Lab Scale Development of Water-Based Adhesive for Flexible Substrate

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CERTIFICATE

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Dedications

This project is heartedly devoted to our

BELOVED PARENTS

who raised us to the point where we can complete this work as our final year project.

We're pleased to dedicate the whole efforts to our

SUPERVISOR & CO-SUPERVISOR.

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Abstract

The purpose of this study is to develop water-based adhesive for flexible and rigid substrates which have better properties than commercially available solvent based adhesive.

Adhesive is a substance which holds two surfaces together by surface attachment process. Polychloroprene rubber is one of the most versatile and widely used base material for adhesive development. The most common and establish polychloroprene adhesive is the solvent based polychloroprene contact adhesive which has been used commercially since many years. Solvent-based adhesive uses volatile organic compounds (VOC) which poses serious environmental and health hazards. Besides this, the antisocial impact due to the sniffing of solvent-based adhesives has created a worldwide concern for the use of solvent-based adhesives. Therefore, it was necessary to develop water-based adhesive which could serve a purpose. Therefor the theme of this study is to produce water-based adhesives which is cost-effective, environmentally friendly, and have better properties than solvent-based adhesives. In this research, 33% antioxidant dispersion and 50% zinc oxide dispersion are prepared, and ball milled for 24 hours. After 1 day these dispersions are added with water, Polychloroprene latex, alkyl phenolic resin and dispersing agent. Five formulations were being prepared and then applied on sample material such as canvas and leather after three, five, seven and 15 days. Peel strength and solid content test are measured and compared with commercially available solvent based adhesive. Peel strength test depicts higher strength in water based adhesive. It has been noticed that water-based adhesive is better than solvent based adhesive for many applications.

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

1.1 Adhesive

Adhesive is a material which is used to create mechanical connection between two layers. Adhesive is applied on the surface due to which surfaces adhere with each other and remain stable because of strong bonding interaction [1]. Adhesives are used worldwide for many applications such as leather industry, product packaging and assembly. Adhesive mostly has low viscosity and is applied as a liquid. Adhesives flow in substrate surface and may fill the crevices. Adhesive may be either from natural or synthetic, organic or inorganic but most commonly from a polymeric material. Adhesion is a multidisciplinary field that involves physics and chemistry of surface and interfaces as well as the mechanism of deformation and fracture of an adhesive bond. The performance of adhesive depends upon the physical and chemical properties. Besides this nature of the adherent surface and prior surface treatment and primer also contributes to the performance. Thus, there are three factors such as adhesive, adherent and surface which have an impact on the service life of the bonded structure. Adhesives are classified based on origin (i.e. natural or synthetic); adhesion method; starting physical state; by chemical reactivity and polymer type (thermoset or thermoplastic) [2]. The choice of these adhesives depends upon the application method and the material on which it is applied. Some of the other classifications are based on composition are water-based adhesive, solvent-based adhesive or solvent less adhesive. There are four proposed mechanisms of adhesion such as mechanical interlocking, adsorption and surface reaction, inter diffusion, and electronic/ electrostatic attraction theory. The strength of the adhesive bond obtained is determined by destructive testing such as peel strength, tensile lap shear, fatigue, and cleavage tests. These tests are carried out under specific environmental conditions [3].

Adhesive is a material which can join two substrates because of various chemical and physio-chemical mechanism. The application of adhesive between substrate results in strong bond on curing. The three important concepts in adhesives are substrate, adhesion, and cohesion. [4].

1.2 Substrate

A substrate is a material on which adhesive is applied. For example

- If we bond two steel sheets, then the substrate used here is steel. In this case both the substrates are made of same material.
- If we bond steel with Aluminum, then the Al is substrate material. In this case both the substrate is of different material.

1.3 Adhesion

Adhesion refers to the mechanism or forces that keep together the adhesive with substrate. Moreover, adhesion refers to the forces or mechanism that are in boundary layer between the substrate and adhesive itself.

1.4 Cohesion

Cohesion is the mechanism (forces) that holds the adhesive itself. This is illustrated in Figure 1.1.

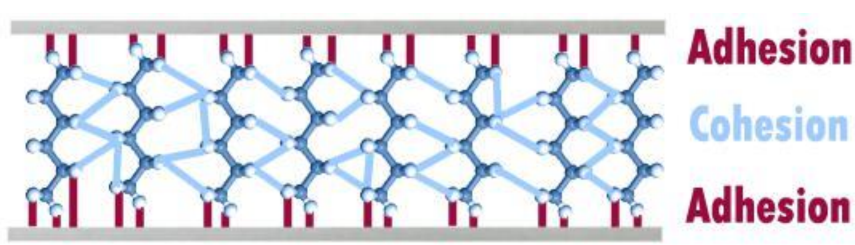

Figure 1.1 The intermolecular forces and chemical bonds are responsible for cohesion and adhesion mechanism [5].

1.5 Theories of Adhesion

Adhesive bonding is the result of various physio-chemical interaction taking place between substrate and adhesive. There is need to understand the processes occurring during adhesion. There are different theories to describe adhesion mechanism such as mechanical linking, electrostatic theory of adhesion, diffusion theory and surface reaction. Adhesive bonding is the result of combination of these mechanisms, but each theory has its role for adhesive system. An important factor in adhesive bonding is the scale at which adhesive and adherend interaction takes place. Table 1.1 shows a rough scale of action of mechanism.

Table 1.1: Theories of Adhesion [3]

Traditional	Recent	Scale of Action
Mechanical Linking	Mechanical Interlocking	Microscopic
Electrostatic	Electrostatic	Macroscopic
Diffusion	Diffusion	Molecular
	Wettability	Molecular
Adsorption/surface reaction	Chemical Bonding	Atomic
	Weak Boundary Layer	Molecular

Source: Book-Adhesive Technology handbook by Sina Ebnesajjad Page (5-10)

1.5.1 Mechanical Theory

Mechanical theory is one of the oldest theories and was presented by Hopkin and McBain in 1925 [4]. This theory is based on assumption that adhesive bond is formed by the dispersion of adhesive into the crevices, pores, voids, and surface irregularities of bonded substrates resulting in mechanical links which can transmit loads. The two adherends are bonded by the penetration of adhesive into the surface of two materials. When mechanical interlocking of adherent and adhesive occurs then adhesive bond is formed. According to this theory a stronger bond is formed between porous and abraded surfaces as compared to smooth surfaces however this theory failed because strong bond could also be formed between smooth surface. Figure 1.1 shows the

adhesion mechanism of mechanical theory. Wake [4] proposed a simple equation to estimate the joint strength G as follows:

G=(constant)*(mechanical key component) *(interfacial interaction Component)

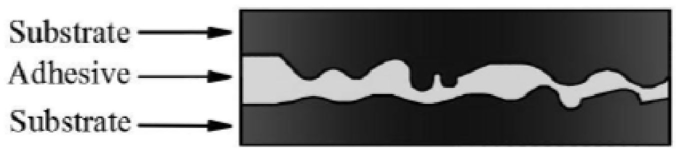

Fig 1.2 - Mechanism of mechanical theory

By improving surface morphology and physiochemical properties, adhesion mechanism is increased between adhesive and substrate. Important criticism on mechanical interlocking theory is that, increase in adhesion cannot be always attributed to mechanical keying mechanism, but because of energy loss in the surface roughness.

1.5.2 Electrostatic Theory

This theory is since adhesion take place between adherend and adhesive due to electrostatic force of attraction. Theoretically electron transfer takes place between the adhesive and substrate surface because of unlike electronic band structures. Adhesive forces are formed due to the electrical double layer. These forces act as resistance to separation. This theory gains support from the fact that electrical discharges have been observed when an adhesive is peeled from a substrate.

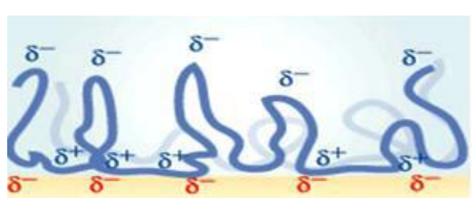

Fig 1.3: Mechanism of Electrostatic Theory [4]

1.5.3 Diffusion Theory

Voyutsi [5] proposed diffusion theory as adhesion being result of macromolecules inter diffusion. According to this theory, adhesive and substrate should be polymeric in nature and have mutual compatibility with each other. Figure 1.3 shows adhesion between two polymeric materials due to inter diffusion of macromolecules at the interface. This model states that contact between two macromolecules is the result of diffusion of molecules of super facial layers. The average penetration depth in case of adhesion between two identical polymers is given by Fick's' Law as:

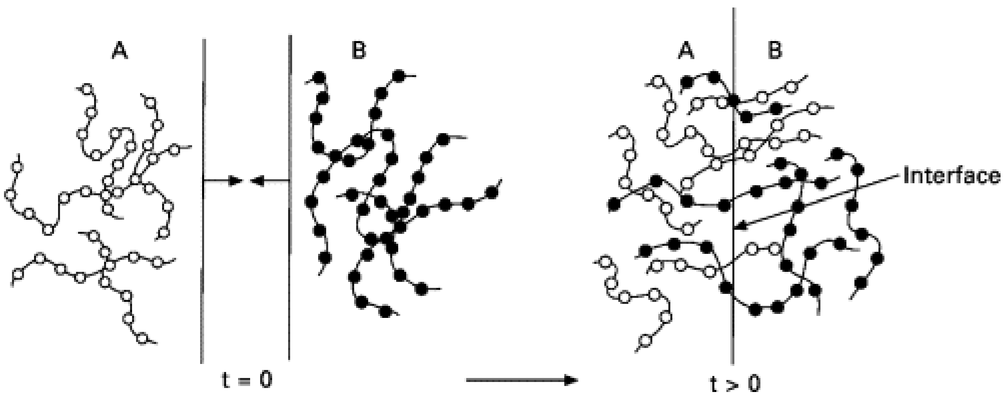

Fig 1.4 - Mechanism of Diffusion theory [4]

$$x \propto \exp\left(-\frac{E}{2RT}\right) t^{\frac{1}{2}}$$

eq. 1

where R is molar gas constant, t is contact time, E is diffusion activation energy, T is temperature. This model has limitation of diffusion of well-matched polymers and welding of thermoplastics. For metal to polymer adhesion, diffusion occurs across the interface between metal and polymer when few metals are dispersed onto polymeric surfaces.

1.5.4 Model of Weak Boundary Layer

Adhesive bond Interface has several properties that are different from bulk materials. So, it was thought that failure of adhesive bond will not occur at interface of adhesive and substrate rather because of formation of weak boundary layer will be the cause of bond failure. Bikerman [4] stated that while determining the level of adhesion, a weak boundary layer (WBL) cohesive strength must be considered even if failure is propagated at interface. From this assumption, cohesive energy Gc (WBL) is equal to adhesion energy. The seven classes of WBL considered by Bikerman as illustrated in Figure 1.5.

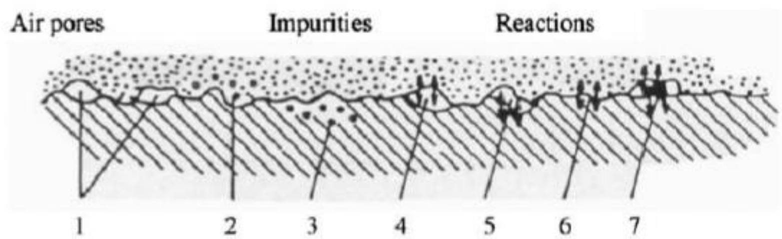

Fig 1.5: Mechanism of weak boundary layer with seven Bikerman classes: 1. Air pores, 2 and 3. Impurities at surface; 4 to 7. Reactions between components and medium [4].

1.5.5 Adsorption Theory

This is most acceptable model proposed by Sharpe and Schonhorn. According to this theory the intermolecular and interatomic forces established between molecules and atoms of adhesive and substrates after they are brought into contact are responsible for adhesion. This theory is also called thermodynamic theory (identified as wettability theory). The two substrates in contact should have good wettability for good adhesion. Contact angle which is form of calculating adhesion by physical adsorption, and bonds formed by this adhesion are very weak but are enough to make strong bonds. To develop a successful adhesive, it must have the property of wetting the surfaces to be bonded. Many low surface tension materials have been developed after this theory. Epoxy is good example of this theory, as it wets steel providing a strong bond however, it doesn't wet PP, olefins PE, PTFE and doesn't form any bond.

1.6 Types of Adhesive

Adhesives classified based on different medium are,

1.6.1 Solvent Based Adhesive

- Natural Rubber
- Polychloroprene
- Styrene butadiene rubber
- Butyl Rubber
- Epoxy rubber
- Nitril rubber
- Polyurethane
- Polyacrylates
- PVC solvent cement
- Cynoacrylates

1.6.2 Water Based Adhesive

- Polyvinyl acetate
- Polyvinyl alcohol
- Starch/Dextrin
- Sodium Silicate
- Lignin
- Sodium carboxymethylcellulose

Adhesives are also classified based on structural and non-structural adhesive. Beside this, adhesive can be classified according to mechanical performance in tensile, shear and peel on exposure to various service temperature [7].

1.6.3 Solvent less Adhesive

1.6.3.1 Hot Melt

Adhesives are also classified based on bonding temperature. This classification is based on the temperature required by adhesive to establish a bond. Thus, based on setting temperature adhesive are classified as,

- Cold setting which have temperature below 20 ^{0}C
- Hot setting has a temperature above 100^{0}C
- Room temperature setting which is in range of 20^{0}C- 30^{0}C
- Intermediate temperature setting works in between 31^{0}C-100^{0}C

1.7 Water-based adhesives

Water based adhesives are generally formulated from either Natural polymers or Synthetic polymers.

Sources for Natural Polymer are Vegetables (e.g. starches and dextrins), Protein sources (e.g. fish, casein, soybean, blood, milk albumen) and animals (e.g. hides or bones). Sources for Synthetic Polymers are from polymers that include Cellulose ethers, carboxymethylcellulose, Polyvinyl Alcohol, methycellulose and polyvinylpyrrolidone.

These adhesives can be supplied as solutions or as dry powders that have to be mixed before application with water. When water is lost by evaporating or absorbing the substratum from the bonding line, the strength of the adhesive is achieved. This condition requires that at least one substrate be permeable for the application of these adhesives [8]. Where neither substrate is permeable, the adhesive can be thinly wiped or dried by a wet brush or roller or sprayed with water, then activate the adhesive.

It allows the system to be tacky enough in very short time period and the water content in the glue line is so minimal, that it does not require a porous substrate.

Since the polymers are water soluble, these bonds are of limited water and moisture resistance [4]. Some plant glues and casein glues have the special property that the basic raw material in atmospheric water is insoluble and must be dissolved in alkaline materials (sodium hydroxide or ammonia). Such adhesives have better humidity tolerance relative to water-soluble adhesives. Most adhesives dependent on water are perishable and so do not no possess longer possible storage capability.

1.7.1 Limitations on the Usage of Organic Solvents in Adhesives

Following are the limitations on the usage of organic solvents in adhesives:

- Environmental pollution (ozone depletion, smog).
- Health Hazards to industrial workers.
- Restrictions on volatile organic compound (VOC) content in adhesives.
- Heavy taxes on TCE and phasing out the production of TCE.
- An antisocial impact due to sniffing of solvent based adhesives.
- Labelling requirements for products containing or made with ozone depletes.
- Restriction and phasing out manufacturing solvents with a high VOC content.

1.7.2 Alternatives to Solvent Based Adhesives

In view of the environmental issues and legal pressures leading to changes in the way industry must operate, the alternatives that are available are discussed below. The first possibility is to utilize a hundred percent solids adhesive such as hot melt. This choice would require significant investment in new equipment and acceptance of lower line speeds. The second alternative is to switch to water-based adhesives. Slow drying rate of water relative to solvents would result in low line speed. This could be eliminated, by using a drying chamber with a moderate investment in drying equipment.

1.7.3 Need for Development of a Water Based Polychloroprene Adhesive

Environmental concerns and governments imposing restrictions on the use of solvent with high VOC contents will lead to restrictions on producing solvent-based adhesives in the future. The primary goal in developing a water-based adhesive is to produce an environment-friendly and a cost-efficient adhesion, matching the properties such as contact ability and bond strength, of solvent based adhesives which have been in market for years.

1.8 Water Based Chloroprene Adhesive

A water-based adhesive can be defined as an adhesive that is apparently dry to the touch and which will adhere itself instantaneously upon contact. These adhesives rely on the auto adhesive characteristics of the dried polymer. This is often enhanced by the resin modification; the classical example is natural rubber. However, natural rubber has not very good properties as required for modern day adhesive therefore alternative elastomers are used and polychloroprene is therefore most widely used for this purpose.

Polychloroprene contact based adhesives are mainly solvent based but with increasing environmental pressures and concerns over solvent toxicity, there is a need for the alternative solution. Water based contact adhesives is a suitable alternative as WBA is eco-friendly and beside this, polychloroprene is available in latex form for water-based formulation. Originally, these lattices were anionically stabilized but latterly carboxylated versions employing nonionic stabilizers have become available. Certain soft acrylic latices have also been suggested as the base for water-based contact base adhesive. However, it is regarded that their performance fall somewhat short of solvent based counterparts and this has led to the development of new formulations for water borne contact adhesives based on polychloroprene latex and vinyl acrylic copolymer.

1.8.1 Mechanism of Water Based Polychloroprene Adhesive

In the polychloroprene latex adhesive, the polymer is solid and fully crystallized to begin with. It is dispersed in water together with the tackifier resin, zinc oxide and stabilizers. As the water evaporates after application of the adhesive, a phase inversion occurs so that the solid particles from a continuous phase and water becomes the dispersed phase. Once the water is completely removed, a solid compact film is formed. During this period of coalescence, the polymer and resin particles develop some tack. The level contributed by the polymer depends on its gel level and the time depends on the crystallization rate of polychloroprene.

After bonding crystallization and cross linking of the polymer occur in the same way as that of the solvent based adhesive. Difference in properties are due to the coarser dispersion of ingredients and the residual surfactants in the adhesive. This is illustrated in the figure 1.6. Different polymer types are available to provide the right balance of properties for a given application; high gel level gives good hot bond strength but relatively little tack; low gel level gives high tack and allows heat reactivation of the adhesive film. The use of co-polymers can produce interesting combinations of properties.

Therefore, it is possible to achieve a performance comparable to solvent based adhesives with water-based adhesives formulated very specifically for a given application, however solvent based adhesives are much more versatile.

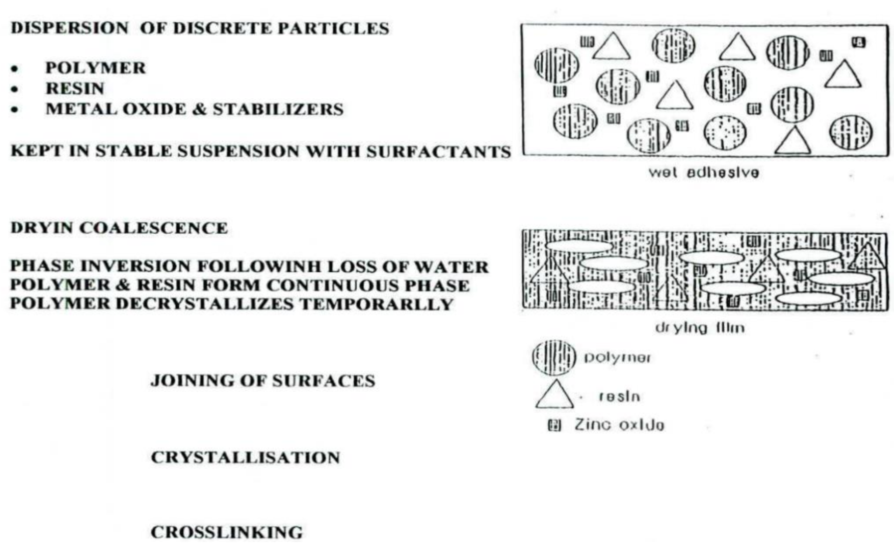

Fig 1.6: Mechanism of Water Based Polychloroprene Adhesive [6]

1.9 Types of Water Based Adhesives

Water based adhesives have four main types:

- Latex cements.
- Vegetable glues
- Resin cements
- Animal / protein glues

The individual adhesives are designed exclusively for their own specific purposes. The resulting bond will appear as either a rigid resin or a more film-like finish depending on which adhesive you use, but they are all solvent-free, making it safe to work in close quarters and non-ventilated areas [9].

The types of water-based adhesives are described in detail below:

1.9.1 Vegetables

Adhesives based on vegetables are one of the most popular types of water-based adhesives. Such adhesives have a foundation of starch and a more porous finish. Therefore, they are usually used for bookbinding in the paper industry [10]. Such adhesives are very durable if they are used with materials such as paper but are more vulnerable to failure if they are exposed to water.

1.9.2 Animal/Protein Glues

Animal or protein sticks are produced from either organs that are directly processed to create hot sticks or proteins that are present in animal milk and used to make casein sticks. While hot animal glue mostly is for fast-fixed / quick-set applications, casein glue is used mostly in the beer and wine industry, which is resistant to water and moisture.

1.9.3 Resin Cement/Adhesive

Ethylene vinyl acetate, vinyl acetate, and acrylic resin emulsion polymers are the primary components in resin water-based adhesives. Emulsions are liquid blends that cannot be combined. Water is combined with the ethylene vinyl acetate (EVA) and polymers polyvinyl acetate (PVA) for a smooth combination of white liquids in order to produce these types of water-based adhesives. However, after applying and drying, the adhesive creates a clear, flexible bond which is also used for wood and plastic. It is also used for paper binding.

1.9.4 Latex Cements

Latex cements are made of emulsified elastomers or rubber. Latex binding must be applied on the ground surface like polymer adhesives and can either be drained into a strong bond or, depending on the formulation, into a weak, flexible bond [11]. The primary use for bonding stamps, envelopes, cloth, leather and wood is this type of water-based adhesive.

1.10 Why Water Based Adhesives?

The technology of Water-based adhesive is an adhesive formulation which considers safety of the environment. There are no volatile organic compounds (VOCs) in it so there is no harm to the people or the environment with water-based adhesives [12]. When the water within the formulation evaporates or is absorbed into the substrate, the water-based adhesive forms a bond between two substrates, leaving the adhesive behind. This makes it a popular choice to bind porous substrates [13].
The most convincing reasons for opting water-based adhesives are as follows;

- **Cost**: Solvents are more costly than water, so solvent based adhesion is always more costly than water-based adhesion in terms of production and processing.
- **Bond consistency**: water-based bonding materials have a consistency equal or greater than solvents over a long period of time [14].
- **Uniformity**: Consistency is easier to maintain and uniformly spread with a wet bonding adhesive. Water-based adhesives often contribute to the rapid extraction of adhesive from the product and reduce the risk of obstructions.

- **Friendly to the environment**: A water-based formulation, because of its low VOC content, is safe and environmentally friendly.
- **Versatility**: A variety of substrates, including natural and synthetic textiles, glass, silverware, paper and cardboard, can be effectively used with wet bond adhesives.
- **Odor**: Water based adhesives have very low odor.
- **Consumer safety**: Water based adhesives are free of solvents thus safety of user is assured.
- **Good heat resistant** as compared to solvent based adhesives.
- **High tack ability** making it able to bear high loads and shear stresses.
- **Good water resistant**: Although water exposure is dangerous for the bonding, but water-based adhesives have well resistant to water until a specific limit of exposure is reached [15].

1.11 Ingredients of Water Based Adhesives

In formulation of Water based adhesives, following materials were used:

- Polychloroprene latex
- Resin
- Antioxidant
- Metal oxide
- Dispersing Agent
- Wetting agent
- Gum Arabic
- Water

The above-mentioned ingredients are discussed in detail below;

1.11.1 Polychloroprene Latex

It is used as a base elastomer in adhesive production due to its good mechanical strength and high resistance to ozone and weather conditions. It also shows other remarkable properties as well such as:

- Moderate oil and fuel resistance
- Good chemical resistance
- Low flammability
- Good aging resistance

1.11.2 Resin

Resins are synthetic polymers obtained from the condensation reaction of phenol with formaldehyde. The figure below shows chemical structure of Phenolic resin [16].

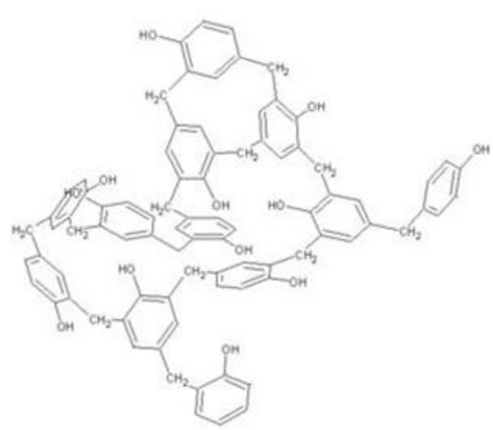

Fig. 1.7: Structure of Alkyl Phenolic Resin [16]

Resin enhances the peel strength, impact strength and most important of all, it improves the tack time of the adhesive bond. It also improves creep and fatigue resistance. So, the choice of resin is of great interest [17]. Most used resins are hydrocarbon resin, epoxy resin, phenolic resin, carboxylate resins etc.

1.11.3 Antioxidant

It is responsible for protecting the polymer (latex) from oxidation as exposure to oxygen causes generation of free radicals that eventually react with polymer and reduce its mechanical properties. So, Antioxidant scavenges these free radicals and form inactive products with those radical [17].

1.11.4 Metal Oxides

They play a very important in adhesion as they act as acid acceptor. With the aging of adhesive, small amount of HCl is released which must be absorbed as it causes degradation of the substrate. This prevention becomes very crucial when the substrate being used is highly sensitive acid material such as cotton.

Usually, Zinc oxide and Magnesium oxide are used as acid acceptor [18]. They can be used separately or as a combination as well.

Metal oxide also serves as a curing agent in adhesives. A curing agent can increase heat resistance of most adhesives. ZnO has high efficiency as a curing agent, thus leading to increased strength as adhesive bond is aging. Whereas Magnesium oxide is used for high temperature applications in higher levels (20-40) phr.

1.11.5 Dispersing agent

They are specialized chemicals that wet out the surface of particles in dispersion process. This ensures that the particles being dispersed do not re-combine to form agglomerates. Dispersing agents prevent re-agglomeration either by electrostatic repulsion or steric hindrance. Dispersing agent consists of a polar head that is attached to the particle being dispersed and a polymer chain that stable and compatible in the media of dispersion [10].

1.11.7 Gum Arabic

It is used in small quantities as it has great properties. Gum Arabic is extracted from Acacia tree and is bio-friendly, but the main reason of its use is the binding power it possess. When the adhesive dries, leaving all the moisture out of its system, gum Arabic play an important role in binding the particles together and thickening them as well. It improves cohesive properties of the adhesives [20].

1.11.8 Water

Water is the backbone of adhesive being discussed as it is incorporated in every ingredient.

Dispersion of antioxidant and dispersing agents is done in aqueous solution. After application of adhesive, it is important to remove the water content as much as possible for initiation of adhesion [21].

1.12 Applications of Water Based Adhesives

Water based adhesives are becoming very popular due to their non-toxic nature and enhanced compatibility. Some of the major applications are discussed below;

1. Water based adhesives have great capacity to be used in self – sealing envelopes of the type where two lips are coated with adhesives and can adhere to each other when activated [22]. Storage life is better than conventional adhesives that lose their bonding strength in less than a year. Similarly, they can also be used in self-sticking notepads.
2. Adhesives for bubble wrap-film are in demand now a days that must be friendly as well. Adhesive based on water are on the best choice for this purpose. When coated on the bubble film and stacked on the glass surface, they don't leave residues when peeled away [23]. This makes It a good choice for use in protection of architectural glass, picture frame glass, screens, stainless steel metal surfaces refrigerator doors, transportation and storage purposes as well.
3. Water based adhesives offer high strength for tapes application such as films, removable applications and masking.
4. Water based adhesives are used in paper-to-paper application. In paper industry, for binding purposes this adhesive is a preferred choice due to high and quick tack ability and eco-friendly nature. [15]
5. Due to the strong bond capacity and relatively low cost, water-based adhesives are mostly used in wood industry to do almost everything from applying veneers to securing joints. [13]
6. Another major application of water-based adhesive is its remarkable use in shoe

industry. For assembly of leather, canvas, toe lasting, folding, preparing uppers and jointing uppers with counters, water-based adhesives are used. [24]

7. It has application in textile industry for apparel, home and commercial usage.
8. Electronic industry uses water-based adhesives for potting, over-molding and masking purposes.
9. A huge application of water-based adhesives is in automotive industry for interior and exterior body parts, sensors and more.

Chapter 2

Literature Review

2.1 Introduction

The focus of this chapter is on the working mechanism for the water-based adhesives while discussing their major advantages and disadvantages. It will introduce the basic composition and percentage contribution of each component. After the formulations of adhesives, the methods to apply them will be discussed along with the pros and cons. Several techniques for the better mixing of the constituents will be discussed.

2.2 Formulation of Water Based Adhesives

Water based adhesives contain several constituents with the basic polychloroprene latex or acrylic latex, antioxidant, dispersing agent, metallic oxide, fillers and adhesion promoters [25]. These are used in various percentages in order to obtain the correct water based adhesive mixture. The purpose of each of the component has already been discussed in the previous chapter.

The mixtures are prepared by using the various methods. Paradinitroso Benzene millbase was formulated by the addition of 100 parts of dinitrosobenzene 5 parts of surfactant Polywet Z1766; 5 parts of an acid scavenger such as a lead salt; 40 parts of carbon black Sterling NS; 0.07 parts of sodium hydroxide; 1 part of a dispersant aid such as Marasperse 5 CBOS-3 and sufficient deionized water to bring the millbase to 45% total solids content. Following table illustrate one of the formulations of water-based adhesive based on Patent Number 5036122 [26].

Table 2.1: Formulation Of Water-Based Adhesive Based On Dichlorobutadiene Latex

Ingredients	Batch A	Batch B	Batch C	Batch D	Batch E	Batch F	Batch G
Dichlorobuta-diene Latex	87	87	87	87	87	87	87
Para-dinitroso-benzene millbase	149	149	149	149	149	149	149
M-20 Polymalei-meide	0	2.5	5	7.5	10	12.5	15
Sufficient Water	40	40	40	40	40	40	40

The percentages of these components may vary in order to obtain the correct properties according to the application. Such as, for industrial purpose, the higher adhesion is required so the percentage of adhesion promoters is enhanced. Addition of1% adhesion promoters can increase the adhesive strength up to 5%.

Another formulation of water-based adhesive is shown in the following table:

Table 2.2: Composition of Water-Based Adhesive In Phr

Ingredient	**Parts per hundred rubber (phr)**
Dispercoll K-8464	35.4
Neorez R-9630	25.3

Neorez R-9320	11.9
Uniplex 108	150
Airflex320	9.2
Desmondur DA	5.0

The above-mentioned components are written as the commercial names as per available in the market. They are mixed in this proportion to obtain a higher strength for the industrial applications.

2.3 Advantages & Limitations of Adhesives

Depending upon the application, adhesives have a number of advantages over the mechanical joining. Besides the advantages, when we discuss about the strength and efficiency of the joints, it has many shortcomings as compared to the mechanical joints. Therefore, the application decides whether to use the adhesives for joining or the mechanical fastening would work better [27].

2.3.1 Mechanical Advantages

Adhesives are given more importance in the field of joining due to following main advantages:

- Reduced weight
- No stress concentration at a single point
- Uniform load distribution
- Joints with higher fatigue resistance and many more [28].

Considering the aircraft industry, the joining of similar or dissimilar substrates using rivets or nut & bolts can cause an increase in the weight of aircraft as well as reduced efficiency due to hole in the substrate for bolt application. It also damages the structure of composites or metal substrates by penetration. The reduction in structural efficiency is caused along with the reduced fatigue strength occurs. For the above facts, the adhesive joining is utilized preferably instead of riveting or mechanical fastening.

2.3.2 Mechanical Limitations of Adhesives

The use of adhesive is limited by the nature of their performance degradation over the period. Their effectiveness is reduced as time passes due to shorter high strength life span. The degradation is more pronounced when the temperature is increased above 150^0C. The crosslinking between the bulk adhesive layers can also lead to a fire or burn [29].

There comes another limitation when selecting the proper adhesive for the substrate. Certain substrates don't allow the adhesion with the adhesives. So, they need an extra step of surface preparation through surface coatings. It can increase the cost also.

2.3.3 Design Advantages

For adhesives application, there is no need of special design of the components. The adhesives allow to the joint flexibility and size variation. There is no limitation regarding the size of substrates. Also, the shape limitation is removed. The thin metallic or composite sheets can be easily joined without any problem as produced by the mechanical fastening [30].

2.3.4 Limitations regarding design

The shelf life of the adhesives is to be predicted with the same design and environmental conditions in which the assembly is going to serve the purpose. Hence, the prototype designed shall be in the similar working conditions to avoid sudden failure [31].

2.3.5 Advantages in packing and production

The adhesives are easy to apply and store in the vessels or in the form of glue. It helps them to be able to use them on spot and ready mixture is available. The cements require a specific deal of work and labor costs which make them expensive. But cements can serve for longer times [9]. Moreover, the production of adhesives is cheaper and faster as compared to the cement and other compounds.

2.3.6 Packing Limitations

The sticking of adhesives with the walls of its container is to be overcome with special inner wall coatings. The life span of adhesives is subjected to the storage conditions which require special measurements such as avoiding the heat contact, temperature variations, impurity considerations etc. During the production, the sticky components wastage is higher. It can lead to reduced production efficiency.

2.4 Correct choice of adhesive

Adhesives have many uses in footwear, automotive, construction, design and aerospace industries. Cost, Bond strength, Easy application, Toxic effects on the surroundings, environmentally friendly, Adhesive's nature are the basic factors for selecting an adhesive for specific purpose.

The application of adhesive to get the bond strength depends not only on the ingredients it has, but also on the type of materials which are to be bound using it. It also depends on the nature of surface either it is rough or smooth. Also, the environment in which it is to be used, affects the bond strength.

Adhesive bond is dependent on tensile, compressive and shear stresses to which different adhesives responds differently. Seek advice from a specialist before selecting an adhesive.

2.4.1 Efficient joint configuration

Efficient joint configuration can confer strength to the joint. Proper bond design with effective adhesive bond can build powerful bond and can fulfil the requirements more accurately.

2.4.2 Preparation of surface

To adhere the surfaces of two substrates strongly, preparation of surfaces is essential. Surface treatment makes the bond strong and long lasting. Research shows that there is a direct relation between surface treatment and service expectancy of adhesive joint. Contaminations like dirt, grease and oil on the surfaces of substrates are removed by surface treatment for better adhering of the surfaces [11]. Some of the methods for surface preparation are given below:

1. Cleaning by solvent
2. Chemical treatment
3. Mechanical treatment
4. Etching by using chemical
5. Plasma treatment
6. Corona treatment
7. Primers

2.4.2.1 Cleaning by solvent

Cleaning by solvent is the removal of oil from the surface of substrate by using the organic solvent. No change occurs in physical and chemical properties of the surface. Toluene, methyl alkyl alcohol, methyl ethyl ketone solvents are used for the cleaning purpose. In vapor degreasing, surface is rubbed with hot vapors. The purpose of this process is to remove oil, grease and waxes from the surface of substrates. For vapor degreasing, specific solvent and equipment is essential. Trichloroethylene and perchloroethylene are the commonly used solvents for vapor degreasing. Vapor degreasers are usually available with built-in transducers in solvent tank. After vapor degreasing, the surface is plunged into ultrasonic scrubber complying by solvent spray [32].

2.4.2.2 Chemical treatment

In this process, surfaces are cleaned by using chemicals. Alterations are made in chemicals nature to increase the adhesion properties of the surfaces. Chemical treatment is used for polymeric substrates where the cleaning of solvent may not be able to work. Caustics, chelates and acids are the agents which are widely used in this process.

2.4.2.3 Mechanical treatment

The process of removal of rust, scale or weld splatter from the surface by using the tools like sandpaper, wire brushes and scraper is called the mechanical treatment. But in huge areas these tools are slow to use. One drawback of abrasion process is, particles of the debris are filtered on the abraded surface. Surface contamination, abrasive and surface of material generates these particles [30]. Removal of these particles is necessary before the application of adhesive. Brush or cloth or compressed air can be used for this purpose. As abrasion causes the surface to be rough, we have to clean the surface before the application of an adhesive for joining. To apply the solvent, cloth is utilized. This cloth is cleaned after short intervals in order to decrease the contamination arising from the contaminated cloth.

2.4.2.4 Chemical etching

The desired surface which is to be etched is immersed into the chemical solution. This solution enhances the activity of surface by dissolving containments or by transforming it. This makes it more favorable for bonding. After this process, the surface is placed in water bath followed by high temperature drying. The treatment of plastics surfaces for bonding is done by this method. Sometimes cleaning is done before chemical etching. The chemical etchant Sulfuric acid-dichromate is commonly used for surface treatment. The composition of this solution is determined by tough rules. The strength of adhesive bond after testing determines the exact formulation [14]. However, some cavities may occur on the surface but the improvement in higher bond strength and wettability is observed in numerous cases.

2.4.2.5 Plasma treatment

The composition of charged particles, atoms, molecules and radicals is called the Plasma. Due to high reactivity of plasma it is used to improve the surfaces. Surfaces become more hard, rough and conductive to adhesion due to plasma. The exposure time or contact time is different for different surfaces. For example, the reaction time for polyethylene is 9 seconds whereas for PTFE it can take several minutes for surface preparation. Plasma treatment forms the bond which are two to four times stronger than the bonds formed by chemical and mechanical treatment [15].

2.4.2.6 Corona treatment

Plasma generated at atmospheric pressure is called corona discharge. Electric field accelerates the particles like ions and electrons produced by the corona discharge. These accelerated particles are used to clean the surface and circulates polar groups to substrates surfaces. Instant bonding is made because the corona discharge effects are short lived. This technique is used for bonding the polyolefin films.

2.4.2.7 Primers

Primers work as bonding layer between adhesive and substrate. They improve the adhesion property that is why they are also named as adhesion promoters. Primers and adhesives both have same polymer chemistry. Primer increase wettability and gives protection to surface in dry conditions. Primers and adhesives are chemically same in dry conditions. Primers change adherent surface to polymer surface which is more appropriate in adhesive technology than inorganic surfaces [16]. Primer layer has low thickness, but it is sufficiently good to refer the phenolic resin primer as epoxy resin adhesive which has best adhesion property. In aircraft industry Anti-corrosive primers are used and they have different structure than normal primers. Epoxy resins, resole, hardening agent and functional components like strontium chromates are included in the composition of these primers. As the primers can change the surface properties therefore primer must be selected carefully.

2.4.2.8 Contact angle

Contact angle is used to find surface free energy, surface tension and changes which occur on surface layer when surface is reshaped. Various factors such as surface porosity, physical and chemical properties of adhesive and solid surface, contamination and rigidity of surface, temperature and dampness can affect the contact angle.

2.6 Dispensing Method

The application of adhesive on substrates for bonding is called dispensing method. Several types of dispensing methods are being practiced including Pin transfer, spray application, brushing and troweling, nozzle dispensing method, roller transfer etc. These methods are described below.

2.6.1 Brushing

The most commonly used method for the application of adhesive on substrates is brushing. When adhesive is to be applied on certain specified areas and the adherent possess intricate geometry. Stiff brushes give a relatively better layering of the adhesive. The major disadvantage of using brushes is the uneven adhesive application which causes differences in adhesive film thickness at different regions.

2.6.2 Spraying

This method is used to apply adhesive on substrates having large areas. The advantage of this method is even adhesive layering and high production rates. The parameters such as viscosity and content of the adhesive must be efficiently controlled for even layering. The equipment used resembles that of a spray paint apparatus. The adjustments and variance in the spray paint equipment can result in adhesive application on different sorts of substrate designs and areas. Safety precautions for using this kind of apparatus must be strictly followed. The use of solvent based adhesives can be hazardous for human health. Proper ventilation should be provided for safe usage [17].

2.6.3 Roller Coating

The technique used to apply adhesives to flat sheets and films is called roller coating. This method involves the progressive transfer of adhesive from a storage tank to different rollers and then finally applied to the substrate. Uniform coating of adhesive and high production rates can be achieved. If multiple adhesive coats are to be applied, the time lapse between the progressive layers must be properly controlled. If the next coating is applied after a long time, it will result in lifting of pre-applied layers. If the coatings are applied too fast; bubbling, sagging and blistering may result.

2.6.4 Knife coating

In this method, the substrate sheet passes under an adjustable knife blade and the deposition of adhesive occurs simultaneously through the blade. The distance between the substrate and the knife blade tip is the thickness of the adhesive film.

2.6.5 Flowing/ Nozzle dispensing method

This technique uses a nozzle or hollow brush for adhesive deposition. If nozzle is used for application, it is called flow gun while if brush is used, it is known as flow brush. For the substrates having irregular surfaces, liquid adhesive can be applied effectively with this technique [18]. This method has a higher productivity and even layer thickness in comparison to other methods such as brushing. The adhesive is swept smoothly with a brush in one single stroke.

Different nozzle dispensing methods are described below:

2.6.6 Squeeze Bottle

This technique involves the feeding of adhesive by squeezing or inverting a bottle. The amount of adhesive depositing is difficult to control in this process due to gravity effects.

2.6.7 Pressure Pump

A pressurized syringe system is used in this process for adhesive deposition. The adhesive is deposited over the substrate by operating an air button while the flow of adhesive is controlled by an air nozzle.

2.6.8 Jet Dispensing

In this process, cyclic deposition of adhesive is achieved by a spring-driven pin which pushes the adhesive though a nozzle. The pin is elevated in through air pressure in the adhesive reservoir and then forces the adhesive into the nozzle by force of the spring.

2.6.9 Silk Screening/ Stencil printing

In this process, the adhesive is applied to different regions of the substrate manually. This technique is suitable for adhesives having a low viscosity so that they can be easily and evenly spread onto the substrate surface with the help of a cloth. The disadvantage to this method is that it can only be used for thin film deposition. This method is not suitable for fast-drying and gluey adhesives.

2.6.10 Spatulas, trowels and knives

Hand tools for the application of adhesive are termed as spatulas. Spatulas are categorized as knives and trowels. The equipment has notched edges. The spacing between the adjacent notches and notch depth in knives and trowels allows for controlling the quantity of the adhesive. Blades should be kept perpendicular to the surface of the substrate. The notch shape must be kept square. An even, uninterrupted and unbroken film can be achieved by use of closely spaced and round notches, if the adhesive used has a higher liquid content.

Chapter 3

Experimental Procedure

3.1 Introduction

This chapter deals with the experimental procedure which is followed during the lab work. Experiments are performed for the water-based adhesives synthesizing using the various steps. These steps are the formulation and then preparing the samples of leather and canvas for tests. The test procedures are discussed with the details of apparatus being utilized.

3.2 Materials

Following materials were used in the formulation of water based adhesive.

- Polychloroprene Latex
- Alkyl Phenolic Resin
- Sodium Silicate
- Zinc Oxide
- Setalmol BL
- Gum Arabic
- Water
- Vulknox SKF
- Wettem 9938

All material was supplied by local industry and chemicals were commercial grade having 80-90% purity.

3.3 Formulation

Formulation is based on wide trial of experiments. Maximum strength is obtained by adding the optimum amount of material during the experiment. Polychloroprene Latex is the main ingredient of water based adhesive. The strength of water-based adhesive is obtained due to the evaporation of water [19]. Therefore, the formulation is being calculated and performed in the laboratory in order to get the optimized results. The procedure was repeated by varying the percentage of alkyl phenolic resin. The calculations are in phr which is Parts per Hundred rubber. The strength is varied by the contents added and the time of mixing, curing and drying time. The results are varied in an increasing manner to follow the industrial standards.

Table 3.1: Water-based Polychoroprene Adhesive Formulation

Sr. No	Chemicals	Grams
1	Polychloroprene Latex	714
2	Alkyl Phenolic Resin	178
3	Sodium Silicate	5
4	Gum Arabic	60
5	ZnO	71
6	Wettem 9938	4
7	Setalmol BL	7
8	Water	171
9	Vulknox SKF	29

3.4 Method of Production of Adhesive

Water based adhesive is produced in different stages. At first ZnO and antioxidant dispersion is ball milled for 24 hours and then they are mixed to obtain a solution of water based adhesive. This solution is cured for 2 hrs and they are applied on the sample. During the first stage we must make ZnO dispersion by using following composition [20].

Table 3.2: Formulation of ZnO 50% dispersion

Ingredients	**Amount (Grams)**
Zinc Oxide	100
Dispersing agent (Setalmol BL 10% aqueous solution)	30
Gum Arabic- 10 % Aqueous solution with 0.5 parts biocide (Proxal GXL/zinc pyrithione/Sodium petachlorophenate,)	30 (29.5 aqueous sol+0.5 biocide)
Sodium silicate (10 % aqueous solution)	5
Water	35

During the second stage Antioxidant dispersion is added in final solution by using the composition given below.

Table 3.3: Formulation of Antioxidant 33% dispersion

Ingredients	**Amount (Grams)**
Antioxidant (Vulknox SKF)	100
Dispersing agent (Setalmol BL 10% aqueous solution)	30
Gum Arabic- 10 % Aqueous solution with 0.5 parts biocide (Proxal GXL)	30 (29.5 aqueous sol+0.5 biocide)
Wetting agent (Wettem 9938)	4
Water	136

During the final stage these dispersions are added to form water based adhesive.

Table 3.4: Formulation of Water-Based Adhesive

Ingredients	Parts per hundred Rubber (phr)
Polychloroprene Latex	100
Dispersing agent	1
ZnO	10
Antioxidant	4
Alkyl Phenolic Resin	25

3.5 Apparatus Used During the Experiments

For the formulation and preparation of adhesives, several equipment is used in the laboratories [21]. The list and use of basic apparatus are listed below:

1. Roller Mill
2. Magnetic Stirrer
3. Adhesive Mixer

3.5.1 Roller Mill

Roller mill consists of a motor and 2 rollers adjusted side by side. The bottle in which the dispersion is to be made is filled with the ingredients. It is tightly closed and then put horizontally on the rollers of roller mill. The distance between the rollers is so adjusted in order to fit the bottle in for proper rotation. The speed (rpm) is adjusted from the knobs present on the side of roller mill. The rpm can be 35rpm to 1000rpm.

Roller mill is used for the uniform mixing, dissolution of particles and milling of powders. In case of adhesive formulation, the roller mill is used for the dispersion formation of ZnO and additives as well as for the antioxidant dispersion. These are used in the later stages of adhesive formation [22].

Fig 3.1: Roller Mill [22]

3.5.2 Magnetic Stirrer

Magnetic stirrer is an apparatus which is used for the thorough mixing of the solution contents. It is used for the adhesive mixing in a beaker. The apparatus consists of a magnetic rotor in the bottom and a magnetic rod of various sizes is available, which is added in the beaker. As the rotor rotates, the magnetic rod in beaker also rotates. Eventually, uniform mixing of solution is achieved [23].

Fig 3.2: Magnetic Stirrer [23]

3.5.3 Adhesive Mixer

The adhesive mixer consists of various parts. These are listed below:

- Closed Vessel
- Heating element

- Impeller
- Temperature sensor
- Temperature and rotation controller
- Insulation

3.6 Procedure

The procedure followed is divided into three stages for the water based adhesive formation.

3.6.1 Stage 1: Preparation of ZnO Dispersion

In the first stage, the ZnO dispersion is to be prepared. For this purpose, the calculations are carried out as discussed earlier in the table. Various solutions are prepared and then mixed using roller mill at low rpm. The milling is carried out at varying intervals and then tested for the resulting peel strength.

3.6.2 Stage 2: Preparation of Antioxidant Dispersion

In the second stage, antioxidant named Vulknox is mixed with various solutions which are performed. These are also mixed using roller mill to produce uniform dispersion. The amounts of different reagents are calculated using the table.

3.6.3 Stage 3: Synthesizing the Water Based Adhesive

First of all, polychloroprene latex is added in the mixer. Then, ZnO dispersion, antioxidant dispersion, dispersing agent and water are added in the latex. The mixer is then turned on to get the uniform mixing at room temperature which is 25 Degree Celsius [24]. The mixing is carried out for 15 to 20 minutes. Pale yellowish adhesive solution is obtained.

3.7 Sample Preparation

In order to test the adhesive peel strength, sample preparation is carried out. The substrates used for the testing purpose are leather and canvas.

3.7.1 Standard followed

The standard followed for the strength measurement is ASTM standard D903 (2017).

3.7.2 Leather Samples

Sample dimensions are given in the figure:

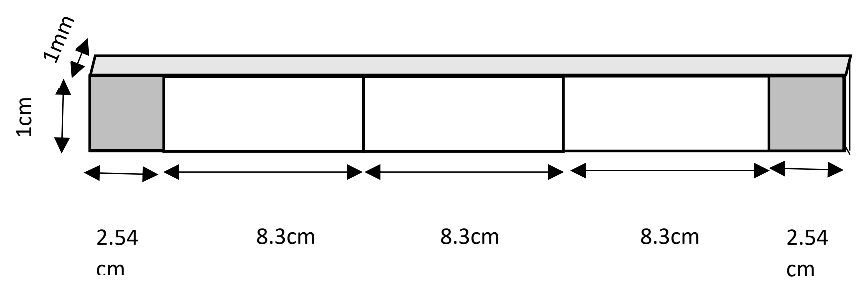

Fig 3.3: Sample Dimensions for Peel Test

The 1cm section is for the grip in universal testing machine UTM. The sample dimensions are cut according to the ASTM Standard D903. Usually 5 samples are tested and then, average is taken for the peel strength.

3.7.3 Canvas Samples

Canvas samples are also cut from the bundle in the dimensions as described above.

3.7.4 Applying Adhesive

The adhesive layer is applied using brush and 5 layers are applied one after the other with 2 minutes drying time for each layer.

3.7.5 Drying Time

Drying time for the adhesives i.e. curing is kept varying to get the optimized results of the peel strength samples. The drying time is given 1 day, 3 days, 5 days and 7 days.

3.8 Peel Test

For many purposes, adhesive resistance is measured. Some bonds have been designed to be used that must not break (e.g. construction materials), some have been designed to allow the separation in normal use (e.g. foil cover), and some have been designed to be re-sealed again and again (e.g. re-sealing bag and bandage).

Tensile tests, peel tests, shear tests or compression tests can be used to measure adhesion bond strength, but peel tests are most appropriate for flexible substrate tests. Peel experiments are used to measure localized stress tolerance in flexible substrates [25]. As a rule of thumb, peel strength depends on the bond thickness of adhesive especially the elastomer present into it. As the bond thickness increases, the load is distributed to larger areas thus bond strength increases.

Peel test is done on universal tester. The tester captures every data point corresponding to the applied load and draws a curve on the basis of these data points. The smoothness of the curve represents the uniformity of applied adhesives over the surface [26].

There are two configurations for peel test based on the angle of force applied for peeling.

1. Angles that are, > 0 degree and < 180 degrees
2. 180 degree

We have used the 180-degree configuration with the Shimadzu Universal testing machine. A steel plate is used as a support for fixture of samples (leather and canvas).

The following diagram shows the schematic of the configurations;

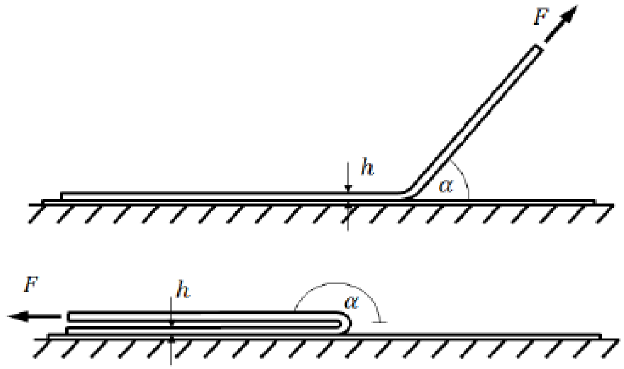

Figure 3.4 - Schematic of Configuration

Our interest is in the second configuration in which angle α is 180 degrees and force F is applied in the pointed direction. The peeling starts from the point of bent and proceeds in the direction of force F.

The advantage of using Shimadzu is that it can also be used for shear strength, applied coating pull-off and tensile strength measurements as well [25].

Peel test can be conducted by different types of methods that are illustrated with the diagram below;

Figure 3.5 - Methods of Peel Test

3.8.1 Purpose of Peel Strength

The main purpose of peel test is that it provides data about bond strength of adhesive along a curved path. The adhesive strength can also be referred to as "stickiness" [27]. This stickiness is the source of resistance that is provided the applied force for peeling. The estimated strength by this test provides insight on the material's capability and whether more processing is required or not for strength enhancement.

3.8.2 Test method approaches

There are two general approaches for peel test depending on the nature of separation,

1. Static-Mass Approach: In this method, two adhered surfaces are separated by gravity acting on the mass.
2. Machine method: In this method, machine is used to apply force thus separating the adhered surfaces. We have used this approach for conducting our tests.

These tests are applied under some specific conditions such as a measured force enough to break the bonds, the rate at which force is applied and layer of reasonable thickness at adhered surfaces.

The result is maximum force required to break the adhered bond between the surfaces [28].

3.9 Determination of Solid Content (%)

Another essential test is to measure the total solid content in the prepared adhesive. The % solid content is the mass of total usable adhesive per Kg. In water-based adhesives, moisture is dried off after curing and this mandatory of adhesion properties. Water is there to maintain the viscosity and thus increasing the adhesive setting time as well. So solid content should be high for high peel strength [29]. But too much solid content means great increase in viscosity and this the peel strength decreases and material becomes more brittle.

3.9.1 Test Method

The total solid content is obtained from the calculation of adhesive mass before and after drying.
The loss in mass shows that some of the material is evaporated and the material left is all solid [30].

If M1 is the mass of initial (Wet) sample and M2 is the mass of sample when dried completely,

$$\boldsymbol{Dry\ Solid\ Content} = \frac{(M_2 * 100)}{M_1} \qquad \textbf{eq. 2}$$

Chapter 4

Results & Discussion

4.1 Introduction

In this chapter the test results of strength of adhesive (Bond strength) are illustrated by Pull-off method or Peel test. Effects of Resin content and crosslinking agents are also discussed.

4.2 Peel Test Result

Peel test were performed on the leather and canvas samples as described in experimental methodology. For characterization of adhesion between materials, peeling force is a very important property to observe. Peeling force is defined as the required force that is applied to separate the adhesive film and substrate [31].

4.3 Effect of Resin Content

Resin is considered to be a versatile commodity in many industries because of its high quality of adhesive properties. It is of great importance that which resin is to be used as it affects the whole adhesive system. It offers heat and chemical resistance, which makes it an ideal product for everyone who needs a high pressure holding system. It is used at a major scale for adhesive purposes, one of the most common uses of (Alkyl Phenolic) resin. The strong characteristics of this resin make structural and engineering adhesives possible.

The major effects of Alkyl Phenolic content in adhesive formulations are;

1. Provides low initial viscosity;

   In adhesive preparation, viscosity is a very important factor as it affects the mixing capability of the system. When the fluid has low viscosity, the atoms and molecules can move relatively easily and the additive can form contacts with these moveable molecules (stirred) throughout the fluid system.

So at first, low viscosity is desired so that the ingredients and dispersions can be mixed in the adhesive system easily.

2. Viscosity-stability;

   Along with initial viscosity, Alkyl Phenolic resin also support in optimizing the original viscosity of the system that it will possess throughout its storage life. This is just like modifying the setting time of concrete according to the requirements. So, Alkyl phenolic resin is partially responsible for setting time of adhesive by maintaining a stabilized viscosity throughout.

3. Good Heat Resistance;

   Alkyl phenolic resin imparts good heat resistance properties in the adhesive which is a very desirable requirement. As the adhesive may be applied at hot surfaces or where there is heat involved even at occasion. This heat can be detrimental to adhesive strength and holding capability. Alkyl phenolic resin helps in maintaining good structural properties even at higher temperatures.

Although all above mentioned properties are required in the adhesive system but these property aren't linearly related to resin content. There is a specific range of Resin content in which these properties occur and show peak performance but after that, they begin to deteriorate so we have optimized a specific value after experimentation that is explained below.

Figure 4.1& 4.2 below shows the effect of changing resin content on the average peel strength of leather to leather (Fig 4.1) and canvas to canvas (Fig 4.2) samples with different curing periods. First sample was composed with 25% resin content and second sample was composed with 30% resin content. Both samples are illustrated in graph showing that peel strength of adhesive increases as we increase the resin content.

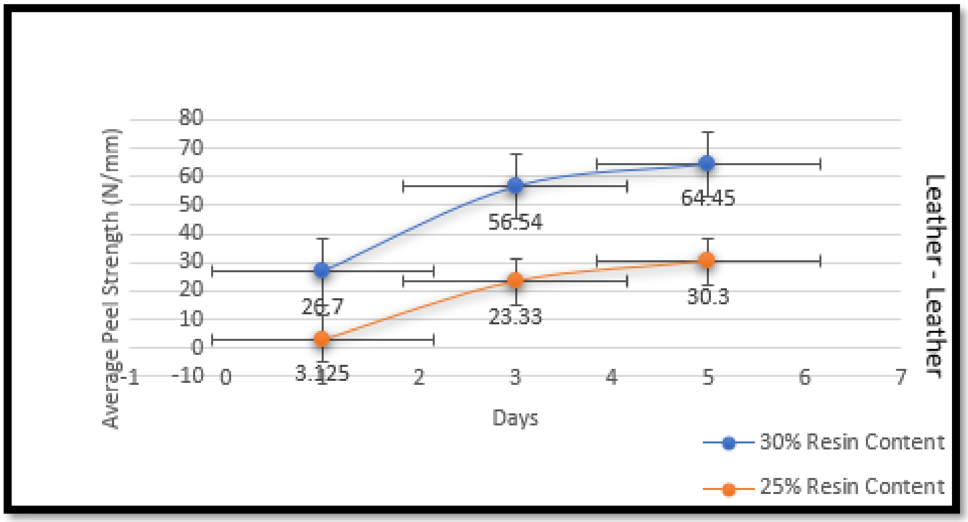

Fig 4.1: Effect of Resin Content on Peel Strength of Leather Samples

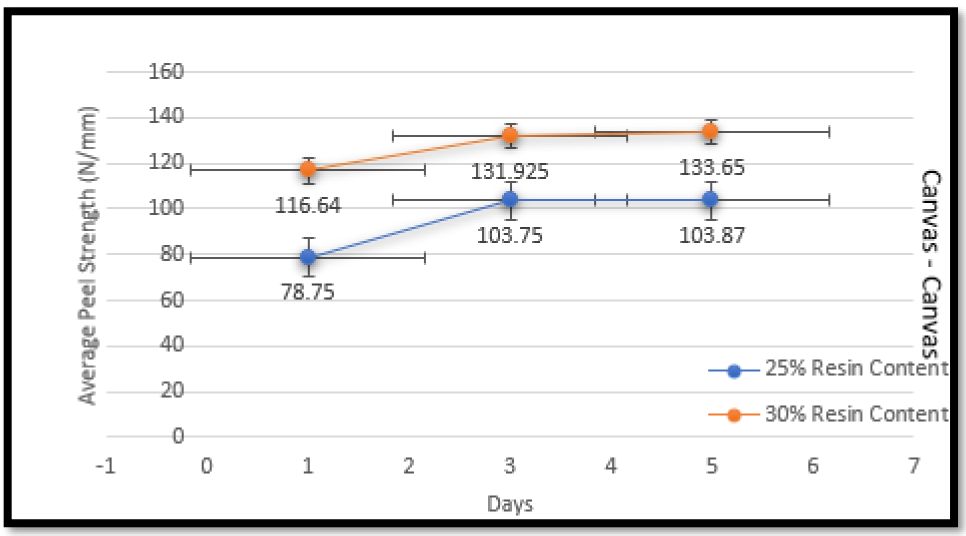

Fig 4.2: Effect of Resin Content on Peel Strength of Canvas Samples

As clear in the results, the peel strength for both type of samples (Leather – Leather and Canvas – Canvas) increases with increase of in resin content but up to a certain limit only. For both samples, the maximum attainable increase is shown at day 5 curing period. This limit is interpreted in a way that excess of resin content after a limit actually compromises the flexibility and reduces the "tack" of adhesive system thus hindering the absorption of impact, lowering the cohesive property and resulting in relatively brittle cracks that cause the adhesive film to break at even lower strength when resin content is higher than 50% or 100phr. That's why the 30% value is the optimized value for our composed system.

4.4 Effect of Crosslinking Agents

Crosslinking means the formation of chemical links between molecules thus increasing the structure strength. Cross linking is usually the result of unwanted free radical degradation of metal oxides but when controlled with specific amounts and forming dispersion as we did in this experiment, it provides high physical properties such as heat resistance and durability that are very important long term properties of any adhesive. [33]

But excess of these agents is not good for peel strength as clearly illustrated in the Fig 4.1 & 4.2. As the content of crosslinking agent is increased, the peel strength of adhesive start to diminish. The reason being that at higher concentrations of crosslinking agents the flexibility of system (adhesive layer) is compromised. Similarly, using high molecular weight crosslinking agents will cause a decrease in shear strength of adhesive.

Another fact is that at higher concentrations of these agents when the viscosity is increased, the wettability of adhesive is also utterly degraded. To overcome these scenarios, a precisely low and optimized amount of crosslinking agent (ZnO) is used.

Metal oxide (ZnO) not only provides crosslinking but it also serves as Acid Acceptor. As the adhesive film ages with time after its application, HCl is released from this film that causes degradation over time. This released HCl must be re-absorbed by the adhesive so that it doesn't degrade. For this purpose, ZnO works just fine as an acid acceptor and absorbed HCl back into the system. This is a very useful property when applying adhesive in acidic zones. [34]

ZnO also serves the purpose of curing agent as well. It is very effective in increasing the strength as the bond line of adhesive film ages with time. This also prevents alienation of system by some external element through these bond lines.

Another secondary function that ZnO serves is that it often reacts with the alkyl phenolic resin and forms a metal resinate (infusible), that further helps in increasing heat resistance of over all system [34].

MgO is also an option as an effective crosslinking agent but as it has to be used in higher quantities as compared to ZnO, it is less preferred as to keep adhesive more clear.

4.5 Effect of aging period on Peel Strength

It is essential for a good adhesive to have good peel strength so that it can resist mechanical forces which act on it. Moreover, it also important to study the endurance of this adhesive to withstand the exposed conditions. One of these conditions is the time period for which adhesive has been kept drying also known as "Curing" or "Aging".

The developed adhesive is cured under organic sun light for different intervals (1, 3 and 5 days) and the Peel strength test had been performed after these intervals. This required preparation of several samples for both leather to leather and canvas to canvas substrate. All this data was recorded and compiled to generate the following graph explained previously as well.

It can be observed that as the curing days are increased the Peel strength of adhesive film and substrate keeps on increasing until a point where the strength doesn't differ that much and starts giving a linearity trend in the graph. This happens after 4th day for both leathers to leather and canvas to canvas samples.

4.6 Determination of Solids' Content

In adhesive formulation, there are some volatile components present that are if not added on purpose may be still present as a by-product of any reaction taking place.

During curing these components are also removed from the system along with water and thus linkage becomes better. So, the solid content helps in determining the total content of these component integrated in the formulated adhesive [32].

The procedure for this test consists of weighing samples before and after drying. Sample is prepared and weight is measured instantly and then the samples is kept for drying. Drying at room temperature or in oven both are viable options as this adhesive was tested in both ways.

Table 4.1: Resin Content vs. Solids' Content

Resin Content (%)	**% Solids' Content**
25	42
30	48

Conclusion

In this project, we have developed a composition of Water based adhesives and tested in the lab conditions. The strength of synthesized adhesives is tested and modified using various percentage of resin. With increasing percentage of resin, the strength is increased. Overall, peel strength testing is used for quantification of strength of adhesives. Also, increase in solid content percentage has increased the strength of Water based adhesives.

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