

Development of Polychloroprene Rubber Based Industrial Contact Adhesive



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2017

Development of Polychloroprene Rubber Based Industrial Contact Adhesive



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**This work is submitted as a MS thesis in partial fulfillment of the
requirement for the degree of
(MS in Chemical Engineering)**

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Feb, 2017



Form TH-1

National University of Sciences & Technology (NUST)

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S/No	Code	Title	Core/Elective	CH	Grade
1	EME-921	Momentum heat and mass transfer	Core	03	B+
2	CHE-847	Chemical Kinetics and reactor design	Core	03	B+
3	CHE-843	Separation processing in chemical Engineering	Core	03	B+
4	CHE-814	Product Technology	Elective	03	A
5	CHE-873	Membrane Technology	Elective	03	B
6	CHE-816	Molecular Nanotechnology	Elective	03	C+
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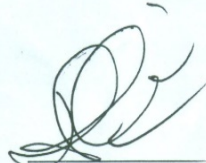
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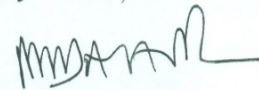
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Dedication

This thesis is dedicated to my parents

For their endless love, support, and encouragement

Acknowledgments

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 divings 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. Arshad Hussain** and **Dr. Muhammad Shahid** for their endless support, supervision and affectionate guidance to steer me in the right the direction whenever he thought I needed it. I would also like to extend my gratitude to committee members; **Dr. Abdul Qadeer Malik** and **Dr. Muhammad Bilal Khan Niazi** for their valuable suggestions and guidance.

I would also like to thank **Dr. Muhammad Mujahid** (Principal, School of Chemical and Materials Engineering) and **Dr. Arshad Hussain** (HOD, Department of Chemical Engineering) for providing a research oriented platform to effectively utilize my skills in accomplishing this research work.

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 Junaid Afzal** and **Mr. Muhammad Younis** for being with me through this research period, helping me for conducting the experiments in laboratory.

Muhammad Hamran Mahmood

Abstract

The purpose of this research is to develop a polychloroprene rubber based industrial contact adhesive with higher strength as compared to the commercially available adhesives.

The focus of this new adhesive would be on the higher bond strength, compatibility, and durability for practical applications in shoe, plastic, leather, and automotive industries depicting higher performances than the current commercially available adhesives for the same purpose. This will include the formulation of new adhesive experimentally by arranging, examining, and testing the different proportions of the chloroprene rubber of different commercially available grades, Phenolic resins, MgO, antioxidants and the solvent. With varying amount of resin up to 85 phr the best results are obtained. The drying time for the adhesive is optimized to the 4 min. The %of solids are 58 percent which depicts the presence of high usable adhesive in the set formulations. The Understanding and depicting the reaction kinetics during the reaction of rubber, phenolic resin and the metal oxide, formation of new bonds and the possible adhesive and cohesive forces for the bonding illustrated by different characterization techniques. The peel strength test gives the bond strength when applied to canvas-canvas and leather-leather substrates which are of 60 and 55 N/mm. The formulated adhesive is 1.5 times better than the commercially available adhesive.

Keywords

Polychloroprene rubber, Phenolis resins, MgO, Canvas, Leather, Antioxidants.

Nomenclature

Roman

G	Joint strength
D_f	Diffusion coefficient
X	Polymer perforation

Abbreviations

PCP	Polychloroprene
PU	Polyurethane
SIS	Styrene Isoprene Styrene
PCA	Polychloroprene Adhesive
PSA	Pressure Sensitive Adhesive

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Chapter 1

Introduction

1.1 Adhesive

An agent that is used to attach two layers or surfaces together is called adhesive. It is applied to join the two layers or parts. The surfaces which are to be joined are compressed initially after applying the adhesive. When it is dried, the strong bond is formed between both the surfaces [1]

1.2 Contact adhesive

The adhesive that is applied between two surfaces in such a way without applying any pressure. When the two surfaces are dried after applying the bond, their surface is pressed slightly [2].

1.3 Pressure sensitive adhesive

In pressure, sensitive adhesive, two surfaces are married together without any pressure, heat, solvent and water. They normally form a viscoelastic bond of high strength. This kind of adhesive attaches' surfaces only by slightly applying finger on the surfaces [3].

1.4 Contact adhesive and its properties

Mostly contact adhesive is used because of its good mechanical properties. Best adhesive strength, setting time very fast and easily applied on every layer of the material. Contact adhesive is applied on the both surfaces, which are to be attached [4]. Solvent from the surface evaporate quickly after applying and bonding happens between both the surfaces [5]. Very high strength and a firm grip can be observed immediately after applying and it increases further with the time. It is available in solvent-based technology as well as in water-based technology. In contact adhesive, a major polymer which is to be used is polychloroprene. In different cases, blends of different polymers are used in contact adhesives like polyurethane, acrylic polymers, styrene, natural rubber, butyl rubber and butadiene rubber [6]. The degree of elasticity and flexibility determines the characterizations of rubbers and elastic materials.

1.4.1 Bond strength of contact adhesive

Contact adhesive is available in the market with different bond strengths. But even in the low quality of contact adhesive, strength is enough to attach the both surfaces together [7].

1.4.1.1 Particularization of contact adhesive

Particularizations which are present in the contact adhesive involve optical and electrical, mechanical, and thermal properties. The coefficient of thermal expansion, heat conductivity, and operating temperature are key parameters [8], [9]. Ductility and yield strain are major mechanical properties. For optical and electrical particularization of contact adhesive, refractive index, transmission, and dielectric constant are major parameters [10].

1.4.1.2 Coating ability of contact adhesive

Humidity in adhesive and binding temperature of adhesive are two major components to determine the coating ability of contact adhesive [11]. They also affect the rate at which bond cement between two surfaces. As the temperature is high, the binding adhesive bonds the two surfaces quickly. In low temperature, adhesive takes much time to bond the surfaces. Drying rate in the high humid adhesive is very low, but in adhesive where the humidity level is low surfaces bond very quickly. When time is less, the high value of temperature and low humidity level is ideal for the strong bonding [12].

1.4.2 Adhesive mechanism for contact adhesive

Intermolecular diffusion occurs between the surfaces in contact adhesives. The liquid which is organic in nature evaporates and bonding between the layers get strengthen. When two properly coated bonding surfaces are brought together auto adhesion starts to take place [13]. 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 [14]. 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 [15].

The polymer or binding material must have diffusive properties. Diffusive property of binding material depends on solvent and polymer to be used [16]. There are selective materials and polymers which have good auto adhesive properties. 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 [17]. 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 [18]. When the adhesive is properly coated on the material and dried in a lap of time under specific parameters of temperature and pressure, this time is called open time. Adhesive layer alters all the physical properties in the open time due to evaporation of the solvent, interfacing of polymers, the base of polymer changes and crystallization of binding polymers [19]. When the open time has been passed, auto adhesive or good adhesive property of the surface can't be achieved.

1.4.3 Contact adhesive's characteristics

Contact adhesive can bear the load for a longer time than PSA's because peel strength and shear strength of contact adhesive are very high. Contact adhesive is normally called as semi-structural adhesive, its properties lie between conventional adhesive like urethanes and thermosetting epoxies and more pressure sensitive adhesive elastomeric polymers which are nonstructural in nature. After joints are formed, contact adhesive exhibit very high bond strength [20]. Without attaching components together, finishing operation gets completed soon. In fact, owing [21] to the green strength of contact adhesive difficulties mostly occur in working with contact adhesive to prevent from any misalignment or repositioning.

The resistance to attacking chemicals and temperature properties of contact adhesive is very close to the non-structural and structural adhesive. The bonding strength of binding component is very good. In many situations, hot bonding strength gets a firm grip after it gets dried [22], [23]. Before the moisture is released, the solution is sticky but once it is dried best thermoplastic properties appears on the surface. The best thermal, mechanical, and bonding properties of the adhesive make it useful for the construction projects, automotive industries, heavy machinery equipments and sports industries. Heat resistance, chemical resistance, and strength properties of contact adhesive lies between the structural adhesive and thermoplastic adhesives [24], [25].

1.4.4 Advantages of contact adhesives

When immediate intensive bond strength is needed contact adhesive bond can be used. The hand can anywhere apply it. The application can be made manually by any equipment easily. Extremely fine adhesive properties of contact adhesive make an effective bond strength even on porous surfaces. Bonds which are formed between

the surfaces are elastic in nature due to the polymer used in the adhesive. Contact adhesive can tolerate the high-temperature range between the -40°C to 130°C . In indoor of the bonding surfaces, good aging resistance has been reported but in outdoor, aging resistance depends on the polymer's base (to be used) and the composition of bond [26], [27].

1.4.5 Disadvantages of contact adhesive

When the bond gets immediately dry and set, repositioning of the bonding surfaces is almost impossible in contact adhesive. So, for repositioning, some organic flammable solvents are used. Though, these solvents are toxic. Systems in which water is used for repositioning, take too much time to get dry. The performance of bond is also very poor in water based systems. Critical drying of the bond surface, filling of gap and time to set depends on the composition of the formulation [28], [29].

1.4.6 Using methods of contact adhesive

Contact methods are generally used by spraying the bond on the surface, which is to be attached. It is also being used by applying the bond with the help of brush on the surface to be joined. Roller coating and curtain coating of adhesive contact bond have also been observed in many industries. Among all, the spraying of bond on the joining surface is a most effective method at commercial level because of its rapid drying time and high strength [30], [31]. In the case of plane sheets and flat skins, a preferable method are curtain coating and roller coating. Bonds in which organic solvents dry very slowly, curtain and roller coating is preferred there also. In slow drying adhesives, when the coating is applied through curtain coating and roller coating, it is must take care that bond is not getting concentrated on the one surface. I

In that case, solvents are expelled by high-speed air passing through the bonding surface or heat the bonding surface at very high temperature. Few contact adhesive bonds which are applied by spraying are also known as dry spraying adhesives [32], [33]. This type of bond is normally used in those conditions in which industrialists need fast drying time and substrate used in it are normally polystyrene foam. There is another way also to make it more effective by using hot spraying. In hot sprayings, adhesive pass through the hot bed of high temperature initially [34]. Then it moves through the atomizing gun for the purpose of spray, so when the spray is applied from atomizing gun, bubbles of bond come out of the surface. As the bubbles come out of the gun, immediately solvent from the bond evaporates and pure bond gets attached on the surface within a short time with effective strength.

1.4.7 Types of contact adhesives based on polymer

In the history of mankind, natural rubber was the human being using the first contact adhesive. But with the development of human society, the synthetic materials have replaced the natural materials. Similarly, synthetic rubbers have replaced the natural rubbers [35]. Currently, many polymers are being used as part of contact adhesive including polychloroprene, acrylic polymers, polyurethanes, acrylic polymers, styrene butadiene copolymers used in the normal bond formulations. The types of bond formulations of contact adhesives are listed below.

1.4.7.1 Neoprene

Neoprene bond shows very high bond strength. Rapid development and with high strength makes it very effective for the bonding surface. Shear strength with high temperature absorbing capacity and chemical resistance parameters of neoprene rubber are quite unique in nature. The open time of this formulation is limited and capability formulation is also limited.

1.4.7.2 SBR

Bond strength is very good. Strength properties depend upon the ratio of styrene and butadiene in the composition. The base polymer also plays the critical role in it. The chemical and heat resistance in SBR is less than other polymers. To get better thermal and mechanical properties, some tackifiers are added to it.

1.4.7.3 Polyurethane

In it, plasticizer does not get removed from the bonding surface. Molecules of the bond freely move. It can be adhesive to many substrates. It is not substrate specific. But it has one major drawback that when it is mixed with the substrate it should be in amorphous form. In this type of bond, Chemical and thermal resistance are very low.

1.4.7.4 Acrylic copolymers

Bonding strength and tack strength is less in this type of bond. It forms food adhesive with other LSE substrates. Solvents drying time is good. Solvents release in the environment quickly. It is mostly used in latex emulsions. Moisture resistance is very low in acrylic copolymers in comparison with other contact adhesives.

All the contact adhesives of these polymers are in two forms. Either in a solution of water or a solution with the organic solvent. However, solvent-based solutions are superior in term of thermal, mechanical and abrasive properties. Water based adhesives may cause many problems including less smoothness, less tacking, less drying rate and microorganism can have a little chance to grow in the wet adhesive.

The Little amount of solvent is used to improve the coalescing of the latex particles in wet solution (solution based on water) called coalescing aide. This coalescing aide is soluble in both elastomer and water. However, contact adhesive can be further divided into two types.

- 1) Curing contact adhesive
- 2) Non-curing contact adhesive

Curing contact adhesives are very firm in nature, exhibiting great thermal and mechanical properties due to cross-linking of polymer molecules. But the pot life of non-curing contact adhesive is very short. Contact adhesives having base polymer and carrier molecules also have tackifiers, fillers, cross-linking chemicals, pigments, and stabilizer [36], [37], [38]. Major commercial adhesives are listed below

1.4.7.5 Polychloroprene

Mostly contact adhesives are manufactured by using polychloroprene as a major ingredient. Short open time with the effective bonding strength is the key quality of polychloroprene rubber. Polychloroprene rubber has high elevation stature among all the polymers in terms of all major properties [39]. Polychloroprene rubber of which selection grade should be used depend on the desired quality of the product in terms of strength, mechanical properties, thermal properties and open time [40].

Polychloroprene rubbers (elastomers) are usually prepared for organic solvents based adhesive formulation. It can be dissolved in different kind of polar and nonpolar solvents for bonding. In this way, industrialist can make a binder of different compositions with different viscosities, strength, and bonding parameters. Porous and nonporous substrates both can be used with polychloroprene. Which solvent should be used in contact adhesive is selected based on its dissolving ability and drying rate [41]. Crystallization rate can also be affected by the choosing of organic solvent.

Polychloroprene bonds can also be manufactured by water dissolved elastomers [42]. The Polychloroprene contact bonds have not replaced the organic solvent based bonds as it appears in perception [43]. But water based rubber takes enough time to get dry. To get drier in short time, a lot of energy will be utilized. So, it will be an expensive process. Auto adhesiveness in water based rubber is lower. Initial bond strength is also very low even when applied pressure is very low.

Heat, shear stress, moisture resistance, and mechanical strength are also very lower in these water base adhesives than solvent contact adhesives due to presence specific ingredients. But in this area lot of work has been done [44]. Many

developments have been reported till now. In 1931, DuPont first developed the synthetic polychloroprene and chloroprene rubber replacing the synthetic one [45]. This newly developed synthetic rubber was being given the name of Duprene. This after few years was given name Neoprene. It is still the most used synthetic rubber with annual production of more than 30,000 tons [46].

The latest process of converting butadiene to chloroprene is quite fast and economical on industrial bases [47]. When the polychloroprene is produced in the form of solid granule/grade. First coagulation of latex is done then coagulated latex spread onto a flat sheet. After that, it chopped and dusted to get fine particles. Then chips or granules are further processed for packing [48].

1.4.7.5.1 Structure role of polychloroprene

By varied polymerization conditions, we can change the structure of polychloroprene. These three parameters play a key role in polymerization i.e. polymerization temperature, monomer conversion rate and the process of polymerization. The initial reaction of polymerization and molecular weight of polychloroprene plays a major part in the polymerization of the process. Chloroprene can also be classified based on the linear structure of the chain [49].

Polychloroprene which is used in solvent based bond is highly linear. The lower molecular weight of polychloroprene can be easily dissolved in an organic solvent by stirring and heating. Polymers which are (Latex based) anionic Olly based with emulsifiers rosin acid based.

1.4.5.7.2 Application areas

60 percent of CR produced used in conveyor belts of the cement industry, electricity transmission lines, and jackets of wires and molded material packagings. Almost one-third of CR is produced to produce adhesives. CR production has many areas of application like cricketing material for players i.e. gloves, pad, and guards etc. It is also used to make foam and matrices. In history, polychloroprene was being used as an alternative to natural rubber when natural rubber went short in world war one and world war 2. Synthetic polychloroprene has an advantage over natural rubber due to its strength and cost. Polychloroprene based contact adhesives are used in household, industries, and construction materials etc.

Polychloroprene contact adhesive was first used in shoe industry of United States and then its use was enhanced further. Though the shoe industry of polychloroprene is in decline from last 15 years but still shoe industry is still the most

adhesive using industry of the world. In industries like furniture base contact, adhesive plays a key role. In past days, contact adhesives were being mixed with solvents to join the woods and chlorine based solvents and solvents having a low flash point were being used. Organic solvent based adhesives are very easy to apply. Now around the globe researchers are working to replace organic solvent based adhesives to semi-organic aqueous solvents or aqueous dispersed solvents to make environment-friendly contact adhesives.

1.4.8 Properties of contact adhesives

The most useful property of contact adhesive is its auto adhesion to the surface. For efficient bonding, contact adhesive gives efficient strength and immediate bonding. Green strength is the most positive aspect of the contact adhesive. The substrate is coated with adhesives and then can dry. After drying, the surfaces are combined under light with moderate pressure. Instant bonding is seen reported then. It is not a simple process of diffusion but also the complicated process of diffusion with solubility. Solvent's amount remained after drying plays a key role in bonding [50].

The two major factors that affect the bonding strength of the polymers are viscosity and rate of crystallization of the adhesive polymers.

1.4.8.1 Crystallization rate of contact adhesives

When the auto-adhesive starts developing the starting strength of the contact adhesive the crystallization rate of contact adhesive plays the key role. Polychloroprene of the very high grade gives very high first strength to the base polymer and adhesive additives. When the polymer gets crystallized at the very early stage, it affects in a negative manner on the surface of the bond. First, the diffusion process of polymer slows down and second the adhesive capability of the bond gets very low. There should be an equilibrium between the adhesive properties of adhesives and the strengthening particularization of the bond [51], [52], [53].

Not like the chemical polymers which are being used as cross-linking agents and are reversible in nature, the auto-adhesive bond is very reversible in nature. The crystallization rate of the bonding polymers is very temperature dependent. At different temperatures, they exhibit different properties. At lower temperatures, the rate of crystallization is very slow, while at higher it is very fast. Those all polymers which are crystallized at lower temperatures can be easily de-crystallized at the exalted temperatures. When the temperature is raised to a very high level, the plasticity and

shear strain of the polymer increases directly [54], [55]. When the polymer melts down and elasticity is increased, the bond between the adhesive can easily be broken down. The adhesives which are based upon the polychloroprene are very sensitive at higher temperatures [56]. This property of polymer based material makes it produce the heat sensitive industries.

1.4.8.2 Viscosity of auto contact adhesives

Viscosity plays the major key role in the manufacturing of contact adhesives. The strength of the bond is directly related to the viscosity and molecular weight of the polymer. Higher the viscosity of the polymer, bond strength with lowers value of solid content is very good [57].

1.4.8.3 Polarity of auto contact adhesives

Versatility in the production of the of the different contact adhesives is only be created by the polar nature of the solvent. Polychloroprene based adhesive rubber gives a solution to different industries by making solutions with different solvents [58]. Stability of the bond, evaporation rate of the solution and different viscosities of the solution are varied according to the desires of the industrial demand.

1.4.8.4 Tack time of contact adhesives

This time of bonding gives a critical solution to the bonding. At the pressure, which is called contact pressure, the bonding of adhesive can be increased at a specific time called contact adhesive. Those adhesives which have lengthy tack time to settle the components, before setting the bond strength. The major user of the bond is the shoe industry of United States. Solvent based polychloroprene adhesives are manufactured by the adding different components like antioxidants, acidic components, and resins [59], [60], [61]. Polychloroprene are used in different grades in different industries with different formulations. The selection of different solvents and different additives play a key major role in determining the properties of the different polymeric adhesives like shear stress, peel strength, bond strength and tack time. The adhesive bonds which are cured in nature have resistance for the heat, water, oxidation of chemicals and solvents which are mostly organic in nature.

1.4.8.5 Solvent selection of contact adhesives

Solvents based contact adhesives are normally manufactured by polychloroprene rubber. Owing to environmental safety issues, the chlorinated solvents which have intense ability to catch fire are banned. So, those environmental health standards can be maintained. Solvents are not only being selected not on the

basis of the ability to dissolve the solutions but also the drying rate of the solvents. Non-solvents are also being blended with the solvents so that bond solution could not break down. The rate at which solvents dry also depend on the permeability of the solvents, retention time of solvents and absorption of the solvents [62], [63].

1.4.8.6 Acid accepting components and anti-oxidants of contact adhesives

In the manufacturing of auto contact adhesives, acid accepting components and antioxidants are being blended in the solution mixture of auto contact adhesives [64]. To avoid dehydrochlorination of the polymer, zinc oxide and magnesium oxide are being blended in the solution mixture of the polymer adhesives. Zinc oxide is being blended in the powdered form. It not only enhances the viscosity of the bond but also the strength of the bond by increasing the cross-linking [65], [66].

Magnesium oxide and zinc oxide, both are acid accepting agents as well especially the minute amount of acidic hydrogen chloride. The minute amount of the zinc and magnesium oxide not only enhances the life of bond but also the stability of bond with desired characteristics in long-term. Storage potential of the bond is also increased by using magnesium and zinc oxide [31], [55]. To provide the maximum heat resistance in the polymer, zinc oxide plays a key role in the bond solution. Zinc oxide is normally blended 4 percent of the bonding solution.

It has been proved since the work has been begun on the bond adhesives. The fine powder of zinc oxides is normally being used for the maintaining the suspension of auto contact adhesives. The blending of extremely fine or ground particles of zinc oxide increases the strength of the adhesive solution with proper suspension. As per the demand of the industries, metallic oxides can be blended up to 20% maximum to the minimum 2% of the solution [67], [68].

1.4.8.7 Resins in contact adhesives

Alkyl phenolic resins are the most commonly used resins for the manufacturing of adhesives. Resins have very little influence on the crystallizing rate of the contact adhesives and adhesive properties of the polymer. Resins can be blended up to 30 percent maximum. These resins increase both the antioxidants resistant and stability of the adhesives [68]. Adhesives having these resins increase the maximum bond strength, lower open time, and maximum auto-adhesive strength. Many alternatives have been tried after the use of alkyl phenolic resins. Modified rosins based adhesives can be easily applied for the use of contact adhesives [69], [66].

The aging particularizations of contact adhesives can be affected using resins. The aging can be increased and decreased using the resins. Resins must be blended with the antioxidants to get the best mechanical properties of the adhesives. In different regions of the world, shoe industries use different bonds. Like in tropical regions, footwear industries use heat resistant adhesives. but in the cold and extremely hard Russian conditions, different sort of adhesives is applied for the attaching of shoe components. Water Bourne adhesives have many factors which make it un-useful are, evaporation of water makes rubber adhesive less effective [70]. Thus, it is clearly needed a water based system to be worked more for research. Because water based system lack many outstanding mechanical and other properties which non-water based system normally poses [71].

1.5 Factors involved in producing satisfactory bond

- Choice of adhesive should be appropriate. It should be well suited and compatible with the surfaces ever adhesive is going to be applied.
- The raw materials used to produce adhesive should meet the minimum standard set by ASTM in terms of adhesive quality specification.
- The substrates preparation has very vital significance and it should be treated accordingly before applying the adhesives.
- The amount of thickness applied on the surface should be right and should give proper time for drying of the adhesive over the surface. It should be ensured that uniform and enough pressure is applied after assembly.
- When applying the adhesive with brushing method, the steadiness should keep in view.
- Before using any adhesive, the container of adhesive should be shaken well.

1.6 Motivation

The industrial sector is growing in Pakistan rapidly with each year. Foreign investments and emerging local markets are boosting the growth and production of industrial goods. Adhesives are used widely in the manufacturing of the end products and as a product itself. Textile, rubber, leather, footwear, furniture, automotive industries have high demands of adhesive for their end products. These industries mostly manufacture and produce the goods and products that have a daily use. Depending on the quality and category of the products different types of adhesives on the basis of their strength are utilized. The local industries and small industrial setups

that add sufficient revenues to the economy are the main consumers. Though adhesives are being produced locally, yet high quality and high strength adhesives are imported from European markets, that in terms are much expensive, affecting and increasing the final cost of the manufactured or assembled goods. The demand for adhesives is increasing with increase in local industrial setups and high demand of their products. Mostly available adhesives are nearly satisfactory in terms of strength. Though developed and produced locally, adhesive costs are still higher but imported adhesives such as Bison and CementX etc. even surpass them in cost.

Currently no cheaper, high quality and high strength adhesive are available that can meet the market demands. Available products are expensive, imported ones are more expensive. Therefore, the need of a locally made, cheaper, high quality and high strength adhesive need to be fulfilled. This development will not only fulfill the demands of adhesives at lower rates but decrease the dependence on imported adhesives too. The low costs adhesive, when available, will ultimately increase the profit margin of local Industries and small industrial setups. Thus, reducing the cost of their end products, making them available and affordable for more portion of the population. The main motivation if summarized is to develop a high strength and high-quality adhesive. The developed adhesive must have higher strength as compared to the commercially available local and imported adhesives. The developed adhesive is to be used primarily in footwear industry but must be multipurpose too, such that it can be used in other relative industries. Being a high strength and multipurpose adhesive, it's cost must be lower too.

1.7 The aim of the study

Aim of this study is to develop a polychloroprene rubber based contact adhesive. The purpose of developing the adhesive to achieve high strength for multipurpose use with primary usage in the shoe industry. Most of the commercially available adhesives have chloroform as the solvent which makes them vulnerable to drug use. Another aim of this study is to replace the chloroform with other suitable solvents to stop the use of adhesives as a potential drug source. Besides the high strength and chloroform free conditions, the developed adhesive will be relatively low in cost as compared to the adhesives available in the market. The set objectives can be achieved by achieving an optimum formulation obtained through extensive experimentation.

Chapter 2

Literature Review

2.1 Polychloroprene rubber based adhesives and their components

There are many Polychloroprene rubber based adhesives which can operate at a wide temperature range. The polychloroprene rubber based adhesives are designed to join various materials. Researchers have designed and synthesized polychloroprene-based adhesives used to glue metals, wood, concrete, plastics, and leather [72]. The basis of polychloroprene based adhesive is rubber or its combination with various other polymers. Most polychloroprene rubber based adhesives have several components such as zinc and magnesium oxides, resins, and solvent [73].

The common solvents used in polychloroprene rubber based adhesives are water, dichloroethane, ethyl acetate, methyl acetate, acetone, amyl acetate, t-butyl acetate, xylene, benzene, toluene, dioxane, ethyl benzene, diethyl benzene, and mesitylene, terebinthine, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, isopentane, isohexanes, isopentanes, isooctanes, 2,2-dimethylbutane, cyclopentane, cyclohexane, petroleum ether, kerosene naphthas and others. Furthermore, as a solvent for polychloroprene adhesives, instead of individual single solvents (xylene, benzene-ethyl acetate) a combination can also be used with a suitable mixture of two or more solvent systems [74], [75].

In polychloroprene-based adhesive, polychloroprene rubber is a largest single solid component on a weight basis. polychloroprene includes polymers that derive from the polymerization of halogenated dienes and optionally monomer which can be polymerizable. Researchers have used several different types of rubber for the formulation of adhesives such as polymers of chloroprene which can either be such as homopolymer neoprene or a copolymer of chloroprene with minor amounts of comonomers such as butadiene, isoprene, or vinyl monomers such as acrylonitrile, acrylates, or methacrylate's, such as methyl methacrylate.

More crystalline forms of the polychloroprene have also been used for adhesives used for the various industrial application. Such forms of polychloroprene include Neoprene AD, Neoprene AC, Neoprene CG, Neoprene W. Blends of distinct

polychloroprene or polychloroprene copolymers may be employed to achieve a desirable balance of properties [76], [77].

Di and polyphenols, hexamethylenetetramine, and other products of the condensation of amines with aldehydes, di-phenylaniline, and structuring substances that contain polyisocyanates are used as accelerators for self-curing adhesives. para-hydrocarbon-substituted phenol-aldehyde resin has also been used by several researchers; the general method for their preparation involves condensing the phenolic component such as p-propyl phenol, p-n-butyl phenol, p-t-butyl phenol, p-t-aryl phenol, p-octyl phenol, p-cyclohexyl phenol, p-phenyl phenol, p-benzyl phenol with the aldehyde, compound containing aldehydes such as paraformaldehyde, hexamethylenetetramine. Several promoters are also used to accelerate the vulcanization such as 20% alcohol solution of potassium hydroxide, in its presence the vulcanization takes place in almost 1 day at room temperature. One of the commonly used resin in polychloroprene rubber based adhesive is butyl phenol-formaldehyde [78], [79], [80].

To enhance the strength of multilayer resin products the adhesives are applied with the reactive functional group. The number of functional groups in the adhesive can be increased by introducing the additives allowing to enhance the adhesion to resins. Several researchers suggest that to increase the gluing properties of the polychloroprene adhesives that consist of different resins, e.g., indene cumarone or resole phenol resins, or resins based on cyclopentadiene. It was also suggested that the products of the co-condensation of phenol, acetaldehyde, and acenaphthene, as well as resin polymerizate of α -methylstyrene or copolymer of cyclopentadiene with unsaturated dicarboxylic acid or its anhydride, can also be used as resins [80], [81].

Adhesive compositions that include Baipren polychloroprene resin, filler, solvent, and water are also formulated. The polychloroprene adhesives with phthalic acid anhydride condensation with resorcinol as modifying agents are also noted to be used in viscose and textile industries. Furthermore, per gun, thiuram, and there have also been used as modifiers in polychloroprene based adhesives. Polychloroprene based adhesive for use in tire and resin technical industries are also formulated by some researchers [82], [83].

The said polychloroprene-based adhesive includes chloroprene rubber, zinc oxide, near as, and ethyl acetate as solvents, and, additionally, colophony and colloidal silicon acid and a molecular complex of resorcinol with urotropine and stabilizer as a

modifier. The use of this modifier enhances the adhesion ability and contact strength between resin mixture in polychloroprene rubber based adhesive. The adhesion properties in polychloroprene based adhesives can be enhanced and significantly improves by introducing compounds that contain different reactive functional groups in their formulation [84].

2.2 Adhesion and theories of adhesion

Adhesion occurs by interfacial forces when two of the surfaces of a substrate are joined and held together. These forces are of attraction, resulting from the interaction of atoms, molecules, and ions present on the surfaces. The chemistry and concept of the adhesion need understanding of the intermolecular forces, physical and chemical properties of the materials and forces that will affect when materials will be joint together. The forces range from the chemical bonds to the weak Vander Waal's forces [66], [67], [81]. There are different theories of adhesion proposed by several types of research over the course of time. Some of them are discussed below:

2.2.1 Theories of adhesives

Table 1. Theories of adhesion

Traditional	Recent	Scale of Action
Mechanical interlocking	Mechanical interlocking	Microscopy
Electrostatic	Electrostatic	Macroscopy
Diffusion	Diffusion	Molecular
Adsorption/surface reaction	Wettability	Molecular
	Chemical bonding	Atomic
	Weak boundary layer	Molecular

Source: Book - The Science of Footwear (Human Factors and Ergonomics) by Ravindra S. Goonetilleke. Page (200-206).

2.2.1.1 Mechanical Theory

Usually, surfaces of any material are not smooth, there is always roughness to some extent. It contains a maze of peaks and valleys responsible for the friction over the surface of material. The mechanical interlocking theory was proposed by McBain and Hopkin in 1925. Per the mechanical interlocking theory, the adhesive must breach into the pores and holes of the substrate surface. Which tends to displace the trapped air at the interface and lock on mechanically to the substrate. The physics of adhesion can be illustrated as “Hook and eye” [85], [86]. The porous substrate like woody material, fibrous material, and textile etc. the main factor for joining the surface

(adhesion) is mechanical anchoring. This phenomenon was further lighted up by Baroff and wake. Their work on textile cords and rubber casing proved that penetration of the fiber ends into the rubber was the only significant factor for their adhesion. Wake proposed that the effect of both mechanical interlocking and thermodynamic interfacial interactions as multiplying factors the estimating joint strength G [57].

According to Wake;

$$G = (\text{mechanical interlocking}) \times (\text{interfacial interacting component}) \dots \dots \dots \text{eq. 2.1}$$

As the above equation, it is illustrated that improved structural behavior and surface physiochemical characteristics of any substrate will result in higher adhesion and bonding between the surfaces. But mostly increase in interlocking results in enhancing the interfacial area [51].

The major drawback and criticism of the theory are that it is only valid for the smooth surface and shows higher results for such surfaces. Tabor *et al* and Johnson *et al* studied the adhesion between two surfaces of mica and rubber which are perfect texture and optically smooth, clearly, exhibit that theory is valid for only smooth surfaces. Thus, preexisting intrinsic adhesion mechanisms can be observed in such cases due to mechanical interlocking [73].

2.2.1.2 Diffusion Theory

This theory is valid when both the adhesive and substrate are polymeric in nature. It states that the adhesion between the substrate and adhesive is because of the mutual diffusion of polymeric material across the interface. This theory is applicable when both the adhesive and substrate are polymeric. The adhesive and adherent must have long-chain molecules with significant chain movement. cAdhesive and polymeric material should be chemically well-suited in terms of diffusion and miscibility. This theory can also be applicable in rare cases when both adhesive and adherent are soluble in each other. Vasenin developed a model by using Fick’s law of diffusion, exhibiting the amount of material ‘w’ diffusing in each direction by [87],

$$\partial w = -D_f \partial t \frac{\partial c}{\partial x} \dots \dots \dots \text{eq. 2.2}$$

Where, D_f = Diffusion coefficient, $\frac{\partial c}{\partial x}$ = Concentration gradient and t = time.

However, this model is only valid for steady-state diffusion where concentration within the systems does not vary with time. It does not occur for polymer chain segment's perforation into the substrate surface. In most of the diffusion through polymers, the perforation increases linearly with the square root of contact time.

$$x^2 = 2D_f t \dots \dots \dots eq. 2.3$$

This is also valid for diffusion of rubber into rubber along with the liquid. The inter-diffusion of polymer chains across polymer-polymer interface requires mutual solubility of the polymers and sufficient chain flexibility. These conditions are normally met in the adhesion of the elastomer, where inter-diffusion contributes significantly to the intrinsic adhesion. However, when polymers have different solubility parameters or one polymer is highly cross-linked or crystalline the diffusion is unlikely to be the mechanism of adhesion [33].

2.2.1.3 Electronic Theory

According to this theory, the electrostatic forces are produced between the layers of joined substrate over the adhesive-substrate interface. And this joint junction act as a capacitor. Capacitor tends to increase the Potential Difference until a charge happens. Thus, the potential difference force provides the major part for the adhesion [71]. Deryaguin's approach tells that the potential barrier at the interface of adhesive substrates is the cause of adhesion and adhesion depends on this barrier. Although there is no correlation between the electronic interfacial and adhesion, thus in most cases this potential does not exist [66].

When the insulator substrate surface is subjected to low-pressure glow, after coating of adhesive, the increase in the adhesion of thin layer films over the surface was noted by numerous researchers. Stoddart *et al* studies told us that there was no overall surface discharge produce on adherent but only electronic emission was altered. Thus, the predominance of the electrostatic double layer is handy in certain specialized cases. However, this theory is not valid to the intrinsic adhesion of typical adhesive-substrate interfaces. [82].

2.2.1.4 Adsorption Theory

This theory states that adhesion occurs at the surface due to the surface and molecular force. Material is adhered because of the intermolecular forces and interatomic forces established on the surfaces of the adhesive and substrate. Van der Waal's forces and weak hydrogen forces are established across the interface and chemical bond may be formed. This is called chemisorption and involves ionic, covalent, or metallic interfacial bonds. Other than this there might be Donor-Acceptor interactions occurs at surfaces and become the medium of strength between primary and secondary bonds [66].

2.2.2 Advantages and limitations of adhesive bonding

Adhesives have a wide range of usage carrying from the metals to textile and rubber industries. Adhesives with their attractive applications and use are considered as the alternate for mechanical fastening due to their distinct advantages over mechanical fastening. Beside their promising advantages and use, there are certain limitations too. Some of the major advantages and limitations are given below;

2.2.2.1 Mechanical advantages and limitations

Dissimilar metals have different thermal conductivities making them difficult to weld. Some metals such as aluminum, magnesium, and titanium have unstable oxides and are distorted by the heat of welding. Adhesives can be used to join these substrates avoiding the problems usually encountered with welding or other methods of joining. Adhesive joints are low temperature and high strength. Poly-chloroprene based rubber adhesives are viscoelastic with abilities to expand and contract. This property helps in joining the materials having different thermal expansion coefficients. Being viscoelastic the adhesive act as like touch, relatively flexible materials. Their toughness also provides resistance to thermal recycling and crack propagation. Adhesives also provide a bond with superior fatigue resistance. They also damp vibration and absorb shock [78], [79].

In adhesive based joints the stress is uniformly distributed from one substrate to the other, eliminating localized stress concentrations usually confronted with other means of joining. With the use of mechanical fasteners, the substrates need to be thicker or are strengthened to handle the concentrated stress thus increasing the overall weight and cost of final assembly. While with the use of adhesives low cost and low weight structured can be built [80].

The major drawback of polymeric rubber based adhesives is their degradation with time due to several factors i.e presence of moist, very high temperature or toxic chemicals. The usually can perform at -50 C0 to 150 C0 but some can perform even better than these temperature conditions [81]. This temperature limitation makes the polymeric rubber based adhesives less useful in cases where high-temperature operations and processes are carried out. The strength degradation increases with continues stress and high temperatures. Residual stress inside the joint can also cause notable problems. Certain epoxy adhesives, when applied in bulk can overheat and burn or degrade due to their own crosslinking reactions.

2.2.2.2 Design advantages and limitations

Adhesives have a better strength to weight ratio as compared to the other mechanical joining methods. Unlike rivets or bolts, adhesives produce smooth contour that is aerodynamically and aesthetically beneficial. Adhesive can join a wide variety of solid surfaces regardless of their shape, size, thickness, and different physical properties such as elastic modulus [82].

For effective selection and use of the adhesive for any operation with selected substrates, their design limitations should be considered too. A number of researchers have lighted up that when external forces act on several hard adhesives in nature, do not work. These stresses can be reduced by careful designing of the joint. The shelf life of an adhesive joint is also very difficult to predict. Therefore, to know the design limitations and efficient shelf life of a joint, a prototype should be tested in similar environmental conditions that will accelerate the stress [85].

2.2.2.3 Production advantages and limitations

Adhesives are less expensive and faster in joining as compared to the other conventional methods. When the size of the substrate area to be joined increases, adhesives can save cost and labor and mechanical fasteners take a lot of labor and cost expenditures whilst with adhesives the whole operation can be performed in one go. Furthermore, adhesives minimize or prevent galvanic corrosion between dissimilar metals [69].

Adhesives require a clean surface to acquire optimum results. The cleaning of the substrate may vary from simple cleaning to use of chemicals, depending on the substrate type and required bond strength. The curing often requires sufficient heat and pressure. Jigs and fixtures become necessary for the assembly due to long setting time [87]. The inspection of the finished adhesive joints is also very difficult. Therefore, these production limitations must be considered before selecting the adhesive for any substrates [43].

2.3 Adhesive in footwear industry

Adhesive plays very key role in the joining of the shoes. It is a key component of manufacturing and transformation of the materials of the shoes. It provides a shape and structure to the shoe and footwear. There are number of adhesives used in the footwear industry. But polychloroprene rubber based adhesives are particularly used for the footwear industry due to its high strength and high performance. Although the

adhesive joint performance is high dependent on the footwear materials, substrate surface treatment, and nature of the adherent [56].

Nowadays footwear industry has very close relation with adhesive industries. It is due to the technique involve in the joining of the footwear and its manufacturing process. For the understanding of the adhesive industry and how it works with shoe industry, it is necessary to get knowledge about the manufacturing process of adhesives. Adhesives in shoe industry are of very significance as its producers rapidly producing new formulations for better strength and enhanced improvements. Shoe mainly comprises of eight segments which are shown in the below figure:

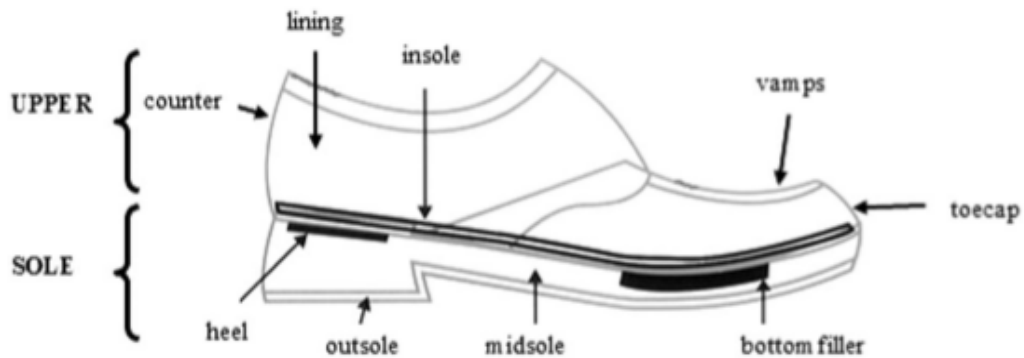


Figure 1. Typical Illustrating of shoe construction

For the good results of footwear, there should be care in the choice of adhesives for joining of sole with the shoe, as per the set standards of EN 1369:1998 and EN ISO 17708:2003. In footwear industry, most prefer a method to joining the shoe component is the use of high-performance adhesives. As with the use of adhesive, the gaps can be covered and it can act as a bridge between the materials which are set to be bonded. Although the selection of adhesive depends on many factors i.e. thermal stability, environmental changes, nature of the substrates and time for complete bonding of the shoe components [57], [73].

Nitrocellulose adhesives are the first adhesives which were used back in 1496. But in 1949 adhesive industry reached the new horizon with the introduction of polychloroprene rubber based adhesive (PCP). It is al because of its versatility, durability, and long lasting effects. PCP also produces very good results in the leather industry, textile, and other materials. Although with the introduction of plastic in the shoe industry, the polyurethane based adhesives are also introduced in late 1970 [45]. Both PCP and PU adhesives are used in footwear industries due to their best and long lasting results. In footwear industry, PCP adhesives are used in the last step due to the requirement of hotmelt adhesive for the joining of the shoe sole. PCP with the solvent

can be applied to any of the substrates depending upon the application (brush and sprayed) [12].

2.4 Types of adhesives

There are number of types of adhesives i.e.

2.4.1 Hot melt

These are adhesives which are thermoplastic in nature and contains 100 percent solid contents at standard temperature. But such adhesives will behave as fluid at elevated temperatures. Usually, hotmelt adhesives are consisting of polymer, resin, and anti-oxidant. The application of Hotmelt adhesive is to join the substrates and then at lower temperature solidify itself and provide permanent bonding [3].

2.4.2 Waterborne adhesives

These adhesives are composed of dispersed polymer and water and usually said to be emulsions. Such adhesives are used due to their toxic-less and inflammability nature. But these adhesives have also limitations i.e. slow drying and higher in cost [2], [3].

2.4.3 Latex adhesives

Natural rubber is usually used for such kind of adhesives which are in nature cis-trans mechanism. Such adhesives contain 60 percent solids in rubber solution. Latex adhesive has very good handling properties due to its viscosity. These adhesives are water based and provide an instant bond to the substrate [47].

2.4.4 Polyurethane adhesives

PU are also water based adhesives and used as coatings in textile, plastics materials, woody stuff, and metals etc. PU are applied to the upper sole of the shoe due to its great flexibility and high stability at low temperatures [23]. Figure 2 shows the bonding phenomena of PU.

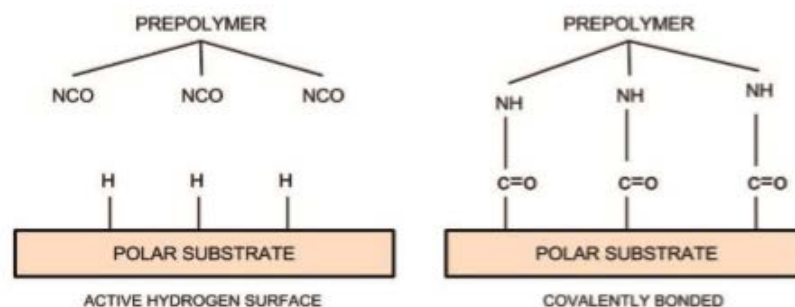


Figure 2. Typical phenomena of bonding in PU

2.4.5 Polychloroprene adhesives

Polychloroprene (PCP) rubber based adhesives have almost same strength as the polyurethane (PU) but PCP shows more flexibility and durability than PU base adhesives. Also, it has a great open time and dries at room temperature providing the enhanced strengths. The solvent based PCP adhesives are referred as contact adhesives and applied on both the surfaces. Figure 3 (a) lights up the behavior of PCP polymer with temperature [37]. In figure 3 (b) with time bond strength will be higher.

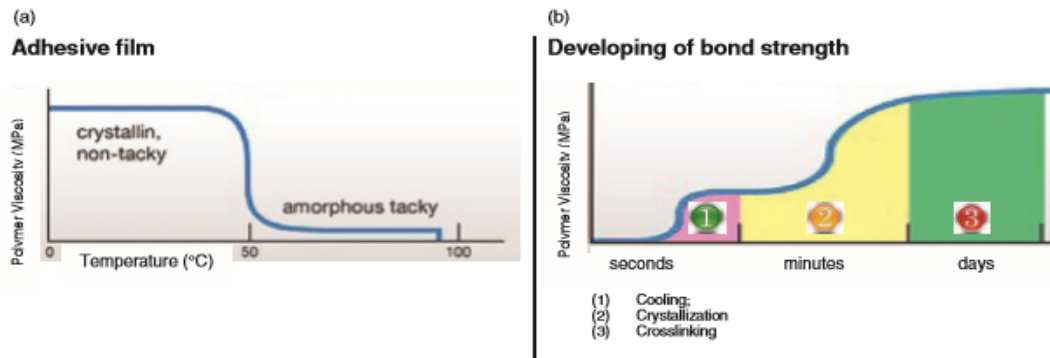


Figure 3. curing procedure of adhesive (a) the behavior of polymer with temperature (b) the effect of time on bond strength

2.5 Dispensing methods

Dispensing is the method of applying the adhesive on the substrate surfaces to be bonded together. There are different methods of the dispensing discussed by the researchers. Commonly used dispensing methods are;

1. Brushing and troweling
2. Roller transfer
3. Spray application
4. Pin transfer
5. Stencil printing
6. Nozzle dispensing methods

2.5.1 Brushing and troweling

Brushing and troweling is one of the most common techniques used to apply the adhesive coating over the surface of the substrates. Brushing, trowels, and spatulas usually do it. The selection of the tools depends on the substrate area and consistency of adhesive. The strength and bond quality depends on the different parameters i.e. levels and extent of coverage, wetting and drying times [45].

2.5.2 Roller transfer

Roller transfer is also called wheel or disc coating. In roller transfer the adhesive, stored in the reservoir tanks, is transferred to a roller and then either directly or indirectly via another roller is applied on the substrate surface. This process is most suitable for conveyor belt production in an application where large substrate surface area is to be coated and bonded [73].

2.5.3 Spray application

This method is also used to coat the large substrate surface areas. Commonly used spraying methods are conventional air spray, hydraulic solid airless spray, hot and hot airless spray [17].

2.5.4 Pin Transfer

Pin transfer is an effective method of applying adhesive patterns to the substrate surfaces. This instrument consists of arrays of pins plotted with specific dot patterns which is immersed in the adhesive. The pins are made to join with the substrate surface along with the transfer of adhesive in a specific pattern. The viscosity of adhesive plays a vital role in this method. The degree of fluidity is pertinent to immerse and wet the pins in adhesive bulk and its successive transfer on substrate surface [21] [29].

2.5.5 Stencil Printing

Stencil printing is a cost-effective method for applying adhesive on the substrate surface. This method involves a patterned stencil with pores analogous to the required placement of adhesives placed on the surface of the substrate. The adhesive is poured over the stencil with the help of a roller. The pore size and adhesive rheology can control the size and shape of the obtained dots. The cleansing and reuse of the stencil is a prolonged process taking a lot of time [33].

2.5.6 Nozzle dispensing methods

Most common nozzle dispensing methods are as follows;

- a. Squeeze bottle
- b. Sealant gun
- c. Pressure pump
- d. Auger pump
- e. Piston pump
- f. Jet dispensing

2.5.6.1 Squeeze bottle

Squeeze bottle method is used to dispense fluid adhesives. The adhesive is flown by inverting or squeezing the bottle. The volume of dispensing adhesive is difficult to control in this method [19].

2.5.6.2 Sealant gun

In this method, the pastes are dispensed from the cartridges. The cartridge is secured in the gun; squeezing or triggering the handle depresses a plunger at the base of the adhesive cartridge that forces the paste out through the cartridge nozzle [79].

2.5.6.3 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. [19].

2.5.6.4 Auger pump

This kind of pump is used to displace the adhesive by rotating screw thread.

2.5.6.5 Piston pump

It includes positive displacement process of adhesive dispensing. The amount of adhesive to be dispensed in controlled the movement of the piston in a closed chamber.

2.5.6.6 Jet dispensing

In this method, the adhesive is applied using a spring-loaded pin which pushes 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 [21].

2.6 Surface preparation

Adhesives are used to join two substrate surfaces together. Since adhesion is achieved by the surface attachment the surface conditions are crucial in achieving the desired bond strength. Mostly the substrate surfaces are pretreated before applying adhesive and joining them together [67]. The surface pretreatment is carried out for one or more of the following reasons;

- i.** To stop the formation of such boundary layer which is weak on the substrate surface.
- ii.** To make the best use of molecular contact between adhesive and substrate.
- iii.** To ensure the sufficient level of intrinsic adhesion forces across the interface for enhanced bond strength and subsequent life of the bond.

iv. To avoid the contamination of the substrate surfaces by impurities that affect the curing time and bond strength.

Surface treatments can either be active or passive. But the passive process does not change the surface chemically. These methods focus on removing contaminations from the substrate surfaces without altering surface chemistry [77]. While active treatment methods alter the surface chemistry. Some of the surface preparation methods are as follows;

1. Solvent cleaning
2. Chemical cleaning
3. Passive mechanical treatment
4. Active chemical surface treatment

2.6.1 Solvent cleaning

The method involves the removal of contaminants such as soil and organic pollutants. This is usually done by using an organic solvent. For this purpose, following solvents are used to remove such contaminants [57].

- Toluene
- Methyl Ethyl Ketone
- Methyl Alkyl Alcohol

2.6.2 Chemical cleaning

Chemical cleaning is used on the substrate where solvent cleaning may degrade the surface such as polymeric substrates. With other surface treatment method, this method is used with them. In chemical cleaning method, commonly used agents are [27].

- Caustics,
- Phosphates, acids
- Chelates etc.

2.6.3 Passive mechanical treatment

This method includes abrasive blasting, wire brushing and abrasion with sandpaper, emery cloth or metal wool. Passive mechanical treatment is effective in removing heavy, loose particles such as dirt, scale, tarnish, and oxide layers [76]. Solid particles from the surface can be removed using blasting and solvent wiping. Cryogenic and hydrodynamic blasting have been used as an abrasive-free surface treatment prior to adhesive bonding.

2.6.4 Active chemical surface treatment

When substrates are treated chemically the characteristic of the substrates changes. For the treatment of substrates chemicals used are of acidic and alkaline nature. Commonly chemical treatment is done by following chemicals [81].

- Sulphuric acid
- Phenol.
- Nitric acid

2.7 Composition of solvent based adhesives

Adhesives for footwear industries are comprised of numerous chemicals which are used to form a bond between the two surfaces. The overall efficiency solely depends on the selection of the components of chemical for the adhesives [63]. The important ingredients to produce adhesives are as following:

- Elastomers
- Resins
- Anti-oxidant
- Solvents
- Fillers/Additives etc.

2.7.1 Elastomers

Generally, elastomers are the most important and significant components to produce adhesives as it carries additives and resin and provides elasticity and viscosity to the solution of adhesives. Different types of elastomers are used in adhesive industry i.e. PCP, PU, SIS and NR etc. [69].

The adhesives which include the PCP, easily crystallize. The major characteristic of such adhesives is that they can adhere to a number of substrates providing them good initial and final strength. These adhesives also provide good cohesion and thermal stability to substrates [57].

PCP adhesives adhere many substrates because of the presence of chlorine atom in every monomer of the polymer. Thus, it contains very good polarity and good physical interactions. The typical formulation for PCP rubber based adhesive is provided in Table 2 for footwear industry [66], [78].

Table 2. Typical formulations of PCP adhesive for Footwear industry

Raw materials	Quantity
PCP	100
Resin	30
MgO	4
ZnO	5
Anti-oxidant	2
Solvent mixtures	500
Water	1

2.7.2 Resin

To enhance the tackiness of an adhesive resin are used. It also enhances the cohesion strength, open time, and resistance to temperature. It has also the long-lasting effect on wettability, the important parameter to check the quality of an adhesive. Thus, resin increases the bonding formation between the substrates due to cohesive interactions [69]. The most common resins which are used in adhesive industries are as followed:

- Colophony
- Hydrocarbon resin.
- Phenolic resin.
- Terpene Phenolic etc.

Phenolic resins are used to enhance the wettability parameter of adhesive by improving the cohesive interactions between the surfaces of substrate providing the immediate bonding between the surfaces without any of the pressure [58]. The table 3 shows the general properties of different resins.

Table 3. General Properties of Different Resin.

Resins	Acidity Index	Strength	Tackiness	Open Time	Temperature Resistance	Elasticity	Life Time
Colophony	150-180	Low	High	High	Low	Low	Long
Hydrocarbon	<0.2	Low	Low	High	High	Low	Long
Alkyl phenolic	--	High	Low	Low	High	Low	Short
Terpene phenolic	50-80	Low	High	High	Low	Medium	Short
Coumarone-indene	<0.6	High	High	--	Low	High	Short
Vinyl chloride/vinyl acetate	--	High	Low	Low	High	High	Long

Chapter 3

Materials and Experimental Setup

3.1 Materials

- Polychloroprene Rubber AC-130 grade (Mw. 120000)
- Phonic Resin (Mw. 700)
- MgO/ZnO > 150 micro-meter
- Fillers (CaCO₃)
- Solvents (Methyl Acetate, Chloroform, Ethyl Acetate, Naphtha, Toluene)
- Anti-Oxidant

Local industry provided all the materials. These materials are of commercial grade and solvents have the purity of 80-85 %.

3.2 Sample Formulation

For setting the best performance adhesive formulation almost 362 experiments were run at lab scale. Some of the core experiments were shown below in table 4, 5, 6.

Table 4. Formulation of Polychloroprene Rubber Adhesive

Formulation No:	Rubber (phr)	Resin (phr)	MgO (phr)	Antioxidant (phr)	Toluene (phr)	Methyl Acetate (phr)	Naphtha (phr)	Ethyl Acetate (phr)
PCA-1	100	50	3	8	180	425	113.5	0
PCA-4	100	60	3	8	180	425	113.5	0
PCA-7	100	70	3	8	180	425	113.5	0
PCA-9	100	85	3	8	180	425	113.5	0
PCA-10	100	85	3	8	180	0	113.5	425
PCA-11	100	100	3	8	180	425	113.5	0

Table 5. Formulation for polychloroprene rubber based adhesive PCA-A

Sr. No	Chemicals	Quantity	Parts per rubber
1	Rubber	10	100
2	Resin	9	49
3	Mgo	0.5	5
4	Anti-Oxidant	10.84	108.4
5	Toluene	17.246	172.46
6	Chloroform	14.73	148.9
7	Naphtha	26.2645	262.645

Table 6. Formulation for polychloroprene rubber based adhesive PCA-9

Sr. No	Chemicals	Parts per rubber
1	Rubber	100
2	Resin	85
3	MgO	3
4	Anti-Oxidant	8
5	Toluene	180
6	Methyl Acetate	420
7	Naphtha	262.645

Table 7. Formulation for polychloroprene rubber based adhesive PCA-10

Sr. No	Chemicals	Parts per rubber
1	Rubber	100
2	Resin	85
3	MgO	3
4	Anti-Oxidant	8
5	Toluene	180
6	Ethyl Acetate	420
7	Naphtha	262.645
8	CaCO ₃	25

The formulations are based on the extensive trial of experiments. After setting the experiments the optimum amounts of different materials are taken to achieve the maximum strength of the adhesive. The chloroform solvent based system is removed by replacing it with ethyl and methyl acetate based solvent system. The compatibility of the solvent is based the evaporation rate, solubility factor and final properties of the solvent which they impart to the adhesive system. The compatibility of solvents can be checked from kidney diagram provided in appendices.

3.3 Method of Production of Adhesive

There are two methods available to produce the contact adhesive. These methods are as followed:

1. Roll mill method
2. Direct dissolving method/Slurry method

Generally, in industries, the direct dissolving method is preferred over the roll mill method as it requires minimum labor force to operate the production process. The schematic of the direct dissolving method is shown in figure 4.

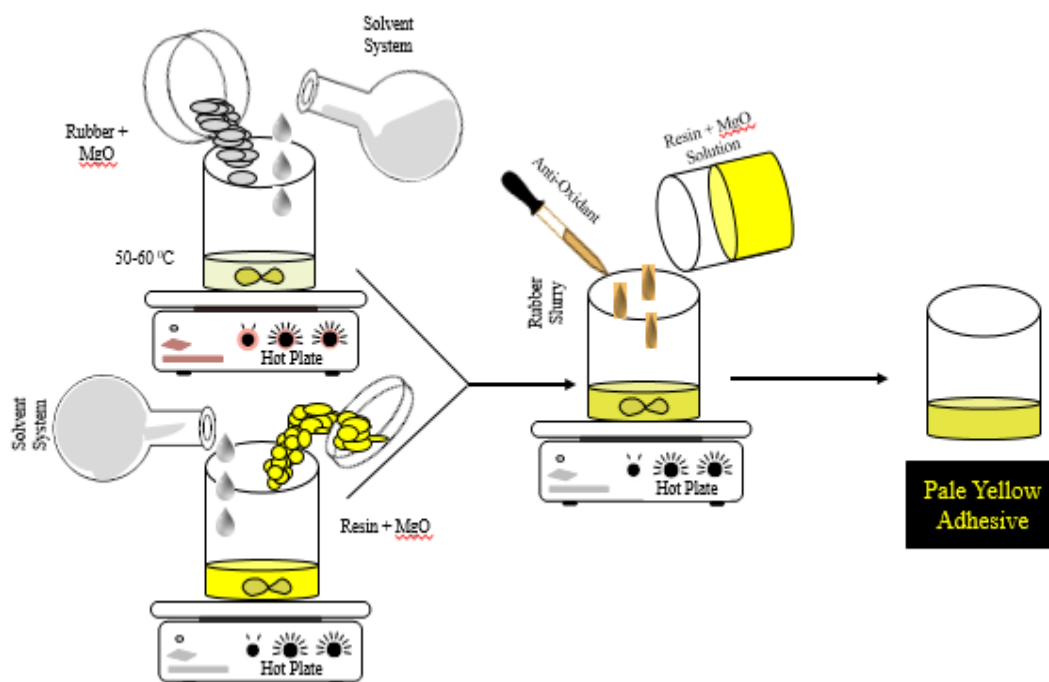


Figure 4. Direct dissolving method to produce the polychloroprene rubber based adhesive

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.

3.4 Building of the apparatus

The bottom impeller mixing machine is fabricated to produce larger batches of adhesives figure 5. 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.
- The speed of the motor is set to be at 150 rpm.

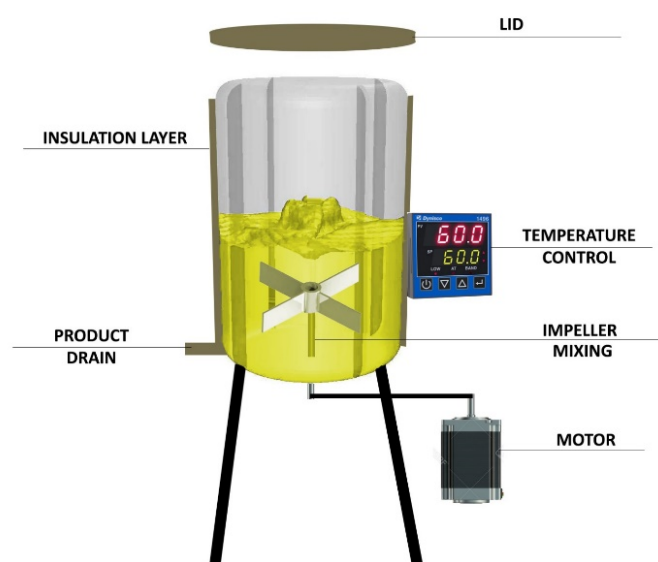


Figure 5. Sketch of fabricated bottom impeller machine.

3.4.1 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 60 °C.
- When the rubber chips disappear and the completely uniform slurry mixture is produced, add 86 phr of phenolic resin and stir it for another 15 mins while maintaining the temperature.
- The pale-yellow color of the mixture appears.
- Now add the Methyl acetate or ethyl acetate about 420 phr and 300 phr respectively.

- Adding 4-5 phr of antioxidant while keeping the temperature at 60 °C.
- After that add 25-50 parts of fillers to lower the cost of overall adhesive and stir it for another 2 hours. In the end, add 113 phr naphtha to lower the viscosity of the prepared solution.

3.5 Testing specimen preparation

For the testing of the prepared adhesives, the different specimen of different substrates was prepared. The substrates used for the analysis of the peel test are as followed:

- Canvas-Canvas.
- Leather-Leather.

The dimension of the two substrates are:

- 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.

3.5.1 Applying the adhesive

After preparation of the specimen, the adhesive was applied to the surface of substrates. It was done by brushing method and two coatings were made with the time interval of 3 mins. The thickness of adhesive layer is about 0.2 cm on the surface of both the substrates.

3.5.2 Drying Time

After applying the coating of adhesives over the layers of substrates 5 min of drying time was provided at room temperature. The specimen was ready for the peel test.

Chapter 4

Resources and Approaches

Successful bonding of parts requires an appropriate process. The adhesive must not only be applied to the surfaces of the adherents but the bond should also be subjected to the proper temperature, pressure, and hold time. The liquid or film adhesive, once applied, must be capable of being converted into a solid in any one of three ways. The method by which solidification occurs depends on the choice of adhesive. The ways in which liquid adhesives are converted to solids are

- Chemical reaction by any combination of heat, pressure, and curing agents,
- Cooling from a molten liquid,
- Drying because of solvent evaporation.

The requirements to form a good adhesive bond, processes for bonding, analytic techniques, and quality control procedures are very significant [86].

Mechanism of adhesives can be described as mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction theories. More recently, other theories have been put forward for adhesive bonding mechanism. It is really difficult to fully describe adhesive bonding to an individual mechanism. A combination of different mechanisms is most probably responsible for bonding with an adhesive system. The extent of the role of each mechanism could vary for different adhesive bonding systems. An understanding of these theories will be helpful to those who plan to work with adhesives [67].

4.1 Characterization

4.1.1 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].

4.1.1.1 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

4.1.1.2 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].

4.1.1.3 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].

4.1.2 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. resealable bag tape). Some things peel without a separate adhesive layer, such as an induction-welded foil, or grip seal bags, and some adhesive joins for security come apart but must not reseal. Adhesive bonding can be measured by tensile testing, shear testing or compression testing, but where there is flexibility in a joined layer, a peel test is appropriate [79].

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. [78], [79].

4.1.2.1 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].

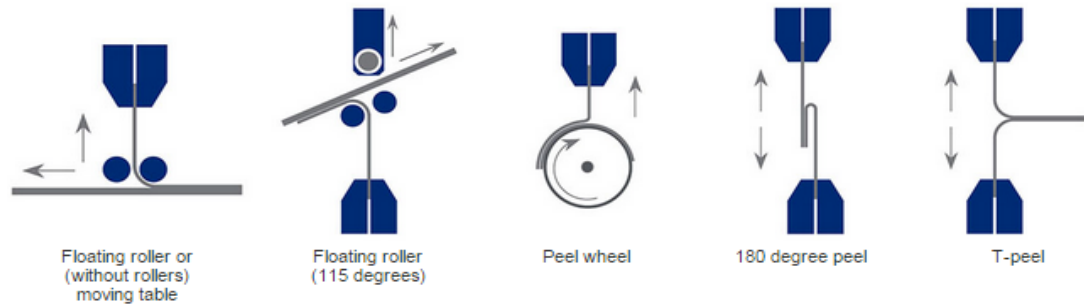


Figure 6. Different types of peel test

4.1.3 Standard test methods for rubber property—adhesion to 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 [43].

4.1.3.1 Test Method

There are two general test methods described as follows:

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

As covered by these test methods, an adhesion test consists of applying to a test specimen, under specified conditions, a (measured) force sufficient to strip from the specimen at a measured rate, a layer of moderate thickness with separation (rupture, tearing) at the adhered surfaces [87]. The numerical 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.

4.1.4 Determination of the % Solids content

This test is carried out to determine the % solids in the adhesive. % solids of the adhesive is the amount of usable adhesive per kg. The solvent is used just for the carrier of the adhesive to provide smooth flowability. Higher the amount 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 5

Results and Discussions

5.1 Effect of Raw materials on peel strength of formulated adhesive

All the raw materials have their effect on the adhesive overall performance. To get high bond strength from polychloroprene rubber based adhesive, the composition in the appropriate amount is needed [87]. Below are the results of different raw materials over the performance of adhesive bond strength.

5.1.1 Effect of Resin Contents

Figure 7 shows that the effect of adding the phenolic resin in adhesive composition on peel strength of canvas to canvas and leather to leather substrates. It clearly shows that the resin content up to 80 phr has an increasing effect on the peel strength of canvas to canvas substrates. But after 80 phr of resin content, the effect of phenolic resin sharply changes and has a severe effect over the bond strength of adhesive. In canvas to canvas substrate after adding 80 phr of resin the flexibility of the system remain same and there is a significant change in the bond strength of the adhesive. While in leather to leather substrates the resin content has also the similar behavior as for canvas to canvas substrates up to 80 phr but after increasing the amount of resin in the adhesive composition for leather to leather substrates the bond strength decreases significantly. It is mainly due to the decrease in the flexibility of the system.

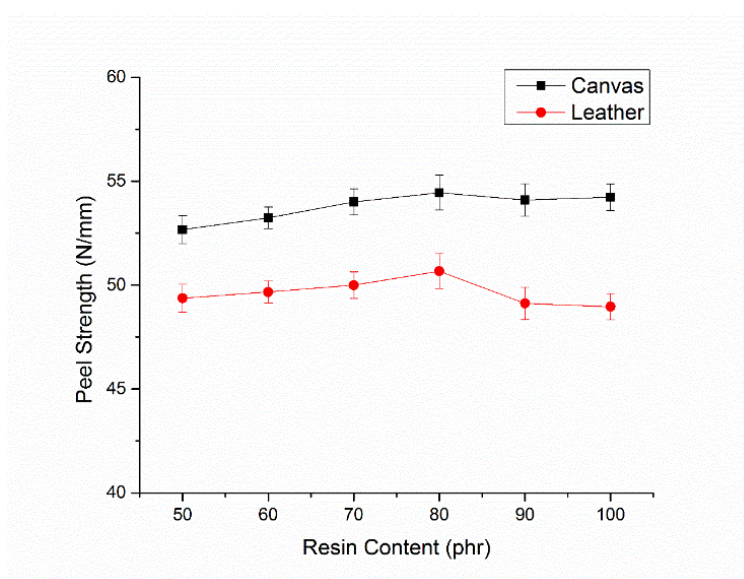


Figure 7. Effect of resin content on peel strength

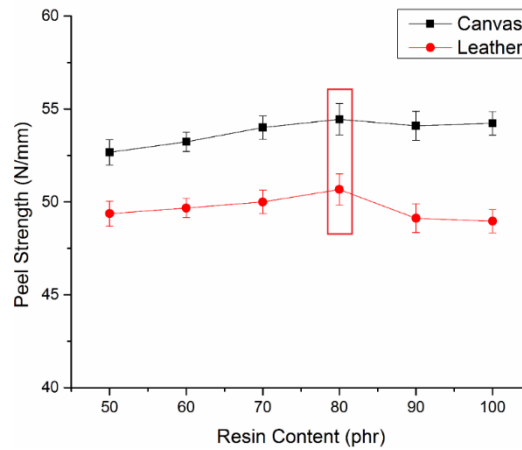


Figure 8. Effect of optimum amount of resin content on peel strength

Figure 8 shows that 80-85 phr of resin contents are optimized values for a high bond strength polychloroprene rubber based contact adhesives. Beyond these value, the overall performance of the adhesives is affected and decrease significantly for some substrates which result in poor performance and the high cost of the product.

5.1.2 Effect of Acid Scavengers/ Crosslinking agent

Figure 9 illustrates that increasing amount of crosslinking agent results in the decreases of peel strength of the adhesive for both the substrates. It is mainly because of the fact, that increasing amount of crosslinking agent reduces the flexibility of films and layers of the adhesive after applying to the substrates. Similarly, the increasing weight of crosslinking agent M_c will lead the adhesive to poor performance in terms of its shear strength as well. It is because of a cohesive characteristic of cross-linked adhesives that depends on the molecular weight of crosslinks M_c .

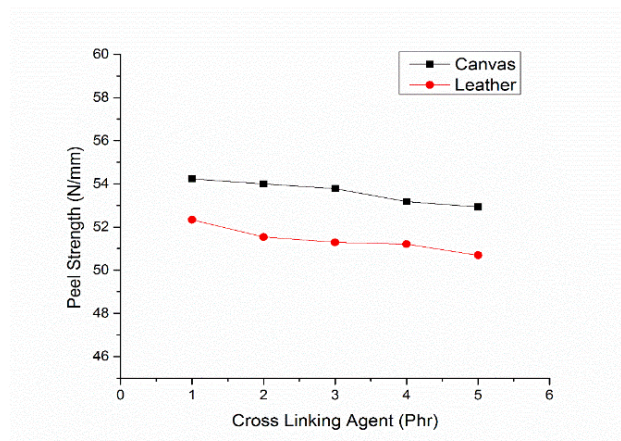


Figure 9. Effect of cross linking agent on peel strength

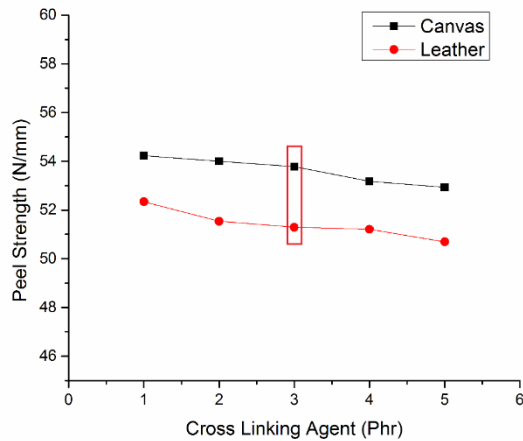


Figure 10. Selection of optimize cross linking agent

It is clear from the figure 10 that 3-4 phr of the crosslinking agent is the optimize value of the crosslinking agent in a good performance adhesive for all the substrates. This amount is significant to hinder the effects of the producing HCL after the use of adhesive over the surfaces of a substrate. As HCL produces when applied adhesive exposes to heat and hot environment.

5.1.3 Effect of Fillers

The addition of fillers in the adhesive composition has significant importance on the cost of the adhesive and overall performance. Figure 11 clearly shows that the appropriate amount of filler should be selected for better performance adhesives. In figure 11 when the amount of filler is increased in canvas to canvas substrates the peel strength decreases. It is mainly because of the overall volume of adhesive is increased but the amount of rubber percentage decreases. Hence the peel strength decreases. While in leather to leather substrates the trend is like the canvas to canvas substrates. As the amount of filler increases the peel strength decreases.

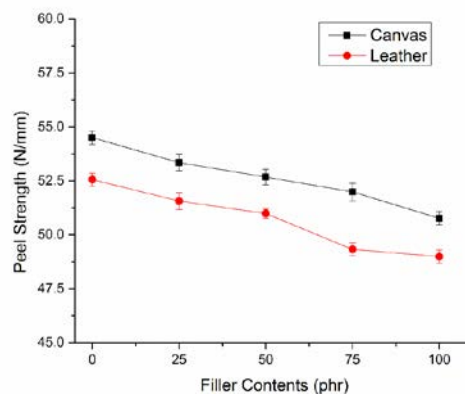


Figure 11. Effect of filler content on peel strength

The optimize value for the filler for a high strength adhesive is about 25-50 phr. As shown in figure 12, 25-50 phr filler content show little variation in the peel strength. Hence the percentage of filler reaches beyond the certain level, the overall peel strength decreases. It is due to that flexibility between the layers of adhesive decreases. Thus, molecules cannot be moved away and towards easily from each other.

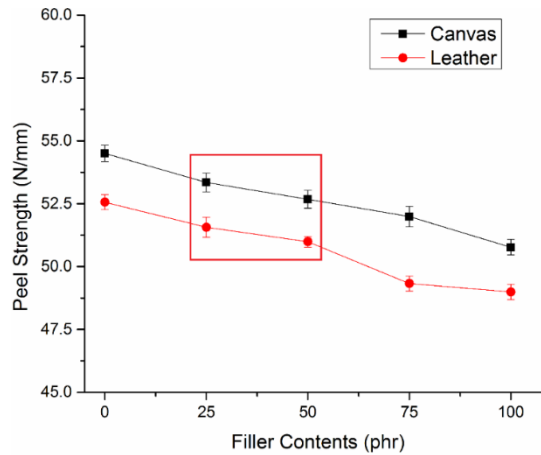


Figure 12. Selection of optimize value of filler content

5.1.4 Effect of Methyl Acetate

Figure 13 shows that increasing amount of Methyl Acetate increases the peel strength up to 400-450 phr. But after that increasing further amount leads the peel strength of the adhesive to the lower values. It is mainly due to the lower polymer contents in layers of the adhesive on the surface of substrates.

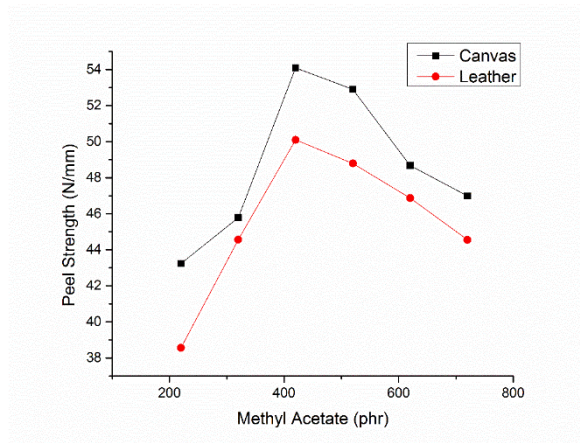


Figure 13. Effect of methyl acetate on peel strength

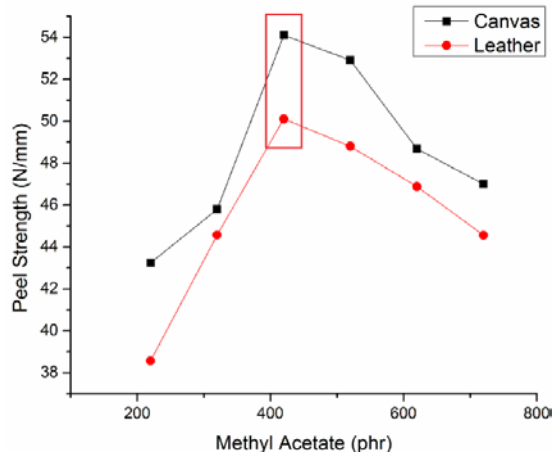


Figure 14. Selection of optimize value of methyl acetate

Thus, the optimum value of methyl acetate is shown in figure 14 which 400-450

5.1.5 Effect of antioxidant on drying time

Figure 15 shows the effect of anti-oxidant on the drying time. It is clearly shown that higher amount of anti-oxidant leads the adhesive for longer drying period. If an adhesive gets longer time for drying, then it will affect the bond strength of the adhesive when applied to the substrates. It is cleared that when 6-8 phr of antioxidant is used in both the formulations the drying time is 4-5 mins.

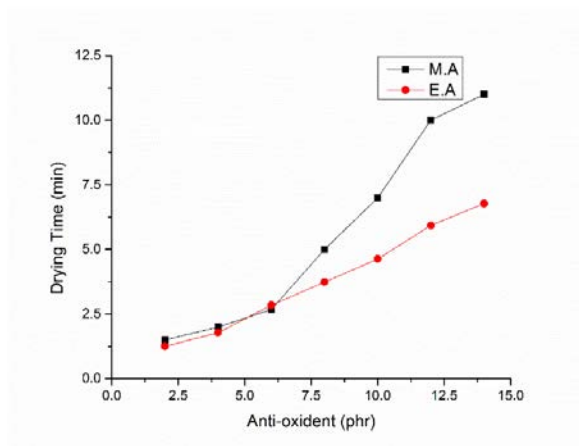


Figure 15. Effect of anti-oxidant on drying time

5.2 Viscosity measurements

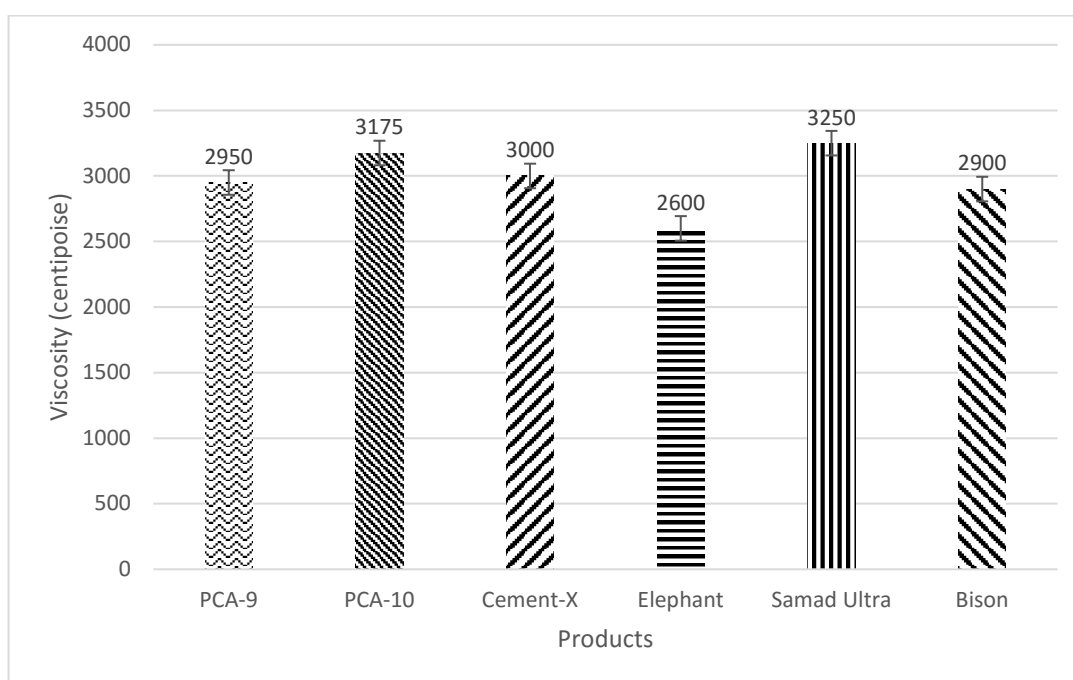


Figure 16. Viscosity of different adhesives

Viscosity effects the applicability and flow ability of the adhesive when it is subjected to the substrates. It is necessary that a good polychloroprene adhesive exhibits the good viscosity. Figure 16 the viscosity measurements of PCA-9 and PCA-10 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 PCA-9 and PCA-10 show that they are well in the standard ranges which 2950 and 3175 centipoises.

5.3 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 100⁰C 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:

$$\% \text{ solid contents} = [(m_2 - m_0) / (m_1 - m_0)] \times 100$$

Where:

m_0 = weight of the dry empty cup.

m_1 = weight of cup containing adhesive.

m_2 = weight of residue in the cup.

Table 8 shows the % solid contents of differently formulated adhesives, PCA-9 contains almost 58% solid contents. Which is according to [17] should in the range of 50-60% in a good quality adhesive having good mechanical properties.

Table 8. Percentage Solid contents of formulated adhesives

Adhesives	Solid Contents (%)
PCA-1	10 ± 1.78
PCA-4	32.33 ± 2.04
PCA-7	41 ± 2.55
PCA-9	56 ± 0.98
PCA-10	58 ± 1.23
PCA-11	10 ± 1.78

The PCA-9 and PCA-10 showed the best results and they have solids content of 56 and 58% which is in the range of 50-60% set by ASTM. The formulated sample have more usable adhesive per kg than the others.

5.4 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.

Several resins utilized as a part of high temperature adhesive details are unbendingly cross-linked or are made - up of a molecular backbone to as a 'ladder structure'. The ladder structure gives high bond dissociation energy and goes about as an energy sink to its condition. The inflexibility of the atomic chain diminishes the likelihood of chain scission by averting thermally disturbed vibration of the concoction bonds.

Water is major source of the issues to the environmental stability of glue joints. Water may enter and change a joint by one or a blend of the accompanying procedures. It might enter the joint by dissemination through the glue, by transport along the interface, by capillary activity through splits and rages in the adhesive or by dispersion through the adherend on the off chance that it is porous. The water admitted can modify the properties of the glue in a reversible (plasticization of the glue) or in an irreversible (creating hydrolysis, breaking or crazing) way. It can likewise affect the adhesive/adherend interface either by dislodging the adhesive film.

5.4.1 Aging under ambient conditions for 3 months

Aging under ambient conditions has been studied of different surfaces of canvas and leather.

5.4.1.1 Canvas-Canvas Substrates

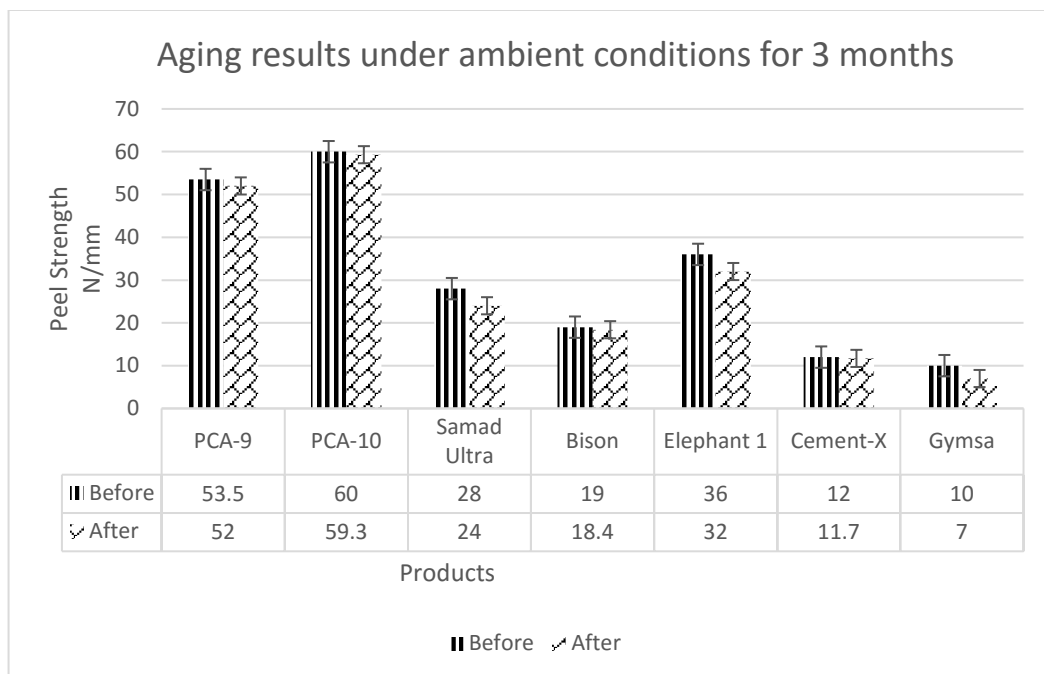


Figure 17. Aging results under ambient conditions for 3 months for canvas substrate

5.4.1.2 Leather-Leather Substrates

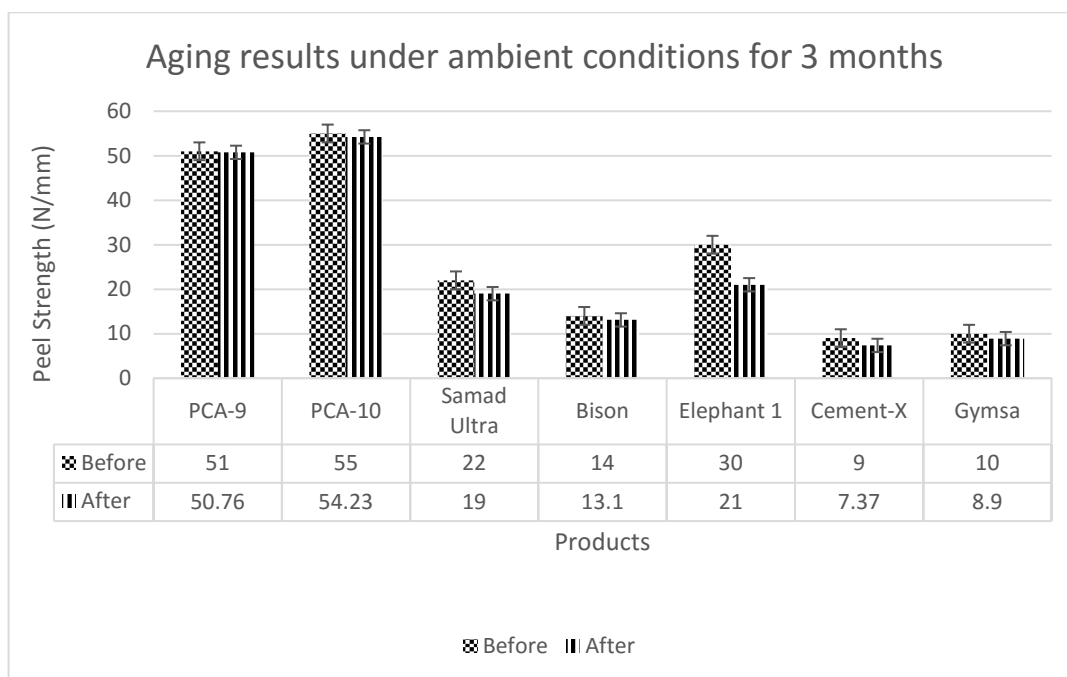


Figure 18. Aging results under ambient conditions for 3 months for leather substrates

Figure 17, Figure 18 and table 9 shows that over the time span adhesive loses its properties at room temperature and 85% humidity. The result shows that at the ambient condition the bond strength will not effect as much. From the table, in formulation PCA-9 the percentage fall is only 2.80 after three months for the canvas to canvas substrates while for leather to leather the percentage fall is negligible. In PCA-10 the percentage fall of peel strength is only 1.16 for the canvas to canvas substrates while for leather to leather substrates it is of 1.4.

Table 9. Characteristic after aging under ambient conditions for 3 – months

Aging Conditions	Type of Adhesives	Canvas-Canvas	Leather-Leather
		% fall of peel strength	% fall of peel strength
Ambient conditions for 3 months	PCA-9	2.80	0.47
	PCA-10	1.16	1.4
	Cement-X	14.28	13.63
	Samad Ultra	3.16	6.43
	Bison	11.11	30
	Gymsa	2.5	18.11
	Elephant	30	11

5.4.2 Aging at 100 °C in oven for 24 hours

5.4.2.1 Canvas-Canvas Substrates

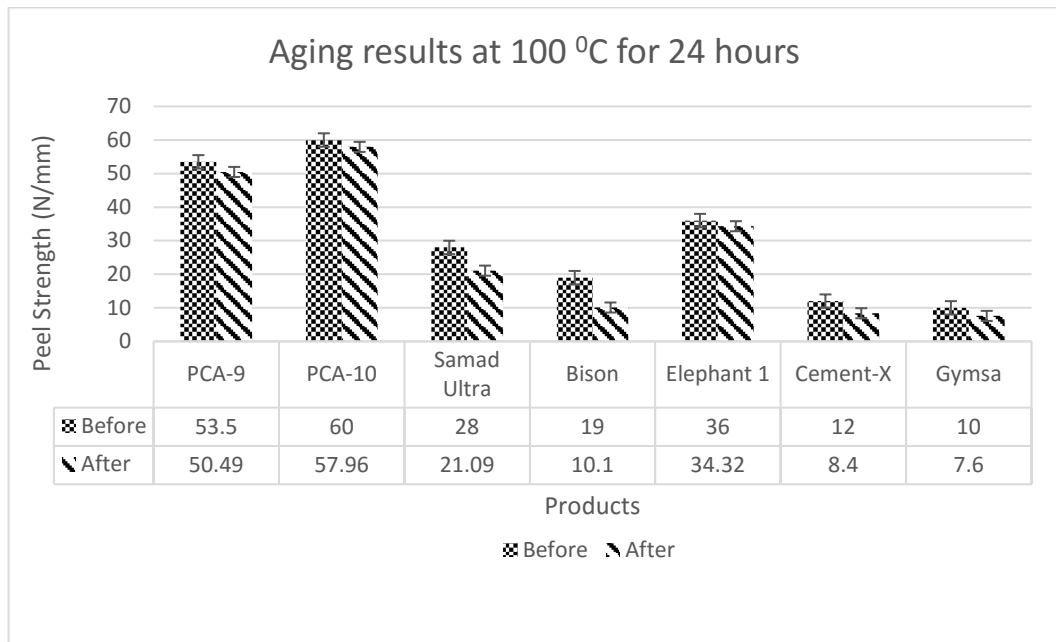


Figure 19. Aging results at 100 °C for 24 hours for canvas substrates

5.4.2.2 Leather-Leather Substrate

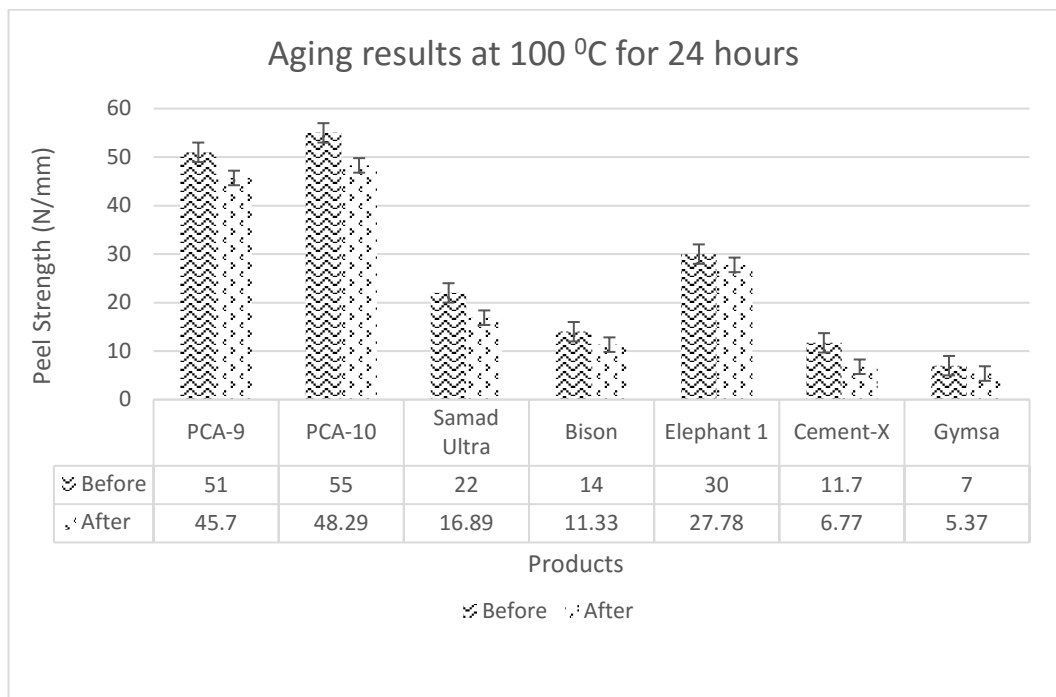


Figure 20. Aging results at 100 °C for 24 hours for leather substrates

Figure 19, figure 20 and table 10 explained the behavior of different substrates bonds when subjected to hot air at 100 °C. More crosslinking is present when higher functionality commercial grade resins used. At high temperatures, more crosslinks happen to result in a highly crosslinked network. Thus, the flexibility of the adhesive

system reduces. Hence the mismatch of adhesive properties over the surface of substrates leads the bond failure even at low loads.

Table 10. Characteristic after aging at 100 0C for 24 hours

Aging Conditions	Type of Adhesives	Canvas-Canvas % fall of peel strength	Leather-Leather % fall of peel strength
100 0C for 24 hours.	PCA-9	5.63	10.39
	PCA-10	3.4	12.2
	Cement-X	24.67	23.22
	Samad Ultra	46.84	19.07
	Bison	4.66	7.4
	Gymsa	30	42.13
	Elephant	24	23.28

5.4.3 Aging due to hot water when in contact for 24 hours

5.4.3.1 Canvas- Canvas Substrates

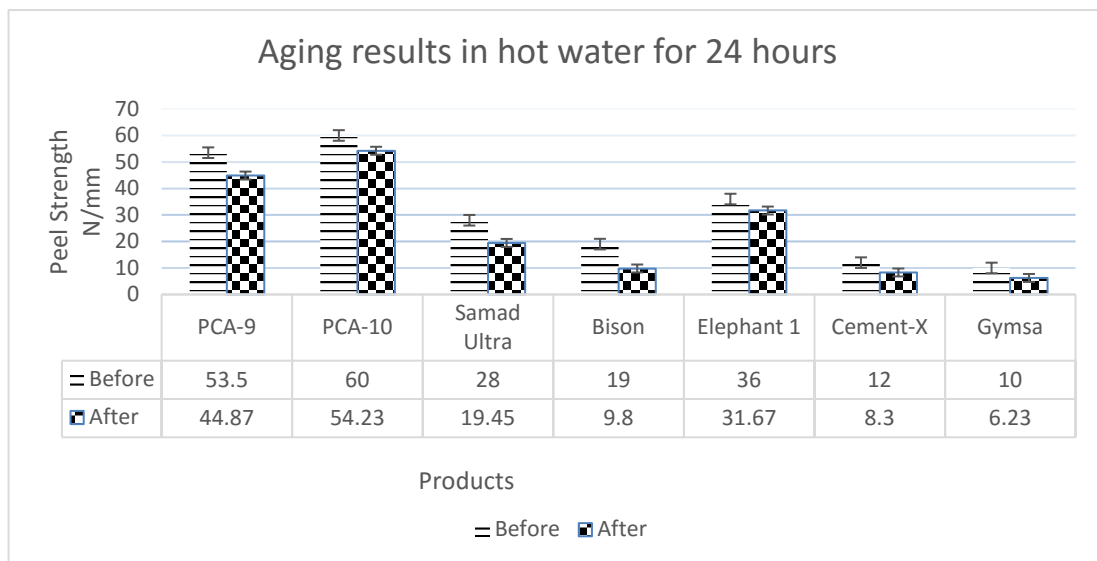


Figure 21. Aging results in hot water for 24 hours for canvas substrates

5.4.3.2 Leather- Leather Substrates

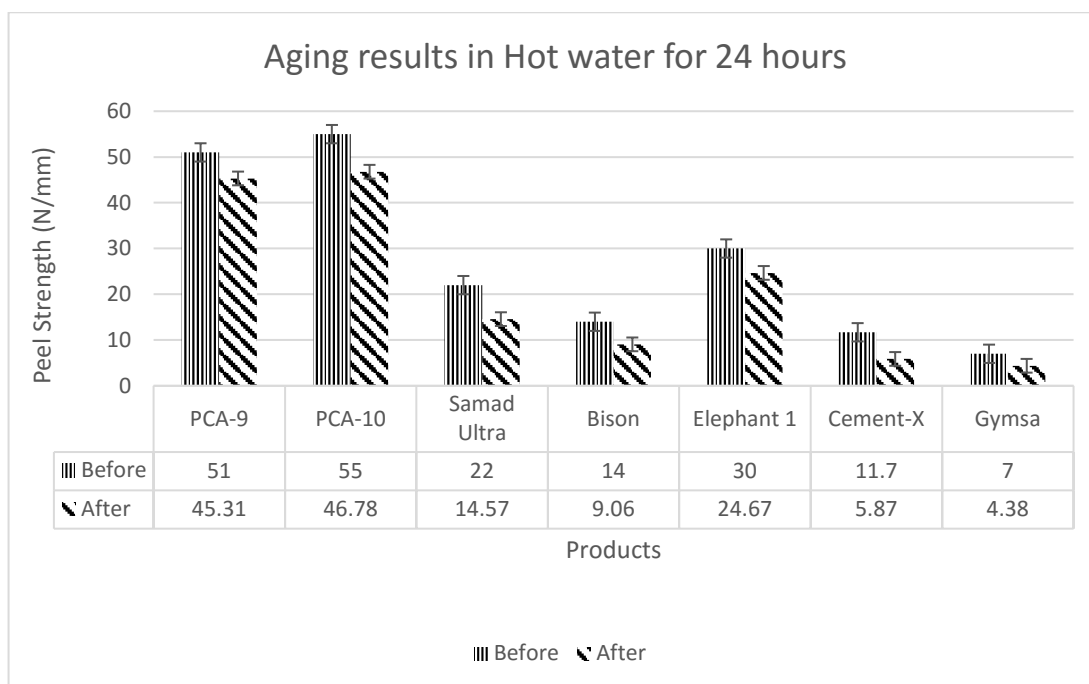


Figure 22. Aging results in hot water for 24 hours for leather substrates

Figure 21, figure 22 and table 11 shows the effect of hot water on different adhesives over the different surfaces of substrates. Water is the major problem for adhesive joints. It is due that water is very polar and permeates most polymers. From the results, it is clearly seen that PCA-9 and PCA-10 have most stability than the commercially available adhesives. The water phobic property of formulated adhesives is due to the presence of the filler namely CaCO_3 .

Table 11. Characteristic after aging in hot water for 24 hours

Aging Conditions	Type of Adhesives	Canvas-Canvas	Leather-Leather
		% fall of peel strength	% fall of peel strength
Hot Water for 24 hours.	PCA-9	16.13	11.15
	PCA-10	9.62	14.94
	Cement-X	30.53	33.77
	Samad Ultra	48.42	35.29
	Bison	12.02	17.76
	Gymsa	30.83	49.83
	Elephant	37.7	37.43

5.4.4 Aging in brine solution for 3 months

5.4.4.1 Canvas -Canvas Substrates

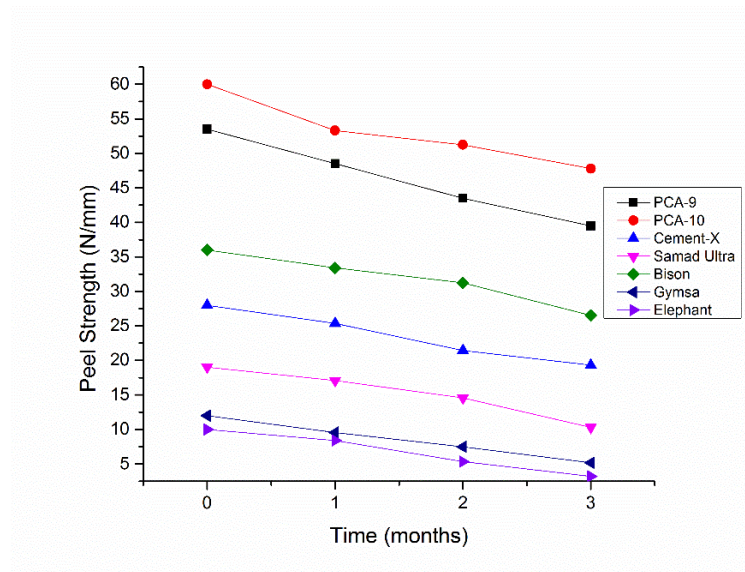


Figure 23. Aging in Salt Water for 3 months for canvas substrates

5.4.4.2 Leather-Leather Substrates

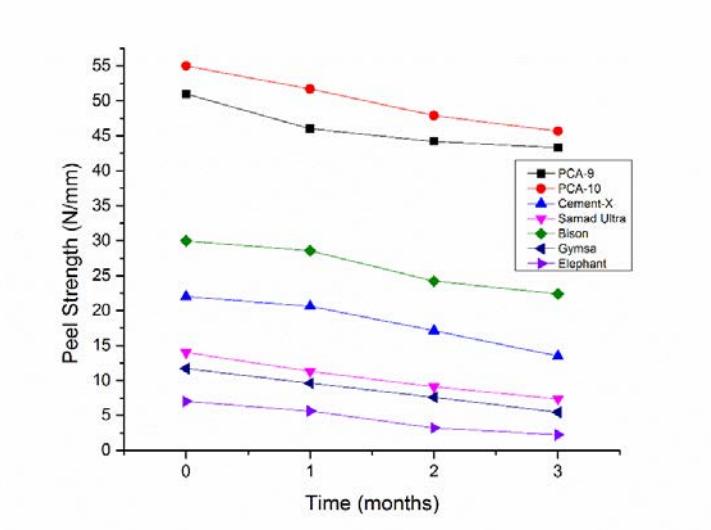


Figure 24. Aging in Salt Water for 3 months for leather substrate

Figure 23, figure 24 and table 12 shows that presence of salt has severe effects on the adhesives 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 PCA-9 and PCA-10 show the resistive result to the salty solution while commercial grade adhesives do not show that resistant and bond breaks.

Table 12. Characteristic after aging in Salt Water for 3 months

Aging Conditions	Type of Adhesive	Canvas-Canvas			Leather-Leather		
		% fall of peel strength	% fall of peel strength	% fall of peel strength	% fall of peel strength	% fall of peel strength	% fall of peel strength
Brine Solution for 3 months.	PCA-9	9.3457	18.6875	26.168	9.8039	13.3333	15.156
	PCA-10	11.166	14.61	20.33	6	12.927	16.963
	Cement-X	9.3928	23.5	31.035	6.36363	22.1363	38.681
	Samad	10.105	23.368	45.736	19.1428	35.1428	47.428
	Ultra						
	Bison	7.2222	13.25	26.357	4.76666	19.3	25.466
	Gymssa	20.166	37.583	57	17.9487	35.1282	53.247
	Elephant	16	46.6	67.9	19.5714	54.142	68.28

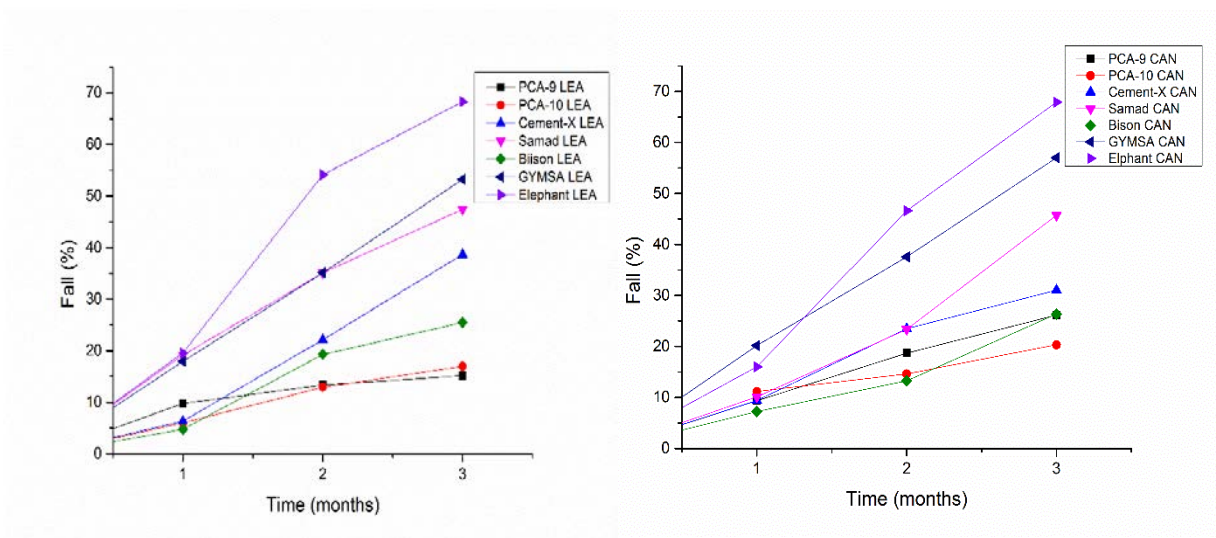


Figure 25. % fall of peel strength a) Canvas-Canvas Substrates b) Leather-Leather Substrates

5.5 Final Bond Strength Results

5.5.1. For canvas substrates

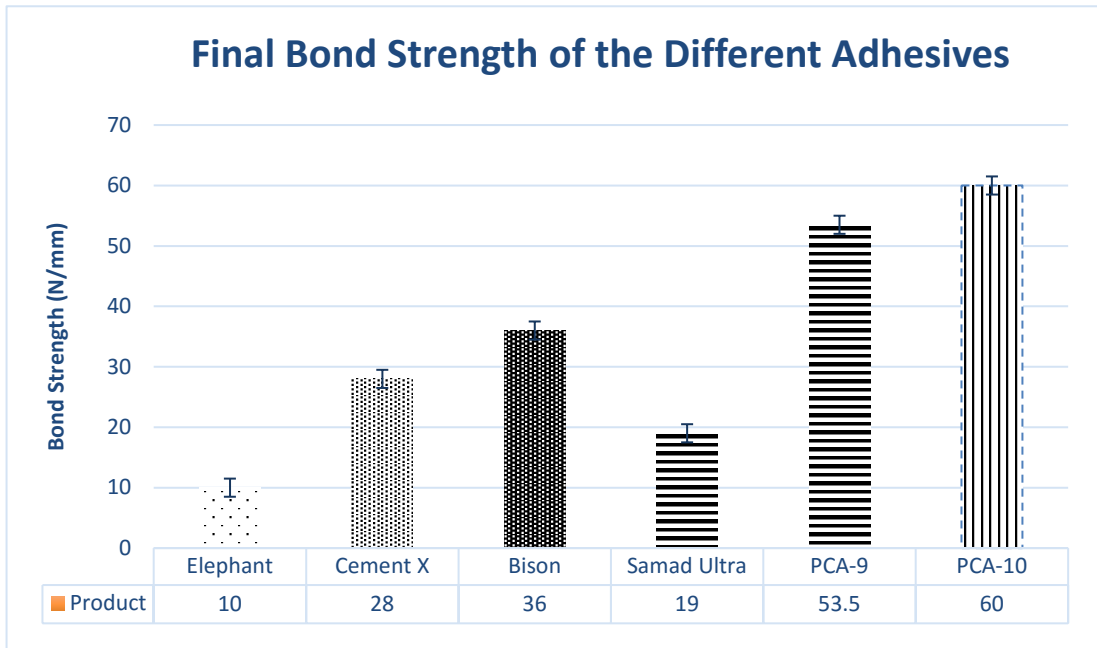


Figure 26. Final bond strength of different adhesives for leather to leather substrate

5.5.2. For leather to leather substrates

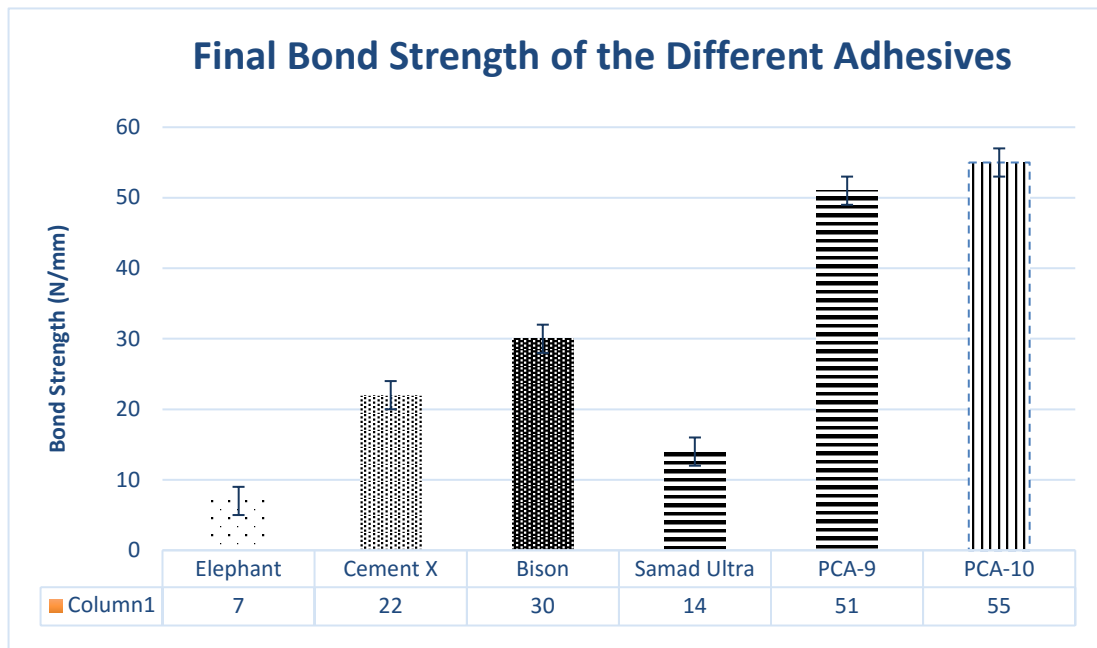


Figure 27. Final bond strength of the different adhesive for canvas substrate

In figure 26 and figure 27 it is clearly explained that PCA-9 and PCA-10 has the better results in term of peel strength. PCA-9 and PCA-10 shows 53.5 N/mm and 60 N/mm strength for canvas to canvas substrates and for leather to leather it is 51 and 55 /mm respectively.

Conclusion

After an extensive trial of experiments experimentation for developing a high strength, high quality, and low-cost polychloroprene rubber based adhesive, finally, the optimum formulations are achieved. Formulations PCA-9 and PCA-10 both showed promising results. With fixed amount of rubber, 85 phr (part per hundred rubber) resin, 5 phr, MgO, 8 phr antioxidant and the solvents in PCA-9 consists of 180 phr toluene, 420 phr methyl acetate, and 113.5 phr naphtha; while PCA-10 have same amounts of toluene and naphtha it consists 420 phr ethyl acetate instead of methyl acetate. Both formulations showed better peel strength than the commercially available adhesives. To further reduce the cost of the said formulations, the filler was added. The peel strength was tested at various filler concentrations and at 25 the compositions showed the optimum results. The compositions with filler contents are said to be PCA-9 and PCA-10. At 25 phr of filler contents, the adhesive still performed better than the commercially available adhesive products.

Hence, PCA-9 and PCA-10 are the finalized formulations. These 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.

Reference

- [1] Ephraim, B. and J. Samual, *Advanced Cycloshift Encryption (ACE) for Point of Sale Barcode System*. Imperial Journal of Interdisciplinary Research, 2016. **2**(10).
- [2] Bi, D., et al., *Study on the preparation and properties of polyurethane elastomers*. Polymer-Plastics Technology and Engineering, 2010. **49**(10): p. 996-1000.
- [3] Adams, R.D., *Adhesive bonding: science, technology and applications*. 2005: Elsevier.
- [4] Akerman, H., *The constitution of adhesives, and its relationship to solvent abuse*. Human & Experimental Toxicology, 1982. **1**(3): p. 223-230.
- [5] Archer, B., *Water-based contact adhesives—new developments*. International journal of adhesion and adhesives, 1998. **18**(1): p. 15-18.
- [6] Baldan, A., *Adhesively bonded joints and repairs in metallic alloys, polymers and composite materials: adhesives, adhesion theories and surface pretreatment*. Journal of materials science, 2004. **39**(1): p. 1-49.
- [7] Bhuvaneshwari, C., et al., *Elastomers and Adhesives for Aerospace Applications*, in *Aerospace Materials and Material Technologies*. 2017, Springer. p. 563-586.
- [8] Branlard, P. and J.P. Merle, *Process for the manufacture of stable polychloroprene latex*. 1978, Google Patents.
- [9] Cepeda-Jiménez, C., et al., *Treatment of thermoplastic rubber with chlorine bleach as an alternative halogenation treatment in the footwear industry*. The Journal of Adhesion, 2003. **79**(3): p. 207-237.
- [10] Challa, G., *Polymer chemistry: an introduction*. 1993: Prentice-Hall.
- [11] Cheng, H., *Adhesive composition*. 2002, Google Patents.
- [12] Christell, L.A., *High-performance water-based chloroprene polymer adhesive composition*. 1994, Google Patents.
- [13] Comyn, J., *Adhesion science*. 1997: Royal Society of Chemistry.
- [14] Creton, C. and E. Papon, *Materials science of adhesives: How to bond things together*. Mrs Bulletin, 2003. **28**(06): p. 419-423.
- [15] Da Silva, L.F., A. Öchsner, and R.D. Adams, *Handbook of adhesion technology*. 2011: Springer Science & Business Media.

- [16] Das, A., et al., *Reinforcement and migration of nano clay in polychloroprene/ethylene-propylene-diene monomer rubber blends*. Composites Science and Technology, 2011. **71**(3): p. 276-281.
- [17] Davis, J.A. and R.C. Koch, *Rubber compositions and articles thereof having improved metal adhesion and metal adhesion retention*. 1984, Google Patents.
- [18] DiStefano, F.V., *High performance solvent-free contact adhesive*. 1993, Google Patents.
- [19] Dubey, K., et al., *Polychloroprene rubber/ethylene-propylene-diene monomer/multiple walled carbon nanotube nanocomposites: synergistic effects of radiation crosslinking and MWNT addition*. Journal of Polymer Research, 2012. **19**(5): p. 9876.
- [20] Dunn, A., *Polymer chemistry: An introduction*. By G. Challa. Ellis Horwood, London 1993. pp. 192, price hardback£ 17.50; paperback£ 14.95, ISBN 0-13-682519-2 (hardback); ISBN 0-13-473687-2 (paperback). Polymer International, 1994. **34**(2): p. 235-235.
- [21] Feldman, D. and A. Barbalata, *Synthetic polymers: technology, properties, applications*. 1996: Springer Science & Business Media.
- [22] FERRÁNDIZ-GÓMEZ, T.d.P., et al., *Effects of hydrocarbon tackifiers on the adhesive properties of contact adhesives based on polychloroprene. I. Influence of the amount of hydrocarbon tackifier*. Journal of Adhesion Science and Technology, 1996. **10**(9): p. 833-845.
- [23] Fisher, J.D., *Alkylphenol resins in adhesive and rubber applications, in Phenolic Resins: A Century of Progress*. 2010, Springer. p. 439-450.
- [24] Fornes, T. and C. Cox, *Adhesive for rubber bonding*. 2016, Google Patents.
- [25] Freitas, R., et al., *Lower purity dimer acid based polyamides used as hot melt adhesives: synthesis and properties*. Journal of Adhesion Science and Technology, 2015. **29**(17): p. 1860-1872.
- [26] Fujita, M., et al., *Effects of miscibility on probe tack of natural-rubber-based pressure-sensitive adhesives*. Journal of applied polymer science, 1998. **70**(4): p. 771-776.
- [27] Gervase, N.J., *One-coat adhesive systems*. 1981, Google Patents.
- [28] Harvey, A., *Footwear materials and process technology*. 1982: New Zealand Leather and Shoe Research Association.

- [29] Howson, J.C. and T.E. Brooke, *Contact adhesives*. 1976, Google Patents.
- [30] Hussey, R. and J. Wilson, *Structural Adhesives: Directory and Databook*. 1996: Springer Science & Business Media.
- [31] Ippen, J. and E.A. Muller, *Article and process for the production of bonds between metals and elastomers*. 1969, Google Patents.
- [32] Keown, R.W., J.W. McDonald, and J.K. Weise, *Process for the preparation of chloroprene polymer solutions suitable for contact adhesives*. 1979, Google Patents.
- [33] Khan, M., *Study about polymer applications in footwear*. 2015.
- [34] Kuhn, L.B., *Rubber to metal adhesive comprising dichlorobutane resin and a chlorinated elastomer and use thereof*. 1952, Google Patents.
- [35] Kulkarni, M., et al., *Primer-less two component polyurethane adhesive*. 2016, Google Patents.
- [36] Lasprilla-Botero, J., M. Álvarez-Láinez, and D.A. Acosta, *Water-based adhesive formulations for rubber to metal bonding developed by statistical design of experiments*. *International Journal of Adhesion and Adhesives*, 2017. **73**: p. 58-65.
- [37] Lee, S.G., et al., *Preparation and properties of emulsifier/N-methyl pyrrolidone-free cross linkable waterborne polyurethane-acrylate emulsions for footwear adhesives. I. Effect of the acrylic monomer content*. *Journal of Applied Polymer Science*, 2016. **133**(34).
- [38] Locks, G.A. and A.K. Deshpande, *Resins and adhesive formulations therewith*. 2010, Google Patents.
- [39] Lux, B.D., N.A. Voicechovski, and D.J. Hellested, *Thin film adhesive labels and methods of making thereof*. 2016, Google Patents.
- [40] Mahler, V., *Rubber*, in *Quick Guide to Contact Dermatitis*. 2016, Springer. p. 159-179.
- [41] Marinović-Cincović, M., et al., *Polychloroprene Rubber-Based Nanoblends: Preparation, Characterization and Applications*, in *Rubber Nano Blends*. 2017, Springer. p. 249-279.
- [42] Martínez-García, A., et al., *Treatment of EVA with corona discharge to improve its adhesion to polychloroprene adhesive*. *Journal of adhesion science and technology*, 2003. **17**(1): p. 47-65.

- [43] Martins, A.F., et al., *Mechanical and dynamical mechanical properties of chloroprene rubber and cellulose II composites*. Journal of applied polymer science, 2004. **92**(4): p. 2425-2430.
- [44] Mayan, O., et al., *Shoe manufacturing and solvent exposure in northern Portugal*. Applied occupational and environmental hygiene, 1999. **14**(11): p. 785-749.
- [45] Menon, A. and L. Visconti, *Studies on blends of polychloroprene and polybutadiene rubber containing phosphorylated cardanol prepolymer: Melt rheology, cure characteristics, and mechanical properties*. Journal of applied polymer science, 2006. **102**(4): p. 3195-3200.
- [46] Mowrey, D.H., *Adhesives for bonding peroxide-cured elastomers*. 2003, Google Patents.
- [47] Osage, S.B. and M. Brandli, *Structural adhesive compositions*. 2016, Google Patents.
- [48] Packham, D.E., *Handbook of adhesion*. 2006: John Wiley & Sons.
- [49] Paiva, R., et al., *Effect of the surface treatment in polyurethane and natural leather for the footwear industry*. Materialwissenschaft und Werkstofftechnik, 2015. **46**(1): p. 47-58.
- [50] Paiva, R.M., C.A. António, and L.F. da Silva, *Sensitivity and optimization of peel strength based on composition of adhesives for footwear industry*. The Journal of Adhesion, 2015. **87**(10-11): p. 801-822.
- [51] Paiva, R.M., C.A. António, and L.F. da Silva, *Optimal design of adhesive composition in footwear industry based on creep rate minimization*. The International Journal of Advanced Manufacturing Technology, 2016. **84**(9-12): p. 2097-2111.
- [52] Paiva, R.M., et al., *Adhesives in the footwear industry*. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials Design and Applications, 2016. **230**(2): p. 357-374.
- [53] Paiva, R.M., et al., *Adhesives in the footwear industry*. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications, 2016. **230**(2): p. 357-374.
- [54] Papacchini, F., et al., *5.2 Effect of thermocycling on composite-to-composite bond promoted by different intermediate agents*. A study into the materials and techniques for improving the composite repair bond., 2006: p. 170.

- [55] Pastor-Blas, M., et al., *Failure analysis of surface-treated unvulcanized SBS rubber/polyurethane adhesive joints*. International journal of adhesion and adhesives, 1997. **17**(2): p. 133-141.
- [56] Pastor-Blas, M.M., J.M. Martín-Martínez, and F. Boerio, *Influence of chlorinating solution concentration on the interactions produced between chlorinated thermoplastic rubber and polyurethane adhesive at the interface*. The Journal of Adhesion, 2002. **78**(1): p. 39-77.
- [57] Patel, V., *One-part storage-stable water-based contact adhesive composition with an internal coagulant*. 2002, Google Patents.
- [58] Patel, V. and D.W. Wuerch, *Fast-setting polychloroprene contact adhesives*. 2000, Google Patents.
- [59] Paul, S. and P.C. Schalock, *Glues*, in *Quick Guide to Contact Dermatitis*. 2016, Springer. p. 223-232.
- [60] Perlinski, W., I.J. Davis, and J.F. Romanick, *Neoprene latex contact adhesives*. 1984, Google Patents.
- [61] Pilipović, A., M. Šercer, and J. Kodvanj, *INFLUENCE OF CROSSLINKING PARAMETERS ON MECHANICAL PROPERTIES OF CHLOROPRENE RUBBER*. Transactions of FAMENA, 2010. **34**(3).
- [62] Pizzi, A. and K. Mittal, *Urea-formaldehyde adhesives*. Handbook of Adhesive Technology, 2003: p. 635-652.
- [63] Pocius, A.V., *Adhesives*, in *Physical properties of polymers handbook*. 2007, Springer. p. 479-486.
- [64] Possart, W., *Adhesion: current research and applications*. 2006: John Wiley & Sons.
- [65] Radhakrishnan, N., P. Periyakaruppan, and K. Srinivasan, *Modification of Polychloroprene by Graft Copolymerization and its Application as an Adhesive*. The Journal of Adhesion, 1997. **61**(1-4): p. 27-36.
- [66] Raymond, P.A. and J.S. Piwnlca Jr, *Low VOC solvent-based polychloroprene contact adhesive*. 2002, Google Patents.
- [67] Robbins, J., *Polychloroprene contact adhesive*. Adhesives & Sealants Industry, 2003. **10**(2): p. 30-37.
- [68] Roberts, A.D., *Rubber contact phenomena*. Rubber Chemistry and Technology, 2014. **87**(3): p. 383-416.
- [69] Rodriguez, F., et al., *Principles of polymer systems*. 2014: CRC Press.

- [70] Roy, K., et al., *Development of a suitable nanostructured cure activator system for polychloroprene rubber nanocomposites with enhanced curing, mechanical and thermal properties*. Polymer Bulletin, 2016. **73**(1): p. 187-207.
- [71] Saad, A.L. and S. El-Sabbagh, *Compatibility studies on some polymer blend systems by electrical and mechanical techniques*. Journal of applied polymer science, 2001. **79**(1): p. 60-71.
- [72] Saikumar, C., *Adhesives in the leather industry perspectives for changing needs*. Journal of adhesion science and technology, 2002. **16**(5): p. 543-563.
- [73] Sherry, H.Y., A. Sood, and J.S. Taylor, *Shoes*, in *Quick Guide to Contact Dermatitis*. 2016, Springer. p. 205-212.
- [74] Skeist, I. and J. Miron, *Introduction to adhesives*, in *Handbook of adhesives*. 1949, Springer. p. 3-20.
- [75] Skelley, R., *Two component adhesive*. 1997, Google Patents.
- [76] Souza, E.M., et al., *Behavior of adhesion forces of the aqueous-based polychloroprene adhesive magnetically conditioned*. Journal of Adhesion Science and Technology, 2016. **30**(15): p. 1673-1699.
- [77] Staikos, T. and S. Rahimifard, *An end-of-life decision support tool for product recovery considerations in the footwear industry*. International Journal of Computer Integrated Manufacturing, 2007. **20**(6): p. 602-615.
- [78] Tang, j., *Bonding adhesive and adhered roofing systems prepared using the same*. 2016, US patent 20,160,108,296.
- [79] Tang, J. and J. Carr, *Bonding adhesive and adhered roofing systems prepared using the same*. 2016, Google Patents.
- [80] Taşdemir, M. and E. Uluğ, *Mechanical, morphological and thermal properties of SEBS, SIS and SBR-type thermoplastic elastomers toughened high impact polystyrene*. Polymer-Plastics Technology and Engineering, 2012. **51**(2): p. 164-169.
- [81] Vick, C. and R. Rowell, *Adhesive bonding of acetylated wood*. International Journal of Adhesion and Adhesives, 1949. **10**(4): p. 263-272.
- [82] Voss, G.D. and B.B. Smith, *High adhesion of a variety of rubber compounds to fabric using a single resorcinol-formaldehyde latex composition*. 2001, Google Patents.
- [83] Voyutskii, S., *Types of fracture of adhesive joints made with polymers*. Polymer Mechanics, 1966. **2**(5): p. 453-459.

- [84] Wickramasinghe, L.G., *Development of a water-based polychloroprene adhesive*. 2016.
- [85] Yang, D., et al., *Monocomponent waterborne polyurethane adhesives: influence of the crosslinking agent on their properties*. Journal of Macromolecular Science, Part A, 2011. **48**(4): p. 277-283.
- [86] Zhang, K., et al., *Modification of polychloroprene rubber latex by grafting polymerization and its application as a waterborne contact adhesive*. The Journal of Adhesion, 2012. **57**(2): p. 119-133.
- [87] Zhang, K., et al., *Preparation and properties of a waterborne contact adhesive based on polychloroprene latex and styrene-acrylate emulsion blend*. Journal of Adhesion Science and Technology, 2009. **23**(1): p. 163-175.

Appendices

A. Appendix A

A.1 Basic Definitions

1. Adhesive

A substance used to bond to surface together by the action of adhesive and cohesive forces and exhibits flow when applied to the substrate.

2. Activator

A substance which effects the curing time of the adhesive and enhances it.

3. Adhesion promotor

A substance used to enhance the bonding properties of the adhesive. It can be used in the adhesive formulation or applied directly to the substrate. (ASTM D 907-06). These substances usually known as primer and coupling agents.

4. Adhesive joint

A point where two adherends are held together with adhesive. (ASTM D 907 – 06)

5. Curing

Curing is a process in which adhesive becomes tougher and harder by chemical reaction or the physical action.

6. Chemical Cure

Chemical curing in adhesives occur due to the chemical reaction when adhesive is applied to the substrates.

7. Cohesion

Cohesion is present in similar molecules. These inter molecular forces may be due to chemical bonds.

8. Cohesive Strength

The strength of the adhesive films between the same molecules.

9. Crosslink

Crosslinking is the process due to chemical reaction to form three-dimensional network of the rubber.

10. Curing time

The period in which solvent evaporates from the surface of the substrates and adhesive films get harder to bond the two surfaces together.

11. Diluent

A liquid used to lower the viscosity and solids in the adhesive.

12. Drying time

The time in which adhesive can dry without any external heat or pressure.

13. Elastomer

Such materials which can attain their shapes again after removal of the load. Usually rubbers are elastomer and they are macromolecular materials.

14. Filler

A material used to modify the strength of the adhesive. Also, it is used to reduce the overall cost of the adhesive.

15. Heat resistance.

The ability of the adhesive to withstand at elevated temperature.

16. Latex

A stable dispersion of the material i.e polymer in the appropriate aqueous solution.

17. Loop tack

The initial grabbing of the adhesive when applied to the substrates without any of the pressure.

18. Manufactured unit

A quantity of the finished product processed at one time.

19. Mastication

A process of softening the long rubbers at specified temperature so that rubber can easily be dissolved in the solvents.

20. Nonvolatile contents

These contents are solids which do not evaporate with the solvent.

21. Novolak

A phenolic resin in which ration of phenol and formaldehyde is set to be 1:1.

22. Peel strength

The average load applied to the unit width of the bond line required to separate two joined surfaces.

23. Peel test

A test according to the ASTM standards to separate the two surfaces from each other at machine. These tests can at different angles i.e. T peel, 90° peel and 180° peel test.

24. Phenolic resin

The thermoset resin formed of the reaction of the phenol and formaldehyde.

25. Physical Cure

Physical curing is the process due to physical action such as evaporation of the solvents when applied to substrates and make the adhesive harder.

B. Appendix B

B.1 Standard Test

1. ASTM D903 (98) 2010

The test is carried out on the universal testing machine. The specimen is prepared according to following procedure

- One substrate is of 400 mm long and 35 mm wide.
- Second substrate is 300 mm long and 53 mm wide.
- Adhesive should be applied up to the mark region and 1 inch gap should be provided from the bonded region so that easy gripping can be achieved at machine's jaws.
- The 100 mm/min strokes are set on the machine for the peel test of the flexible substrates.
- The calculation is carried out by taking the average of the peel strength.
- At least 5 specimens should be tested for accurate calculation.

2. ASTM D1583 (98) 2010

This test is used for the determination of the nonvolatile solids in the adhesive. The test is carried out on different substrates of rubber, canvas, leather, and flexible material.

- The test is conducted by weighing the dry cup first then
- Pour 3 to 5 grams of the adhesive and weigh the cup again then
- Place it for 3 hours in the oven at 100°C after drying of the sample weigh it again.
- The weight of the solids in the dry cup is the solids content.
- The amount is calculated in percentage and that percentage is the bonding agent and usable adhesive in the sample.

$$\% \text{ solids content} = \frac{m''' - m'}{m'' - m'}$$

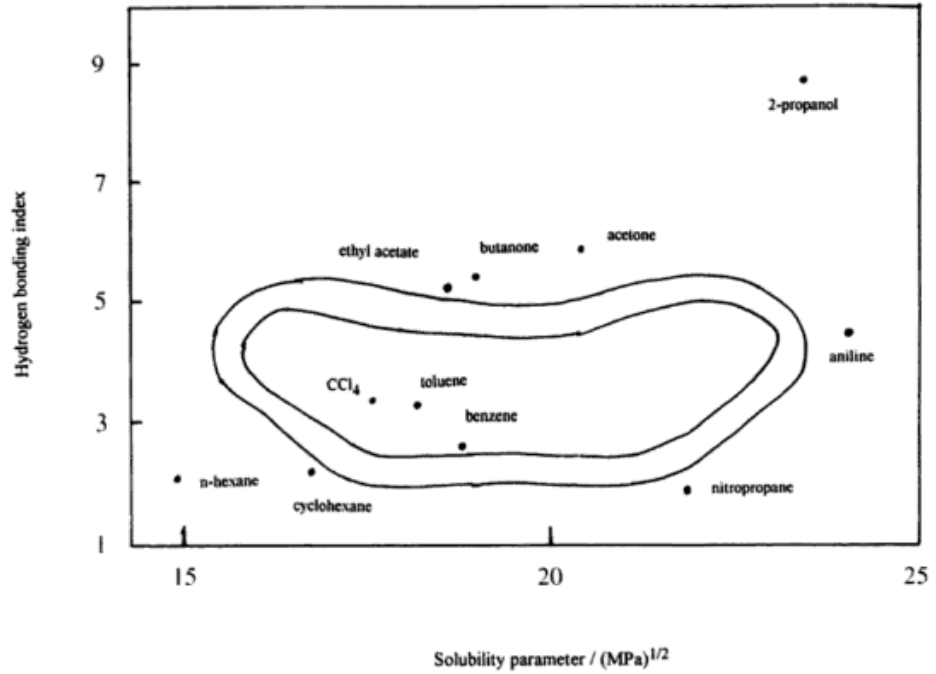
m' = weight of dry clean cup

m'' = weight of cup along with sample

m''' = weight of dried cup

C. Appendix C

C.1 Solubility map for polychloroprene



Source: Adhesion Science by John Comyn