TO STUDY THE EFFECTS OF ADHESIVE PARAMETERS ON MULTILAYERED LAMINATE PERFORMANCE

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CERTIFICATE

This is to certify that the Major project report **“To study the effects of adhesive parameters on multi-layered laminate performance”** being submitted for the partial fulfillment of the requirement for the award of **Master Degree of Engineering** in **Polymer Technology** of University of Delhi is a record of student own work carried out by him.

To the best of our knowledge the report has not been submitted to any other university or institution for the award of any degree or diploma.

He bears a good moral character, and we wish him every success in his life.

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ABSTRACT

Flexible packaging is now becoming increasingly popular due to their lightweight, cost saving, barrier and aesthetics. Today flexible packaging is being used in almost all the products including food items e.g. bakery, confectionary, snack food, oil, tea, coffee, milk, chewing tobacco etc and non food grade items like seeds, bearing etc. Flexible packaging laminates are being manufactured by printing and laminating the transparent, opaque or metallised films of PET, PP, PE, HDPE, LLDPE, PVC, PAPER, Aluminums Foils etc. The most common laminate in the converting industry is PET/METALLISED-PET/POLY; various types of adhesives are being used for laminating these films but polyurethane adhesives are most popular. In the present work, effect of various parameters on laminate performance has been studied. Two component polyurethane adhesives has been used in which hardener concentration, curing time, curing temperature are being varied. The effect of varying these parameters on bond strength, viscosity, GSM, etc. have been studied and sported.

Chapter- 1

INTRODUCTION

1.1 Packaging is a mean of providing the correct environment conditions for goods/material during the length of time it is stored and distributed to the consumer. A good packaging should keep the product clean, should prevent loses, contaminations, chemical and physical damage and must provide identification and instructions.

1.2 Packaging can broadly be classified into three categories: Rigid, semi rigid, and flexible. Rigid packaging includes containers made up of glass, wood and metals. The example of rigid packaging is glass bottles, drums, crates boxes etc. Semi rigid packaging includes material, which lie in between the rigid and flexible packaging for example toothpaste and cosmetic tubes. Flexible packaging constitutes the material made up of polymeric films, cloth, and papers either alone or in combination with each other.

The example of the flexible packaging is shampoo pouches, chips packets and bags etc.

Amongst these packaging materials flexible packaging is gaining enough market share. In many applications flexible package has replaced rigid packages due to several advantages. These are: -

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

1.3 In flexible packaging polymeric films, cloths, papers and foils are used alone or in combination with each other either printed or unprinted. The conversion of a single layer film to a printed or unprinted laminate is called converting process. It is basically required to improve the functional properties of the materials. In conversion process printing is the first step, which is required to decorate the pack, to give information, instructions etc of the product to be packed. Polyester films are most commonly used for printing due to its inherent characteristic of ink adhesion. These printed films are then laminated with other films to improve the mechanical properties, barrier properties, to protect the inking layer, and to make it seal-able for pouch formation. In the lamination process adhesive is applied to one of the substrate and the second substrate is combined with the first substrate under heat or pressure and sometimes both.

Figure 1: Some flexible film laminates

1.4 The laminating process can either be solvent based or solvent less depending on the type of adhesive used and process of lamination. The lamination process is the most important step in the conversion process as it offers the advantage of using two or more layers, hence combining the properties of both the substrates. The adhesive used in lamination is generally two component adhesives, which are combined in, prescribed ratios. Today numbers of adhesives are present in the market but suitability of adhesive for a particular application depends on various factors. A good laminating adhesive must have following properties: -

- It should wet the surface on which it is to be applied,
- It should be flexible, even after curing,
- It should be transparent, colorless and odorless and non-toxic as it is to be used for food articles,
- It should be non toxic and non hazardous,
- It should sustain the environmental conditions and remain intact during handling and transportation,
- It shouldn’t affect the properties of the film on which it is to be applied,
- It shouldn’t loose bond by heating and aging after curing,
- It should give sealing properties.

1.5 The functional properties of an adhesive depends upon various factors such as adhesive and hardener ratio, curing time curing temperature, amount of adhesive applied and type of adhesive to be used. As in packaging two component-based adhesives are being used the major factor, which governs the adhesive performance, are adhesive-hardener ratio, curing time and curing temperature. Although lot of commercial literature is reported on ratio of hardener to be used, curing time and temperature, but no consolidated information is reported. In the present work the effect of hardener ratio, curing time, and curing temperature, on bond strength and adhesive GSM is studied. A two component polyurethane adhesive from converter adhesive and chemicals (CAC) having trade name CAC-1580 is being used in the present work. The two components in this adhesive are modified diisocnate and polyester. The adhesive-hardener ratio, curing time and temperature as reported in literature are 70:30,12 Hours, 60^0C respectively. Main objective is to validate these conditions by evaluating the performance of adhesive their bond strength.

Chapter – 2

LITERATURE

2.1 Polymeric Films

2.1.1 A plastic material below 0.010 inches or 0.25 mm in thickness is generally considered a film, above this thickness is called sheet. Film thickness also is described in mils, which are equitant to thousands of an inch. Hence 0.010 inches equal to 10 mils. However the unit micron is widely used for measuring the film thickness.

2.1.2 Orienting or stretching the film, under carefully controlled temperatures, can improve the properties of films. This causes a realignment of molecules and yields a much tougher film often it also increases strength and barrier properties.

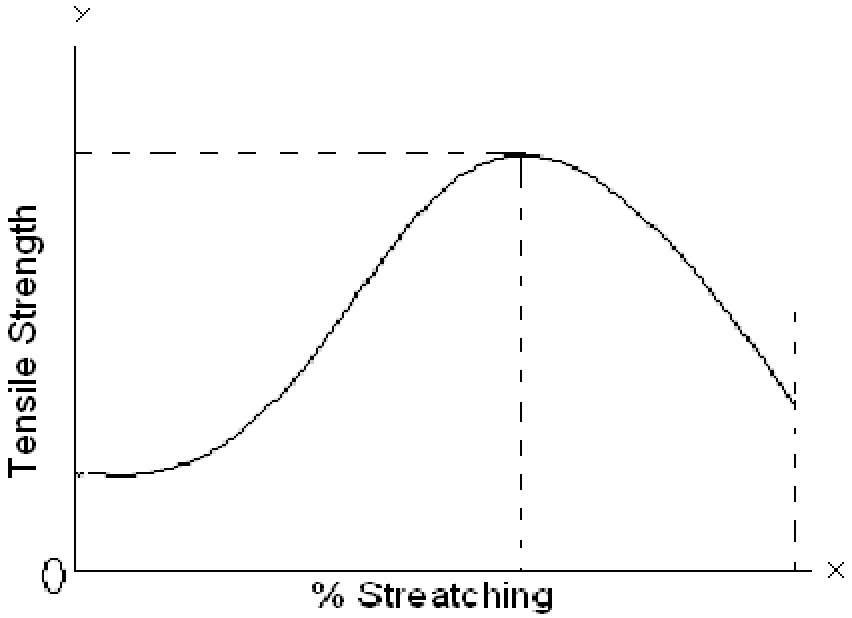


Figure 2: Effects of streaching on tensile strength of polystyrene film

2.2 Classification of Polymeric films

2.2.1 Polymeric films can be classified according to their manufacturing material as follows: -

i) Cellulose

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

ii) 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 two forms i.e. Bi-axially oriented polypropylene and Cast polypropylene.

iii) Polyethylene

Polyethylene can be classified further as follows: -

a) **Low density polyethylene (LDPE): -** It is heat sealable, inert, odor free, shrinks when heated, good moisture barrier but has high gas permeability, sensitivity to oils and poor odor 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 (121^0C) 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 film has high puncture resistant, high tear strength. It provides comparable properties to other olefins even in thinner gauges.

iv) Polyvinyl chloride (PVC)

Unplasticized PVC films is shift, high tensile strength, high water vapor permeability greater than LDPE but gas permeability is lower. Plasticized PVC films are soft having limpness and used for shrink warping trays containing cuts of fresh meat and fresh produce.

v) Polyvinylidine chloride (PVDC)

It has very strong and therefore used as thin films. It has very low gas and water vapor permeability and is heat shrinkable and heat seal able. However it has a brown tint, which limits use in some applications.

vi) Ethylene vinyl Acetate (EVA)

Compare to have a greater elongation, elasticity & impact strength but low barrier properties and used as stretch films.

vii) Polyesters

It is very tough and strong and is normally transparent. Slip additives are added and this makes the film slightly hazy. Water vapor permeability is of the same order 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. It is also one of the most metallized films.

viii) Styrene polymers and co-polymers

Biaxial oriented poly styrene films are used for some packaging which require high water vapor transmission.

ix) Nylon

It is tough with high tensile strengths, softening point, barrier properties but high moisture permeability. Used for vacuum packaging of foodstuffs, for boil-in-bag packs and packaging of surgical equipments.

x) Inomers

It is flexible, tough, extremely clarity perform well in extension coating and skin packaging application. It is also used in co-extruded film because of their grease resistance in thin gauge.

xi) Fluro-polymers

Good transparency, especially when in contact of liquids, low gas permeability, but higher water vapor permeability than LDPE, PVC.

xii) Acrylic Multipolymers

It has good transparency, especially when in contact of liquids, low gas permeability, but has higher water vapor permeability than LDPE, PVC.

xiii) Acrylonitrile methyl acrylate co-polymers

It has good clarity and high barrier properties. In combination with LDPE it has been used for cheese and meat packs.

xiv) Poly methyl pentene

It has high heat resistance but it has found limited applications as packaging film because high water vapors and gas permeability.

xv) Polycarbonates

Outstanding combination of high impact strength, high temperature resistance, and clarity. Water vapor permeability is higher than that of polyolefin, P.V.C., useful for boil-in-bag packs, and for skin packaging.

xvi) Metallized films

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

xvii) Aluminum 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 vapors and gases.

xviii) Co-extruded films

It is multi-layered co extruded film to meet the properties of different polymers in a single film. It has high tensile properties, good seal ability and barrier properties. It is widely used in oil packaging and a lot of other products packaging.

xix) Pearliesd 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.

2.3 Processes

2.3.1 Surface Preparation of Adherends for Adhesive

Most industrially useful polymeric materials are not found in the pure state but in a compounded state. Compounding ingredients normally used are plasticizers, antioxidants, slip agents etc. In addition most plastics are not of a single molecular weight. In particular free radically polymerized materials can have a rather broad molecular weight distribution. The low molecular weight materials often bloom or rise to the surface especially in semi crystalline plastics. The surface of an industrial semi crystalline plastic may be similar to the one shown in the figure below: -

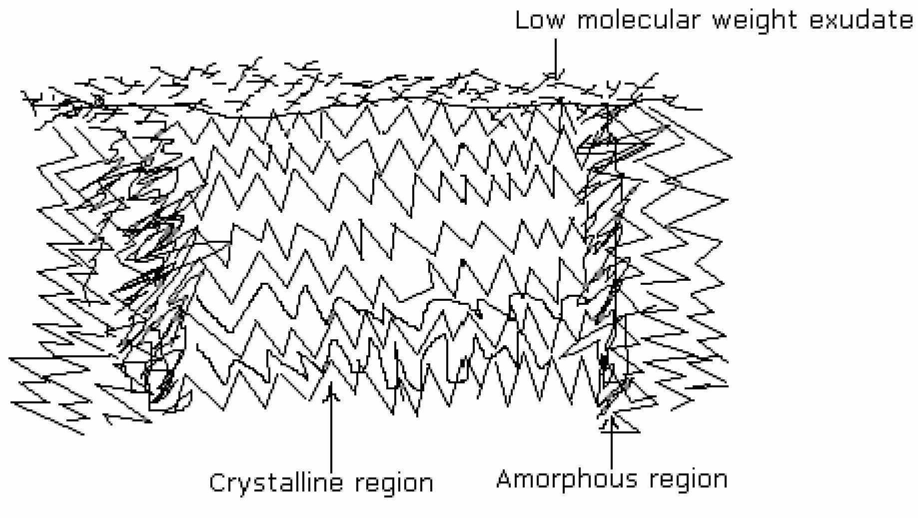


Figure 3:Surface of a semi-crystalline plastic

The squiggly lines in the figure interior to the polymer signify the amorphous region of the polymer, while the zigzag lines represents the crystalline region of a polymer surface. On the surface of the plastic are shown some shorter curved lines representing the low molecular weight exudates. Using adhesives with plastics has more problems than those caused by the low molecular weight exudates. Plastics are low surface energy materials and most high strength adhesive do not spontaneously wet these surfaces. So the first reason for surface preparation is to provide a reproducible surface so that the bonding operation is consistent. The second reason to use a surface preparation is durability.

To generate a better surface for adhesive bonding, first the weak boundary layer of low molecular weight exudates needs to be removed. Alternatively it must be chemically modified to provide a cohesively strong layer well bonded to the polymer surface, second the surface energy of the weak boundary needs to be increase so that it is higher than the surface tension of the adhesive to be used (If however the weak boundary layer has been removed by the surface preparation, the remaining polymer surface energy must be increased), third the polymer surface topography should be improved to enable capillary action by the adhesive.

There are two distinct type of surface preparation of plastics *physical and chemical methods*. This classification is somewhat improper since the “Physical method” usually changes the surface chemistry in addition to providing physical changes. The differentiation comes from the fact that the physical methods usually use some form of high-energy radiation to change the surface. The “Chemical methods” usually involve immersion of the plastic in a bath or wiping the surface with a cleaner or primer. These treatment methods can be subdivided as following: -

a) Corona Discharge Treatment

This process is used most often for the continuous surface treatment of plastic films. The corona discharge system consists of a generator, transformer, and a treater. The generator raised the frequency of the 60 Hz AC to a much higher level 25 to 30

KHz is a commonly used frequency. The transformer steps up the voltage to the 15,000 V to 30,000 V required producing a corona discharge consisting of many small uniformly distributed sparks. The treater is a capacitor with the plastic material to be treated placed between the electrodes. The arrangement of the treater elements varies, depending on the equipment design.

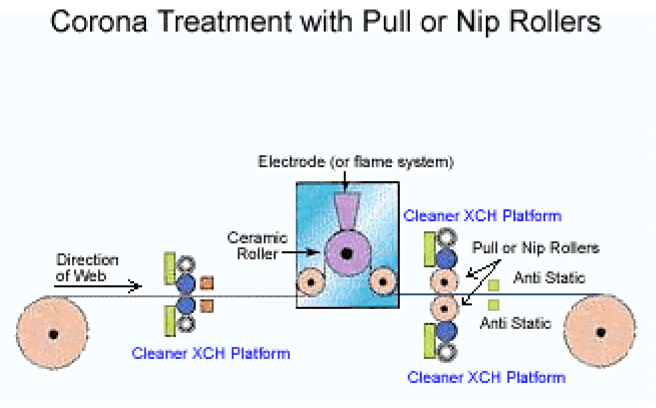


Figure 4: Corona Treatment

The process that takes place during the Corona discharge treater are not entirely understood. Electron, proton, exited atoms, and ions in the corona discharge break carbon to carbon and carbon to hydrogen bonds on the plastic surface, cause radical formulation. The radical reacts with O_2 and N_2 in the air introducing polar groups to the plastic surface, other process also takes place during corona discharge treatment.

b) Plasma treatment

Plasma technology is increasingly used for the surface treatment of plastic parts. Plasma treatment is quite effective but is a batch process carried out in an evacuated chamber and energy supplied by radio frequency. Continuous systems are expensive and have been made only for narrow webs. Plasma treatment causes ablation (micro etching), surface cleaning, cross linking and surface activation by reaction of plasma gas with the plastic surface. In the plasma treatment process various activated gases may be used for example N_2, O_2, NH_3, CO_2 etc

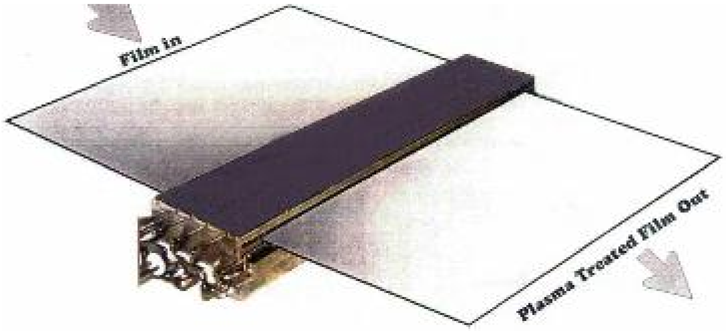


Figure 5: Plasma Treatment

c) Flame Treatment

Flame treatment is the most often used process to improve the bond ability of molded plastic articles. It is especially useful in treating irregularity shaped parts although flame treatment of polymeric films sometimes also used. An oxidizing flame at a temperature of 1090^0C to 2760^0C contacts the plastics surface for a period of less than a second causing its oxidation among other surface changes.

d) Other Treatments

Mechanical abrasion usually sandblasting removes surface impurities in addition to increasing the surface area both actions helps to improve the adhesion. *Chemical etching* is the treatment of plastic surface by exposure to solution of reactive chemical compounds usually oxidized. In *ion beam itching* a gas is ionized and then directed toward a target by a series of electrical lances. The ions are accelerated to a high velocity so that when they impinge upon the surface, material is ablated. In radio *beam sputter-etching* polymer to be treated is attached to an electrode connected to a radio frequency source. Another electrode, an anode, is also within the evacuated chamber. When a gas is admitted into the chamber, capacitatively coupled radio frequency plasma is initiated. Ions in the plasma are accelerated from the anode to cathode, at which point the polymer surrounding the cathode is ablated by the action of the ions.

2.3.2 Printing, Lamination, Slitting and Pouching

a) Printing

The printing is used to decorate the product and giving information about it a broad variety of methods of printing are available e.g. lithography, ink jet, letterpress (relief printing), etc

however the following process are widely used for printing the flexible polymeric films: -

i) Gravure

Gravure printing (also called as rotogravure) is used for indicate designs and colors but requires long runs in the million plus range to amortize the high cost of engraved rolls. Color lay down is excellent, make-ready time is very short and printing results are very consistent.

The process chemically or mechanically incises small and larger cells into the surface of copper plated mild steel cylinder that usually is chrome coated afterward for wear resistance.

Today electrochemical, laser, electron beam engraving have largely replaced the traditional chemical etching. Printing is a web process with the roll immersed in a pool of low viscosity ink that is wiped from the outer surface by a doctor blade, leaving the cell filled with ink. The roll stock is fed between the engraved and impression roll and the ink is drawn directly from the stock and printing rolls. The thin ink, often containing a solvent, which dries between printing stations, thus avoiding the problems of wet on wet multi color printing as in offset.

ii) Flexography

This is the most widely used method for the decoration of plastic film. A thin, fast drying solvent-based ink is applied to the film surface by mean of a flexible rubber plate with raised characters on it. This is mounted on a plate cylinder by means of an adhesive. Ink is transferred to the rubber plate from the ink fountain via rubber ink roller and on anilox roller. The anilox roller is an engraved stainless steel roller, which holds ink in the recesses of the design and acts as a metering device to the rubber plate. The process offers a combination of high speed and comparatively low printing plate cost but unable to reproduce fine details.

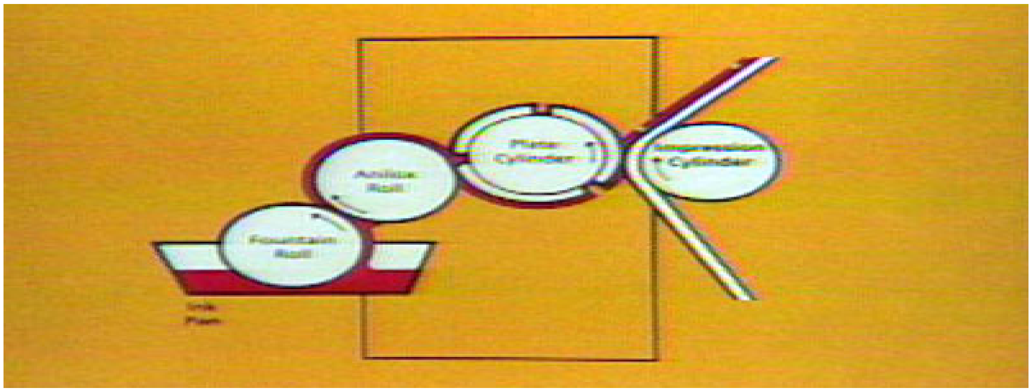


Figure 6: Flexography

iii) Screen Printing

Screen-printing is widely used for plastic decorating for several reasons, the equipment is simple and inexpensive good quality multicolor printing is possible including the coverage and good abrasion resistance are obtained. However the process is slow one, mainly suitable for short runs.

b) Lamination

The fundamental action involved in lamination of flexible materials is the bringing together and bonding of two or more web by means of some adhesive agent to create single web. The reason for packaging this function is to create a structure that contains all required packaging properties, which in many cases have to be supplied by more than one material.

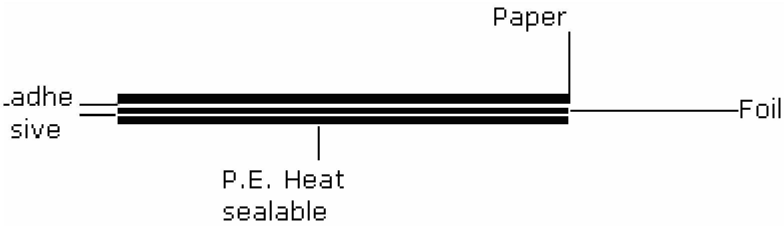


Figure 7: flexible Laminate

Classification of laminating processes

Laminating process can be divides as follows: -

i) Dry bond laminating

It is the process of coating either water based or solvent based adhesive to a substrate, drying the adhesive with heat and airflow and heated compression nip that makes the films together to form laminate.

ii) Wet bond laminating

It involves the metering of a low viscosity adhesive onto a multiple application roll configuration that applies the adhesive to the first substrate, which is then mated to a second substrate using a heated nip. In case the adhesive used is solvent borne one of the substrate must be permeable to the solvent vapor.

iii) Thermal or pressure laminating

The thermal laminating adhesive takes one or more of the following forms: -

- A previously applied thermoplastic adhesive, which is activated by the heat and pressure of the thermal laminator,
- A special sealing layer one or two side of a structural film,
- Adhesive in dry film form,
- A coated adhesive on a non-reactive career. Some of these adhesives function at room temperature as well,

- A relatively low melting point film treated and introduced partially as a sealant.

iv) Extrusion laminating

A thin layer of molten polymer is used in this type of laminating. It is directly extruded between the two webs and laminated by nipping rolls as given in the figure below: -

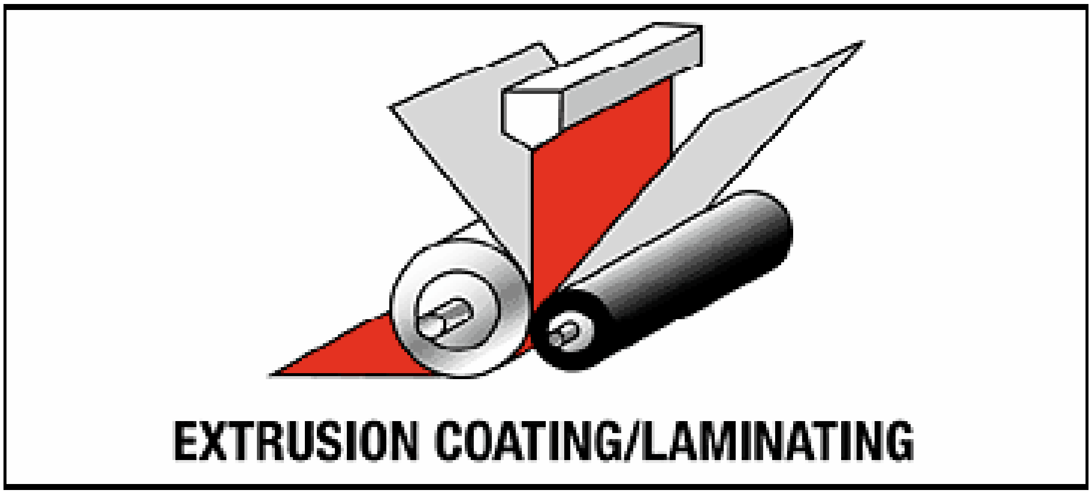


Figure 8: Extrusion Lamination

c) Slitting

Flexible packaging materials generally do not have perfectly flat surfaces. The material in a parent roll contains stretch lines and varies in gauge by about 1-5% across the web width. In slitting process the laminated web is cut to give specific width and defected material is removed from the laminated rolls with the help of a sharp blade, before dispatching the material to the pouching or consumer.

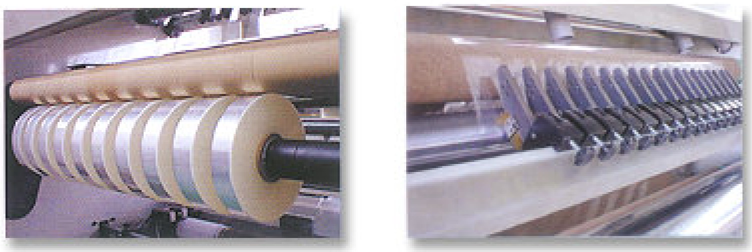


Figure 9: Slitting

d) Pouching

It is the final stage of making packaging material for converters. 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, die punch handles, spouts, performed handles, self sticking tape zipper, pilfer proof membrane etc.

Figures 10: Some kind of pouches

Chapter – 3

ADHESIVES AND THEIR CLASSIFICATIONS

3.1 Adhesives

3.1.1 Adhesives are the substances capable of holding two substrates together by surface attachments and are widely used in many industrial sectors, where their use is essential in manufacturing thousands of products. There are different kinds of materials for joining of various substrates. The adhesive material must be capable of wetting the surface to which it is applied, at least for an instant so that it forms a joint capable of transmitting stresses, and be both lightweight and strong. Adhesive often provide advantages over mechanical fastening techniques as a result of flexibility, weight reduction and labor savings.

3.2 Classification of Adhesives

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

3.2.1 Adhesive Classification on Application basis

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

a) Solution Adhesives

These adhesive are available in the form of solution. These can be organic solvent or water based with a homogeneous solution form. The bond is formed when the career (water/solvent) is lost through absorption into the substrate or evaporation.

b) Hot melt Adhesive

These are available in the form of sheets or molten mass and are process-able at high temperature 100^0C or more. They form a strong bond quickly by cooling are compatible with most of the materials and unaffected by water and humidity.

c) Emulsion

It is a mixture of polar solvent to non-polar solute with very small droplets suspended in the medium. It can be prepared with or without an emulsifying agent for example natural latex adhesive.

d) Pressure sensitive Adhesive

These adhesive are highly tacky and activates with finger pressure applied at ambient temperature. In such type of adhesives curing does not take place. For example adhesive used in cellophane tape.

3.2.2 Adhesive Classification chemical basis

All adhesives contain a binder, which provides toughness and cohesive strength. The chemical makeup of this binder gives the most important properties of the adhesives i.e. what it will stick to and what the bond will resist in service. Some of the important types of adhesives are: -

a) Acrylics

It covers the large range of polymers and co-polymers based on acrylates, methacrylates and other co-monomers, and are available in several forms of which emulsion and solution are most important.

b) Ethylene-Vinyl Acetate

These are based on ethylene vinyl Acetate co-polymer, available in the form of Hot-melt and solution and are widely used in the packaging industry. They have poor solvent, oil resistance and also heat sensitive.

c) Poly-Vinyl acetate

It is synthetic resin, which is relatively hard and brittle, but it can easily be plasticized to yield an adhesive polymer of remarkable versatility.

d) Polyvinyl Alcohol

It is a synthetic resin, which dissolves in water to give colourless solution. It is used in woodwork, packaging etc.

e) Polyurethane

It is a family of products containing urethane group formed by the reaction of isocynates and hydroxyl groups and are widely used in packaging, dentistry, aircrafts etc.

f) Natural rubber

An elastomer obtained from rubber tree in thin film is non-tacky but makes strong bonds with itself on contact. It is available as aquas latex or as a solution in solvent. It is a major component of cold seal adhesives.

g) Animal Glue

These are based on protein extracted from animal bones And Hides can be in the form of solid, jelly or liquid.

3.2.3 Adhesive Classification on Component basis

a) One Components Adhesive

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

b) Two components 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.

3.3 Polyurethane Adhesives

3.3.1 These are the high molecular weight polymers and come as molded articles, films, fibers in solution or dispersion. Properties of polyurethane can be tailored as per requirements e.g. flexible foam, rigid foam, semi rigid integral skin foam for automotive parts, thermoplastic elastomers, high performance rigid coating for a diversity of substrates and requirements, flexible coating for textile leather, elastic fibers and adhesives. In spite of the wide variety of applications the decimal composition of all these products is generally quite similar. Polyurethane are prepared by poly addition polymerization two or poly functional hydroxyl or amino group containing compounds with di or poly isocynates

$$\mathrm{RCNO} + \mathrm{R'OH} \rightarrow \mathrm{RNHCOOR'}$$

$$\mathrm{RHO} + \mathrm{R'NH_2} \rightarrow \mathrm{RNCONHR'}$$

Polyurethane constitutes wide variety of polymers with quite different compositions and corresponding different properties. In practice polymer containing no or very low amounts of urethane group are also classified as polyurethane as long as these products are derived from di- or poly-functional isocynates e.g. Polyetherureas, Polyisocynurates, polyureas & polycarbodimides.

3.3.2 **Manufacturing of Polyurethane**

Polyurethane is prepared from two compounds: -

a) Polyols

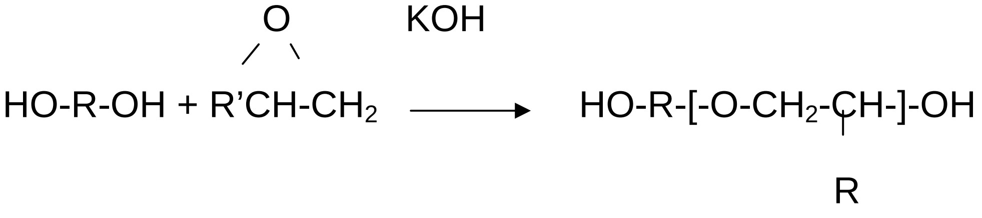
b) Isocynates

a) Polyols

Polyols of adhesive applications can be generally divided into three main categories: -

i) Polyether polyols

These are the most widely used polyols in urethane adhesives because of their combination of performance and economics. They are typically made from ring opening polymerization of ethylene, propylene and butylenes oxides with active proton initiator in the presence of strong base.



$$HO\text{-}R\text{-}OH + R'CH\text{-}\overset{O}{}\text{-}CH_2 \xrightarrow{KOH} HO\text{-}R\text{-}[\text{-}O\text{-}CH_2\text{-}\underset{R}{CH}\text{-}]\text{-}OH$$

Initiator Alkylene Oxide Polyester Polyols

Where initiator = Glycol-diols, Glycerin- triols, Sucrose- octols

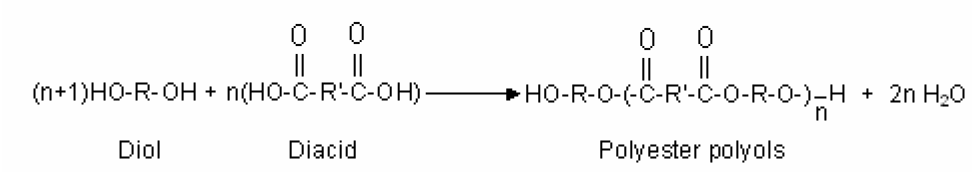
R’=H, Ethylene Oxide, R’=CH_3, Propylene Oxide,

R’=C_2H_5, Butyl Oxide

The polyether backbone is resistant to alkaline hydrolysis, which makes them useful for adhesives used on alkaline substrates such as concrete. They are typically very low in viscosity and exhibit excellent substrate wetting. In addition their low cost and ready availability from a number of suppliers add to their attractiveness. The more commonly used polyether polyols for adhesives range in molecular weight from 50 to 2000 for diols and 250 to 3000 for triols.

ii) Polyester polyols

These are widely used in urethane adhesives because of their excellent adhesive and cohesive properties. Compared to polyether-based polyols, polyester based adhesives have higher tensile strength and improved heat resistance. Drawbacks of these adhesives are low hydrolytic resistance, low temperature performance and chemical resistance. One of the more important application areas for these products is in the solvent borne thermoplastic adhesive used in shoe sole binding.



$$(n+1)HO\text{-}R\text{-}OH + n(HO\text{-}\overset{\overset{O}{\|}}{C}\text{-}R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH) \longrightarrow HO\text{-}R\text{-}O\text{-}(\text{-}\overset{\overset{O}{\|}}{C}\text{-}R'\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}R\text{-}O\text{-})_n\text{-}H + 2n\,H_2O$$

b) Isocynates

A number of isocynates are used for polyurethane manufacturing however some isocynates from the adhesive point of view are described as follows: -

i) Toluene di-isocynate(TDI)

ii) Methylene di-phenyl diisocynates (MDI)

iii) Blocked Isocynates

i) Toluene di-isocynate(TDI)

It is colorless, volatile low viscosity liquid commonly used in the adhesive to manufacture low viscosity polymers for flexible substrates. It is typically supplied as an 80:20 mixture of 2,4 and 2,6 isomers, respectively.

2,6-T.D.I.

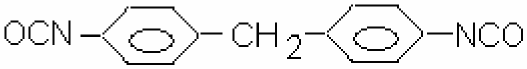
2,4 -T.D.I.

Toluene Di-Isocynates (TDI)

TDI is used in adhesives for the textile and food packaging laminates because of its low viscosity and low cost.

ii) Methylene di-phenyl diisocynates (MDI)

It is used where high tensile strength, toughness and heat resistance are required. MDI is less volatile than TDI making it less of an inhalation hazard.

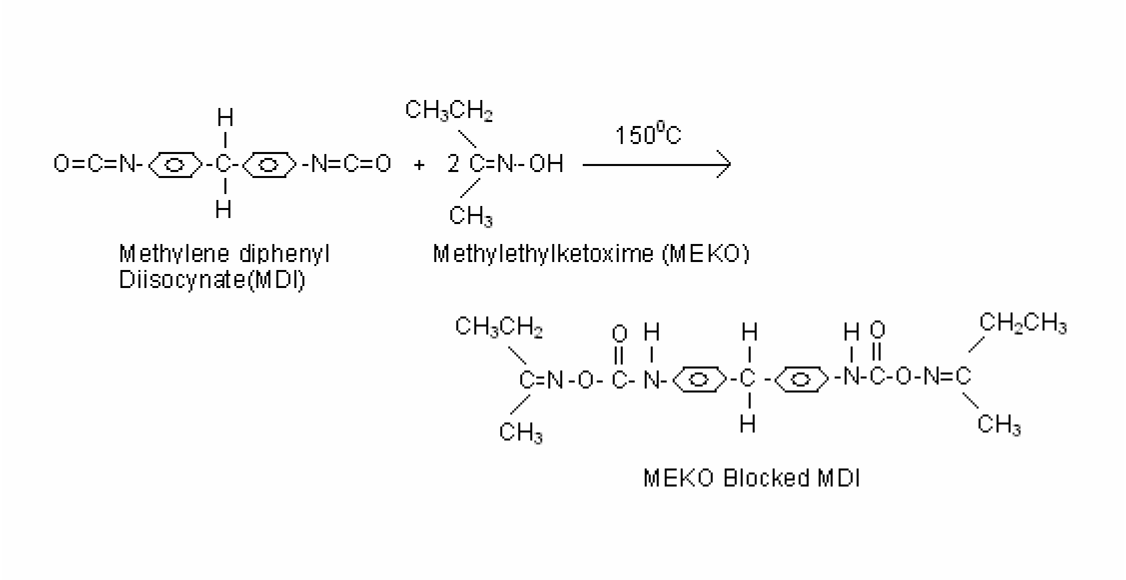


4,4 Methylene Diphenyl Diisocynates (MDI)

MDI is a solid at room temperature reacts faster than TDI and used in packaging adhesives, structural adhesives, shoe sole adhesives and construction adhesives.

iii) Blocked Isocynates

Blocking or Masking refers to reacting the isocynate group with a material that will prevent the isocynate from reacting with active hydrogen containing species at room temperature but will allow that reaction at elevated temperatures. Blocked isocynates are widely used for laminating adhesives and tire cord adhesives.



3.4 Urethane Polymer Morphology

The Advantage of polyurethane adhesive is that it can be formulated as per requirements economically. Polyurethane derives much of their toughness from their morphology. These are made up of long polyol chains that are di-isocynate and chain extenders if present.

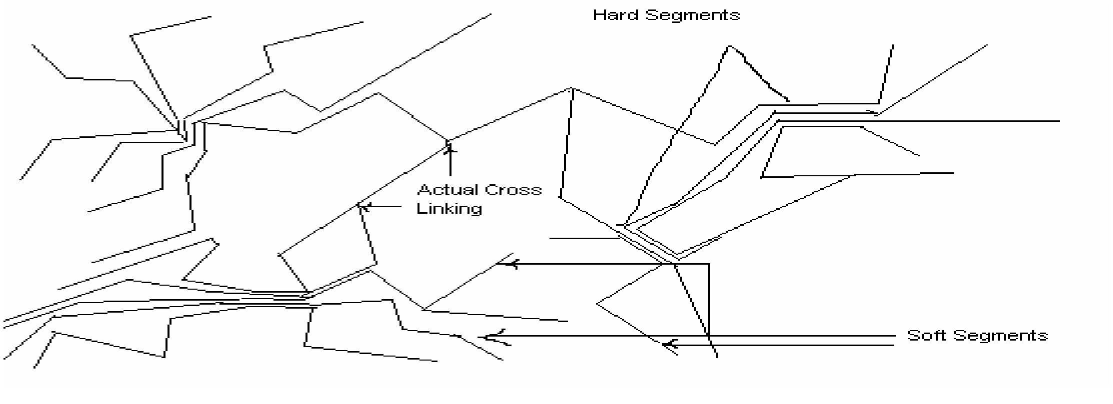


Figure 11: Polyol Chain Structure of Poly Urethane

The polyol chains impart impact low temperature flexibility and room temperature electrometric properties. Typically the lower molecular weight polyols give the best adhesive properties, with most adhesive being based on product of molecular weight less than 2000. Generally the higher the soft segment concentration the lower will be modulus, tensile strength, hardness and tear strength, while elongation will increase. Varying degree of chemical resistance and heat resistance can be designed by proper choice of the polyols.

Short chain di-ols or di-amines are typically used as chain extenders. These molecules allow several diisocynate molecules to link forming longer segments hard chain with higher glass transition temperature. The longer segment hard chains will aggregate together because of similarities in polarity and hydrogen bonding to form a pseudo-cross-linked network structure. These hard domains affect modulus, hardness, tear strength and also serve to increase resistance to compression and extension. The hard segment will yield under high shear forces or temperature and impact determine the upper use temperature of the product.

The presence of both hard and soft segment domains for polyurethane gives rise to several glass Transition temperature, one below -30^{o} C which is usually associated with segment, transitions in the range of 80^{0}C to 150^{0}C, and transition above 150^{0}C.

Transition in the range of 80^{0}C to 150^{0}C is associated with the breakup of urethane hydrogen bonds in either the soft segment or hard segment. Transition higher than 150^{0}C are associated with the breakdown hard segment crystallites.

Product wise choice of either the isocynates or polyols actual chemical cross-links can be introduced in either the hard or soft segments that may be beneficial to some properties. Highly cross-linked polyurethane is essentially amorphous in character with high modulus, hardness and few elastomeric properties.

3.5 Adhesives in Flexible Packaging Industries

3.5.1 Adhesive used for flexible packaging must provide excellent clarity and bond strength, resistant to heat, humidity and in some cases, chemicals. In addition they must resist tunneling. Tunneling often occurs when the two films differ in extensibility and stretch, or relax of different rates. These localized delaminating can have a potentially damaging effect on the package content. Although adhesive manufacturers evaluated several polymer system during the early stage of development, solvent born adhesives based on polyester and polyurethane polymers vary quickly become the standard for the flexible packaging industry because of their excellent adhesion, wide range of substrates and excellent cohesive strength when designed properly. Both classes of polymers consist of individual building and performance characteristic of the final adhesive.

3.5.2 Laminating adhesives are classified according to their functional properties (e.g. bond strength, chemical; resistance and heat resistance) as follows: -

- General purpose adhesive
- Medium performance adhesive
- High performance adhesive
- Ultra high performance adhesive

General-purpose adhesives are the most economical and are used for low requirement, relatively simple end uses. A general-purpose application includes packaging of snacks foods and non-aggressive dry products. The relatively more expensive medium, high and ultra performance adhesives are used in laminates where higher thermal/ chemical resistance is required. Typically applications include laminates for packaging liquids, pastes and boil in bag and heat sterile-able laminates.

Chapter - 4

THEORIES OF ADHESION

4.1 Adhesion Theory

4.1.1 The main application of adhesion is bonding by adhesives, which is replacing the more classical mechanical attachment techniques such as bolting/riveting. It allows to save weight to ensure a better stress distribution and after better aesthetics. Adhesive is involved whenever solids are brought into contact, as in coating, paints, multi-layered sandwiches etc

4.1.2 Since the final performance of these multi-component materials depends significantly on the quality of the interface that is formed between the solids. It is understandable that a better knowledge of the adhesion phenomena is required for practical applications.

Many theoretical models of adhesion have been proposed by scientists, which together are both complementary and contradictory and are illustrated. These models are given below : -

a) Mechanical Interlocking

b) Electrostatic Interactions

c) Adsorption Theory

d) Diffusion Theory

e) Chemical Bonding Theory

f) Theory of Boundary Layers and inter-phases

a) Mechanical Interlocking

This is the oldest and simplest explanation of for adhesion. The adhesive flows into the cavities or interstices of the adherents and solidifiers. This mechanical anchoring between the adhesive and the adherent prevents the removal of adhesive from the substrate and the spreading of adhesive plays a significant effect on the adhesive bond.

b) Electrostatic Interactions

This theory compares the adhesive substrate system with a condenser and the double electric layer produced at the interface of, say, two different polymers are compared with plates of condenser. In stripping the adhesive from the substrate a potential difference is established whose magnitude increases with increased clearance between the moving surfaces, and when a definite limiting distance is reached a discharge occurs.

The work of adhesion, $A = 2.\pi.\sigma^2.h/D$

Where σ is the surface discharge density, h is the discharge gap and D is the dielectric constant of the medium.

c) Adsorption Theory

According to this theory in the event of intimate contact between the adhesive and the adherent the adhesive strength arises as a inter-atomic and intermolecular forces at the interface. The forces between the adhesive and the adherent are usually grouped into two categories: -

i) Primary Forces

ii) Secondary Forces

Primary forces include ionic, covalent and metallic bonds; Secondary bond may include Vander wall's Forces, hydrogen bonds, and Lewis acid-base interactions.

d) Diffusion Theory

This theory characteristically applies to polymers when they show self-adhesion and when they adhere to each other. It is of obvious importance to adhesive, for when two solids are to be joined by a contact adhesive it is applied to both the surfaces, solvent and water allow evaporating and the surfaces are than united. The union of the adhesive across this interface is a diffusion process. It is based on the most essential features of high polymers e.g. chain structure and flexibility of their molecules and the ability of the latter to exhibit micro Brownian motion. Two criteria must be satisfied if the diffusion theory is to be applied: -

i) The polymers must be mutually soluble

ii) The macromolecules or their segments must have sufficient mobility.

e) Chemical Bonding Theory

It is understandable that chemical bonds across the adhesive substrate’s interface can greatly participate to the level of adhesion between both materials. The formation of chemical bond depends on the reactivity of both adhesive and substrate. The bonding to brass and rubber cured with sulfur, adhesion resulting from the creation of polysulfide bonds. One of the most important adhesion field involving interfacial chemical bonds is the use of adhesion promoter molecules, generally called coupling agents to improve the joint strength between adhesive and substrate. These species are able to react chemically on both side one end with material and other end with polymer, thus creating a chemical bridge at the interface.

f) Theory of Boundary Layers and inter-phases

According to this theory the cohesive strength of a weak boundary layer can always be failure appears to be interfacial. According to this assumption the adhesive energy, is always equal to the cohesive energy of the weaker interfacial layer. This theory is based primarily on probability consideration showing that the fracture should never propagate only along the adhesive-substrate interface and that cohesive failure within the weaker material near the interface is a more favorable event.

Chapter – 5

EXPERIMENTATION

5.1 Experiments for flexible polymeric films

5.1.1 Package yield of film (ASTM-D-4321-99)

It is important to determine the number of packages from the given mass of film. To determine package yield of a film, 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 one gram.

The sample was then weighed accurately and converted it in gram per unit area as follows-

$$\textbf{Package yield or GSM = weight/area (gm/m}^{2}\textbf{)}$$

Or $$\textbf{GSM} = \boldsymbol{\rho} \textbf{. T (gm/m}^{2}\textbf{)}$$

Where ρ is the density of the sample material and T is the thickness of the sample. The average of at least three samples has been reported.

5.1.2 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 particular mixture.

Formamide % (CH_3NO)	**Ethyle cellosolve %** ($C_4H_{10}O_2$)	**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

Note:

i) 100% Water used for 72 dyne/cm wetting tension

ii) Rhodomine -B die can be used to color the solution for easy observations

5.2 Experiments for Adhesive

5.2.1 Solid Content in adhesive

First a clean and dry petridish was weighed and noted it’s weight as W_1. Approximately 2.0 gm of properly mixed adhesive was taken in a clean and dry petty dish and weighed on a balance noted down the weight as W_2, now petridish had kept in a oven at 100^0 C to 110^0 C than for 1-2 hrs and than cooled, after cooling the weight was noted as W_3 again. Keeping the same petridish in oven for 5.0 min and weighted it after cooling there was no change in weight than noted the weight as W_3. The % of solid content was determined as follows: -

$$\textbf{\% Solid contents} = (W_3-W_1)^* \, 100/(W_2-W_1)$$

5.2.2 **Measuring Viscosity using Ford B-4 Cup (Viscometer) (ASTM D1200-94)**

The Ford B-4 cup viscometer was placed on its stand. Allowing the adhesive to stabilize at room temperature a small container was placed under the Ford cup. The cup was filled all the way to the top until a small adhesive overflows into the outer ring, preventing the adhesive from running out of the cup. Stopwatch started and immediately removed the finger. Allowing the adhesive to efflux (run out) into the container below. As soon as the adhesive stream stopped flowing, stop the stopwatch. Recorded time (in seconds) it took for the adhesive to efflux from the cup was reported as *the Viscosity with Ford B-4 Cup* of the adhesive.

5.2.3 Bond strength measurement

a) Sample Preparation

i) Mixing of adhesive

Accurately weighed adhesive and hardener were taken in a 100 ml beaker after that adding 50 ml inert solvent (Ethyl Acetate)was added into the mixture. The mix was then prepared by constant stirring for not less than 2.0 minutes.

ii) Adhesive Application

A hand bar coater (No 4) was used for coating the bare PET film on treated side (>44 dyne/cm). The metalised film (metal side) was laminated with the help of a rubber hand roller by pressing it against the adhesive coated bare PET film. The laminates were then placed into the hot air oven for curing at different time & temperature requirement. The sample laminates were prepared in a way that:

- The pressure applied was approximately same for all the laminates.
- The adhesive deposition was taken 1.5±0.5 GSM.
- During the preparation of laminates air bubbles and creases were avoided.
- Solvent must be removed completely before laminating the films.

c) Curing of laminates

All the laminates were cured in a hot air oven for desired time & temperature. The samples were removed from the oven half an hour before the testing.

d) Sample size for bond strength measurement

The sample was cut from the laminate with the help of a sharp cutter of size 25 mm in width and 250mm in length.

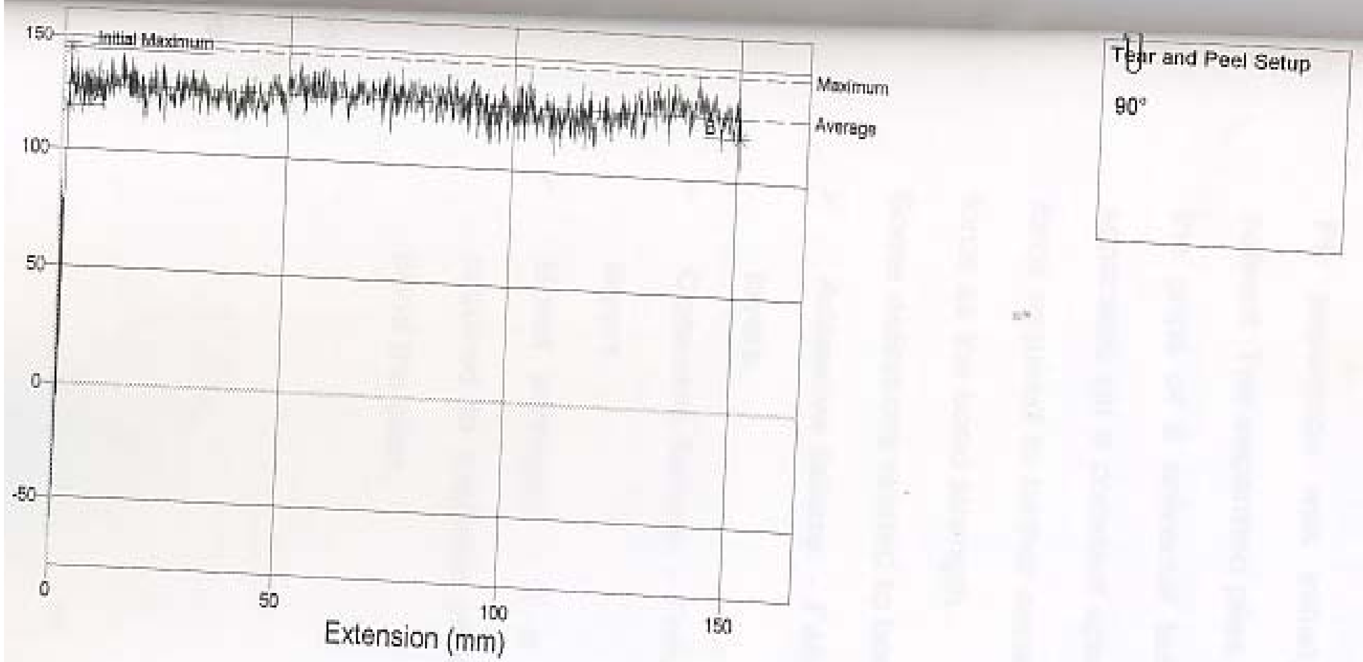


Figure 12

BOND STRENGTH MEASUREMENT GRAPH (TESTED BY U.T.M. LLOYD-LR 5K)

e) Bond strength or ply adhesion of laminates made from flexible materials (ASTM-F-904-98)

Ply separation was initially started mechanically by using a solvent. The separated plies of the test specimen were placed into the grips of a universal testing machine. The grips were than separated (at a constant speed of 250 mm/min) and the average force required to further separate the plies was reported in gram-force as the bond strength.

Some definitions related to bond strength are as follows: -

- **Adhesive failure: -** Failure at the interface of two adjacent layers.
- **Cohesive failure: -** Failure with in one of the two adjacent layers.
- **Bond strength: -** It is the amount of force or energy required to separate plies of material(s) plus the force to bend the plies.

Chapter – 6

RESULT AND DISCUSSION

Table: 1 -Results from the experiments

	Package yield of film (gsm)	Wetting tension (dyne/cm)	Total solid content (%)	Viscosity (sec)
Values	17.12	44	81.19(OH) & 80.07(NCO)	11.6

Table: 2-Bond strength of various laminates prepared by varying hardener ratio, curing time & curing temperature.

S. No.	Adhesive Ratio	Hardener Ratio	Curing Temp. (^{0}C)	Curing time (Hours)	Bond Strength (Gram-force)
1	100	0	20	5	32.2
2	100	0	20	10	45.2
3	100	0	20	15	47.6
4	100	0	20	20	54.7
5	100	0	30	5	36.5
6	100	0	30	10	83.6
7	100	0	30	15	109.4
8	100	0	30	20	113.5
9	100	0	40	5	43.6
10	100	0	40	10	98.7

11	100	0	40	15	122.7
12	100	0	40	20	127.8
13	100	4	20	5	83.5
14	100	4	20	10	119.8
15	100	4	20	15	130.4
16	100	4	20	20	181.1
17	100	4	30	5	116.2
18	100	4	30	10	130.9
19	100	4	30	15	140.6
20	100	4	30	20	197.6
21	100	4	40	5	130.4
22	100	4	40	10	138.6
23	100	4	40	15	154.2
24	100	4	40	20	206.3
25	100	8	20	5	109.6
26	100	8	20	10	145.2
27	100	8	20	15	150.6
28	100	8	20	20	196.6
29	100	8	30	5	119.4
30	100	8	30	10	151.2
31	100	8	30	15	163.7
32	100	8	30	20	206.3
33	100	8	40	5	154.4
34	100	8	40	10	168.3
35	100	8	40	15	174.9
36	100	8	40	20	242.5
37	100	12	20	5	121.6
38	100	12	20	10	152.3
39	100	12	20	15	164.7
40	100	12	20	20	210.3

41	100	12	30	5	130.6
42	100	12	30	10	168.9
43	100	12	30	15	183.3
44	100	12	30	20	250.6
45	100	12	40	5	154.3
46	100	12	40	10	193.3
47	100	12	40	15	204.8
48	100	12	40	20	270.2
49	100	16	20	5	129.9
50	100	16	20	10	168.3
51	100	16	20	15	177.3
52	100	16	20	20	235.7
53	100	16	30	5	140.6
54	100	16	30	10	178.6
55	100	16	30	15	192.7
56	100	16	30	20	284.5
57	100	16	40	5	182.8
58	100	16	40	10	200.2
59	100	16	40	15	230.1
60	100	16	40	20	303.4
61	100	18	20	5	182.1
62	100	18	20	10	185.1
63	100	18	20	15	211.9
64	100	18	20	20	284.9
65	100	18	30	5	196.6
66	100	18	30	10	210.3
67	100	18	30	15	254.6
68	100	18	30	20	324.9
69	100	18	40	5	209.8
70	100	18	40	10	234.7
71	100	18	40	15	267.5

72	100	18	40	20	352.3
73	100	20	20	5	189.5
74	100	20	20	10	192.4
75	100	20	20	15	229.7
76	100	20	20	20	299.2
77	100	20	30	5	214.6
78	100	20	30	10	221.6
79	100	20	30	15	271.3
80	100	20	30	20	348.7
81	100	20	40	5	238.4
82	100	20	40	10	243.2
83	100	20	40	15	286.6
84	100	20	40	20	368.9

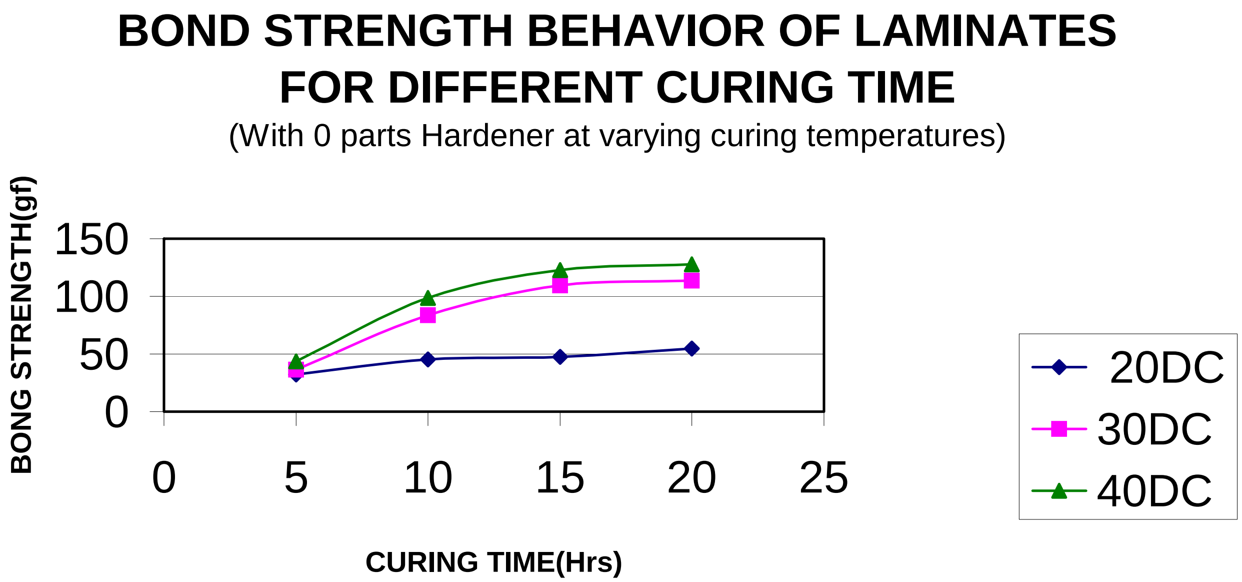
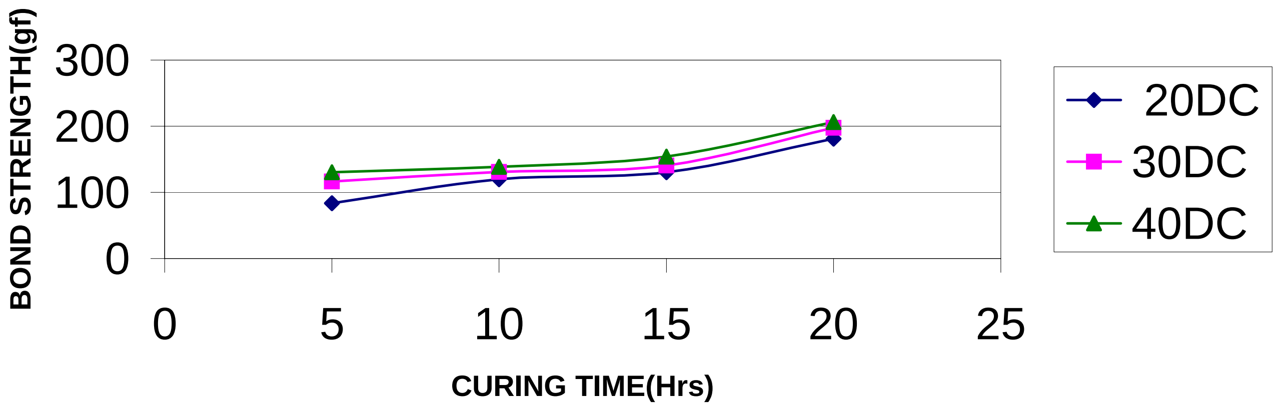

BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME
(With 0 parts Hardener at varying curing temperatures)
BONG STRENGTH(gf)
150
100
50
0
0
5
10
15
20
25
CURING TIME(Hrs)
20DC
30DC
40DC

Figure: 13


BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME

(With 4 parts hardener at varying curing temperatures)

Figure: 14

BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME

(With 8 parts Hardener at varying curing temperatures)

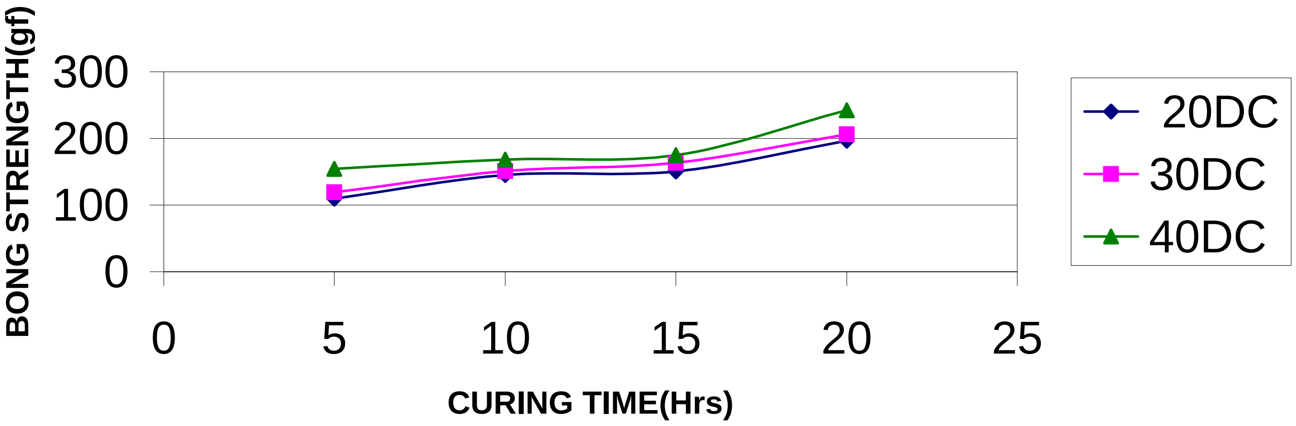
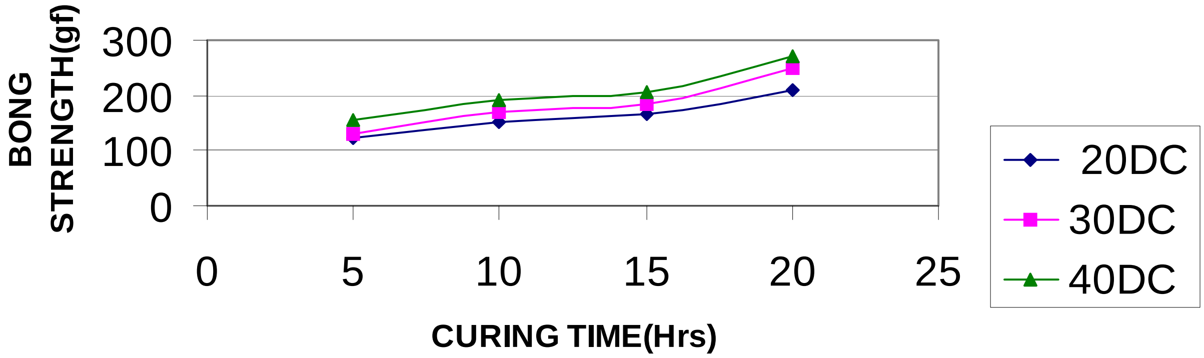
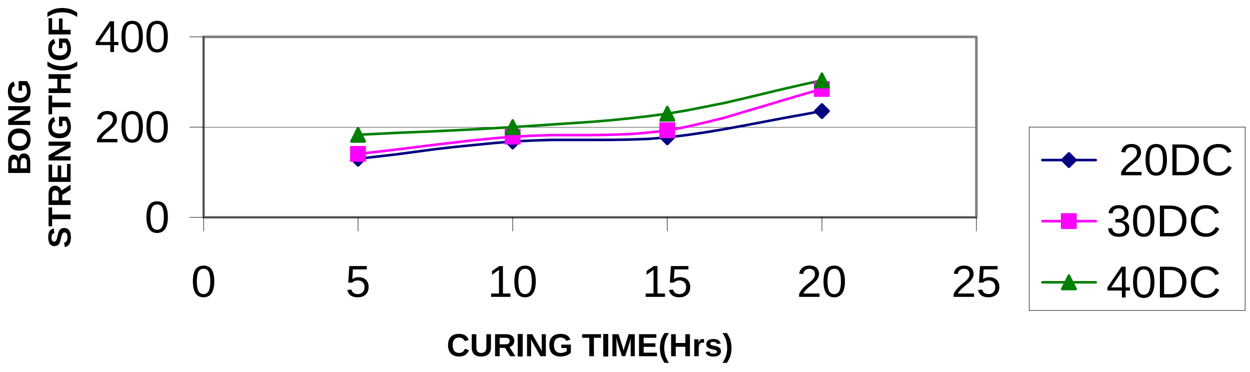


Figure: 15


BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME

(With 12 parts Hardener at varying curing temperatures)

Figure: 16



BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME

(With 16 parts Hardener at varying curing temperatures)

Figure: 17

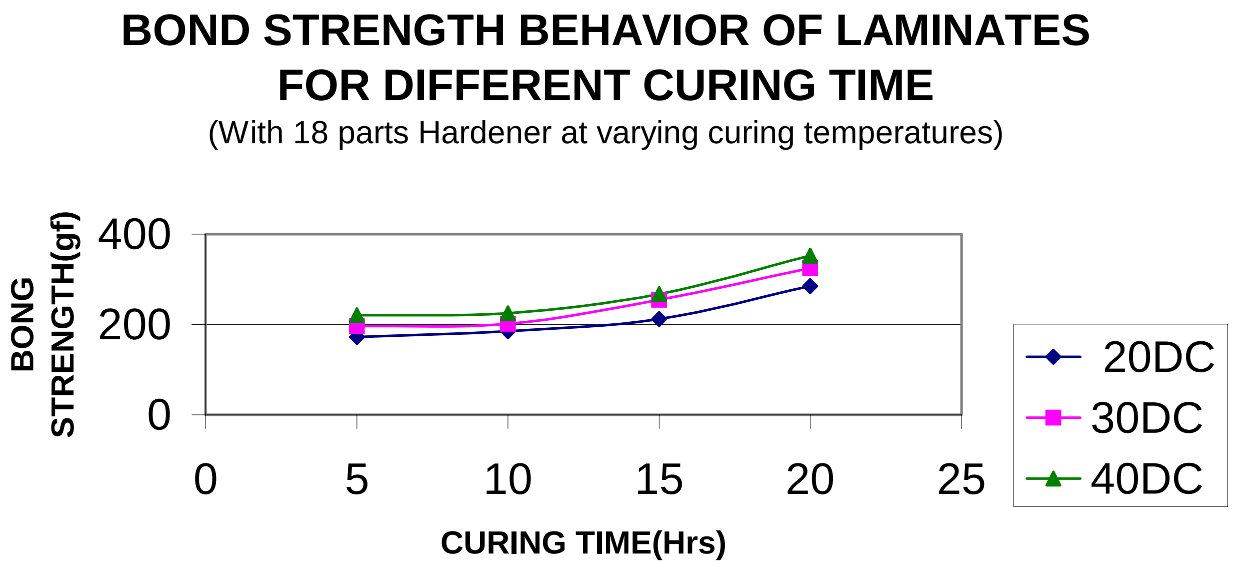
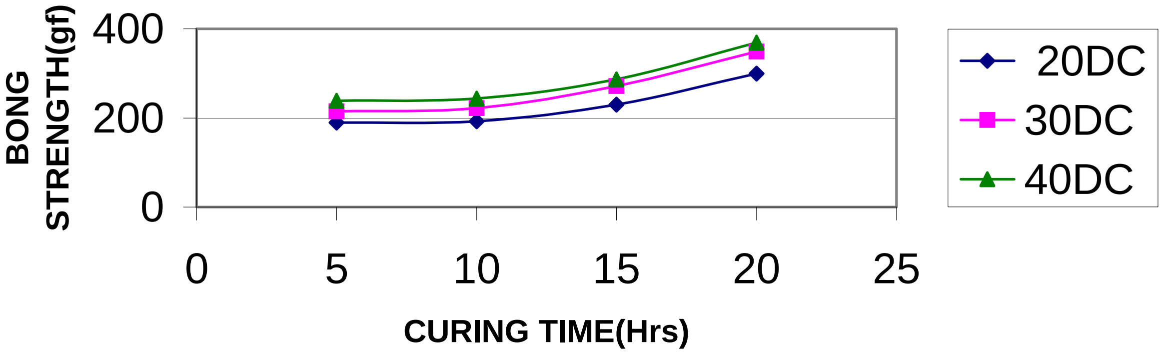

BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME
(With 18 parts Hardener at varying curing temperatures)
BONG STRENGTH(gf)
400
200
0
0
5
10
15
20
25
CURING TIME(Hrs)
20DC
30DC
40DC

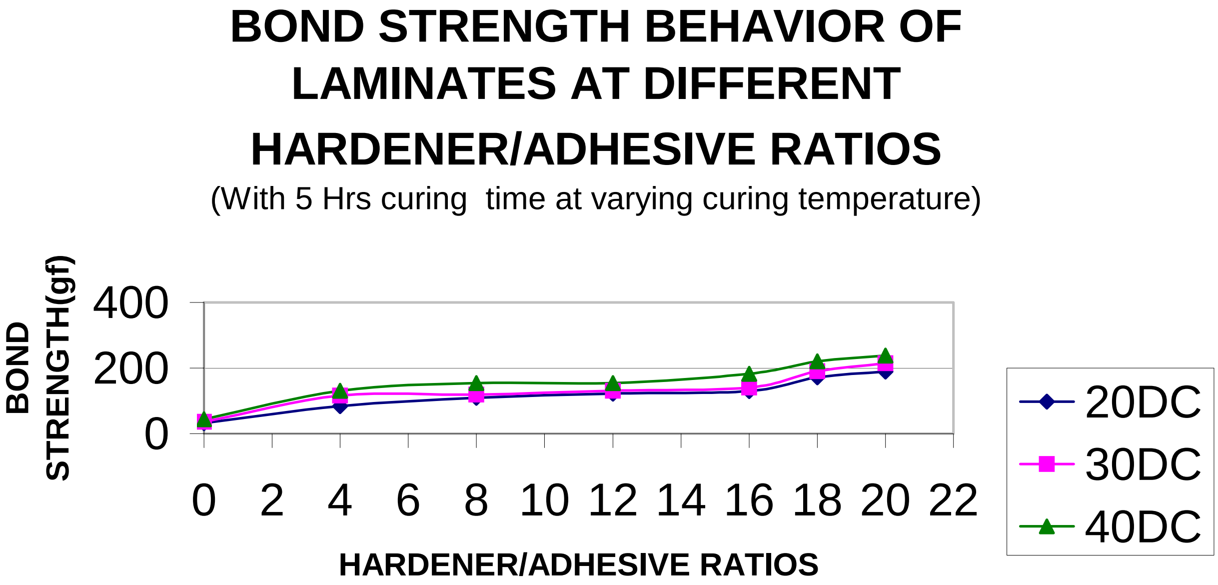
Figure: 18



BOND STRENGTH BEHAVIOR OF LAMINATES FOR DIFFERENT CURING TIME

(With 20 parts Hardener at varying curing temperatures)

Figure: 19



BOND STRENGTH BEHAVIOR OF LAMINATES AT DIFFERENT HARDENER/ADHESIVE RATIOS

(With 5 Hrs curing time at varying curing temperature)

Figure: 20

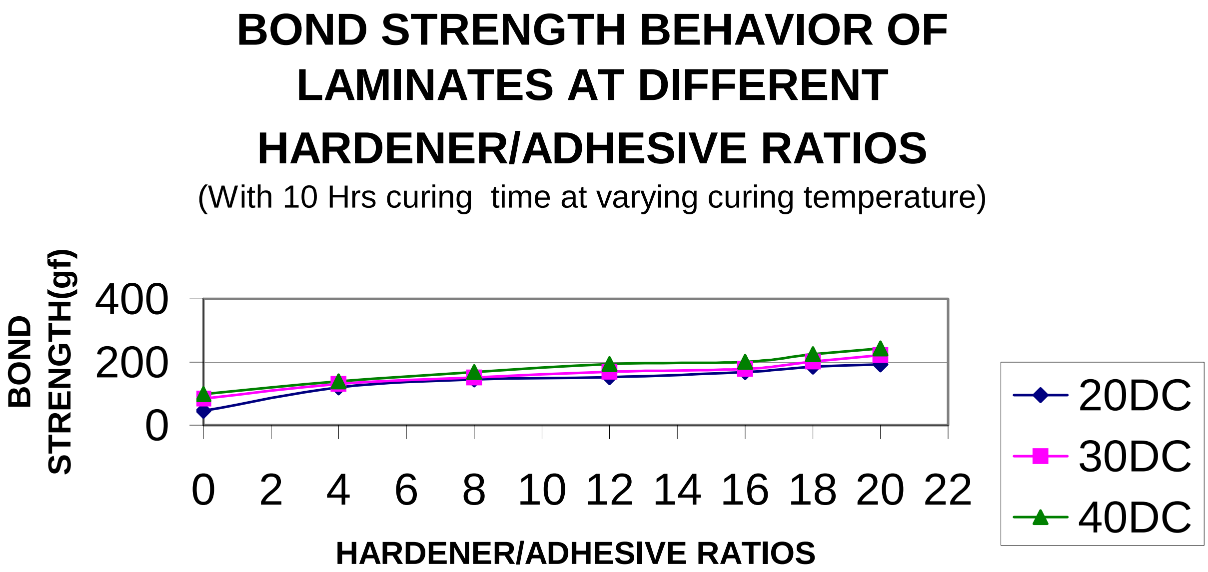

BOND STRENGTH BEHAVIOR OF LAMINATES AT DIFFERENT HARDENER/ADHESIVE RATIOS
(With 10 Hrs curing time at varying curing temperature)
BOND STRENGTH(gf)
400
200
0
0
2
4
6
8
10
12
14
16
18
20
22
HARDENER/ADHESIVE RATIOS
20DC
30DC
40DC

Figure: 21

BOND STRENGTH BEHAVIOR OF LAMINATES AT DIFFERENT HARDENER/ADHESIVE RATIOS

(With 15 Hrs curing time at varying curing temperature)

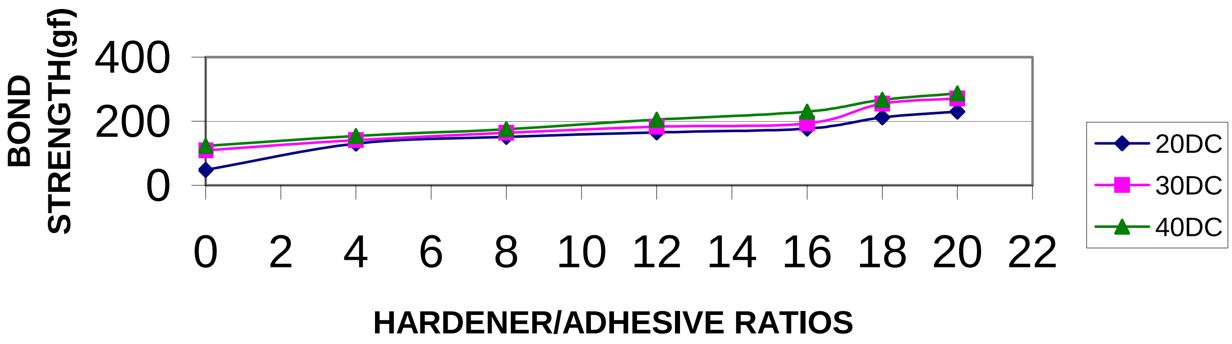
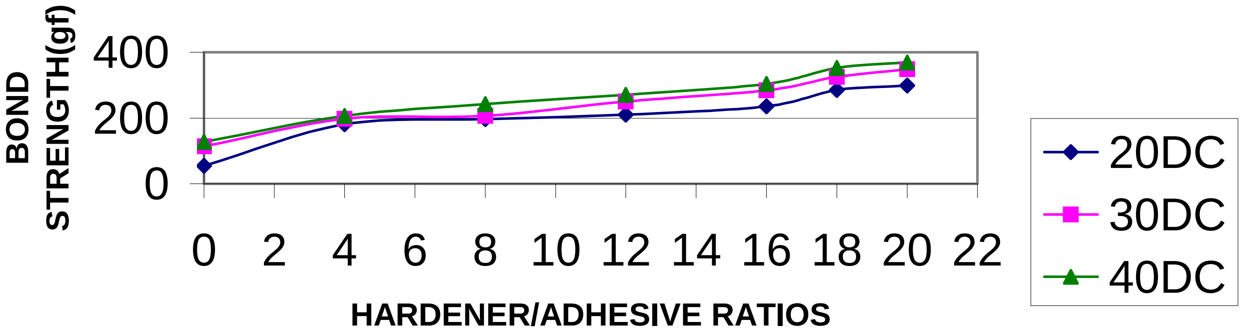


Figure: 22



BOND STRENGTH BEHAVIOR OF LAMINATES AT DIFFERENT HARDENER/ADHESIVE RATIOS

(With 20 Hrs curing time at varying curing temperature)

Figure: 23

6.1 Figure-13 to figure-19 shows the bond strength behavior of laminates at different curing time and temperatures. Curing time was varied from 5, 10, 15 and 20 hours, 20^0C, 30^0C & 40^0C and hardener ratio 0,4,8,12,16,18,20.

6.1.1 As observed from the figure-13 (0 hardener) for all the temperatures, the bond strength is very low at 5 hours curing time. There is a sharp increase in bond strength on increasing the curing time to 15 hours. However this increase is higher for 30^0C and 40^0C temperatures. After 15 hours curing, further increase in curing time has negligible effects on bond strength.

The above observations infer that adhesive can cure without hardener at high temperature and longer curing time. It is also observed that for adhesive curing 15 hours curing time and 30^0C curing temperature is optimal.

6.1.2 In figure-14 to 17, a similar trend is observed; there is a sharp increase in bond strength on increasing curing time from 5 to 10 hours. However, the increase is not significant on increasing curing time from 10 hrs to 15 hrs. Further, increase in curing time to 20 hrs increases the bond strength abruptly. Bond strength is increasing slowly on increasing curing temperature 20^0C to 30^0C. However this increase in bond strength is more effectively shown at curing temperature 40^0C.

From the above results it is inferred that 20 hours curing time and 40^0C curing time is sufficient to obtain considerable bond strength.

Although there is some bond formations at lower curing time i.e. 15 hours & 10 hours, but the bond strength is not significant. This shows that although at 10 hours & a15 hours some cross linking and polymerization take place but 3-D network structure between polymeric chains is formed after 20 hours curing time. Similar trend is observed for curing temperature also. In case of curing temperature at 40^0C 3-D network structure is formed.

6.1.3 Figure-18 & 19 show that an increase in curing time increases from 5 hrs to 10 hrs bond strength increases, but increase in bond strength in very low at all the temperatures. The bond strength increases slowly up to 10 hrs curing time increase is abrupt after 15 hrs curing time. Bond strength also increases significantly on increasing the curing temperature from 20^0C to 40^0C.

Above results infers that 15 hours curing time and 40^0C curing temperature is sufficient to obtain good bond strength.

From the above results, it is observed that on increasing the hardener ratio/concentration beyond 16 parts the cross linking take place at 15 hours curing time, which shows that on increasing the hardener ratio laminate adhesive cures early as compared to lower hardener ratio.

6.2 Figure-20 to 23 shows the bond strength behavior of laminates at different hardener/adhesive ratios and curing temperature. Hardener adhesive ratios was varied from 4 parts per 100 parts of adhesive to 20 parts per 100 parts of adhesive at an increment of 4 parts per 100 parts adhesive. Curing temperature was varied from 20^0C, 30^0C & 40^0C at constant curing time.

6.2.1 Figure-20 to 23 indicate similar trend that is there is a sharp increase in bond strength on increasing the hardener/adhesive ratio from 0 to 4 parts of hardener per 100 parts of adhesive. The further increase in hardener ratio from 4 to 16 parts of hardener per 100 parts of adhesive shows slow but considerable increase in bond strength. There is a sharp increase in bond strength once again on increasing hardener ratio from 16 to 18 parts per 100 parts of adhesive. This increase becomes slow on further increasing the hardener ratio from 18 to 20 parts per 100 parts of adhesive. There is considerable effect on bond strength on increasing curing temperature from 20^0C to 40^0C. Following inference are drawn from the study:

i) Adhesive cures without hardener but may not achieve significant bond strength, which is attributed to the fact that only NCO part get polymerized by taking atmospheric moisture. It is also observed that bond strength is very low in this case, which shows that although polymerization has taken place but 3-D network structure was not formed.

ii) 18 parts hardener per 100 parts of adhesive is sufficient to achieve good bond strength. On increasing the hardener concentration from 16 parts to 18 parts bond strength of laminates increases considerably, but it is observed that on increasing the concentration from 18 to 20 parts there is not significant change in bond strength. This observation concludes that 18 parts hardener is the required optimal hardener concentration for cross-linking.

CONCLUSIONS

- Bond strength increases abruptly on account of 3-D network formation of adhesive molecules due to cross-linking, which is dependent on curing time curing temperature.

- 40^0C curing temperature is optimum for achieving higher bond strength.

- 15 hrs to 20 hrs curing time is optimum for achieving significant bond strength.

- Hardener /adhesive ratio is optimum at 18 parts of hardener per 100 parts of adhesive.

- Bond strength is also observed at 0 parts of hardener per 100 parts of adhesive but that is not considerable.

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