Development of High Strength Adhesive for Bonding Metallic Substrates

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2019

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Regn No: NUST2016NSE04-00000171859

This thesis is submitted as a partial fulfillment of the requirement for the degree of

MS in Nano Science and Engineering

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April, 2019

Dedication

This thesis is dedicated to my beloved parents who have been source of inspiration and strength for me

Acknowledgement

Praise is due to **ALLAH** whose worth cannot be described by speakers, whose bounties cannot be counted by calculators, whom the height of intellectual courage cannot appreciate, and the diving's of understanding cannot reach; He for whose description no limit has been laid down, no eulogy exists, no time is ordained and no duration is fixed.

I would like to acknowledge and express my sincere gratitude to my research **supervisor, Dr. Muhammad Shahid** for his endless support, supervision and affectionate guidance to steer me in the right direction whenever I needed it. I would also like to extend my gratitude to committee members; **Dr. Usman Liaqat** and **Dr. Mohsin Saleem** for their valuable suggestions and guidance.

I would also like to thank **Dr. Arshad Hussain** (Principal, School of Chemical and Materials Engineering) and **Dr. Zakir Hussain** (HOD, Department of Material Engineering) for providing a research-oriented platform to effectively utilize my skills in accomplishing this research work. Also, I would like to acknowledge all the lab staff for providing all the technical help during the whole research.

In the end, I must express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Last but not least I would like to thank **Mr. Muhammad Awais** and **Mr. Talha Butt** for being with me through this research period, helping me for conducting the experiments in laboratory.

Fariz Aneeq Mufti

ABSTRACT

Grafted Polychloroprene adhesives have been available since the 1990's. However, companies exercise propriety restrictions due to which there is limited information about their formulation. In this research grafting of Methyl Methacrylate (MMA) onto chloroprene rubber using hydrogen peroxide as an initiator is carried out by free radical polymerization. Rubber radicals react with MMA forming graft copolymers. Eighty-two formulations have been carried out during studies. Fourier transforms infrared (FTIR) spectroscopy showed an absorption spectrum of the grafted copolymer at 1730 cm-1 which is characteristic of carbonyl band (>C=O) of PMMA not present in PCP. The grafted copolymer is then mixed with phenolic resins, magnesium oxide, anti-oxidants and solvents to use in adhesive applications. Grafting factors such as grafting time, grafting temperature, monomer and initiator concentration and their effect on the properties of grafted adhesive is investigated. The adhesion strength of adhesively bonded joints is calculated by 180-degree peel testing of aluminum, canvas and leather substrates. Peel strength increases with increasing the monomer and initiator concentration until a certain limit and then it starts to decrease. Also grafting temperature of 70 ^{0}C gives the adequate grafting reaction with maximum peel strength. The grafting time is 1 hour at 60 ^{0}C and 45 minutes for 70 ^{0}C to achieve the desired properties of adhesive. Viscosity, wettability and solid contents are also measured and compared with the commercially available adhesives. The drying time for the adhesive is optimized to the 4 min for canvas and leather while for aluminum the drying time is 7 minutes. The percentage of solids contents are 55% which depicts the presence of high usable adhesive in the set. Peel tests in different environmental conditions show that grafted adhesive has greater weather and thermal stability than non-grafted adhesive. The formulated adhesive is 1.8 times better than the commercially available adhesive.

Abbreviations

HPO	Hydrogen Per Oxide
MgO	Magnesium Oxide
MMA	Methyl Methacrylate
MMA-g-PCP	Methyl Methacrylate-grafted-Polychloroprene
PCP	Polychloroprene
PSA	Pressure Sensitive Adhesive
PU	Polyurethane
SBR	Styrene Butadiene Rubber

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CHAPTER 1

INTRODUCTION

1.1 Adhesive

Adhesive is a material which as a result of various chemical and physio-chemical phenomenon is used to create mechanical connection between two surfaces or layers. The surfaces are compressed after applying the adhesive, which result in strong bond when adhesive is dried [1].

1.2 Adhesion Mechanism

The phenomenon of transferring loads from adherend to adhesive joint is known as adhesion. Mechanical properties of base polymer control the interfacial forces necessary for good adhesion. Sustaining sufficient stresses at the interface is basis for high adhesion. There is always intermolecular diffusion taking place between the surfaces joined together by adhesives. Intensive fast diffusion occurs between the surfaces due to the interface formed between the bonding polymers. The strength of bond initially formed is very high. Within a few minutes' interface of polymers disappears and strength of the bond is at its peak for binding polymers. Several major parameters play a pivotal role in the auto adhesive to take place. The polymer or binding material must have diffusive properties. Diffusive property of binding material depends on solvent and polymer used. Intimate and close contact of the substrate is compulsory for the highest diffusion. Elastic stress, elastic strain and plastic flow of the whole recipe determine the diffusive properties and bonding. Elastic stress and rheology of composition affect the high quality of bond strength. To get optimum diffusion pressure, time and temperature play a key role at the place of joint. Adhesive layer alters all the physical properties due to evaporation of the solvent, interfacing of polymers, the base of polymer changes and crystallization of binding polymers.

1.3 Theories of Adhesion

Adhesive bonding is the result of various physio-chemical interaction taking between materials to be joined and adhesive. So, adhesive bonding needs some understanding of these processes taking place on the surface of materials [2]. Different theories to describe adhesion mechanism are 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 particular adhesive system [3]. 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 particular mechanism.

Table 1-1 Theories of Adhesion [3]

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

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

1.3.1 Mechanical Theory

It is the oldest of all theories and was presented in 1925 by McBain and Hopkin. It is based on assumption that adhesive bond is formed by the dispersion of adhesive into the pores, voids and surface irregularities of bonded substrates resulting in mechanical links which can transmit loads. The two adherends are bonded by penetration of adhesive into the surface of two materials. High adhesive bond is formed by the Mechanical Interlocking of adherend and adhesive. According to this theory a stronger bond should be formed between porous and abraded surfaces as compared to smooth surfaces, however, this theory failed because strong bond can be formed between smooth surfaces as well. 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) … ….Eq 1-1

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 [5].

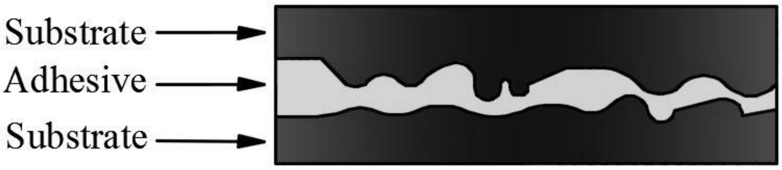


Figure 1.1 Mechanism of Mechanical Theory [4]

1.3.2 Electrostatic (Electronic) Theory

This theory was proposed in 1948 by Deryaguin and his co-workers [6]. According to this theory, electrostatic effects among adherent and adhesive is responsible for adhesion mechanism. Both adhesive and substrate have distinct structures, due to which electron transfer takes places between them. Electrostatic forces are formed at adhesive-adherent interface due to electrical double layer [7] [8]. This theory treats adhesive-substrate system as capacitor. An electrical double layer is formed on the plates of capacitor when they are brought close to each other when the plates of capacitor are moved away from each other, the potential difference between them increases, until discharge takes place. Figure 1.2 shows the electric double layer formation [7], [9], [10]. The separation energy of interface G_e is related to potential difference as follows [8]:

$$Ge=\frac{h\varepsilon d}{8\prod} \qquad \text{Eq 1-2}$$

Where h is discharge distance and Ed is dielectric constant. This theory says that adhesion strength depends upon the magnitude of potential barrier, however there are several situations where this barrier doesn’t exist. Furthermore, energy dissipation during failure analysis is not abstractly explained in electronic theory. So, electrical phenomenon during failure processes are consequence rather than source of high strength [9], [5],[11].

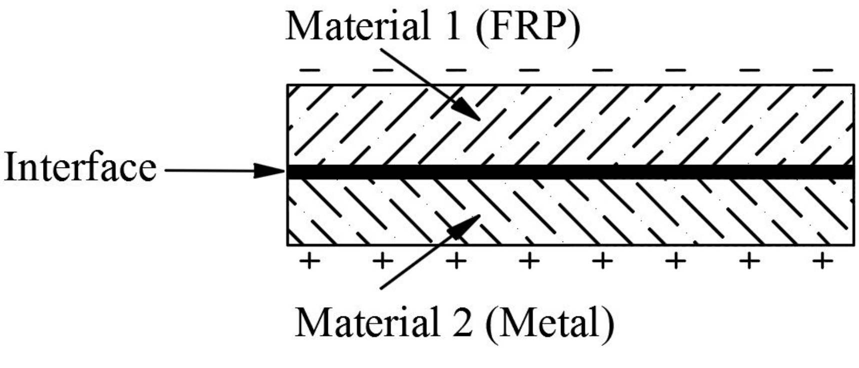
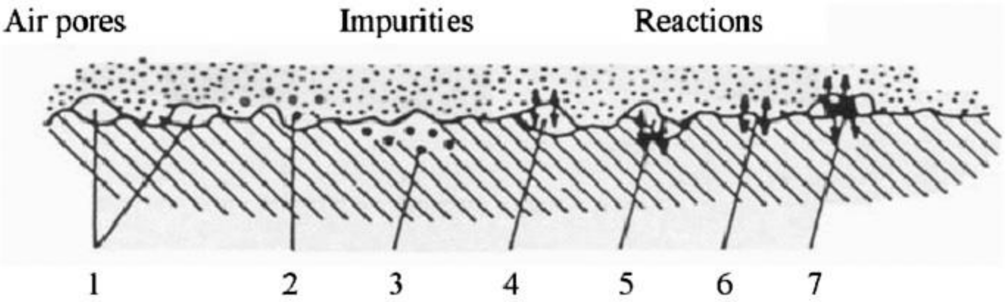


Figure 1.2 The electrical double layer (electrostatic mechanism) [9]

1.3.3 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 [12]. Bikerman 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 1.3 [13],[9].



Model of weak boundary layers. The seven Bikerman classes:
1) air pores; 2) and 3) impurities at the interface; 4) to 7) reactions between components and medium.

Figure 1.3 Seven classifications of weak boundary layers [13]

The weak boundary layer should be eliminated for an adhesive to perform satisfactorily. Failure in metals take place by formation of scaly oxide layer. However, this problem doesn’t occur in aluminum, because it has coherent layer of oxide on its surface. a low-molecular weight additive is present in polyethylene throughout its surface leading to weak interface. In both cases surface treatments can be performed to remove these weak layers [7], [14], [15].

The two objections or drawbacks of WBL are:

- Interfacial failure has been observed in Many systems experimentally
- Failure at the interface in any of the material in contact may be cohesive cannot be attributed to presence of WBL. Many authors stated that stress concentration close to tip of crack shows the failure propagation is near to interface, but not at interface [9], [5].

1.3.4 Diffusion Theory

Voyutsi proposed diffusion theory as adhesion being result of macromolecules inter diffusion [16]. According to this theory, adhesive and substrate should be polymeric in nature and have mutual compatibility with each other. Figure 1.4 shows adhesion between two polymeric materials due to inter diffusion of macromolecules at the interface [9], [16], [17]. 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 [15] as:

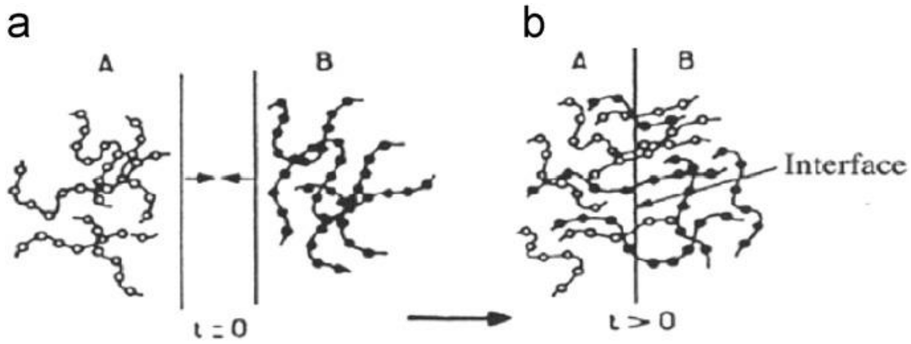


Figure 1.4 Inter Diffusion Across Interface [18]

$$x \propto \exp\left(-\frac{E}{2RT}\right) t^{\frac{1}{2}} \qquad \text{Eq 1-3}$$

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 [19]. For metal to polymer adhesion, diffusion occurs across the interface between metal and polymer when few metals are dispersed onto polymeric surfaces [20]. When concentration remain constant with time, (Steady State Diffusion),then according to Fick's First Law [19] of diffusion , flux (F_x) in x direction varies with concentration gradient c as:

$$F_x = -D \frac{\partial c}{\partial x} \qquad \text{Eq 1-4}$$

Where D is diffusion Coefficient. Diffusion constant for concentration variation with time is given by Fick's second law [20] of diffusion as:

$$D = \left(\frac{\partial c}{\partial t}\right) \qquad \text{Eq 1-5}$$

Optimum diffusion can be achieved by maintaining the solubility characteristics of polymers equal. Macromolecules chain length, temperature T, an concentration c all have significant effect on mobility pf macromolecules, which leads to intermolecular diffusion and on adhesive strength [9]. There is direct relation between contact time and concentration gradient. Vasenin [5] stated that peel energy G is proportional to number of chains crossing the interface between adhesive and substrate as well as to the penetration depth as given below [5]:

$$G \sim K\left(\frac{2N\rho}{M}\right)^{\frac{2}{3}} Dd^{\frac{1}{2}}tc^{\frac{1}{4}} \qquad \text{Eq 1-6}$$

Where K is constant which depends upon the contact polymers molecular characteristics.

One important objection on Vasenin model is that the energy dissipation occurring during viscoelastic or plastically in peel measurement is not included in Eq. (1-6). Diffusion model doesn’t explain adhesion phenomenon between highly crystalline or cross-linked polymeric substrates, or when contact occurs far below glass transition temperatures of these polymers. This theory is generally applicable to rubber-based elastomers or to the surfaces that are layered with contact adhesives are pushed together [21].

1.3.5 Adsorption Theory

This is most acceptable model proposed by Sharpe and Schonhorn [22]. 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[19], [22]. 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 sufficient enough to make strong bonds [9]. 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 [21].

1.4 Types of Adhesives

Adhesives can be classified in many ways, but the three very important classification of adhesives are by Source, by chemical Composition and by function

1.4.1 Classification by Source

Adhesive in these categories are either natural or synthetic adhesive.

1.4.1.1 Natural Adhesives

All adhesives based on natural sources such as animal based or vegetable oil-based adhesives and natural gums include in this category. They have long shelf life and are easy to apply. They are used to join paper, light wood and foils etc. [3].

1.4.1.2 Synthetic Adhesives

Synthetic adhesives are not found in nature. They are designed and manufactured by man. These are the most widely used adhesives because of their far superior properties than natural adhesives. All Structural adhesives are synthetic adhesives [23].

1.4.2 Classification by Chemical Composition

All synthetic adhesives can be thermoplastic, thermosetting or elastomeric.

1.4.2.1 Thermosetting Adhesives

They melt as they are applied onto application and do not require heating to cure. Curing generally occurs by chemical reaction at temperature depending upon type of adhesive. One-part system cure at high temperature and their shelf life is limited, while two-part systems have longer pot life and cured at room temperature. Solvent can be added to facilitate their usage [5]. Their bonds can withstand temperatures of 93-260 ^{o}C. They offer good peel strength. Thermosetting adhesives include epoxy, polyester, acrylic, Urea-Formaldehyde and polyimide etc.

1.4.2.2 Thermoplastic Adhesives

These adhesives are heated to high temperature where they can flow and then applied to the substrates where they develop strength upon cooling or evaporation of solvent. They can be used up to 80^{o}C however they are not recommended to use at elevated temperatures. Their creep resistance is poor, and their peel strength is just fair. Generally, they are not suggested for structural applications. Some common thermoplastic adhesives are polyvinyl acetate, polyvinyl chloride, phenoxy and acrylics etc. [24].

1.4.2.3 Elastomeric Adhesives

They are based on natural or synthetic polymers. They can be used from 60-204^{o}C. They have low bond strength but high flexibility. They are modified with resins to improve bonding for leather, paper, rubber, fabric and plastic films. Examples of elastomeric adhesives are natural rubber, butyl rubber, polyurethane, neoprene rubber, nitrile rubber.

1.4.3 Classification by Function

There are two types of adhesives based on their function i.e. structural and non-structural adhesives.

1.4.3.1 Structural Adhesives

They have high strength. They are used to hold structures together and can bear high loads. They can transmit stresses within the bond without loss of integrity.

1.4.3.2 Non- Structural Adhesives

They do not endure heavy loads but are used to hold materials in place. They are useful in filling gaps and bond paper to paper. Pressure sensitive adhesives is an example of non-structural adhesive [25].

1.5 Contact Adhesive

The adhesive which rapidly dries when applied to substrate and strong joint is formed between the joining substrates in a short time. Auto adhesive properties of polymer is major constituent of contact adhesives [26].

1.6 Pressure Sensitive Adhesive

Pressure sensitive adhesives have the ability to wet the surface more efficiently because they do not solidify and remain viscous. Strong bond is formed when substrates are brought close to each other and pressure is applied thereafter [27].

1.7 Properties of Contact Adhesive

Contact adhesives have excellent mechanical properties, high strength, fast setting time and easy applicability and durability [28]. In solvent based technology, solvent evaporates very quickly from the surface and very high bond strength is observed which increases with time [20]. Some of the properties which affect the strength and its performance are described below.

1.7.1 Viscosity

During joining process, adhesive is acting as a bridge between the two surfaces, and it has to fill and penetrate into small features thereby filling microscopic irregularities which are present on the surface. So, the viscosity of the adhesive should be low enough to flow into the available spaces within the surfaces [29].

1.7.2 Storage Life

The time during which working properties of an adhesive can be retained is known as storage life or shelf life. Adhesives should be stored in dark or opaque containers. Storage life is dependent on temperature. Storage life is generally between 6 to 12 months [30].

1.7.3 Working Life

This term is used in multi-component systems. It is the time during which multi-component system can be applied after its components are mixed together. It depends upon the temperature of mixing and quantity being used, mixing conditions, and method used for end use [30].

1.7.4 Tack Time of Contact Adhesive

Time required for drying the adhesive before joining the two materials is known as tack or open time. For contact adhesives, this time varies from 5 to 60 minutes depending upon the conditions and type of application [31], [32].

1.7.5 Acid Accepting Components and Anti-oxidants

Anti-oxidants are added in small amount because they prevent aging process of adhesives, increase pot life and also effect the viscosity of contact adhesives. The aging process may result in degradation, color changing or other physical properties of adhesives. This results in decrease in adhesion strength of bonded joints [33].

Metal oxides are added in contact adhesive as acid accepting agents. Typically, these acids accepting agents are magnesium oxide and zinc oxide. Hydrochloric acid is released after some time, which cause discoloration and substrate deprivation. So, these metallic oxides act as stabilizing agent in solvent borne adhesives [31]. Both Zinc and magnesium oxides resist neoprene adhesive against dehydrochlorination. Further, zinc oxide helps in vulcanization of rubber.

1.7.6 Wettability, Contact Angle, Surface Free Energy

Liquids wet surfaces to some extent and form a contact angle with the solid surface. This wettability results from atomic and molecular interactions between the surfaces. Strong adhesive bond depends upon the good wettability of adhesive material. Contact angle depends upon the viscosity, externally applied loads and adhesive forces present between the surfaces. For last four decades it is known that a Zero contact angle between the adherends results in excellent adhesion between the two materials. [34], [35].

1.8 Resins in Contact Adhesive

ISO 472 and ISO 4618/3 define resins as “solid, semisolid, or pseudo solid organic material that have high molecular mass, and generally become soft or melt over temperature range”. Resins act as tackifying agent in adhesives. Tackifying resins increase wettability of non-polar elastomers, changing viscoelastic properties and polarity thereby, increasing their adhesion. Resins are added in contact adhesives formulations to modify viscosity, tack time and strength of adhesive. [31].

1.8.1 Selection of Solvent for Contact Adhesive

Solvent based adhesives are widely used in packing, automotive, construction, footwear and furniture industries. The advantage of solvent based adhesives is availability of range of raw materials and change the formulation to meet the requirement of application. However due to safety and environmental issues, chlorinated solvents are banned [36].

1.9 Polymers Based Contact Adhesive

Animal glue has been used for thousands of years as an adhesive material. But with the development of synthetic materials natural glue has been replaced by synthetic adhesives. Nowadays, many polymers are being used as contact adhesives, most common of which are chloroprene, polyurethane, acrylic, styrene butadiene polymers etc. Different properties of these polymers-based adhesives are discussed below:

1.9.1 Styrene Butadiene Rubber (SBR)

They have low tensile strength because of low crystallization rate. The heat and chemical resistance are also low as compared to other polymers however these properties can be increased by adding different reinforcing agents. On the other hand, they offer good abrasion resistance, better aging and uniformity than other polymers.

1.9.2 Acrylic Polymer

They can be used at low temperature conditions and have low toxicity. Although their bond strength is less as compared to other polymers but they have good water resistance and easy formulation. They have good drying time because solvent release in the environment very quickly [3].

1.9.3 Neoprene

It is one of most important type of polymer used as contact adhesive. It shows very Strong bond strength with good tack time, high temperature absorption and chemical resistance to many compounds. It is used to bond variety of substrates including wood, leather, laminated, automobile assembly etc. It has limited open time and also it is formulation limited [23].

1.9.4 Polyurethane

Its properties depend upon chain reaction and the resultant chain length produced as a result of this reaction. Its major advantage is its versatility to bond many substrates with very high strength. It is not substrate limited. They have application in footwear industry for bonding sole-to-upper layer of shoes, in electrical systems, in automobiles and in metal to metal bonding [25].

1.9.5 Nitrile Rubber

It has appreciable resistance to oils because of higher nitrile content i.e. about 25%. They have good adhesive strength as they are compatible with almost every type of resin available. Nitrile rubber-based adhesives are used to bond polar adherends as proteins, wood and textile, vinyl’s where good resistance to water and oil are required.

1.10 Contact Adhesive Bond Strength

Strength of adhesive joint is predicted by the physio-chemical properties of adhesives [37]. Contact adhesives attain 50 percent of their final strength immediately after applying. Contact adhesives are basically natural or synthetic rubbers or polyurethane elastomers having higher molecular weight. Uniform thin coating of adhesives are essential for obtaining higher strength [30].

1.11 Polymerization

Polymerization is process in which large molecules are formed by bonding of small building blocks (monomers).

1.12 Co-polymers

A copolymer is formed by linking of two or more different types of monomers. These monomers can be arranged by head -to-head, head-to-tail or tail-to-head.

1.13 Block Copolymer

A copolymer that consist of to two different groups of monomers joint together or two different homopolymer joined together is termed as block copolymer. It can also be defined as the polymer which consist of large groups of each monomer.

1.14 Grafting

Grafting is a technique used to modify the polymer structure by adding different functional group on the polymer structure. Grafting increases thermal, mechanical and adhesive properties of polymers, thereby, enhances the applicability of these polymers [23].

1.15 Contact Adhesive Coating Ability

Coating ability of contact adhesive is determined by humidity level and binding temperature of adhesive. At high temperatures, adhesive bonds the surfaces very quickly as compared to low temperature. But humidity level should be low to bind surfaces quickly. So. For bonding the materials quickly in less time, the temperature should be high while humidity level should be low [38], [39].

1.16 Factors Involved in Producing Satisfactory Bond

- Choosing appropriate adhesive.
- Compatibility with the surfaces on which adhesive to be applied.
- . The raw materials should meet the minimum standard set by ASTM in terms of adhesive quality specification. •
- Essential Surface treatment before applying the adhesive layer on the substrate.
- A thin uniform layer of adhesive should be applied and proper time for drying the adhesive over the surface must be given.
- Shake the container whenever use the adhesive.

1.17 Motivation

Economy of any country depends largely upon local industries and their products. This sector is largely supported by Government from past few years which is resulting in creation of new industries as well. Outside financial specialists and developing neighborhood markets are boosting the development and creation of modern merchandise. Adhesive industry is one of those enterprises which is developing quickly and has extensive variety of market to catch. Glues are winding up more vital in the assembling of the finished results and furthermore permitting the advancement of new items. Adhesives are used in automobile industry, material, aviation, dentistry, microelectronics and footwear applications. These businesses for the most part fabricate and create products have an everyday utilization. Variety of glues are used depending upon type of application.

There is a large opportunity in adhesives department. Adhesives which are producing locally either don’t have required properties or they lack in quality of adhesive technology. Hence, the imported adhesives have made a strong hold in Pakistan. There are big names such as 3M solutions, Cement X, UHU, samad ultra which are being used and hold the adhesive market. But these products are costly which contrast developing needs of market.

So, high quality and less expensive adhesive is still not available in the market to fulfil customers demand. This advancement won't just satisfy the requests of glues at lower rates yet diminish the reliance on imported glues as well. The low costs cement, when accessible, will at last increment the overall revenue of nearby Industries and little modern setups. Consequently, reducing the expense of their finished results, making them accessible and reasonable for more part of the population

1.18 Aims and Objectives of Study

The objectives and aims of this study are as follows:

1. Developing a general purpose grafted polychloroprene adhesive and effect of grafting on the strength of PCL adhesive
2. Adhesive should of high strength and suitable for footwear industry.
3. The adhesive should be low in cost and environment friendly.
4. To explore the result of time, temperature and environmental conditions on the performance of grafted PCL.
5. Comparing the formulated adhesive with the commercially available adhesives.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter introduces the advantages and disadvantages of adhesive bonding, after which grafting of polymers will be discussed in detail. Different techniques used for grafting are described briefly as well. Following that, different techniques used for applying the adhesive and their effect on adhesive bonding are discussed. Finally, various adhesive formulations carried out over the period of time are described.

2.2 Polychloroprene Adhesive

Polychloroprene is the largest and most widely used group of rubber adhesives. It was discovered in 1920s by DuPont. The first paper regarding Polychloroprene was published in 1931 under trade name DuPrene. Later on, it was termed as Neoprene. The new polymer was designated as synthetic natural rubber due to its superior properties and many similar natural rubber characteristics. Few promising properties of Neoprene adhesive were better aging, resistance to temperature and chemicals [40]. PCP adhesive gained its market after World War II as demand of rubber-based adhesives increased and people turned towards PCP based contact adhesive for bonding applications. General Purpose (GN) and fast crystallization (CG) were two Neoprene polymers used at that time [41].

Neoprene proved to be satisfactory in shoes industry during early time of its manufacturing. It was used for both temporary and permanent bonding of shoe soles [42],[43]. But Neoprene faced two problems during its early stages of manufacturing:

1) Convert to black color when stored in steel tanks
2) Decrease in viscosity upon aging

The discoloration was due to oxidation of Neoprene on aging. This oxidation was due to formation of hydrochloric acid. The HCL reacts with iron forming ferric chloride, which upon further reaction with thiuram sulfide yields black color compound of iron sulfide. This drawback was removed by incorporation of magnesium and zinc oxides [44]. Gerrard et al [45] formulated PCP adhesive having composition of Polychloroprene, phenol aldehyde resin, solvent blend for providing viscous composition and magnesium oxide. The claimed adhesive rapidly dried upon application and has excellent strength at both normal and elevated temperature. Adhesives prepared before Gerrard had drying time of hours to days before developing a strong bond between substrates [46]. The adhesion properties specially in case for metal joining increases by incorporation of isocyanates in adhesive composition. Type of isocyanates do not have any effect on adhesion strength or adhesive composition. However, Sulphur compounds along with isocyanates do increase the adhesion of polar substrates [47].

Neoprene type AC has better resistance to discoloration along with viscosity stability. However, they cure more slowly at room temperature. The more stable neoprene type AD was developed in 1958. It has good degradation resistance as compared to type AC and their solutions has stable viscosities. Both Neoprene AC and AD are now considered as base product for solvent based adhesives.

Neoprene is produced by emulsion process from 2-chloro- 1, 3- butadiene and chloroprene monomer. Monomer can be added in many different ways which determine the crystallization rate and reactivity of polymer. Trans, 1-4 is the most common method of monomer addition. High percentage of this structure results in higher crystallinity and rapid development of bond strength. Both Neoprene AD and AC contains 90% of Trans 1, 4 structure and Neoprene W contains 85% of this structure. Due to higher percentage of Trans 1, 4 structure AD and AC have higher crystallization rate than Neoprene W. A general-purpose formulation of Neoprene contact adhesive is shown in Table 2-1Table 2-1 General Formulation of Neoprene Adhesive [50]. Incorporation of nitrile containing compounds in about 3 to 10 wt. % of adhesive composition in place of sulfur compounds results in increased adhesion properties of adhesives and better viscosity control The resistance to discoloration can also be achieved by adding anti-oxidant containing phenol or phosphorous compound [48], [49].

Fillers such as silica improves strength and viscosity and bonding properties of cured adhesive. Addition of epoxy resin and phenol aldehyde resinous in Neoprene adhesive composition increases the storage life adhesive at room temperature and also capable of bonding metals, plastics and automobile interior decoration parts. Superior advantage of this adhesive composition was that it can be easily sprayed on the surfaces to be joined. So different shapes of joints can be designed with the help of this adhesive composition [50], [51]. Lower molecular weight Epoxy resins which are liquid a room temperature should be used as higher molecular weight epoxy resins are incompatible with PCP. In solvent based systems susceptibility to gelation is higher specially system comprising of chloroprene polymer, magnesium oxide as cross-linking agent, phenolic resins and absence of oil soluble ingredients. It was observed that storage stability of Neoprene adhesive comprising of chloroprene, magnesium oxide, acrylic acid can be increased by adding 2 parts of water in adhesive composition [52].

An organic solvent which can dissolve chloroprene polymer and phenolic resins can be used in adhesive application with improved resistance at higher temperature. Polychloroprene polymer and resin must be thoroughly mixed and have intimate contact in order to obtain excellent adhesive properties. For thorough mixing, resin and Polychloroprene can be dissolved in mutual solvent [53]. Aromatic hydrocarbon resins provide greater compatibility than aliphatic resin. As a result of which there is no phase separation, decreased tack time and greater adhesion to surfaces as compared to aliphatic hydro-carbon resins [54].

The chloroprene and carboxyl group should be blended in such a way that mixture contains carboxyl group from 0.02 to 0.4 wt. % [55]. Spector et al achieved same adhesive properties of Neoprene adhesive by using three different chloroprene polymers. The other components of adhesive composition were phenolic resin, Magnesium oxide and metal anhydride. The three different chloroprene polymers included a high crystallization type, a reactive type and medium crystallization type [56].

Anti-oxidants are added in PCP adhesive to prevent premature curing and deterioration of adhesive di-alkyl thio-dipropionate and nickel butyl dithiocarbonate were the very first anti-oxidants used in adhesive composition. During the early days a combination of anti-oxidants were used however later on, it was found that a single anti-oxidant serves the same purpose as used in mixture of anti-oxidants [57].

The adhesion properties of adhesives can be increased by adding about 1 wt. % of adhesion promoters. These adhesion promoters can be increased specially for bonding elastic materials. Phosphorous containing compounds enhances the flexibility of PCP polymers, leading to increase in diffusion depth, facilitating better bond between substrates [58], [59]. The adhesion strength is increased 0.5-3 times by adding phosphorous-boron containing oligomers (PBO). The solvent systems proposed for copolymer adhesives was toluene, hexane or mixture of these hydrocarbons [60]. The adhesive should be prepared by milling the PCP rubber in solvent solution as the milled adhesive has better storage stability and reduced viscosity as compared to unmilled adhesive solution. However, Keown et al prepared unmilled adhesive having same properties as that of milled adhesive. The proposed adhesive was formulated by heating the rubber in solvent solution at high enough temperature that rubber is completely dissolved in the solvent and then other ingredients are employed in adhesive solution. Vinyl copolymers were used which ensured that copolymers increases the properties of adhesive systems substantially [61].

Neoprene latex-based contact adhesives became available in late 1970s and their market grow because of their easy process ability and environmentally friendly. Latex of formed by blending two or more rubbers. Blending results increase in properties and low cost as compare to single rubber polymer. Researchers worked for their use in different applications and adjust their strength according to Neoprene AC or Neoprene AD based contact adhesives. Latex based adhesives found their applications in leather and metal industries with compromisation in strength [62]. Different properties such as water resistance, temperature degradation, metal adhesion was studied during the 1980s. Both two part and single part aqueous Neoprene latex adhesive was formulated and their systems were studied extensively throughout this period. The green strength of latex neoprene adhesive can be increased by keeping polymerization temperature to under 20 0C. the gel content in non-solvent based adhesive is claimed to be achieved up to 80% which is much more effective and shows greater applicability than solvent based adhesives [63]. However, the adhesive which caught the eyes of researchers was grafted neoprene adhesive.

Grafted Neoprene adhesive offered the opportunity of having low tack time and high ultimate strength even at lower temperatures. Methyl Methacrylate, cyclo hexyl methacrylate, ethyl methacrylate was initially used as grafting monomers with peroxides being used as initiators. The said adhesive was formed with free radical polymerization reaction [64]. Different factors such as grafting temperature, monomer and initiator concentration were major topic of study for the researchers. The monomer concentration was varied from 10-90 weight percent of the adhesive composition.

A solvent free grafted chloroprene system is formed by using blends of chloroprene homopolymer and chloroprene/ acrylates. The resulted blend can be used in formulation latex-based contact adhesive. The most important point was the exclusion of organic solvents from the adhesive system. The said adhesive was used to join plastic to plastic or plastic with other substrates [65]. Grafted adhesives have 40-60 weight percent of solid contents which show their higher applicability even with same viscosity as non-grafted Neoprene adhesive.

Table 2-1 General Formulation of Neoprene Adhesive [50]

General Formulation	Parts	Typical Formulation	Parts
Neoprene	100	Mill Mix	
Magnesium Oxide	4-8	Neoprene AD	100
Zinc Oxide	5	Magnesium Oxide	8
Anti-Oxidant	2	Zinc Oxide	5
Resin	As Required	Antioxidant	2
Solvent	As Required		
		Chum Mix	
		Milled Stock	115
		t-butyl Phenolic Resin	45
		Water	1
		Toluene/Hexane/Acetone	640
		2/4/4	

Effect of grafting factors such as monomer concentration, monomer type, grafting temperature and time on grafting percentage was first time studied by Chang at al [66]. He used MMA and acrylonitrile as grafting monomers and benzoyl peroxide as initiator. He concluded that maximum grafting efficiency can be reached at 80 ^{o}C when toluene is used as solvent and AN as monomer. However, grafting efficiency levelled off when ratio of AN-MMA is reached to 3.0. It was also concluded that grafted PCP has better weather stability than PCP polymer. Same conclusion was stated when cyclo hexyl methacrylate was grafted on PCP later on [67]. MMA-g-PCP adhesive has greater peel strength for upper leather to sole than ethyl acrylate grafted PCP adhesive. However, both grafted adhesives have peel strength greater than PCP adhesive. Pure toluene, benzene or mixture of these two were extensively used as solvent in grafted adhesives. However due to environmental and safety concerns different solvents such as ethyl acetate, methyl ethyl ketone, were developed and used in neoprene adhesive systems. The temperature range for these solvents were 40-60 ^{o}C for dissolving PCP rubber and resins respectively [68].

2.3 Advantages and Drawbacks of Adhesive Bonding

Adhesives have a wide range of applications carrying from metal to rubber and textile industries. Adhesives due to their large applications and demand are considered as alternate for mechanical bonding. Some of important advantages and draw backs are given below:

2.3.1 Mechanical Advantages and Limitations

Adhesives distribute loads over entire area and don’t have any stress concentration points leading to joints with excellent fatigue resistance. Significant amount of weight can be reduced by using adhesives over other joining techniques specially in aircraft industry where adhesive joints are gaining interests for bonding aluminum alloys to reduce weight of aircrafts [69]. In the past two to three decades use of composites in aircraft industry has increased drastically which has drawn attention of engineers to use adhesives as joining technology. Joining dissimilar structural parts by riveting can create local defects in the composite and breakage of fibers in composite material may occur thereby damaging the composite as well as creating residual stresses along rivet holes. Lap joints formed by riveting have lowest fatigue and static performance [70]. Adhesives can be used to join heat sensitive materials which will be destroyed by welding or brazing methods.

One of major drawback of polymer rubber adhesives is their degradation with time. This degradation depends upon number of factors such as time, temperature moisture and toxic chemicals. The working temperature of adhesives is usually between -50 C^o to 150 C^o. strength of adhesive bonded joints decreases with continues stress and high temperature. Certain crosslinking reactions can cause over heating or burning when applied in bulk. Low joint strength is often due to poor adhesion between substrate and adhesive. So, Proper surface preparation is required for strong bonding. Mostly adhesives have low peel or cleavage strength.

2.3.2 Design Advantages and Limitations

Adhesives can be used to join variety of solid substrates regardless of their shape, size thickness. Adhesives have improved strength to weight ratio as compared to other methods. Dissimilar materials even with different modulus and thickness can be joined by adhesives. Adhesives can be used to join thin sheet materials where other joining techniques can cause distortion. For choosing adhesive for any application, its design limitations must be considered. Shelf life of an adhesive joint cannot be predicted, therefore a prototype model should be made and tested in same environmental conditions to estimate the shelf life and design imitations of adhesives [71].

2.3.3 Production Advantages and limitations

Glues are more affordable and fasters in joining when contrasted with regular strategies. At the point when the span of the substrate region to be joined builds, cements can spare expense and work and mechanical fasters take a great deal of work and cost uses while with cements the entire activity can be performed in one go. Moreover, galvanic erosion can be limited between divergent metals with cements. Glues require a spotless surface to gain ideal outcomes. The cleaning of the substrate may change from straightforward cleaning to utilization of synthetic compounds, contingent upon the substrate compose and required security quality [87].

2.4 Neoprene Solvent Based Adhesive Composition

Adhesives contain many other components in addition to parent material. These components include adhesive base, hardener, resin, solvents, fillers, reinforcements, diluents, cross-linking agents. Each of these components has an effect on properties of adhesive. The details about each component and its effect on properties of finished product is discussed below.

2.4.1 Elastomer

This is the key constituent of adhesive. The name of adhesive is given on the name of binder e.g. neoprene rubber in this case. Neoprene type AC and AD are normally used in solvent-based adhesive.

2.4.2 Resin

Resin improves the tack time and increases strength of adhesive bond. So, proper choice of resin in any solvent based adhesive in given application is of great interest. Commonly used resins are hydro carbon resins, epoxy resins, carboxylate resins, phenolic resins etc. Para tertiary butyl phenolic are most widely used family of resins. They provide much higher heat resistance at similar melting points as compared to other resins. It can provide excellent bond strength up to 80^{o}C**.** The effect of different resins in Neoprene adhesive is shown in Table 2-2 [31].

The use of resins to provide viscosity stability, increased wettability, low tack time and desired adhesion properties. The resins are generally added at level between 30 to 60 phr.

Optimum level for adhesive applications is 50 to 60 phr. Low levels are mostly used when low adhesion is required while high levels are used when a strong adhesion is required such as for metal-metal bonding. Adding higher amounts of resin may result in incompatibility between resin and rubber which may adversely effect on adhesive properties [72], [73].

2.4.3 Fillers

Fillers have limited use in Solvent borne Neoprene adhesive. They are primarily added to decrease cost of adhesives and increase the viscosity of adhesive. The most commonly used fillers are carbon black, asbestos flour, kaolin, calcium carbonate, clay, silica particles. Optimum filler concentration depends on type of filler used. Increasing filler content to 20 phr causes decrease in impact resistance. Generally, there is decrease in cohesive strength and adhesion strength by introduction of fillers. For these reasons, they are not used much often in contact adhesives. Fillers can accelerate setting time and slightly increase heat resistance of adhesive bond [31].

2.4.4 Effect of Adhesion Promoter

To obtain synthetic glue capable of joining any material and forming long, firm and durable joints is important problem. This problem can be solved by either developing novel adhesives or modifying known adhesive

The second option is more preferable for industries because developing new adhesive is not economically or technically profitable to them. Modification can be done by adding adhesion promoters in small quantities. The adhesion promoters increase number of functional groups, which results in better adhesion to polar and non-polar surfaces. The adhesion promoters include silane coupling agents, para- ox diphenylamine (PODA), N-nitroso diphenylamine (NPDA) etc. The introduction of these materials is generally added in range of 0.1-o.3 wt. %. the addition of these adhesion promoters improve shear and peel strength for metal-metal bonding [58] [59].

Table 2-2 Effect of Resin Type on Neoprene AH Hot Bond Strength [74].

Adhesive Properties	**Rosin Resin**	**Terpene Resin**	**t-butyl Phenolic Resin**	
			Low Reactivity	**High Reactivity**
Bond strength after 1 day at R.T., pli				
Tested at R. T	5.4 C	9 C	20 C	21 C
Bond Strength After 7 Days				
Tested at R. T	8 C	21 C	34 A	42 A
Tested at 60 0C	-	-	18 C	28 C
Tested at 80 0C	-	-	6 C	16 C
Tested at 100 0C	0.3 C	0.8 C	2.5 C	7 C
Tack Time for Paper to Steel	60	16	10-14	4-8

C= Cohesive Failure, A= Adhesive Failure

2.4.5 Anti-Oxidants

Anti-oxidants protect adhesives against oxidative break down and acid tendering of substrates so, presence of anti-oxidants is very crucial in all adhesives. 2 phr of anti-oxidant is sufficient but its quantity can be increased depending upon application. Agerite Stalite which is acetylated biphenyl amine oxidant offer best protection but its use in limited where staining doesn’t has any effect [3], [5].

2.4.6 Curing Agents

Curing agents such as thiocarbamide, isocyanates, Vanax mixture with Sulfur can be used to increase the heat resistance of Neoprene adhesives. G-type systems cures faster at room temperature than those with A-type systems. Also, solutions with these curing agents are not so stable and two-part system is required. For shoe industry, isocyanates is widely used as curing agents in Neoprene adhesive [74].

2.4.7 Metal Oxides

Primary function of metal oxide is act as an acid acceptor. With aging small amount of HCl released which should be absorbed to prevent degradation of substrates. This is very important when substrate is highly sensitive acid material as cotton. Zinc oxide and magnesium oxide serves as acid acceptors. They can be used alone or combination can also be used. Former is found more effective than alone.

Metal oxides can be used as curing agents in adhesives. Zinc oxide is more effective, leading to high strength as bond is aging. Magnesium oxide is effective at high temperatures if it is added at higher levels (20-40 phr) [75]. Metal oxides react with resins in solution resulting in infusible metal resinate which increases heat resistance of adhesive films. Generally, zinc oxide is used about 3-5 parts and magnesium oxide in 4 to 8 parts are used in formulation of adhesives. About 2 to 4 parts of Magnesium oxide act as acid acceptor and stabilizing agent. While rest of magnesium oxide is utilized in reaction with phenolic resins [76].

2.4.8 Solvents in Adhesive Systems

Solvent can affect viscosity, open time, cost, development of bond strength and ultimate strength to some extent. Blends of solvents can be used, consisting of aromatic, aliphatic solvents e.g. ketones and esters in varying quantity. Chlorinated solvents can also be used when nonflammable systems are prepared. Tack time of an adhesive is dependent upon evaporation rate of solvent, so proper choice of solvent system is necessary to control this property. Xylene can be added in small percentage (about 5 %) to increase the open time of adhesives [5] [77]. Solvents can affect application properties. Solvents such as toluene and 1, 1, 1-trichloro ethane give strong solutions which binds more rapidly forms cobweb when sprayed. Water in quantity about 1 phr is added to catalyze reaction between resin/magnesium oxides and improves the viscosity of Neoprene adhesives. However, excess addition of water can reduce hot strength of adhesive. Therefore, generally less than 3 phr of water is used [76].

2.5 Polymers and their modification

Polymers play an important in modern world. They are used in medical and bio-medical applications, automotive industry, in textile products, in coating and adhesive applications as well. In fact, every individual is relying on polymers to fulfil his needs. But sometimes polymers cannot meet the properties which are demanded from them so, improvement in their properties can broaden their scope of applications. Modification of polymers bring specific properties to the material, e.g. increase in thermal stability, compatibility, rigidity, physical response, flexibility and improves the polymer process ability. Polymers are made up of thousands of molecules of monomer. So, monomers are the building blocks of polymers. When different monomers combine together, then “Co-polymer” is formed and copolymerization is the process by which these monomers combine together. Alignment of different monomers in the polymer chain alter the properties of copolymers [78][79].

2.6 Grafting of Polymers

Process of attaching (grafting) on monomer onto polymer chain is known as grafting. Grafting because of its easiness to control various reaction parameters considered as promising method for polymer modification. Grafting introduces cross linking bonds by chemical modification of polymers. Grafting reaction may occur within few minutes or it may take several hours or even days. Graft reactions can be initiated by several ways, few among which are: by free radical initiation, plasma induced, photo irradiation and enzymatic mechanisms [80]. Some of these reaction mechanisms are shown in fig.1 [78]

2.6.1 Free Radical Polymerization and its Mechanism

This is the most common type of polymerization used for modification of polymers. There are many ways through which radicals can be introduced such as decomposition of an initiator mainly organic peroxides, species undergoing redox reaction, photo initiator excitation. There are three main steps in this process i.e. initiation, propagation and termination [81].

2.6.1.1 Initiation

It is the first step where new covalent bonds are generated by the reaction of chain carrier with monomer or polymer molecule. As a result of this reaction, reactive center site is shifted to new location. Some possible reaction for grafting of vinyl acetate and poly butadiene is shown is

Figure 2.1 [78]. The initiating radicals will abstract acetoxy hydrogen and allylic hydrogen from vinyl acetate and polybutadiene respectively. A single initiator radical can generate abundance of possible species in the reaction while a small quantity of defected structures may disrupt the formation of radical.

The overall rate of reaction depends on the system physical properties. Small molecules will be diffused more rapidly than those from large sized molecules. This means that small molecules have little opportunity to react with nonradical substrates than large sized molecules. Based on above observations, the initiation rate is proportional to efficiency and initiator concentration as [74], [78]:

$$R_i = d[M]/dt = 2\ f\ k_d[I] \qquad \text{Eq 2-1}$$

K_d is initiation rate constant, f is concentration of initiator to carry out polymerization process. The most common initiators are benzoyl peroxide and 2, 2’-azo-bis—isobutyl nitrile (NIBR). Both of these molecules divide into two parts having unpaired electrons that are called radical initiator.

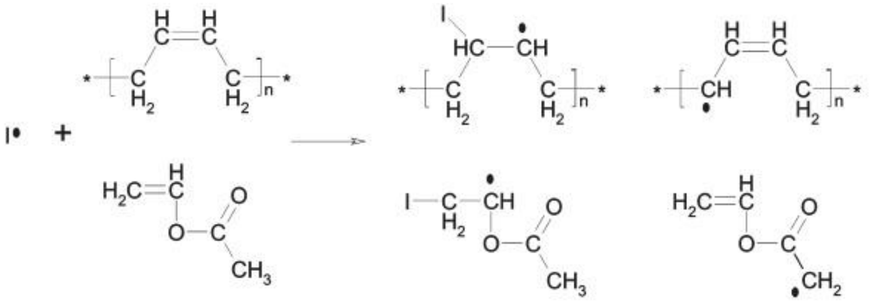


Figure 2.1 possible grafting reactions of poly (butadiene) and vinyl acetate [78]

2.6.1.2 Propagation

In graft polymerization, propagation is the second step after initialization. As initiation step is completed there are number of reaction possibilities that can occur. This step governs kinetics of polymerization. Monomers are added to the active sites resulting in growth of polymer chains. The Figure 2.2 [80] shows the ways in which monomer addition can take place at the active centre. The name is given on how the head or tail is connected at active center. Preferably active center is located on the head group and it reacts with another monomer tail, however head to head addition may takes place which is immediately followed by tail to tail addition so, active center is ended on head side. The propagation enthalpy will be the total enthalpy of polymerization reaction. Consumption rate of monomer is given by

$$-d[M]/dt = kp[M]\,[P] \qquad \text{Eq 2-2}$$

Kp is rate coefficient for propagation, polymer radical concentration is given by [P*]. Kp should not be misunderstood with rate constant, because it depends on polymer radical length and medium viscosity [79] [82].

2.6.1.3 Termination

Termination occurs when two radicals combine together to form pair, which results in stoppage of physical polymer chain and kinetic chain reaction. This is called termination via combination of radicals shown in

Figure 2.3. Another route through which termination may occur is called disproportionation as given in Figure 2.4 [78]. In this route radical activity is passed between species. This step is very rapid and usually controlled by diffusion under all conditions [83] [84].

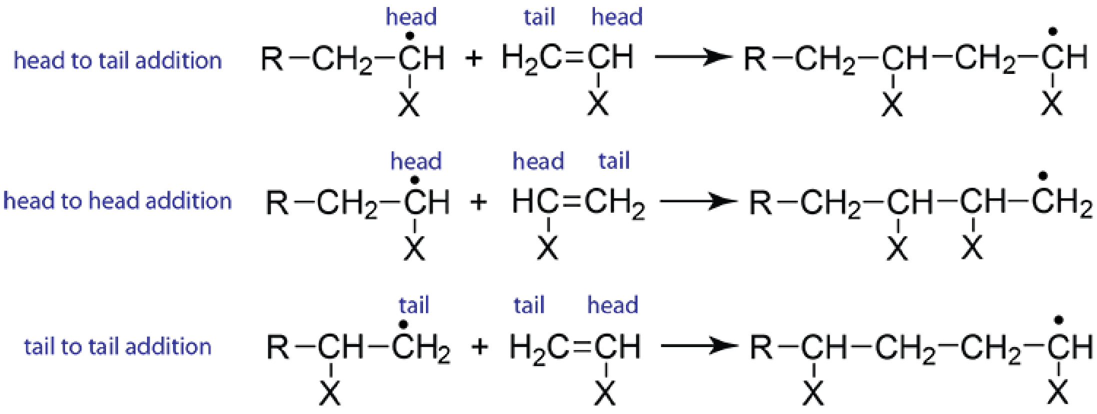


Figure 2.2 Configurations in which a monomer can add to an active center during the propagation step of free radical polymerization [80]

2.6.2 Radiation Grafting

High energy gamma radiations can cause induction of free electrons, radicals and cations by bringing changes in the polymer structures similar to photo-initiated grafting technique. Grafted chain polymer is formed when these radicals react with the monomer in same way as discussed in free radical section. This process is beneficial as no initiator chemicals are used in this process thereby excluding contamination factor. Also, gamma radiation has greater penetration capability than photo-initiated means, requires polymer, monomer and suitable solvent. There are two path ways for progress of radiation grafting:

I. Free radical grafting
II. Ionic grafting

These are analogous to chemical means of grafting but with the exception that this process is carried out in dry or semi dry environment

2.6.2.1 Radiation based Free Radical Grafting

The treatment of polymers can cause hemolytic fission generating free radicals on the polymer. Initiator is not much significant in this process and is rarely used. The key thing in this method is the medium in which this process is carried out for example peroxides are formed on the molecule if the process is carried out in presence of oxygen in open air. Life time of free radicals depend upon the polymer back bone and its nature [80],[85]. This technique is achievable in following ways:

2.6.2.1.1 *Pre-Irradiation Approach*

In this approach, free radicals are generated by treating polymer backbone in vacuum or under an inert gas e.g. nitrogen atmosphere. Grafting is initiated by treating this irradiated polymer with monomer in liquid or gas state or in suitable solvent solution. The advantage of using pre irradiation technique is that no homopolymer formation takes place as monomers are not irradiated in this technique [80],[86].

2.6.2.1.2 *Peroxidation Approach*

In this technique polymer backbone is treated in oxygen or air forming hydrogen peroxide or di peroxides. Formation of peroxides depends on the polymer nature and irradiation conditions. In this approach, grafting is initiated by combining the oxides formed during irradiation with monomers at high enough temperatures so that peroxides decompose and form radicals. The advantage of peroxides products is that they can be stored for long period of time before carrying out the grafting step however, scission of polymer takes place due to direct irradiation which results in block co-polymer formation [87].

2.6.2.1.3 *Mutual Irradiation Approach*

In mutual irradiation approach both polymer and monomer are simultaneously exposed to radiation to form free radicals subsequently causing the molecules to synthesize graft. The limitation of this method is it is unselective and is forced along the direction of incident beam radiation; which shows that radical generation is unfocused. This technique is very harmful and can cause decomposition of certain polymers. Also, the hazard of isomerization and homopolymer formation also takes place in this method as monomers are radiated [85], [87], [88].

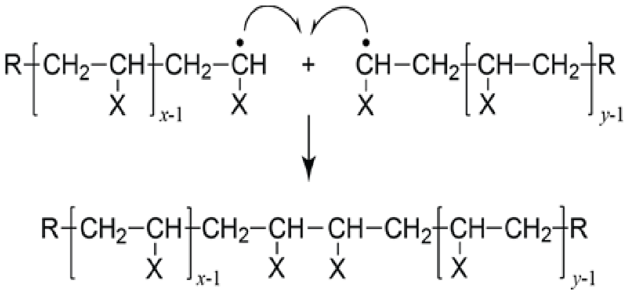


Figure 2.3 Termination by combination

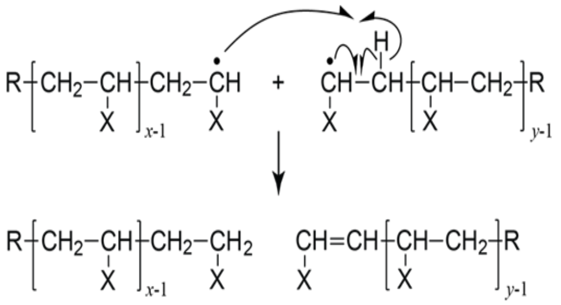


Figure 2.4 Termination by disproportionation

2.6.2.2 Ionic Grafting

The ionic grafting resembles the free radical grafting with the exception that ionic centers (cationic or anionic) are generated instead of free radicals to initiate the grafting process. One example of ionic grafting is shown in fig in which initiator chemical tertiary butyl phosphorene is used for anionic modification of polyethylene oxide. Cationic center is created on initiator by the reaction of acid with initiator molecule as represented in Eq 2-4. [80].

$$[\text{t-BuP}_4] + H^+ \xrightarrow{yields} [\text{t-BuP}_4\text{H}]^4 \qquad \text{Eq 2-3}$$

2.6.3 Photo Initiated grafting

Electromagnetic spectra consist of large number of light sources depending upon difference in their band energy, however, not all of these sources can provide enough energy for excitation of molecules to produce free radicals. The two main sources majorly utilized are microwaves and ultraviolent sources. This is more simple and effortless process which requires limited number of steps to produce the grafted product. Figure 2.5 shows the photo initiated grafting through electromagnetic radiation thereby producing free radicals which is capable of reacting with acrylonitrile [89] [90].

Grating by photo-initiation can occur through two different approaches, one by employment and other devoid of sensitizer. Both these approaches depend on the properties of polymer which is to be used. In photo-initiation grafting, polymer or sensitizer absorbs light and movie to excited energy state. This exciting state initiate grafting process by dissociating the excited molecule which results in generation of free radicals. This process can occur on surface of molecule if conditions are correct. However if free radicals are not formed by direct absorption of light on the polymer surface, then photo sensitizers such as benzophenone, benzoin ethyl ether, or acrylate dyes can be added to initiate grafting process [91]. This photo-initiated procedure is favorable due to short irradiation times and economic equipment. [92],[90],[93].

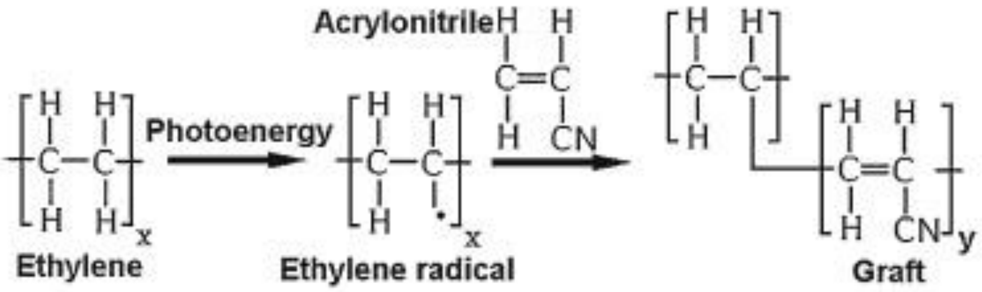


Figure 2.5 Photoinitiated grafting producing radica;s on backl bone of polyethylene without the employment of sensitizer and consequent addition of acrylonitirile monomer to produce graft co polymer [89]

2.6.4 Plasma Radiation Induced Grafting

This technique has gained interest of researches in the recent years. Same possibilities can be achieved through low discharge plasma conditions as with ionization radiation. Plasma radiation involves dissociation, ionization and electron-induced excitation [80], [90], [93].

2.6.5 Enzymic Mechanism

The principle is to initiate the grafting reaction either by chemical or electrochemical means by enzymes. An example of enzymic grafting is the conversion of phenol into 0-quinone by tyrosine, which again undergoes non-Enzymic reaction with chitosan. Polyphenol oxidase has been grafted on polycarbazole by enzymic mechanism successfully [94].

2.7 Controlling Grafting factors

There are many variables which control the grafting factors which include grafting temperature, monomer, nature of backbone, initiator, additives and solvents etc. All of these factors will be discussed in this section.

2.7.1 Nature of backbone

Backbone nature (physical or chemical) plays a vital role in grafting process because of covalent bonding between the monomer and polymeric backbone. Such as grafting of cellulose is difficult to be done as compared to grafting of wool in water [95]. Crystallinity of polymer play an important role in grafting. As crystallinity is decreased the grafting reaction slows down as in case of acrylamide grafted on acetylated wood pulp, the grafting rate decreases with degree of substitution increases. Polymers containing high levels of terminal bonds enhance the chances of getting high grafting rates. As in case, rate of grafting of polyethylene is high in presence of peroxides due to increased cross-linking [96]. Functional groups present in parent polymer also influences the grafting reactions. Acetate-p-nitro benzoate has low grafting efficiency on cellulose than styrene indicating that more effective graft co-polymer can be formed with aromatic nitro group. If the -OH group in cellulose is replaced by -SH group, the grafting level is increased due to initiation by Ce^{4+} ions in place of abstraction of H-atoms from C-molecules having -OH groups. Annealing and chemical treatment can be done to increase the level of grafting [97]–[99].

2.7.2 Effect of Monomer

Monomer reactivity is another important factor in grafting. This reactivity is dependent on numerous factors such as polar and steric nature, monomer concentration and back bone swelling in presence of monomer. Grafting ratio increases by changing the ratios of monomers and also the technique with which grafting has been done. Grafting on polypropylene shows maximum level when monomer composition was 40% acrylic acid and 60% vinyl imidazole by gamma irradiation. The addition of active groups to the binary mixtures increases the grafting of monomers because of enhancement in polymerization rate [100]–[103].

There is different concentration of monomers required when monomer is changed. Such as concentration of vinyl acetate is 2.6 while ethyl acetate is 60.7% on wool. This is due to different nature of each monomer. This concludes that grafting percentage of ethyl acetate is higher due to minimal loss of ethyl acetate in side reactions while vinyl acetate is reduced in side reactions [104]. Generally grafting efficiency is dependent on monomer concentration. It is reported that with increase in concentration of monomer grafting efficiency increases up to a certain point and then it starts to decrease as monomer concentration is increased. This shows that after a certain limit any increase in the concentration of monomer doesn’t affect grafting reaction rather it favors homo polymerization reaction [80], [102], [105].

2.7.3 Solvent Effects

Solvent act as carrier in grafting reaction by transporting monomers to vicinity of backbone. Solvent choice depends on swelling properties of backbone, monomer solubility in solvent, miscibility of different solvents if used, free radical generation in solvent [106]. Solubility of monomers is dependent on polymer nature and solvent used, e.g. for grafting styrene most useful solvents are the alcohols. This is due to swelling nature of alcohol that it can dissolve styrene effectively thus diffusing the monomer in the polymeric structure. However, as alcohol is changed to ethanol or isopropanol from methanol, the grafting efficiency decreases

The relative reactivity for inducing radicals on back bone polymer by monomer and solvent solution will determine grafting efficiency [107]. It is important to generate free radicals of solvent in order to complete successful grafting mechanism in addition to the formation of these radicals on monomers and on backbone polymer. [108].

2.7.4 Effect of initiator

Initiator is required in all chemically induced grafting techniques excluding radiation technique. So, it is important to know which initiator is required, its nature, function, concentration and solubility should be considered. Some typical examples of initiators are K2S2O8, AIBN etc. Grafting efficiency varies linearly with the concentration of initiator. It is studied that after certain initiator concentration, grafting efficiency remains constant and do not change by increasing initiator concentration. The reason for this is that up to certain limits free radicals participate in grafting initialization, however, as limit is achieved after that these radicals don’t participate in graft initialization rather they lead to the termination of polymers. Another primary factor is solubility of initiator solubility in grafting solvent. Ideally, initiator should be fully soluble in the grafting medium to initiate the reaction through monomers [109]–[112].

2.7.5 Effects of temperature

Kinetics of graft polymerization is controlled by temperature. By increasing the temperature grafting yield increases until a certain limit is achieved. As temperature is increased monomeric diffusion process becomes faster facilitating grafting mechanism. When MMA is grafted on silk, the grafting yield increases as temperature is increased due to diffusion rate of monomer increases significantly and silk swelling also increases [113]. However, it was stated that this enhanced graft polymerization is due to thermal decomposition of initiator increased initiator efficiency on base polymer at elevated temperature [114]. One interesting outcome from many grafting results is that maximum grafted efficiency occurs at temperature close to glass transition temperature [115], [116].

2.8 Requirement for Good bond

The basic requirement for formation of strong bond are

1. Proper choice of adhesive
2. Good joint design
3. Surface preparation
4. Wettability
5. Proper bonding process

2.8.1 Proper choice of Adhesive

Adhesives are used in many industries like shoe wear, automotive, construction and aerospace. For choosing a certain adhesive for particular application, the different factors that must be considered are Cost, Bond strength, Ease of application, Toxicity, Sensitivity to environmental conditions, Nature of adherends

Even though adhesives are grounded with polymer structure, but bond strengths of the adhesive material depend upon materials to be bonded, application environment, and nature of adhesive and surface preparation of a substrate. Adhesive bonds are subjected to tensile, compressive and shear stresses to which different adhesives respond in different ways. Sometimes it is advisable to consult an adhesive specialist for proper use of adhesive for certain application [77].

2.8.2 Good Joint design

Proper joint design can impart strength to specific joint. Careful bond design in combination of adhesive bond strength can yield stronger bond and can meet end requirements of parts bonded.

2.8.3 Surface preparation

Since adhesives are applied onto surfaces of two substrates, so proper treatment of surfaces is required to adhere both surfaces. Strength and life time of bond depends largely on surface treatment. According to few researches surface treatment is directly proportional to life and service expectancy of any adhesive joint [2]. Surface treatment is required to remove any layer of containment like dirt, grease or oil which appears to be the surface of substrates for better adhesion [117], [118]. There are different ways to clean these surfaces for better wettability, some surface preparation methods are given below:

1. Solvent Cleaning
2. Chemical treatment
3. Mechanical treatment
4. Chemical etching

2.8.3.1 Solvent Cleaning

The process of removing oil from substrate surface with an organic solvent is known as solvent cleaning. There is no change in physical or chemical properties of surface in this method. Different solvent used are toluene. Methyl alkyl alcohol, methyl ethyl ketone. The part is rubbed with hot vapors of solvent in vapor degreasing. It is used to remove oils, greases and waxes from substrates. Proper solvent and equipment are required for vapor degreasing. Most commonly used solvents for vapor degreasing are Trichloroethylene and perchloroethylene. Vapor degreasers can be available with built-in transducers in solvent tank. The parts primarily cleaned by vapor degreasing are immersed in ultrasonic scrubber followed by spraying of solvent [77], [119].

2.8.3.2 Chemical Treatment

In Chemical treatment, surfaces are cleaned by chemical means. The chemical nature is modified to enhance its adhesion properties of surfaces. This technique is usually applied on polymeric substrates where solvent cleaning may not be used. Commonly used agents for chemical treatment are caustics, chelates and acids etc.

2.8.3.3 Mechanical Treatment

Mechanical treatment involves tools like sandpaper, wire brushes and scrapers to remove any rust, scale or weld splatter present on surface. However, these tools are very slow to use in large areas. One disadvantage of abrasion process is, it causes particles of debris to penetrate in the abraded surface. These particles can come from surface containment, abrasive, and surface of material. These particles should be removed before applying adhesive. This can be done with brush or cloth or compressed air. After abrasion process, surface must be cleaned with solvent before bonding. Solvent- moisturized cloth must be renewed frequently to avoid any contamination from cloth [20] .

2.8.3.4 Chemical Etching

In chemical etching, the surface to be etched is dipped into a chemical solution. This solution makes the surface more active by dissolving containments or transform it, thus making it receptive for bonding. After solution etching part is placed in water bath followed by high temperature drying. This method is widely used for treatment of plastic surfaces for bonding. Chemical etching is sometimes preceded by cleaning. Sulfuric acid-dichromate is widely used chemical etchant used for surface treatment. There are some hard rules that are used to determine composition of this solution. One of composition is shown in

Table 2-3. Exact formulation is determined by strength of adhesive bond after testing. Although some cavities formation may take place on the surface but improve in wettability and higher bond strength has been monitored in many cases [37], [120], [121].

2.8.3.5 Plasma Treatment

Plasma is combination of charged particles, atoms, molecules and radicals. Plasma is very reactive which is the reason it can be used for modification of surfaces. It makes surfaces more hard, rough, and conductive to adhesion. The contact time or exposure time varies from surface to surface such as polyethylene, the reaction time is about 9 seconds while for PTFE it may take several minutes to prepare a surface. The bonds formed by plasma treatment are two to four times stronger than bonds from chemical or mechanical treatment [122], [123].

2.8.3.6 Corona Treatment

Corona discharge is the plasma generated at atmospheric pressure. The charged particles such as ions and electrons produced by corona discharge are accelerated by an electric field. These fast-moving particles are used to clean the surface and impart polar groups to the substrate surface. The bonding should be made immediately because the effects produced by corona discharge are very short lived. Polyolefin films are mainly bonded with this technique [121], [120].

2.8.3.7 Primers

Primers or adhesion promoter's acts as bonding layer between adhesive and substrate and improves the adhesion. Polymer chemistry of primers and of adhesives polymer chemistry used in adhesive technology is same. A primer improves wettability and provide protection to surface in dry conditions. There is no chemical difference between adhesive and primer in dry conditions. Primers transforms surface of adherend into polymer surface which is more convenient in adhesive technology than inorganic surfaces. Primer layer has only minor thickness but it is worth of mention that phenolic resin primer represents a surface for epoxy resin adhesives with excellent adhesive properties [121]. Anti-corrosive primers are used in aircraft industry which have different formulation than normal adhesives. The composition of these primers consists of epoxy resins, resole, hardening agents and functional component such as strontium chromate. Primers may directly be added in adhesive to improve adhesion properties of difficult to bond materials such as nonpolar plastics. The adhesion is improved because components in primer etch the adherent and no oxidative pretreatment is required. It is clear that primer system do affect the surface properties of materials to be joined so, careful consideration should be done while choosing a primer for adhesive applications [25].

Table 2-3 Composition and Processes variable for Sulfuric Acid dichromate etching

Variable	**Typical Value (part by weight)**	**Range (Part by weight)**
Potassium/Sodium dichromate	5	0.5-10
Conc. Sulfuric Acid	85	65-96.5
Water	10	0-27.5
Time	-	10 sec to 90 min
Temperature	-	Room temperature to 7^{o}C

2.8.4 Contact Angle

Contact angle is used to determine surface tension, surface free energy and changes occurring on surface layer when surface is modified. There are numerous factors that significantly influence contact angle, some of which include Surface porosity, Chemical and physical properties of liquid (adhesive) and solid surface, Surface rigidity, Surface contamination, Humidity, Temperature [25],[5].

2.9 Dispensing Method

Dispensing method is to apply adhesive on the substrates to bond together. There are different dispensing methods used, a few of which are discussed below Brushing and troweling, Roller transfer, Pin transfer, Stencil printing, Spray application, Nozzle dispensing method.

2.9.1 Brushing

Brushing is most common method to apply adhesive layers on the surface of substrates. It is used when adhesive is applied to certain areas of surface or when adherends have complex profiles. Best results are obtained with stiff brushes and brushes giving good application should be repeatedly used. On of major disadvantage of brushes is that an even layer of adhesive cannot be applied to the substrates which results in different film thickness at different areas [124].

2.9.2 Spraying

Spraying is used for applications having large areas. Higher production rates with very uniform layer can be achieved with this technique. Solid content and viscosity should be controlled to confirm an even coating. The equipment is similar to that of spraying paints. By varying operating conditions and design of equipment used for spraying paints, almost every design can be covered with uniform layer of adhesives. Health hazards resulting from solvent based adhesives must be considered and proper ventilation must be provided for safe use of these adhesives.

2.9.3 Roller Coating

This technique is mostly used to apply adhesives to flat films and sheets. In this technique adhesive material stored in a tank is transferred from one roller to another roller and via the second roller applied to the substrate. Highest production rate can be achieved with most uniform coverage. When applying multiple adhesive coats, time between coats should be regulated. Too long time lead to the lifting of earlier coats, while if time if too short it will result in blistering , bubbling and sagging [125].

2.9.4 Knife Coating

This technique involves an adjustable knife blade, rod to control the adhesive deposition flowing onto a sheet moving under the blade. The thickness of adhesive layer is determined by measuring distance between tip of baled and adherend surface [126].

2.9.5 Flowing/Nozzle dispensing method

The adhesive is fed through a hollow brush or nozzle under certain pressure. When brush is used it is called flow brush while with nozzle it is termed as flow gun. Liquid adhesives can be applied to surfaces having irregular shapes more effectively by this technique. It can provide uniform film thickness of adhesive layers and high production rates as compared to brushing method. In this method the adhesive should be brushed on in one smooth sweep [127]. Most common nozzle dispensing methods are as follows;

2.9.5.1 Squeeze Bottle

The adhesive is flown by inverting or squeezing the bottle. The volume of dispensing adhesive is difficult to control in this method.

2.9.5.2 Pressure pump

This process involves that adhesive is pushed through the syringing which is based on pressurize system. The flow of the adhesive is controlled by the air nozzle which spread adhesive over the surface by pressing the air button [5].

2.9.5.3 Jet dispensing

In this method, a spring-loaded pin is used to push the adhesive through the nozzle in a cyclic manner. The pin is raised above the adhesive reservoir by the air pressure and dipped back by the spring to force the adhesive through nozzle [124], [8].

2.9.5.4 Silk Screening/Stencil Printing

It is a manual technique in which adhesive coating is applied onto selected areas. This technique is useful for low viscosity adhesives because they can easily be spread onto the substrate by cloth. However, this technique only used to apply relatively thin film. Silk screening cannot be used for tacky or fast drying adhesives [128].

2.9.5.5 Spatulas, knives and trowels

Specula is most effective tool for hard to spread adhesive. Both knives and trowels fall in spatula category. Both knives and trowels have notches in their edges. The amount of adhesive can be regulated by knives and trowels with the help of spacing between the notches and depth of notches. Blade should be kept at right angle to the surface. Square shaped notches are preferred for trowels. Adhesives which have higher liquid content, rounded and closely spaced notches are used as these notches allow adhesive to form unbroken film.

CHAPTER 3

MATERIALS AND EXPERIMENTS

3.1 Materials

Following materials were used in the formulation of adhesive.

- Polychloroprene rubber AD-130 grade
- Phenolic Resin
- Magnesium oxide (MgO) / Zinc Oxide (ZnO)
- Anti-oxidant
- Methyl Methacrylate and styrene as grafted monomer
- Hydrogen Peroxide
- Solvents such as Toluene, Ethyl acetate, Naphtha,

Polychloroprene, ZnO, MgO, phenolic resin and anti-oxidant was provided by local industry. Hydrogen peroxide and methyl methacrylate were commercial grade Daejung Korea chemicals. While toluene and ethyl acetate were supplied by Multi LinkX Enterprises. These chemicals were also commercial grade having 80-90% purity.

3.2 Formulation

Table 3-1 Formulation of grafted PCP Adhesive

Formulation No	**CR phr**	**Resin phr**	**MgO phr**	**Ethyl Acetate phr**	**Naphtha phr**	**Toluene phr**	**MMA phr**	**HPO phr**
GA-1	100	35	3	420	220	180	55	2
GA-3	100	60	3	420	220	180	60	2
GA-4	100	60	3	420	220	180	65	2
GA-9	100	60	3	420	220	180	70	2
GA-11	100	65	3	420	220 phr	180	75	2
GA-13	100	65	3	420	220	180	75	3
GA-16	100	65	3	420	220	180	65	4

The best adhesive formulation was achieved after almost 80 experiments were run at lab scale. Some of core adhesive formulations are given below. These formulations are based on wide trial of experiments. Optimum amount of materials is added during the course of experiments to achieve maximum strength of adhesive. Ethyl acetate and toluene based solvent system is used in all experiments. The compatibility of solvent is based on solubility factor, evaporation rate and final properties of solvent which is imparted in the adhesive system.

Table 3-2 Formulation of Grafted PCP Adhesive GA-11

Sr. No	**Chemicals**	**Parts Per Rubber**
1.	CR	60
2.	Resin	65
3.	MMA/Styrene	75
4.	HPO	2.5
5.	Anti-Oxidant	8
6.	Ethyl Acetate	252
7.	Toluene	125
8.	MgO	3
9.	Naphtha	140

Table 3-3 Formulation of Grafted PCP Adhesive GA-13

Sr. No	**Chemicals**	**Parts Per Rubber**
1.	CR	60
2.	Resin	65
3.	MMA	75
4.	HPO	3
5.	Anti-Oxidant	8
6.	Ethyl Acetate	220
7.	Toluene	140
8.	MgO	3
9.	Naphtha	126
10.	ZnO	3

3.3 Methods of Production of Adhesive

There are two methods to produce contact adhesive which are as follows:

- Roll mill method
- Slurry method/direct dissolving method

Direct dissolving method is mostly used in industries as minimum labor force is required to operate and control production process. Schematic diagram of direct dissolving method is shown in Figure 3.1. The direct dissolving technique is used to carry out the experiments in the laboratory. After successful experiments at smaller scales. The production is scaled up while fabricating the new bottom mixing impeller machine.

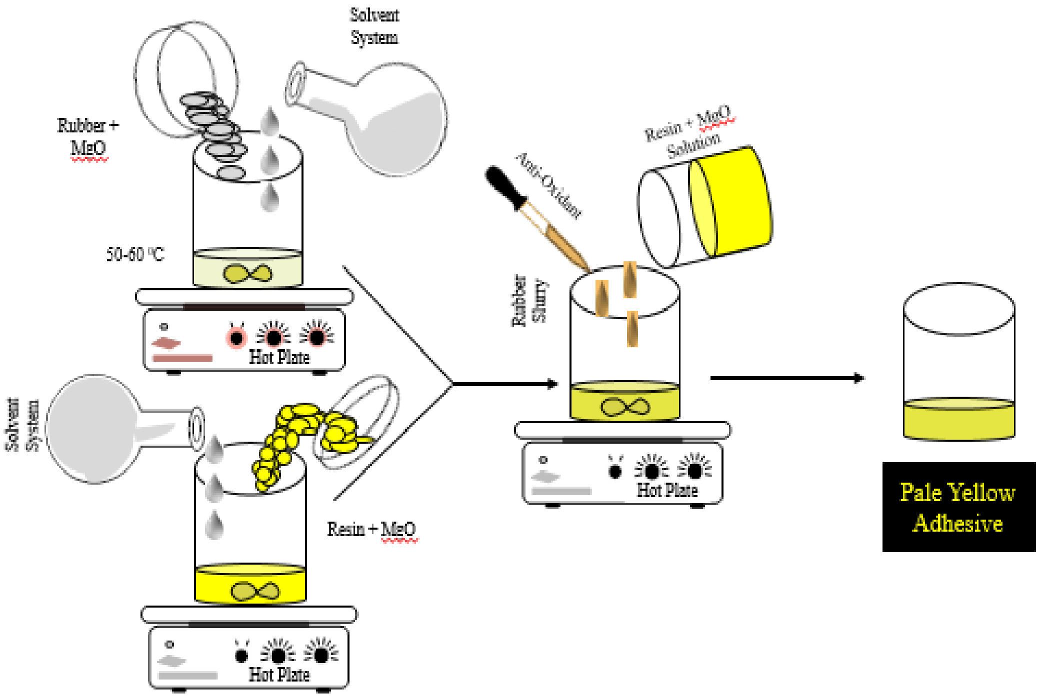


Figure 3.1 Direct Dissolving Method for Producing PCP Adhesive

3.4 Description of Apparatus

The bottom impeller mixing machine is fabricated to produce small batches of adhesives. The machine consists of following parts:

- The closed vessel.
- The impeller is situated at the bottom of the closed vessel.
- Heating element.

- Insulation.
- Temperature sensor immersed in the vessel.
- The panel consisting of the temperature and motor controller.
- Speed of rotor is set to 135 RPM.

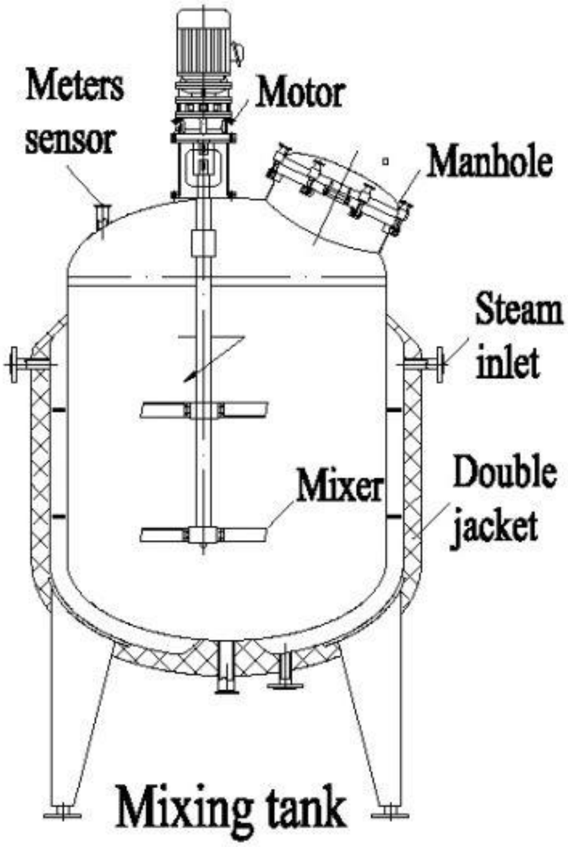


Figure 3.2 Sketch of Verically Impeller Machine

3.5 Procedure

Bottom mixing technique is used to mix all the materials together.

- 100 phr Polychloroprene rubber is dissolved in 180 phr toluene in round bottom stirrer vessel and leave it for 15 min stirring while applying the constant temperature of 35 °C.
- When the rubber chips disappear and the completely uniform slurry mixture is produced, add methyl methacrylate or styrene and raise the temperature to 50°C.
- Add hydrogen peroxide at 50°C and leave it for 35 minutes stirring maintaining constant temperature of 50°C.

- Light Brown color of the mixture appears, drop the temperature to 40^oC.
- Adding 5-8 phr of anti-oxidant at 40^oC and stirring for 15 min at that temperature.
- Now add the ethyl acetate and resin respectively.
- Adding 4-5 phr of antioxidant while keeping the temperature at 60 ^0C.
- After that add 3 phr MgO and 3 phr ZnO and stir for 30 min while maintaining temperature at 60^oC.
- Add naphtha to lower the viscosity of the prepared solution.

3.6 Sample Preparation

Different specimens of different substrates were prepared according to ASTM standard D903 (2017) for testing the prepared adhesive. Peel testing was used for testing all the samples.

3.6.1 Leather Samples Preparation

Leather substrates were abraded by 40 number sand paper before applying adhesive layers.

- **Canvas-Canvas**

The dimension of the two substrates are:

- One substrate was 300 mm long and 25 mm wide.
- The second substrate was 400 mm long and 25 mm wide.

The calculations are carried out according to standards by determining the average values of peel strength of at least 5 specimens.

3.6.2 Applying the adhesive

After preparation of the specimen, the adhesive was applied by brushing method on the surface of substrates. The thickness of adhesive layer is about 0.2 cm on the surface of both the substrates.

3.6.3 Drying Time

After applying the layers of adhesives over the substrates, 5 minutes for leather substrates and 3 minutes for canvas substrates was provided at room temperature.

3.7 Characterization

3.7.1 Digital Krebs Viscometer

The Digital Krebs Viscometer is used for measuring the viscosity of Newtonian and non-Newtonian fluids. The viscosity of a non-Newtonian material varies depending on the rate of shear, but the Krebs viscometer measures the viscosity at a set speed shear rate which provides a consistent standard. The dimensions of the paddle conform to the precise specification of ASTM D562 [49].

3.7.1.1 How does it work?

Samples of adhesive are tested in the container which is placed on the viscometer base. The can is filled to within 3/4" (20mm) of the top.

- Up: Spindle stationary, drive motor off
- Down: Spindle rotating; sample being measured

3.7.1.2 Operation

Fill the container with the sample up to 500 ml and stir it. Now ensure the temperature is at the correct value. Now place the sample container on the magnetic base and down the unit to the level indicated on the paddle shaft. Now press the start buttons and paddle will move at speed of 200 rpm. After this viscosity can be seen on the display of the equipment in desired units. After 10 seconds’ paddle, will automatic stops and display the reading and if the start button is pressed for a long time it will run again. [51], [8]. After measuring and calculating the reading raise the measuring head from the container and allow some time so that all sample drain out from the paddles. The equipment will also provide the printing of the reading while store number is written on the paper along with different units [9].

3.7.1.3 Description

A paddle is immersed in a vessel which contains a fixed volume of the sample material. A constant speed motor drives a paddle at 200 r.p.m. and the torque induced is proportional to the viscosity of the sample and may be converted into viscosity (cP) or weight units (Gms) [10].

3.7.2 Fourier Transform Infrared Spectrometry

Infra-Red spectroscopy has protruding role in field of polymers. It provides important information about the chemical and crystal structure of these polymers. IR spectra of PCP,

PCP-g-MMA were observed by using. A highly polished surface of KBR is prepared, afterwards placing another plate on top of first plate. The liquid adhesive is spread between the two plates forming a thin layer and claiming the plates together. Wipe off the liquid from the edges of plates. Then mount the plate on sample holder. The frequency range for the adhesive is kept between 400-4000 Hz.

3.7.3 Peel test measurements

Adhesive strength is measured for many purposes. Some bonds are designed not to break in use (e.g. construction materials), some are designed to allow separation in normal use (e.g. a foil lid), and others are designed to be resealed several times (e.g. reseal able bag tape). Strength of adhesive bonds can be measured by tensile testing, peel testing, shear testing or compression testing, but for flexible substrates peel test is most appropriate among all. Peel tests are used to calculate resistance to localized stresses in especially in flexible substrates. Peel forces are applied to linear front's therefore high adhesive modulus and more flexible substrates, the stressed area reduces to linearity. Peel strength depends on bond thickness for elastomeric adhesives. As the bond thickness is increased elastomeric characteristics of adhesives absorbs the applied load by distributing the load over large areas [129].

For measuring the value of peel test a universal tester is used. The tester will capture the high accurate frequency data points and make the curve of the strength. The smoothness of the curve shows the uniformity of the adhesive applied to the surface. The advantage of using a Shimadzu universal testing machine that it can be also used for shear strength, applied coating pull-off and tensile strength measurements etc.

3.7.3.1 Purpose of Peel Tests

The aim of testing of peel strength of an adhesive is to identify the bond strength of the material. The adhesive strength can be referred as the “stickiness” of a material. This stickiness provides resistance when force is applied on the sample to separate them. The measured value then provides the estimate that if the strength value is strong enough for a specific material or may be some other bonded process needed [61].

3.8 Standard test methods for flexible substrate

These test methods cover the determination of the adhesion strength between plies of fabric bonded with rubber or the adhesion of the rubber layer in articles made from rubber attached to other material. They are applicable only when the adhered surfaces are an approximately plane or uniformly circular as in belting, hose, tire carcasses, or rubber-covered sheet metal. When the adhered surfaces contain sharp bends, angles, or other gross irregularities that cannot be avoided in preparing test specimens, special test methods must be employed for evaluating adhesion. The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only. This standard does not purport to address all the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use [23].

Figure 3.3 Different types of Peel tests [23]

3.8.1 Test Method

The two general test approaches are described as follows:

1. **Static-Mass Method**, Separation between two adhered surfaces is caused by gravity acting on the mass.
2. **Machine Method,** this method includes the tension machine due to which separation occurs between two adhered surfaces.

These adhesive tests are applied to test specimen under certain conditions, a (measured) force enough to break the adhesive joint at a measured rate, a layer of reasonable thickness with separation (rupture, tearing) at the adhered surfaces [87]. The mathematical value of the adhesion is expressed as

- The average force required to cause separation at a definite rate, or

- The average rate of separation caused by a known or specified force. In the machine test method, the rate of separation is fixed and the adhesion value must be expressed in terms of the measured force. With the static mass test method, either (1) or (2) can be used, but the latter is preferable and will be here employed.

3.9 Determination of the % Solids content

This test is carried out to determine the % solids in the adhesive. % solids of the adhesive are the amount of usable adhesive per kg. The solvent is used just for the carrier of the adhesive to provide smooth flow ability. Higher the number of solids will increase the peel strength but the range for Polychloroprene adhesive is set to be at 50-60%. More solids content leads it to lesser peel strength and it majorly because of the high viscosity. As viscosity effects the applicability of the adhesive when applied to the substrates. The test is carried out according ASTM standards explained in appendices.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Fourier Transform Infrared Spectrometry

The FTIR or both grafted and non-grafted PCP adhesive is shown in Figure 4.1. The absorption peak at 1730 cm-1 is the characteristic of grafted PCP polymer and is due to C=O of PCP and MMA. This peak is not present in backbone of PCP polymer. This peak indicates that MMA has been positively grafted onto PCP. Similarly, -CH2, C-H, and vibration peak of carbon chain is shifted from 1465, 1062 and 1245 to 1485, 1049 and 1241 respectively. All of these peaks show the compatibility between different components of adhesive system. It also shows enhanced molecular interaction between PCP rubber, MMA, resin, MgO and solvent system used.

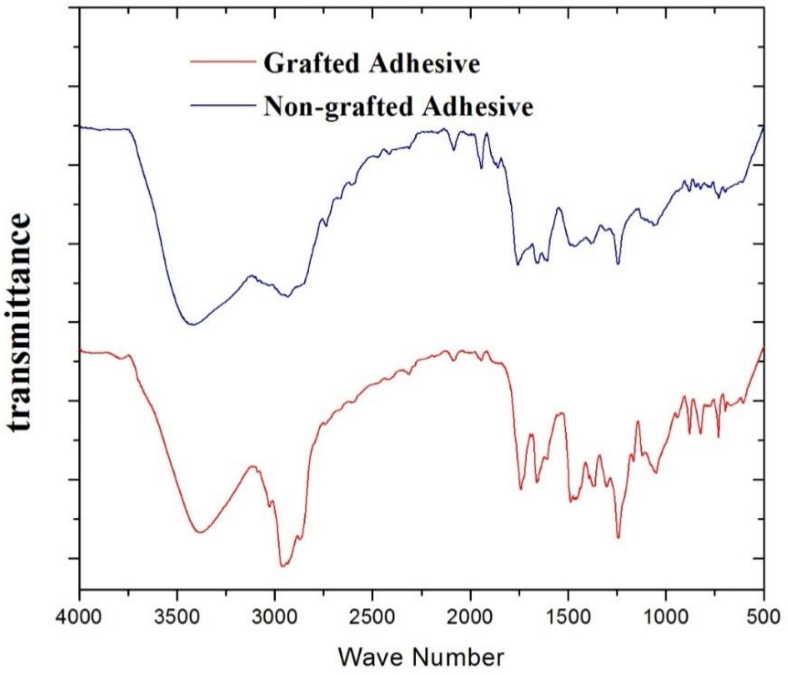


Figure 4.1 FTIR of Grafted and Non-grafted PCP Adhesive

4.2 Effect of Raw Materials on Peel Strength of Formulated Adhesive

All raw materials used in formulation of grafted chloroprene adhesive effects the performance of adhesive. So, appropriate quantity of these materials is needed to get the desired strength of adhesive. The results obtained from these materials on overall strength of adhesive are discussed below.

4.3 Effect of Resin Content

Fig 4.2 shows the effect of content of phenolic resin on adhesive composition on leather to leather and canvas to canvas substrates. Peel strength for both canvas to canvas and leather to leather increases as resin content is increased up to 85 phr. But as resin content is increased from 85 phr bond strength decreases in both leather to leather and canvas to canvas substrates. This is due to decrease in flexibility of the system.

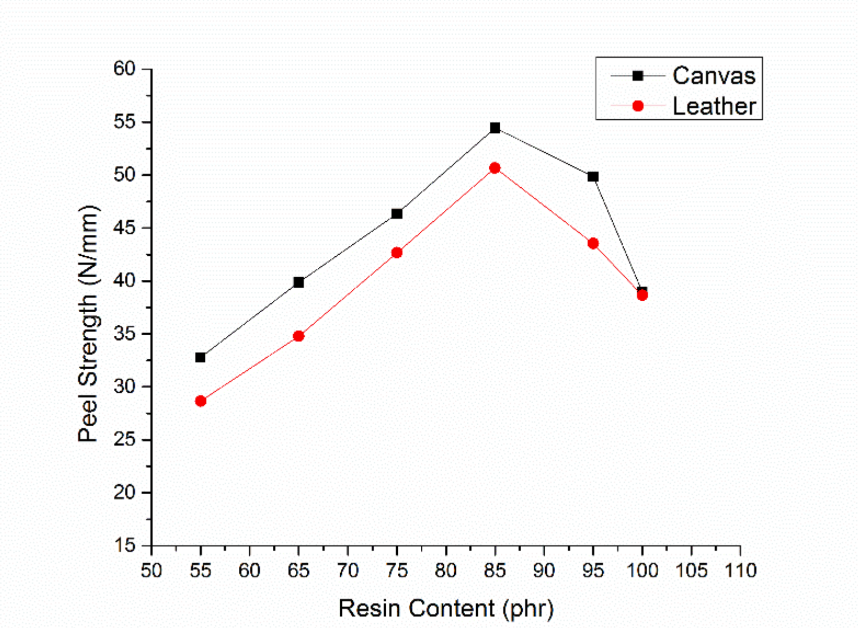


Figure 4.2 Effect of Resin Content on Peel Strength

Fig 4.2 demonstrates that 80-85 phr of tar substance are upgraded values for a high-quality performance of Polychloroprene elastic based contact adhesives. Past these esteems, the general strength of the glues is influenced and diminish essentially for a few substrates which result in poor performance of the PCL adhesive. Improvement in strength and initial tack for different materials is due to compatibility between PCP and resin blends. However, this compatibility decreased as amount of resin is increased from 85 phr, which resulted in reduced tack time and lower cohesive properties of the adhesives. On the other hand, there was a decrease in joint strength which can be related to the change in the locus of failure of the joints, from an adhesion (for a resin content lower than 85 phr) to a cohesive failure of the Polychloroprene (for a resin content higher than 85 phr) [54], [73].

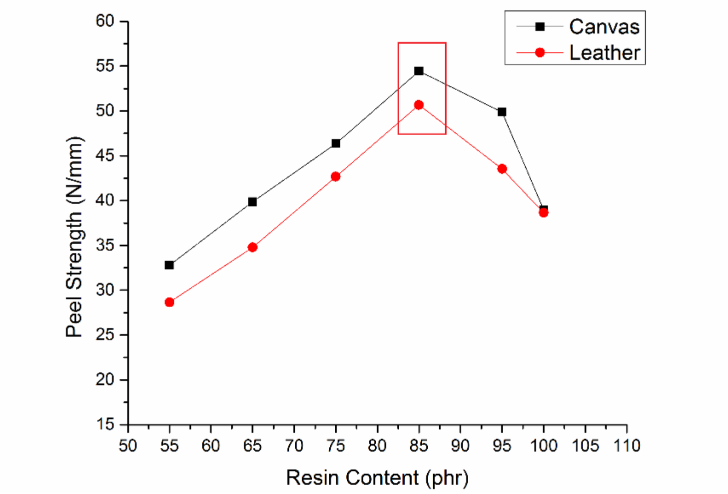


Figure 4.3 Selection of Optimized value of resin content

4.4 Effect of Crosslinking Agents

Peel strength decreases as number of cross-liking agents (MgO and ZnO) increases as shown in Figure 4.4 It can be seen that optimized value of crosslinking agents is 3-4 phr for better performance of adhesive for all substrates. The peel strength decreases because increased number of crosslinking agents decreases the flexibility of adhesive layers on the substrates. Also, by increasing the molecular weight Mc of crosslinking agent will decrease the shear strength of adhesive. This is because of cohesive characteristics of crosslinking adhesives which depends on the molecular weight of crosslinks. At higher phr values the wettability of adhesive is also decreased due to increase in viscosity of adhesive. As a result, the mobility of formulated adhesive is compromised [76].

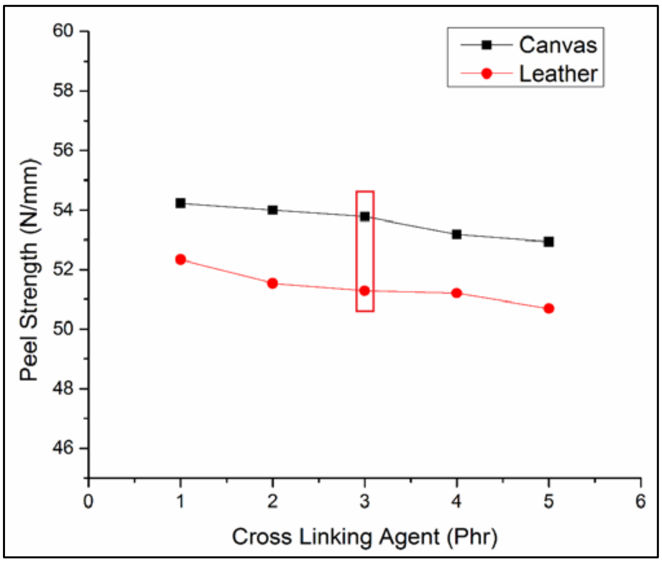


Figure 4.4 effect of crosslinking agent in peel strength and selection of optimized quantity of cross-linking agents

4.5 Effect of Monomer Concentration

The influence of grafting of chloroprene with methyl methacrylate on peel strength is proven in Figure 4.5. The peel strength increases as concentration of MMA in the formulation increases with increase in concentration of MMA, the peel strength increased boundlessly, attaining maximum value at 75 phr, and then it started to decrease. Increasing monomer concentration results in accumulation of these monomer molecules in close proximity to backbone of PCP. The decrease in peel strength is because of reduction in active sites on the polymer backbone after saturation has been reached with more MMA molecules remaining unreacted as co-polymerization proceeds. With this higher monomer concentrations, the primary radicals attack the monomer instead of reacting with the backbone polymer. It can also be noted that, once the graft co polymer radical has formed, the excess monomer will shield the graft co-polymer, which may inhibit the rate of graft co-polymerization. In addition to this the excess monomer will be available for initiator radicals to initiate the homo-polymerization reaction and there by decrease in the peel strength of adhesive.

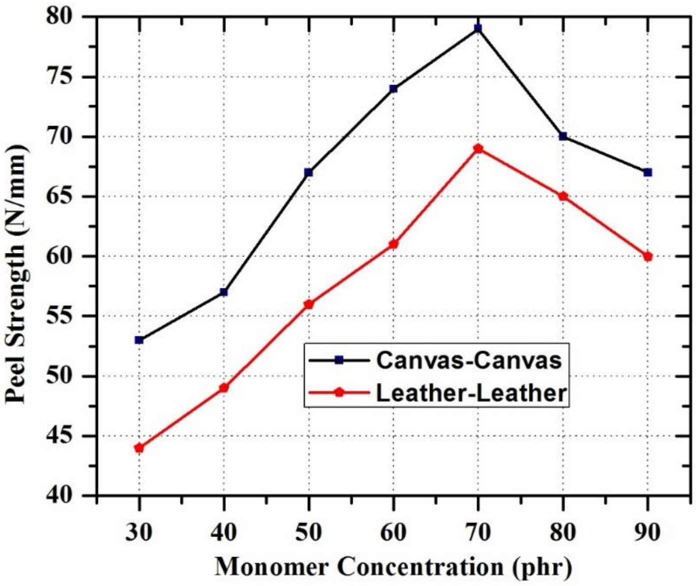


Figure 4.5 Effect of Monomer Concentration on Peel Strength

4.6 Effect of initiator HPO

Hydrogen peroxide (HPO) was used as an initiator in grafting of MMA onto chloroprene rubber. The amount of initiator added was varied from 0.3 to 5 phr. The variation of HPO concentration and its effects on peel strength is shown in Figure 4.6 and Table 4-1. The figure shows that with increase in initiator concentration the peel strength increases and then it hardly changes at higher concentration rate. The high strength of adhesive is due to more free radicals at low initiator concentration. At higher concentration, initiator radicals are in abundance so, the peel strength remains constant even if HPO concentration is increased [115]. The effects of the initiator concentration while keeping other parameters constant on the peel strength for canvas and leather substrates is shown in Table 4-1.

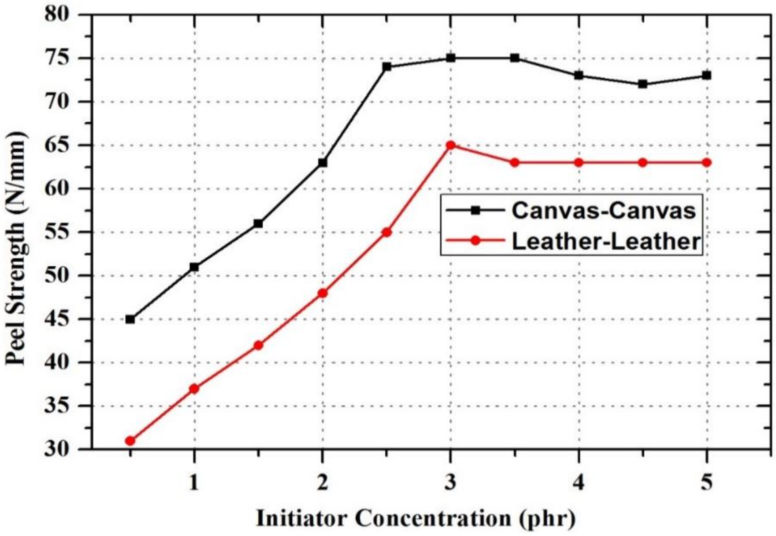


Figure 4.6 Effect of Initiator Concentration on Peel Strength

Table 4-1 Effect of Initiator Concentration

Initiator Conc. phr	**Temperature ^{0}C**	**Peel Strength (N/mm)**	
		Canvas	**Leather**
0.3	30	43	33
0.7	30	50	40
1	35	54	45
1.5	40	59	51
2	40	68	58
2.5	40	77	65
3	40	76	65
3.5	40	76	64
4	50	75	64
4.5	50	75	64
5	40	75	64

4.7 Effect of Grafting temperature

Graft copolymerization is carried out at different temperatures ranging from 50 °C-90 °C. In Figure 4.7 it can be seen that higher temperature results in higher peel strength for both canvas-canvas and leather to leather substrates. The peel strength increased till temperatures of 50 -55 °C. The maximum strength is reached at 55 °C. After that the peel strength decreases for both leather to leather and canvas to canvas substrates. The decrease of peel strength is majorly due to formation of homopolymers of MMA and CR. Graft copolymerization increases till 55°C while further increase in the grafting temperature has promoted homo-polymerization reaction of MMA to Poly-MMA (PMMA) [130]. The maximum adhesion strength has been shown by an adhesive prepared by the grafted polymer sample that was grafted at 55°C. Therefore, adhesion properties of PC can be enhanced by grafting with MMA.

Table 4-2 Effect of Grafting Temperature

Grafting Temperature ^{0}C	**Resin Phr**	**Monomer Concentration Phr**	**Initiator Concentration Phr**	**Peel Strength (N/mm)**	
				Canvas	**Leather**
30	35	50	2	40	28
35	35	50	2	47	34
40	35	50	2	51	39
45	35	50	2	58	47
50	35	50	2	62	53
55	45	50	4	71	60
60	55	50	4	71	60
65	55	50	4	67	58
70	55	50	4	65	56

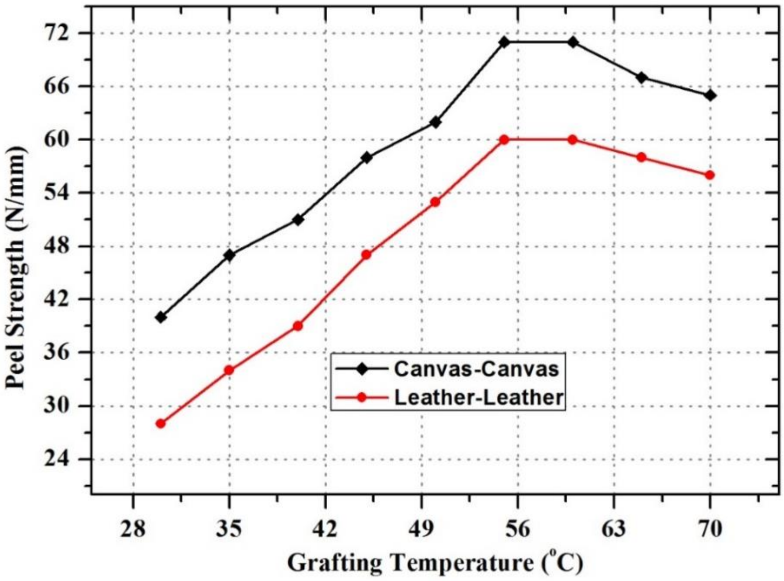


Figure 4.7 Effect of Grafting Temperature on Peel Strength of PC-g-MMA Adhesive

4.8 Determination of Solids Content

The method includes the determination of the non-volatile component present in the adhesive which is responsible for bond strength. The test is carried out according to the standard procedure of ASTM D1582 - 98(2011). The procedure includes the weighing of empty porcelain cup. Then adding 3-5 grams of adhesive in a cup and again weigh the cup. Now place the cup in the oven at 100C^0 for two hours. After two hours take the sample from the oven and weigh it again, the residue remaining are the solid contents which are present in the adhesive. The formula use for calculation is as follow:

$$\% \text{ Solids Content} = \frac{m_2 - m_0}{m_1 - m_0} * 100$$

Where m_0 = weight of empty cup

m_1= weight of cup containing adhesive

m_2= weight of residue after heating

Table 4-3 shows formulated adhesive % solid contents. GA-11 contains the highest % or solids contents i.e. 56 % which shows that the formulated adhesive has good mechanical properties and applicability [3].

Table 4-3 Percentage Solids Contents of Formulated Adhesives

Adhesive	**Solids Content %**
GA-1	20
GA-3	29
GA-4	34
GA-9	45.18
GA-11	56
GA-13	54
GA-16	40

4.9 Viscosity

The applicability and flow ability of the adhesive is affected by its viscosity when it is applied to the substrates. Hence, it is essential that formulated grafted Polychloroprene adhesive exhibits the good viscosity. Figure 4.8 shows the viscosity measurements of GA-11 and GA-13 show that they are well arranged in the standard levels set by Dow chemical USA [33]. The adhesive having good mechanical properties should have the viscosity arrange in 2500 centipoise to 3500 centipoise range. The formulated adhesives GA-11 and GA-13 show that they are well in the standard ranges which 2500 and 2900 centipoise.

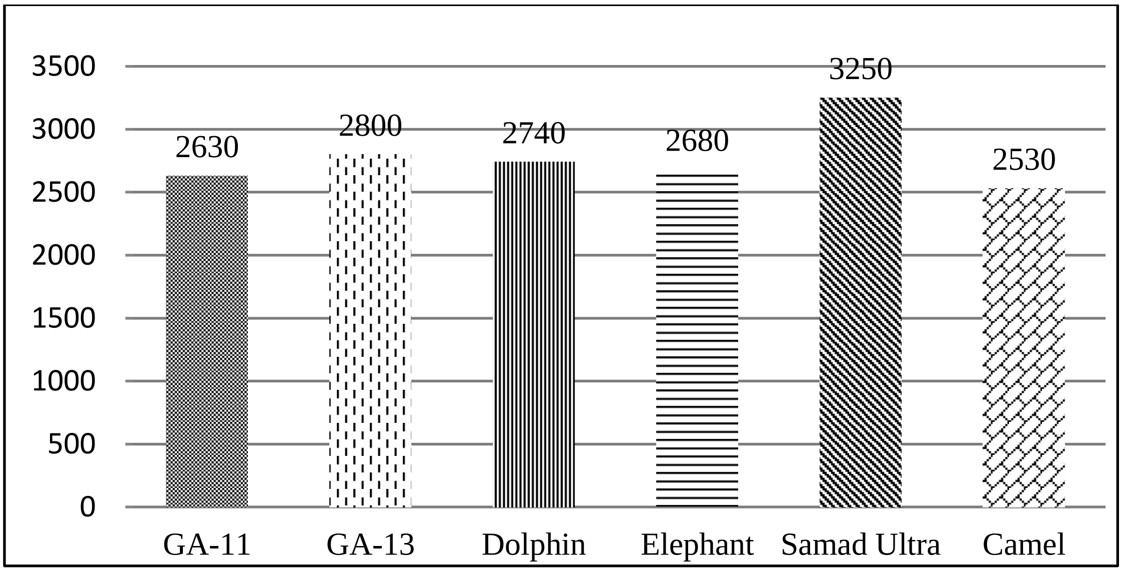


Figure 4.8 Viscosity of Different Adhesives

4.10 Aging Studies of Formulated Adhesive

The adhesive is useful when it with stand to exposing condition. For the good adhesive, it should not only resist the mechanical forces which are acting on it but also it should resist the environmental conditions. In this way, a standout amongst the most imperative qualities of an adhesive joint is its continuance to the working condition. This perseverance is otherwise called joint perpetual quality or toughness. The lastingness of the adhesive joints relies on upon environmental components like high and low temperatures, dampness or relative mugginess, synthetic liquids, and open-air weathering. Every single polymeric material is decomposed to some degree by exposure to high temperatures. To withstand raised temperature, an adhesive must have high dissolving or softening point and imperviousness to oxidation. Exposure to high temperatures brings about chain scission prompting to diminished atomic weight of the bulk polymer. This outcome in both decreased peel strength and fragility.

4.11 Aging Under Environmental Conditions for 4 Months

Effect of aging under environment for different surfaces after span of four months is shown in Figure 4.9. It shows the peel strength for both canvas-canvas and leather to leather substrates. The adhesive loses its peel strength with aging however the drop-in peel strength is less as compared to other adhesives. Table 4-4 shows percentage fall in peel strength of different adhesives. The adhesive formulated by GA-11 and GA-13, percentage fall in peel strength is 1.51 and 1.21 respectively for canvas-canvas, while for leather substrate the percentage fall is 2.60 and 2.89 for GA-11 and GA-13 which is much lower than the commercially available adhesives. This is due to grafting of MMA onto PCP polymer which increases the peel strength on aging.

Table 4-4 Characteristic after aging under ambient conditions for 4 – months

Aging Condition	**Type of Adhesive**	**% Fall of Peel Strength**	
		Canvas-Canvas	Leather-leather
Ambient Conditions for 4 Months	GA-11	1.51	2.60
	GA-13	1.23	2.89
	Dolphin	3.25	7.89
	Elephant	8.33	10.34
	Samad Ultra	14.28	11.36
	Camel	5.26	8.82

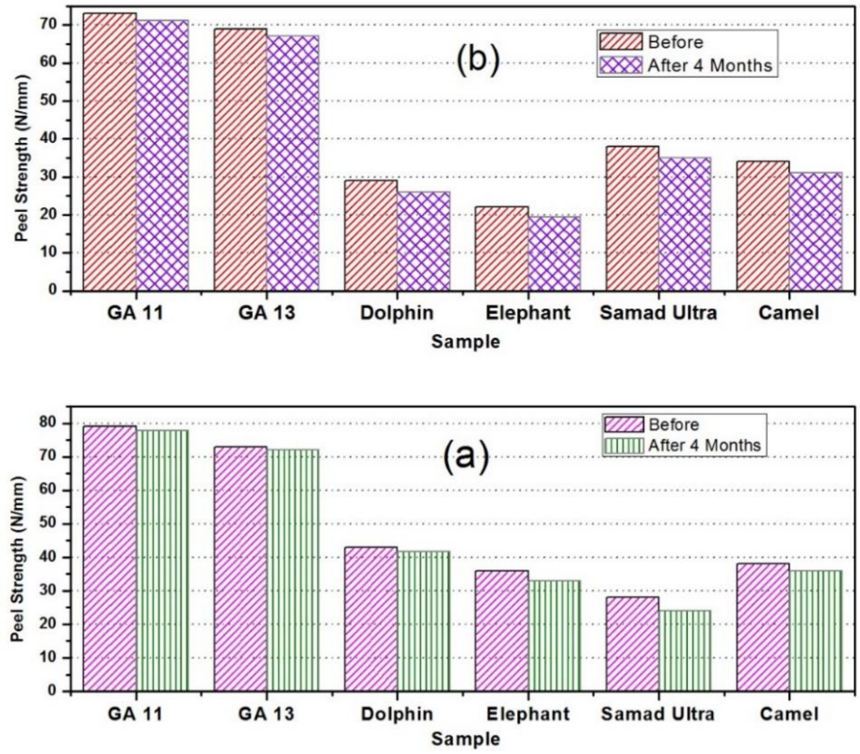


Figure 4.9 Aging results under ambient conditions for 4 months

4.12 Aging Results at 100 ^{0}C

The effect of temperature on adhesive peel strength is shown in Figure 4.10. Fig 4.10 (a) shows the effect of temperature on canvas-canvas while fig 4.10 (b) shows temperature effect on leather-leather substrate. The peel strength decreases at higher temperature because high cross-linking happens at elevated temperature which results in reduction of flexibility of adhesive system. As flexibility of an adhesive system is decreased the bond failure may occur even at lower loads at higher temperatures [131]. The percentage drop in peel strength for both canvas and leather substrates is given in Table 4-5 explain the effect of temperature on different substrates bonded with different adhesives. The percentage peel drops for GA-11 and GA-13 is low as compared to other adhesives which shows the applicability of grafted adhesive even at higher temperature.

Table 4-5 Characteristics after aging for 24 hours at 100 ^{0}C

Aging Condition	**Type of Adhesive**	**% Fall of Peel Strength**	
100 ^{0}C for 24 Hours		Canvas-Canvas	Leather-leather
	GA-11	3.67	4.10
	GA-13	4.10	7.24
	Dolphin	8.37	13.88
	Elephant	13.88	17.24
	Samad Ultra	23.21	22.72
	Camel	8.42	11.76

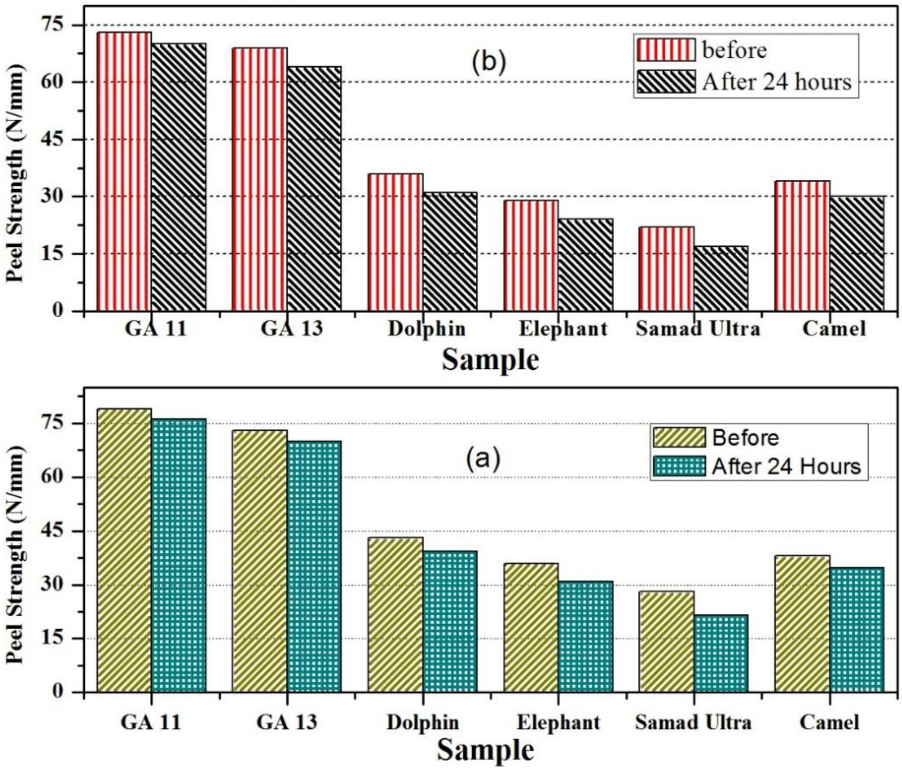


Figure 4.10 Aging results at 100 ^{o}C for (a) Canvas-Canvas (b) Leather-Leather Substrates

4.13 Aging Results in Hot Water

Major concern is water for adhesive joints due to its polar nature. Water can permeate most polymers. Figure 4.11 shows effect of hot water on different substrate surfaces. It can be seen the GA-11 and GA-13 have greater stability in hot water as compared to other commercially available adhesives. The greater stability is due to grafting of MMA onto

PCP polymer which imparts greater thermal stability to the adhesive even at higher temperature loadings [132].

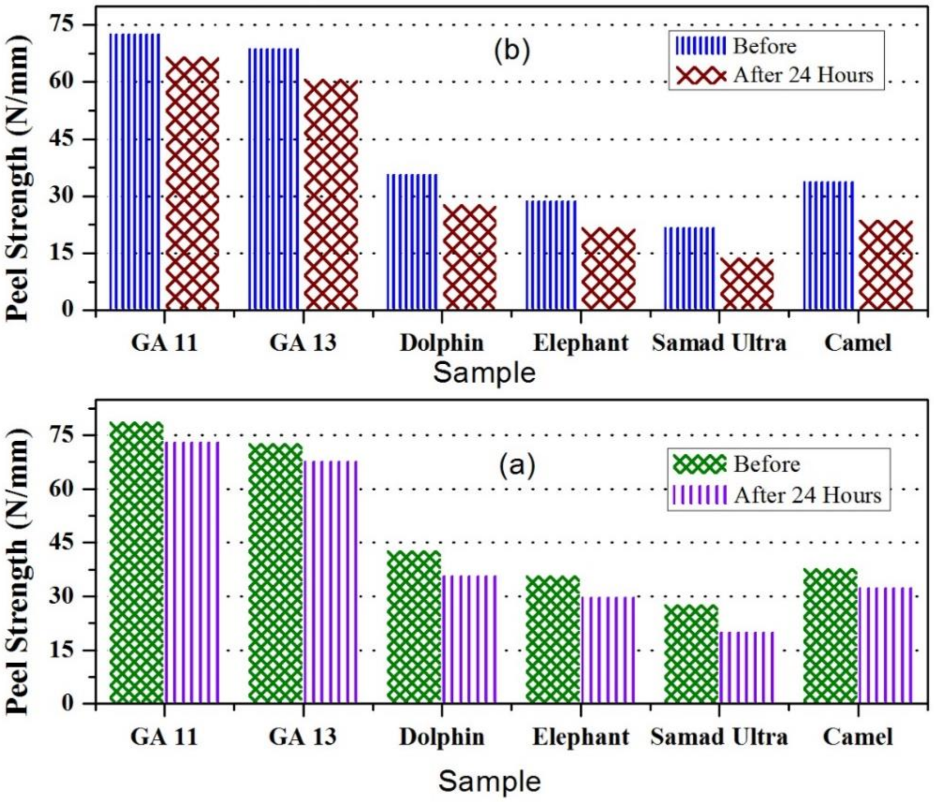


Figure 4.11 Aging results in Hot Water for 24 Hours for (a) canvas-canavas and (b) leather-leather substrates

Table 4-6 Characteristic after aging in hot water for 24 hours

Aging Condition	**Type of Adhesive**	**% Fall of Peel Strength**	
Hot water for 24 Hours		Canvas-Canvas	Leather-leather
	GA-11	7.08	8.21
	GA-13	6.84	11.59
	Dolphin	16.27907	22.22
	Elephant	16.66	24.13
	Samad Ultra	27.5	36.36
	Camel	13.68	29.41

4.14 Aging results in brine solution

Figure 4.11 and Table 4-7 shows that presence of salt has severe effects on the adhesive’s stability. It is due to the corrosive nature of the salt with water. It attacks the bond and then solution diffuse through the layers of the substrates. The formulated GA-11 and GA-13 adhesives show the resistive result to the salty solution while commercial grade adhesives do not show that resistant and bond breaks. The % fall in peel strength for different substrates in given in Table 4-7.

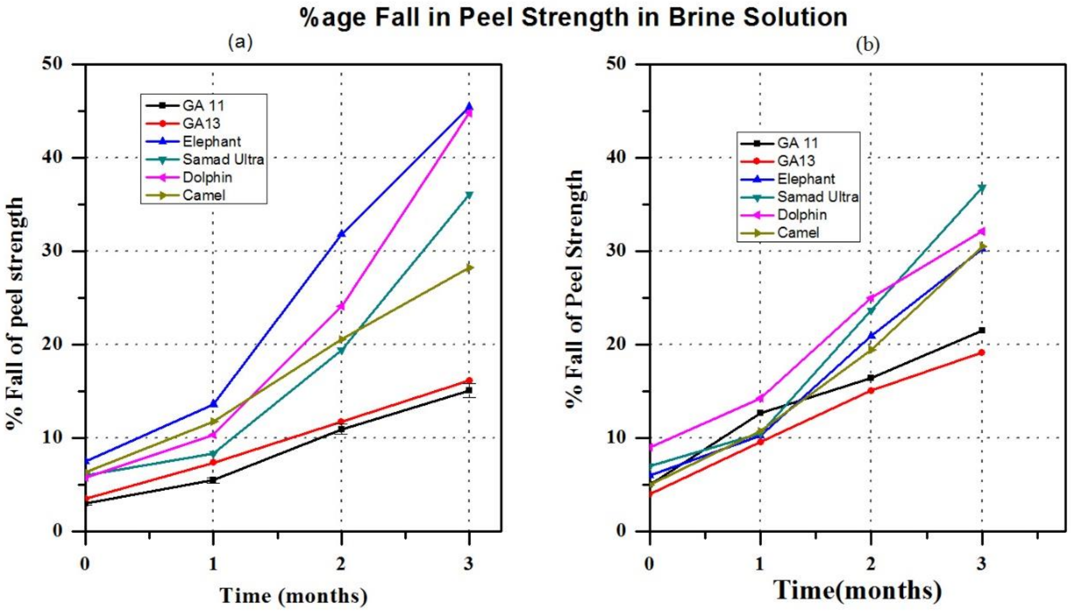


Figure 4.12 % Fall in Peel Strength (a) Canvas-Canvas Substrates (b) Leather-Leather Substrates

Table 4-7 Characteristic after aging in Salt Water for 3 months

Aging Condition	**Type of Adhesive**	**% Fall of Peel Strength**					
		Canvas-Canvas			Leather-leather		
In Brine solution	GA-11	12.65	16.45	21.51	5.47	10.95	15.068
	GA-13	9.58	15.06	19.17	7.35	11.76	16.17
	Dolphin	10.23	20.93	30.23	10.34	24.13	44.82S
	Elephant	8.33	19.44	30.55	13.63	31.81	45.45
	Samad Ultra	14.28	25	32.14	8.33	19.44	36.11
	Camel	10.52	23.68	36.84	11.76	20.58	28.23

4.15 Peel strength of Metallic substrates

The best results obtained from leather-leather and canvas-canvas substrates are then used for formulation of required adhesive for joining metallic substrates. The substrate used is aluminum. The thickness of aluminum substrate was 0.35 mm. The dimension of substrates are as follows:

- One substrate was 300 mm long and 35 mm wide.
- The second substrate was 400 mm long and 35 mm wide.

The calculations are carried out according to standards by determining the average values of peel strength of at least 5 specimens.

4.15.1 Aluminum Surface Preparation

Aluminum samples were first abraded by 20 and 40 number Sand paper. After that, the strips were etched in mixture of acetone, ethyl acetate and toluene in ratio of 2:1:1 for 20 minutes. Adhesive films were applied on both substrates and left them for drying. Initial formulation used for bonding of leather and canvas takes lots of time to dry. A new adhesive was formulated for bonding aluminum surfaces. The ratios of ingredients used in formulation of adhesive is given in Table 4-8. Drying time of 5 minutes was achieved from this formulation which previously ranged from 20-25 minutes. After the adhesive has completely dried, both substrates were joined together

Table 4-8 Formulation for Aluminum substrates

Sr. No	Chemicals	Parts Per Rubber
	CR	60
1.	Resin	50
2.	MMA	60
3.	HPO	2
4.	Anti-Oxidant	8
5.	Ethyl Acetate	300
6.	Toluene	180
7.	MgO	3
8.	Naphtha	94
9.	ZnO	3

4.16 Final Bond Strength

Canvas-Canvas Substrate

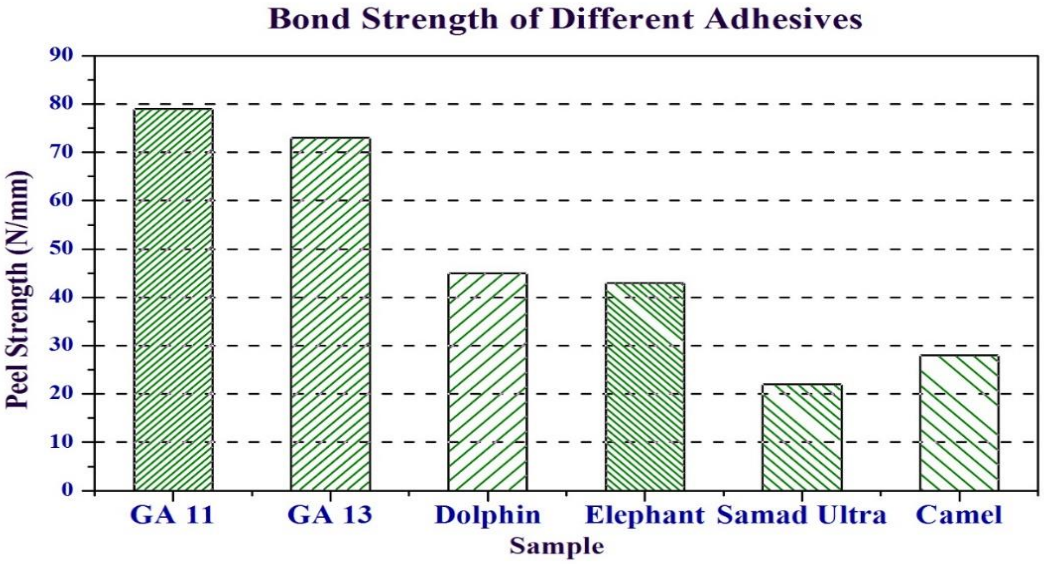


Figure 4.13 Bond Strength for Canvas-Canvas Substrates

Aluminum-Aluminum

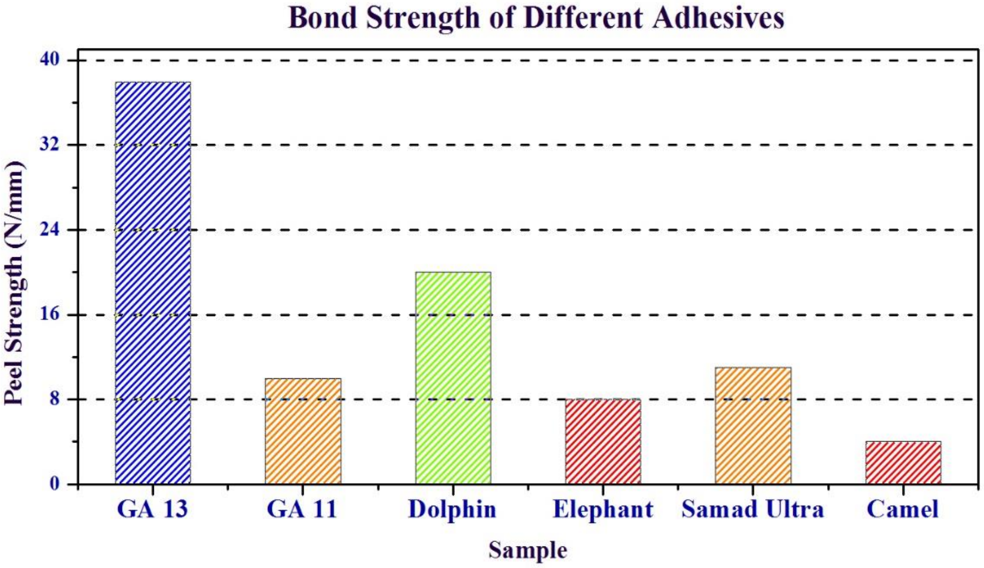


Figure 4.14 Bond Strength of Different Adhesives for Al-Al Substrate

Leather-Leather Substrate

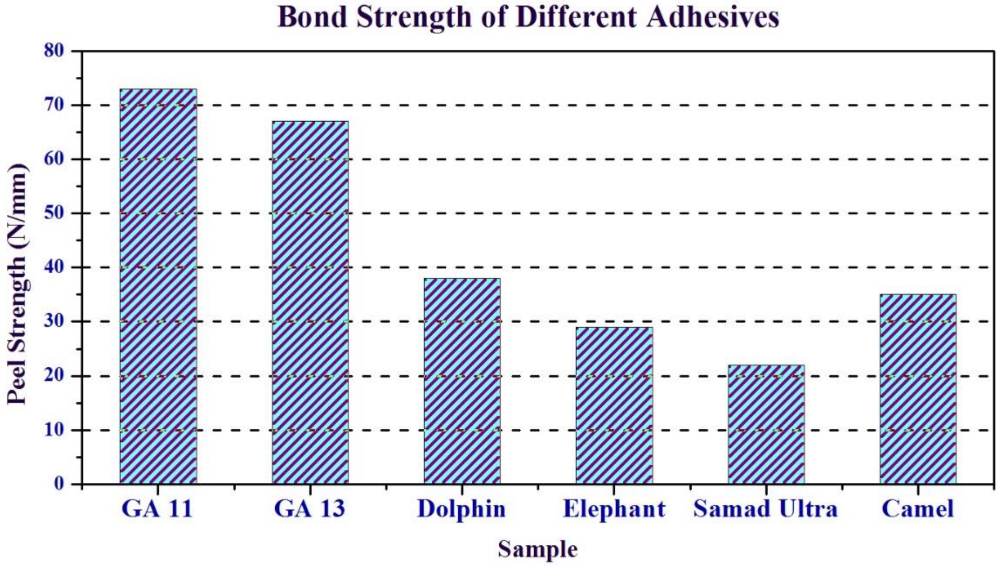


Figure 4.15 Bond Strength for Leather-Leather Substrate

Conclusion

Successful carrying out Graft copolymerization of MMA onto PCP backbone with HPO as an initiator for preparing lower cost, having high strength and high-quality grafted PCP adhesive. MMA has been successfully grafted onto PCP backbone as shown by FTIR results. Different grafting factors such as grafting time, grafting temperature, monomer and initiator concentrations were studied during the course of experiments. Peel resistance increases with increase in amount of monomer and initiator concentration and values depends upon the substrate to be bonded. An optimum amount of monomer i.e. 85 phr and initiator i.e. 2.4 phr concentration has been formulated at which maximum peel strength is achieved. Increasing concentration of monomer and initiator after this decreases the peel resistance of adhesive. Also, the grafting temperature of 60 ^{0}C and time of 60 minutes is calculated for preparation of grafted adhesive. The strength of grafted adhesive is compared with other commercially available adhesives. The strength of grafted adhesive is very high as compared to commercially available adhesives. The adhesive didn’t lose its bonds strength for 4 months. Similarly, the effect of different environmental conditions such as temperature resistance and salt solution on formulated adhesive is low as compared to other adhesives.

GA-11 and GA-13 formulations complete the project objectives. These formulations have better peel strength, are high quality and low cost as compared to the commercially available products. The promising results of this project persist high adhesive demand in the market, makes the finalized formulations as commercially attractive and market capturing products.

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