any_polymer consisting of a chain of organic units joined by urethane links. It is widely used in flexible and rigid foams, durable elastomers and high performance adhesives and sealants, fibers, seals, gaskets, condoms, carpet underlayment, and hard plastic parts. Polyurethane products are often called "urethanes". They should not be confused with the specific substance urethane, also known as_ethyl carbamate. Polyurethanes are not produced from_ethyl carbamate, nor do they contain that substance

5.1 Polyureyhane Adhesives Components

Adhesives based on polyurethane elastomers and diisocynates are now well established in industrial use and also in the customer product markets either as single component solvent based materials such as thermoplastic hot melts, or as two component non solvent based reactive adhesives. These are made by the reaction of Polyols and Isocyanates.

The most important polyurethane adhesive components are toluene diisocyanates (TDI), 4-4'diphenylmethane diisocyanate(MDI), p-anisidene diisocyanate(DADI), hexamethylene diisocyanate(HDI), and tri phenyl methane triisocyanate (Desmodur R) together with various polyesters and polyether glycols. The following polyols are well established in the urethane adhesive fields:

(i) polyesters, often preferred due to their combination of cohesive and adhesive properties

(ii)polyethers, selected when hydrolytic stability and resistance to bacterial attack are predominant requirements

(iii)poly(caprolactone) glycol which offers a compromise in properties between the polyesters and polyethers

(iv)poly(butadiene)-based glycols

Urethane adhesives make good adhesives for a number of reasons:

- > They effectively wet the surface of most substrates.
- > They can interact with the substrate through polar interactions (e.g. hydrogen

bonding).

> Their relatively low molecular weight/ small molecular size allows them to permeate porous substrates (for reactive adhesives).

> They can form covalent bonds with substrates that have active hydrogen atoms (for reactive adhesives).

> Through molecular composition the adhesive stiffness, elasticity and crosslinking can be tailored to suit specific needs.

The most commonly used isocyanates in polyurethane adhesives are MDI (methylene diphenyl diisocyanate) and TDI (toluene diisocyanate), both aromatic isocyanates. Aliphatic isocyanates are also used but in smaller volumes. Polyols of widely different types are used for the production of adhesives. The most commonly used polyols are polyether (polypropylene glycol) and polyester (adipate based) polyols.

Polyurethane adhesives can be classified in the following product segments:

5.2 Non-reactive Polyurethane adhesives:

5.2.1 Solvent borne adhesives:

Polyurethane solvent adhesives consist of a high molecular weight hydroxyl terminated polyurethane (MW approximately 100,000) dissolved in a solvent. The polyurethanes are obtained by reacting a high molecular weight polyester diol with a diisocyanate and differ in solution viscosity and crystallization tendency. The polymer solutions are applied to both surfaces to be bonded. Some time is allowed for the solvents to evaporate and the surfaces are then pressed together, at which point inter diffusion of the polymer chains will occur.

5.2.2 Hot melt adhesives:

. These adhesives also consist of high molecular weight hydroxyl-terminated polyurethane. Chemically and structurally the polymers used in solvent borne and hot melt adhesives are related. Hot melt adhesives are most commonly applied as adhesive film in lamination type of applications. These adhesives form the adhesive bond by cooling from the molten state.

5.2.3 Water based adhesives:

These adhesives are high molecular weight polyurethanes dispersed in water (PU dispersions, or PUD's). The water carrier is eliminated during use, leaving the precipitated and coalesced polymer to form the adhesive bond.

5.3 Reactive Polyurethane adhesives:

5.3.1 One component adhesives:

This is a liquid isocyanate-terminated polyurethane with a relatively high molecular weight (prepolymer) and rather low remaining isocyanate content. The prepolymers are prepared by reacting an excess of isocyanate with high molecular weight polyester or polyether polyols. The free isocyanate groups react with moisture from the environment to form urea linkages. If the functionality of the prepolymer is larger than two (i.e. contains more than two isocyanate groups per molecule) the cured film will be chemically crosslinked.

5.3.2 Two component adhesives:

Such adhesives consist of two relatively low molecular weight components: the polyol and isocyanate. When the two components are mixed they form urethane groups in the adhesive films. The polyols are usually of the ether or ester type. The isocyanates and polyols employed may have a functionality of two or higher. In the latter case a

crosslinked polymer film is formed.

5.3.3 Reactive Hot Melt:

Reactive hot melt adhesives are highly viscous or solid prepolymers with a low melting point. The prepolymers are produced from solid (i.e. crystalline) polyester polyols and isocyanate and have a low number of free isocyanate groups. The adhesive is applied above its melting point and bond through the physical process of cooling (like a conventional hot melt adhesive) as well as through reaction with ambient moisture (as a one component adhesive).

5.3.4 Woodbinders:

Aromatic isocyanates (predominantly MDI) are used as binders to manufacture oriented strand board (OSB), medium density fibreboard (MDF) and particleboard. For these boards, the isocyanate is blended with wood strands, fibres and chips, respectively. The cure takes place in a press at about 200°C. The curing reaction is predominately via the reaction with water and thus the formation of urea groups. Additionally, a wide range of reactions with wood components will also occur depending on the temperature, moisture content and the specific location within the wood matrix.

5.3.5 Crosslinkers:

Although crosslinkers are not seen as 'adhesives' perse, they do improve the adhesive properties of solvent and water born adhesives. Solvent borne crosslinkers are added to solvent born polyurethane or chloroprene adhesives. Water borne 'emulsifiable' isocyanates are added to latex and PUD adhesives. In the bond crosslinking reactions occur and the resulting crosslinked adhesive has improved mechanical properties as compared to the non-crosslinked adhesives.

5.4 Reasons For Adhesive Properties Of Polyurethane

The adhesion properties of the isocyanate-based adhesive involves a combination of several chemical properties which will be examined in details. The characteristics are summarized as follows-

1. Isocyanates react readily with a variety of other functional groups.

2. Di- and polyisocyanates can undergo self polymerization to form three dimensional resins in situ.

3. Isocyanates are quite soluble in many organic substances, and due to their small molecular size readily permeates insoluble porous structure.

4. The reason of di- and polyisocyanates with hydroxyl bearing polyesters and polyethers, co – reactants in many isocyanate adhesive applications, produces the strong, polar ,hydrogenbonded, flexible polyurethanes which when wet, intimately contact and show strong attraction for a variety of surfaces.

5. Isocyanates provide elastomer – metal bonds with flexible to rigid gradation in physical properties between elastomer and metal which affords superior fatigue life.

6. Isocyanates react with hydrated oxide layers on metal surfaces, thus producing an in situ clean surface, and therein most probably allowing the urea groups of the adhesive to form chemical bonds with the residual valencies of the metal lattice.

5.5 Polyurethane Reactions:



There are four basic reactions that can occur in a two component polyurethane. These reactions will occur only after the two components are mixed

1. Reaction of isocyanate with an hydroxyl group to form an polyurethane. This is the primary cure reaction, building most of the molecular weight and crosslink density.





2. Reaction of isocyanate with an amine to form a urea. This reaction occurs mostly as a side reaction, unless amine groups are added for a specific function.

R-NCO + R'-NH R-NH-C(O)-NH-R'



3. Reaction of three isocyanates to form an isocyanurate. This reaction increases the chemical resistance of the cured material.

3 R-NCO + catalysts======= Isocyanaurate

4. Reaction of isocyanate with a urethane to form an allophanate. This reaction produces a fast set speed, increases the thixotropy and increases adhesion to some substrates.

R-NH-C(O)-OR' + R''-NCO R''-NH-C(O)-N(R)-C(O)-OR'

5. Reaction of isocyanate with a urea to form a biuret. This is primarily a side reaction.

R-NH-C(O)-NH-R' + R"-NCO R"-NH-C(O)-N(R)-C(O)-NHR'

Or **R''-NH-C(O)-N(R')-C(O)-NH**

5.5.1 Polyols:

Polyols refer to chemical compounds containing multiple hydroxyl groups. In two technological disciplines polyols have special meaning: food science and polymer chemistry. For information as it pertains to food ingredients, please see the article on sugar alcohols

5.5.2 Isocyanates:

Isocyanate is the functional group of atoms -N=C=O (1 nitrogen, 1 carbon, 1 oxygen), not to be confused with the cyanate functional group which is NCO. Isocyanate is also an organic compound containing the isocyanate group. An isocyanate may have more than one isocyanate group. An isocyanate that has two isocyanate groups is known as a diisocyanate. Di isocyanates are manufactured for reaction with polyols in the production of polyurethanes.

5.6 Recent Developments:

5.6.1 Hybrid Adhesives:

Many recent efforts have focused on developments that create true hybrids. For example, blocked isocyanate prepolymers have been mixed with epoxy resins and cured with amines. These blocked prepolymers will react initially with the amines to form amine-terminated prepolymers that cross-link the epoxy resin. Urethane acrylic hybrids have been reported based on several approaches. Pressure –sensitive acrylic prepolymers with hydroxyl groups have been formulated with isocyanate prepolymers to give adhesives with improved peel strength and high – temperature – performance.

5.6.2 Reactive Hot Melts:

The use of Polyurethane prepolymer with low levels of free isocyanates as a hot melts offers distinct advantages: initial green strength is still achieved, and in addition the isocyanate will moisture cure slowly, converting the thermoplastic adhesive to a thermoset. The tensile strength of the adhesive increases, heat resistance is improved, and the final cured adhesive will not flow at elevated temperatures.

5.6.3 Pressure – Sensitive Adhesives:

Polyurethanes have been somewhat limited to being used as additives to pressure sensitive adhesive to improve their cohesive strength

6.1 Package Yield Of Film (ASTM-D-4321-99)

To determine package yield of a film, it was cut from the film with the help of sharp utility knife and template in a way that the weight of specimen must be more than 1 gram. The sample was weighed accurately and converted into gram per unit area as follows-

Package Yield or GSM= weight/ area (gram/ m2)

Or GSM=p.T

where ρ is the density of a sample material and T is the thickness of the sample.

6.2 Wetting Tension (ASTM-2578-84)

To find out the wetting tension of films drops of a series of mixtures of formamide and ethyl - cellosolve of gradually increasing surface tension are applied to the surface of the film surface. The wetting tension of the film will be approximately equal to the surface tension of that

	• .
particul	ar mixture.

Formamide%(CH3NO)	Ethyl Cellosolve%(C4H10O2)	Wetting Tension(Dyne/cm)
0	100	30
10.5	89.5	32
26.5	75.5	34
42.5	57.5	36
54	46	38
71.5	28.5	42
78	22	44
87	13	48
90.7	9.3	50
99	1	56

(i) Rhodamine-B Dye can be used to colour the solution for easy observations.

(ii) 100% water is used for 72 dyne/cm wetting tension.

6.3 BOND STRENGTH MEASUREMENT:

6.3.1 Sample Preparation :

(a) Mixing Of Adhesive:

Adhesive and Hardeners are mixed according to their optimum ratio and were taken in a 100 ml beaker and required quantity of inert solvent (Ethyl Acetate) was added into the mixture. The mixture is stirred for almost 2 minutes for uniform mixing.

(b) Adhesive Application:

A hand Bar coater (No 3) was used for coating the film on treated side.Adhesive is applied on treated side and second layer is put on it and pressed with the help of rubber hand roller. The laminates were then placed into the hot air oven for curing at definite temperature (40 deg C) .The sample laminates were prepared in a way that :

- The pressure applied should be constant for all the laminates
- The adhesive GSM should remain almost same. (2.0 ± 0.5)
- During the preparation of laminates air bubbles and creases were avoided.
- Solvent must be removed completely before laminating the films.

6.3.2 Curing and Bond Strength Measurments:

4 or 5 laminates of every laminate structures were cured in a hot air oven and at the definite time intervals, one by one taken out for bond strength measurement and observing the tackiness. Bond strength is measured with the help of 15 mm width bar template and sharp edge knife and fixed into the jaw of Universal Testing Machine. The average force for pulling apart the layers is noted

6.4 Experiments:

Adhesive GSM : 2.0 ± 0.5

Curing Temperature: $40 \pm 2^{\circ}C$

Table 1: Curing Time For Important Laminate Structures

S. No.	Structure	Time	Bond	Remarks
		(in hours)	Strength(gf/	
		· · · · · · · · · · · · · · · · · · ·	15 mm	
1	18 μ BOPP(N)-18 μ MET	6	172.64	Tack
	BOPP	10	204.57	Tack
	2011	14	249.68	Low Tack
		18	283.71	Cured
		·	1	
2	$20 \mu \operatorname{BOPP(N)-20} \mu \operatorname{MET}$	6	156.72	Tack
	BOPP	10	189.62	Tack
		14	245.82	Low Tack
		18	297.82	Cured
	1	I	1	I
3	$18 \mu \operatorname{BOPP(N)-20} \mu \operatorname{MET}$	6	126.64	Tack
	BOPP	10	174.98	Tack
		14	229.65	Low Tack
		18	253.21	Cured
		1	1	
4	$15 \mu \operatorname{BOPP(N)-15} \mu \operatorname{MET}$	6	98.35	Tack
	BOPP	10	124.74	Tack
		14	182.94	Low Tack
		18	Tear	Cured
-			50.00	- T - 1
5	$18 \mu \operatorname{BOPP(N)-35} \mu$	6	58.26	Tack
	White BOPP	10	70.46	Tack
		14	85.12	Tack
		18	121.32	Cured
((11(24	T1-
6	$18 \mu \text{BOPP(N)-}25 \mu \text{CPP}$	6	116.24	Tack
	Plain	10	134.83	Tack
		14	Tear	Cured

S. No.	Structure		Time	Bond	Remarks
			(in hours)	Strength(gf/	
				15 mm	
7	18 μ BOPP(N)-	25	6	186.92	Tack
	μ Poly(N)		10	227.86	Tack
			14	249.21	Low Tack
			18	296.67	Cured

8	$18 \mu \text{BOPP(N)-90} \mu \text{Poly}$	6	208.74	Tack
	Plain	10	274.80	Tack
		14	Tear	Tack
		18	Tear	Cured

9	20 μ MET BOPP -	6	243.89	Tack
	12μ PET(Plain)	10	303.76	Tack
	•	14	Tear	Cured

10	18 <i>μ</i> BOPP(N)-		6	156.86	Tack
	18 µ MATT	Finished	10	198.42	Tack
	BOPP		14	256.80	Low Tack
	2011		18	Tear	Cured

11	12μ Plain	PET-	6	78.80	Tack
	12μ MET PET		10	106.56	Tack
	,		14	132.24	Cured

12	12 μ Plain	PET	-	6	198.63	Tack
	20 µ MET B	OPP		10	267.56	Tack
	,			14	329.67	Low Tack
				18	Tear	Cured

13	12μ Plain PET-	6	230.60	Tack
	$12 \mu\text{MET}$ PET	10	380.42	Tack
	+25 μ Poly(N)	14	402.68	Tack
		18	482.68	Tack
		22	Tear	Cured

* Samples Teared while checking the bond strength shows good bond strength

Table 2 : Effect Of Thickness On Curing Time

Adhesive Used: CAC 2511

S. No.	Structure	Time	Bond	Remarks
		(in hours)	Strength(gf/15 mm	
1	12 μ PET-25 μ Poly(N)	6	189.68	Tack
		10	198.94	Tack
		14	267.84	Tack
		18	365.86	Tack
		22	Tear	Cured

		1	152.04	T 1
2	$12 \mu \text{PET-75} \mu \text{Poly(N)}$	6	172.84	Tack
		10	202.68	Tack
		14	273.89	Tack
		18	385.86	Tack
		22	Tear	Cured

3	12 μ PET-100 μ Poly(N)	6	156.78	Tack
		10	198.68	Tack
		14	253.89	Tack
		18	Tear	Low Tack
		22	Tear	Cured

4	12 μ PET-150 μ Poly(N)	6	122.64	Tack
		10	174.52	Tack
		14	198.78	Tack
		18	Tear	Tack
		22	Tear	Cured

* Samples Teared while checking the bond strength shows good bond strength

Table 3:Effect Of Adhesives On Curing Time

S. No.	Adhesive Used	Time (in hours)	Bond Strength(gf/15 mm	Remarks
1	CAC-2511	6	124.54	Tack
		10	234.65	Tack
		14	362.76	Cured

$12\,\mu\,\text{PET-25}\,\mu\,\text{MET CPP}$

2	CAC-1580	6	132.64	Tack	
		10	183.52	Tack	
		14	Tear	Cured	
		-			
3	FCL-480	6	126.56	Tack	
		10	198.94	Tack	
		14	Tear	Cured	

* Samples Teared while checking the bond strength shows good bond strength















.7.1 Effect of laminate structure on Curing Time

Figure 8 shows the curing time vs bond strength values for BOPP-MOPP laminates. As observed from the figure ,bond strength is increasing with curing time. In all the three cases increase in bond strength is slow but steady till 15 hours. After 15 hours to 18 hours a sharp increase is observed which shows the curing time is between 15 to 18 hours. Similar type of results are observed in tackiness results , which are presented in Table1. Here after 18 hours, no tackiness was observed, which shows that curing time for BOPP-MOPP laminate is 18 hours.

Figure 9 shows the curing time vs bond strength values for different structures viz BOPP-MOPP, BOPP-Matt Finished BOPP and BOPP-White BOPP. As observed from the figure that the bond strength is increasing with curing time. In all the three cases, bond strength was increased slowly till the 15 hours. It was increased sharply after 15 to 18 hours. After 18 hours no tackiness was observed which shows curing time as 18 hours. This infers that type of BOPP does not effect the adhesive curing and curing time.

Figure 10 shows the bond strength and tackiness behaviour of different laminate structures. A BOPP was laminated with the CPP, and with the Polyethylene film. It was found that BOPP- along with CPP gets cured after 14 hours whereas BOPP-POLY laminates gets cured after 18 hours. As the bond strength was increased with the curing time.For BOPP and POLY laminates bond strength increases sharply after 15 hours to 18 hours, while on the other hand tackiness was observed at 15 hours while 18 hours, no tackiness was observed. A similar trend was observed in BOPP and CPP laminate which was cured after 14 hours.

Figure 11 shows the bond strength behaviour of laminates of PET and 3 layer structure PET-MET PET-POLY. For the PET-MET PET laminate, curing time is 14 hours. As shown in figure , bond strength increases slowly and no tackiness was observed In case of bond between MET PET and POLY (final pass), bond strength increased slowly upto 14

hours and beyond that, bond strength increases sharply and the sample was cured after 22 hours. The trends are similar in case of PET- MET BOPP which was cured after 18 hours.

As observed in all cases, the curing time is different for different structure irrespective of similar conditions, i.e. adhesive GSM and temperature. This shows that the type of substrate effects. The curing time, which is attributed to surface energy of substrates. The surface energy of BOPP is less than PET which in turn increases the adhesive adsorption on PET films as compared to BOPP films. A thin layer of adhesive adsorbed on BOPP cures faster as compared to PET leading to lower curing time.

7.2 Effect of Film thickness on Curing Time

Figure 12 and 13 shows the effect of varying Poly thickness on the curing time behaviour. In these structures 12 μ PET was laminated with 25 μ , 75 μ , 100 μ , 150 μ poly film. As observed from the figure, there was no change in curing time with Poly thickness. This was further confirmed by tackiness results which are presented in Table 2. It was also observed from figure that bond strength was higher in case of laminate which was prepared with high Poly thickness. This was attributed to the fact that same adhesive deposition is being used for all Polyethylene thicknesses

7.3 Effect of Type of Adhesive on Curing Time :

Figure 14 shows the effect of different adhesive types on curing time of laminates. Three different adhesives viz CAC-2511, CAC- 1580 and 480 from FCL were used for the study. All the above adhesives were used for laminating PET and CPP. It was observed that in all cases the curing time is 14 hours. It was also observed from figure that bond strength of the laminate having CAC-2511 was higher strength as compared to other two adhesives which shows better performance of 2511 against other two adhesives. This is further confirmed by Table 3. results which shows absence of tackiness in all the three cases. This infer that adhesive type does not have any effect on curing behaviour.

7.4 Comparison Of Curing Time With The Actual Production

Table 4 shows the bond strength vs. curing time behavior of some actual production data, taken out from the plant and were cured at 40 °C in the lab conditions. In these samples, variations in bond strength, GSM were observed and tackiness behavior and final curing time was measured to compare with the lab trials. It is shown that for the PET- CPP laminate, adhesive GSM was comparable in both lab and production trials and it was found that bond strength is higher in lab trials whereas curing time was not effected and it was came out to be 14 hours. Another comparison was done by laminating 12 μ PET- 25 μ POLY and 12 μ PET-21 μ POLY sample from production. Adhesive used was the FCL- 480 in both the cases. It was observed that both the samples were cured after 22 hours and all the tackiness was gone after 22 hours. It was again observed that bond Strength of lab trials was higher than the production sample at same time interval. To revalidate the results two other laminates of 12 μ PET -110 μ POLY and 90 μ POLY were compared with different adhesives. As adhesive GSM variation in production samples occurs, some anomalies were seen in the results. Both were laminated with high adhesive GSM and higher adhesive GSM take more time to cure. Printing ink might also have some effect on curing time.

CHAPTER 8

The following results were concluded from the study are as follows-

1. All laminate structures are cured from 14 hours to 22 hours. PET- POLY laminate cured after 22 hours and BOPP laminates takes time in curing upto 14 to 18 hours.

2. Bond strength increases as the curing continues.

3. Curing Time does not depend on the thickness of the substrates. It only varies with type of the substrates.

4.Curing Time does not depend on the type of adhesives. But Bond Strength behavior of CAC-2511 is better as compare to other adhesives.

5. Curing Time also depends on adhesive GSM. Curing time increases with the adhesive deposition on the film surface.

6. Curing time of various laminates are as follows-

PET- POLY	22 Hours
BOPP-BOPP	18 Hours
PET-BOPP	18 Hours
PET-CPP	14 Hours
BOPP-POLY	14 Hours
PET-PET	14 Hours

SCOPE OF THE PRESENT WORK

Today, flexible packaging is going on dominating the rigid packaging, the use of adhesive is going on increasing in all the sections of the market. Curing time is an important operation for all the adhesive, ink and coating industries. A less or no curing time can generate many serious problems like low peel strength, low seal strength, opening of the laminates and existence of the harmful VOC etc.

In the present work, curing time for different laminate structure is observed and validated. Performance of the laminate is wholly depending on the performance of adhesives. Correct curing data are useful for the lamination operations as well as further operations like- slitting, pouching etc.

<u>REFERENCES</u>

- The Wiley Encyclopedia Of Packaging Technology ; Edited By : Marlyn Bakkar ; John Wiley And Sons Publication,1986
- Adhesive Technology ; Edited By Gerald L. Schneberger, John Wiley & sons Publications, 1994
- Advances in Polyurethane Technology Edited by J. M. Buist and H. Gidgeon, Publication Marclaren and Sons Ltd. ,London, 1998
- Polyurethane Handbook Giinter Ortel, 2 nd Edition, Hanser Pulication ,Munich, 1994
- Handbook Of Polyurethane Technology Edited By :A. Pizzi, K.L. Mittal, Publisher Marcel Dekker Inc.
- Handbook Of Adhesives, Edited By: Irving Skeist and Van Nostrand Reinhold ,Second Edition, 1994
- Plastic Materials, Edited by J. A. Brydson, Fourth edition, Published By: Butterworth Scientific, 1982
- Handbook Of Adhesion, Edited By D. E. Pakham, Second edition, Published by: Hanser Publication, 1992
- Industrial Adhesive and Sealants, Edited by : B. S. Jacksons, Published by : Hutchinson Benham, London, 1993
- Plastic Films, by: J. H. Briston, Published by: The Butter Worth Group, 1995
- Encyclopedia Of Polymer Science and Technology, Vol-1Editted By: Kirk-Othemer, John wiley & sons, Fourth Edition ,1991
- Encyclopedia Of Polymer Science and Technology, Vol-7 Editted By: Marc hove grant, John wiley & sons, Fourth Edition ,1991
- Decorating Plastics, Editted By: James M. Margolis Hanser Publication, 1986
- 14. Radiation Curing of Polymers-2, Editted By: D.R. Randel, Published by Royal society of chemistry, 1991

- Polyurethaner Elastomers Second Edition, Editted By: C. Hepburn Published By: Elsevior Applied Science- 1992
- 16. www.packworld.com/articles/Products/76.HTML
- 17. www.rbhmhaas.com/adhesives/articles/pdf/graficarts
- 18. www.hbfullers.com/adhesives/0084
- 19. www.pechineyplasticpackaging.com/secondary/news1202001.asp
- 20. www.media.wiley.com/Product.dat/excerpt
- 21. www.kleiberit.com/Fenster-Tueren-Leimholpattern-English
- 22. www.collano.com/docs/produke/composites/34
- 23. www.dow.com/tone/prodopp/coste34/polyols.HTML
- 24. www.adhesivesmag.com
- 25. www.shellchemicals.com