Development of High Strength Polychloroprene Contact Adhesive with MWCNTs Reinforcement

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Thesis Acceptance Certificate

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Date: -----------------------

Dedication

I would like to dedicate my thesis

to my beloved parents

Acknowledgement

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

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Abstract

Chloroprene (CR) rubber base contact adhesives are an industrially important branch of adhesives commonly used in structural applications e.g. footwear, plastic, leather, automobile, construction industries etc. Various efforts have been made to improve its bond strength for multiple substrates. Variation in processing parameters and addition of useful ingredients may be helpful in increasing peel strength of joined substrates. Incorporation of nanoscale reinforcement is a potential means to move in this direction.

In the current study, an effort has been made to incorporate multiwall carbon nanotubes (MWCNTs) in small quantity and to optimize its ratio in order to obtain improvement in bond strength. The objective of this research was to enhance peel strength on flexible substrates and to improve its resistance at high temperature ($\leq 100^{o}$ C). Most of the adhesives show good performance in normal conditions but their application is limited in extreme ageing environment. The research work was divided into three parts. In first part, a polychloroprene rubber-based contact adhesive was prepared. Then, in second step, the dispersion of multi- walled carbon nanotubes was done using N, N-Dimethylformamide solvent. In final step, dispersed MWCNTs were added in formulated polychloroprene adhesive to prepare a nanocomposite adhesive. Multiple formulations were made using various grades of polychloroprene, along with varying experimental conditions. For example, phenolic resin, MgO, anti-oxidant and solvents were added in various proportions. The best results were obtained with 65-phr phenolic resin and incorporation of MWCNTs up to 1 %. The solids contents 50-52 % in prepared adhesive were found to be optimum. The peel tests after exposure to aggressive environmental conditions showed that nanocomposite adhesive had greater thermal stability and weather resistance compared with commercially available adhesives.

Abbreviations

CR	Polychloroprene rubber
MWCNTs	Multi-Walled Carbon Nanotubes
EDL	Electrical double layer
WBL	Weak boundary layer
PCA	Polychloroprene adhesive
CTE	Coefficient of linear thermal expansion
T_g	Glass transition temperature
CNTs	Carbon nanotubes
CNF	Carbon nanofiber
PA-30	Polychloroprene adhesive (Unreinforced)
PA-N 11	Polychloroprene adhesive (Reinforced)
ASTM	American Society for Testing Materials
FTIR	Fourier-transform infrared spectroscopy
TGA	Thermogravimetric analysis

Table of Contents

List of Figures

List of Tables

CHAPTER 1

Introduction

1.1 Adhesive

A substance that is use to join to separate surfaces or substrates. Surfaces are join in such a way that they resist separation of parts [1], [2].

1.2 Contact Adhesive

“A self-adhesion property”. A material that is applied to both substrates, which are to be joined and then the parts are allowed to dry. After attain tack time of adhesive both the surfaces joined by applying certain pressure. The solvent evaporates immediately and a high strength bond formed [3].

1.3 Pressure sensitive adhesive

Adhesive that is sensitive to pressure. Bonded surfaces do not require any pressure and adhesive remains tacky and viscous [4].

1.4 Properties of contact adhesive

Contact adhesive is mostly use in leather and shoe industry due to its unique property of self-adhesion. Adhesive is coat on both two parts, which are to be married together, and after drying both the surfaces are join together by applying slight pressure. After some time, solvent evaporates and a permanent bond is developed. Place of correction of parts is low because position of surfaces cannot be changed after joining [5]. Solvent and water base contact adhesives are available. Solvent base adhesives are quick to dry, flammable and toxic but water base adhesives have more tack time, inflammable and environment friendly. Peel strength increases with time [6].

1.5 Adhesives basic properties

For effective function of an adhesive, it must have some properties, which are:

1.5.1 Crystallization

Rate of crystallization controls the initial join strength. Grades of polychloroprene play an important role for the development of quick rate of crystallization. Crystallization is directly relating to temperature; it dominates at low temperature but gradually decreases with high temperature. At elevated temperature polychloroprene, adhesive de- crystallizes and gives a unique property of auto-adhesion. This property is useful in manufacturing of heat-activated adhesives [7].

1.5.2 Viscosity

The viscosity of a solution and solid content impacts on strength of the adhesive film. Higher the viscosity of adhesive results higher the bond strength with higher molecular weight polymer [8].

1.5.3 Polarity

Polarity relates to the development of a wide range of adhesives manufacturing. Polar and non-polar organic solvents can dissolve polychloroprene rubber to develop a divergent range of viscosity and open time of adhesives [2].

1.5.4 Open Time

The time after the application of adhesive on the surface of a substrate to build a strong bond. A tacky surface is observable after the open time and evaporation of solvent take place to achieve that time. Temperature, amount of adhesive and structure of the substrate influences the duration of open time[4].

1.5.5 Setting Time

The time to develop a satisfactory bond formation after the joining of two surfaces whom which adhesive is applied [9].

1.5.6 Shelf Life

Useable duration of an adhesive in a container with no change in properties is known as “shelf life”. It can be rise by using anti-oxidants. Temperature, light, exposure to the environment and atmospheric moisture affect the shelf life of an adhesive [10].

1.5.7 Cure time

It is the time require developing the final and full strength of an adhesive. Curing time is gain by polymerization and fully solvent removal from adherend surfaces [11].

To form a strong bond between a substrate surfaces and adhesive, wetting of surface is very necessary [12].

1.5.8 Hardening

To achieve a cohesive firm bond, the hardening of the adhesive is required. It can be achieved by curing and loss of solvent.

1.6 Advantages of contact adhesive

Application of contact adhesive is very easy, even it can apply by hand. It has minimum shrinkage on curing. Contact adhesive can resist a high- temperature range from -400^{o} C to +130^{o} C. Adhesive joint is free from surface deformation and damage of the substrates. A very cheap process of joining of two dissimilar substrates as compared to other joining techniques. A lightweight joining process as adhesive itself has minimum weight as solvent evaporating after curing hence a lightweight product formed. Adhesive joining process has no energy consumption expect labor. Adhesive joint has no vibration, corrosion, vibration. Adhesives have a wide range of ability to join substrates. Adhesives have played an innovative role in new product designs [2].

1.7 Disadvantages of contact adhesive

Once bond formed then repositioning of bonding surfaces is impossible. Organic solvents used to remove the adhesive joint. To use organic solvents special care should be taken because they are toxic in nature. Curing time is required to make a firm bond before that time bond strength is minimum. Contact adhesives are limited to their temperature range and their working performance is poor after that temperature range [13]. The strength of the adhesive bond affected by long-term environmental conditions and use of product. A strong firm bond demands surface preparation. Removal of adhesive bond can damage substrate and it is an expensive process, as it requires organic solvents and time. Application of the adhesive demands special care as solvents in the form of fumes have health issues with human body [14].

1.8 Factors that influence adhesive strength

1.8.1 Adhesive film thickness

A film thickness plays an important role in bond strength. A thick film due to high viscosity of adhesive generates a weak bond due to voids formation. Surface wetting is not proper due to thick adhesive bond film. The bond strength can be improve by applying pressure to remove voids and by adding solvent to lower the viscosity [6].

1.8.2 Physical characteristics of adhesive film

Compressive strength, tensile strength and shear strength have a positive influence in bond strength. Better adhesives have low creep rate under stressed conditions. By adding plasticizers in adhesives, creep rate can be lower.

If difference in adhesive and adherend thermal coefficients of expansion is high then, the bond strength is low under variation in temperature. It can be improve by adding reinforcements and fillers in adhesive and bond strength can be increase [15].

1.8.3 Strength influence by application technique of adhesive

The bond strength is influenced by technique of adhesive applying on adherend surfaces. Temperature, time and pressure are the factors that influence the bond strength of the adhesive. Sufficient time is required to make a firm bond by achieving curing time. In solvent evaporation, temperature plays a key role. Smooth adherend surfaces demand less pressure but in case of porous surfaces sufficient pressure is required to build a firm bond [16].

1.8.4 Polarity of adhesive

Adhesives with polar groups have better strength for organic contacting surfaces as compared to non-polar adhesives. So, introduction of polar molecules causes' strength improvement in non-polar adhesives [17].

1.8.5 Effect of pH

Strong acids and alkalis have a negative effect on bond strength of adhesive. However, the effect of pH on various types of adhesives has a different effect [18].

1.8.6 Complexity of adhesive molecule

Adhesive performance is influence by chain length and complexity of the molecule. High molecular weight phenol-aldehyde case has a positive effect in adhesive performance. Similarly, favorable chain length of fatty acid in cellulose esters is 6 to 14 for better strength of adhesive [11].

1.9 Adhesive strength development

Evaporation of solvent, chemical reaction and proportion of suitable pressure have a key role in development of adhesive strength.

1.9.1 By Solvent evaporation

Adhesive is applied on the surface of two substrates which are marry together in such a way that solvent evaporates and a firm bond is form after joining of two surfaces. The adhesive is disperse in the solvent and curing time is acquire by solvent evaporation to achieve a strong bond [19].

1.9.2 By chemical reaction

By chemical reaction, low molecular weight monomers are convert into high molecular weight cross-linked polymers with strong bond formation [20].

1.9.3 By Applying pressure

The two surfaces are joined together when the removal of solvent by applying suitable pressure. Tacky surfaces join firmly due to pressure but it should be in applying range [21].

1.10 Selection of a satisfactory solvent

Solvent has a key role in adhesive formulation as selection of solvent can vary open time and affects the peel strength of adhesives. Contact adhesives mostly demand solvents. Chlorinated solvent has exceptional ability to catch fire and have malignant consequences on environment and human life. Therefore, chlorinated solvents are banned in adhesive formulation. Choice of solvent not only depends on non-flammable but rate of evaporation of solvent. Non-solvents are also part of adhesives formulations to dissolve polychloroprene rubber. Rate of evaporation is different for each solvent, which can influence open time of an adhesive from few minutes to hours [22].

1.11 Acid accepting components of contact adhesive

The acid accepting components are added in a adhesive formulation to resist dehydrochlorination of the polymer matrix.The zinc oxide and magnesium oxide are mixed in powder form.Their minute amount not only enhances the strength but also increases the life of a adhesive. As these fillers are acid accepting components and they can handle acidic hydrogen chloride.The crosslinking properties of an adhesive are also enhanced by these agents [23].

The primary fuction of magnesium oxide is “acid scavanger”.In vulcanization processs chloride icons are generated. These ions can degrade the polymer chain and slows the the process. By adding zinc oxide in the adhesive formulation, the chloride ions reacts with these fillers and form zinc chloride.The zinc chloride acts as accelerater and enhances the curing process [24].

1.12 Mechanism of adhesion

Adhesion is the mechanism of attraction for the materials that join the surfaces of another substrate. While cohesion is inner strength of the substrate because of variety of interactions with in the adhesive. The figure below describes cohesion and adhesion forces present between an adhesive and substrate and within an adhesive [25].

According to researchers, adhesion is the attraction force between two dissimilar materials whereas cohesion is the attraction force between two similar substrates. The surface molecules interact when two substrates are brought into contact with each other, give rise to attractive forces that can be physical, chemical or electrostatic(adsorption, covalent bonding or van der Waals forces) [26].

1.12.1 Theories of adhesion

Adhesion is the result of various physio-chemical interaction taking between substrates to be joined through adhesive. Therefore, adhesive relationships need to understand some of the processes that are at the surface of the material. There are several ways to define adhesive mechanisms, mechanical intercourse, electrostatic, diffusion, and surface reaction. However, it is difficult to describe adhesive relationships especially on mechanisms or principles. Adhesive relationships are the result of the combination of these mechanisms, but the role of every mechanism changes for various adhesive systems [27]. There are different theories of adhesion proposed by researchers over the course of time. Some of them are discuss below:

1.12.2 Mechanical interlocking theory

Surface of a substrate is not smooth but there is some roughness presence in the form of voids and pores. Peaks of these pores is responsible for friction over the surface of the material. In 1925, McBain and Hopkin proposed the theory of mechanical interlocking; appropriate adhesion only happens when an adhesive enters into the crevices and holes of the substrate and interlocks to the surface of the substrate [28].

Mechanical anchoring is the main factor for bonding of porous surfaces like fibrous, woody and textile materials. Barrof and Wake further explained this phenomenon. They suggested that joint strength “G” is the multiplying factor of both mechanical interlocking and thermodynamic interfacial interactions given below.

G= (mechanical interlocking) x (interfacial interactions component)

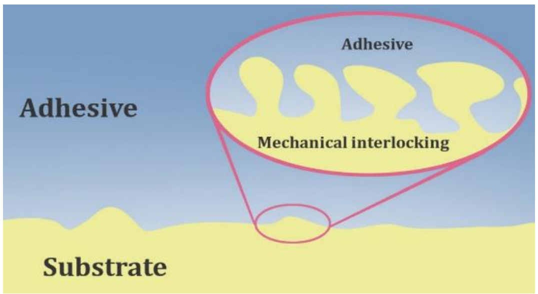

Figure 1.1: Mechanical interlocking between adhesive and substrate [28]

The mechanical interlocking theory proposes that roughness of surface of the material is favorable because of:

- It provides mechanical interlocking
- The total area can be enhanced on which adhesion force progress.

The major drawback of this theory is that it is only effective for smooth surfaces and shows better results for these surfaces [29].

1.12.3 Diffusion theory

The diffusion model is functional with polymer molecules where molecules diffuses into each other. It describes that adhesion between adhesive and material is due to diffusion of polymeric molecules at the interface of the surface of the material. Because of penetration of molecules, adhesion takes place at the interface. Mobility of short polymers chain is high and penetrate into other material before the long polymer chains. Mutual diffusion is the main driving force of polymer molecules for auto adhesion [30].

This theory demands that the adherend and the adhesive are polymer and are mutually compatible and miscible with each other. By maintaining the solubility characteristics of polymers, equal optimum diffusion can be attained. However, inter diffusion requires that both the molecules should be polymer in nature and should be sufficiently soluble. These circumstances can only be filled for healing, auto-adhesion or welding of similar polymer processes [31].

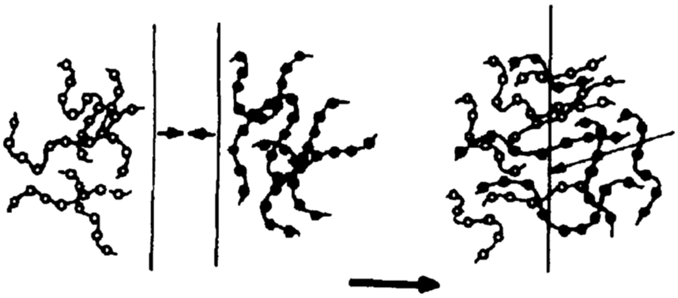

Figure 1.2: Interdiffusion between adhesive and substrate [32]

This is valid for crosslinking and adhesion of polymers which are rubbery in nature, as might occur when two surfaces are coated with contact adhesive [30].

1.12.4 Electrostatic – adhesion theory

Theory of electrostatic describes that the electrostatic forces are generated between the layers of joined substrate over the adhesive-substrate interface. Interface of this joint act as a capacitor. Capacitor tends to increase the potential difference until a charge rises along the interface of bonded layers. Therefore, adhesion between the substrate and adhesive is due to potential difference [32].

Many researchers noted the increase in the adhesion of thin layer films over the surface. Stoddart studies told us that there was no overall surface discharge produce on adherend but only electronic emission was altered.

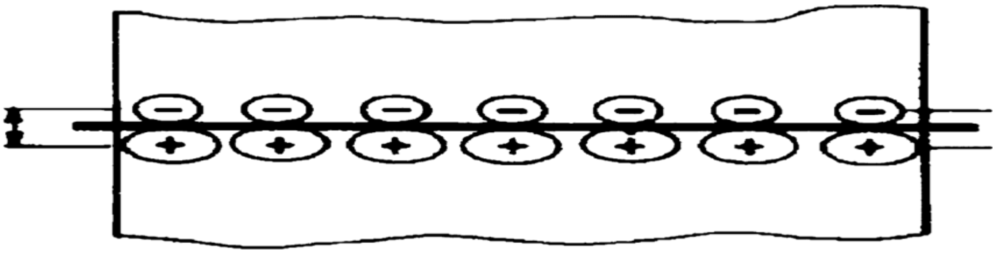

Figure 1.3: Schematic diagram of adhesive-substrate interface [34]

Thus, the predominance of the electrostatic double layer is handy in certain specialized cases. The electronic theory proposes that when two metals are come closer in contact, charges will move from one layer to another layer; give rise to adhesion force by developing an electrical double layer (EDL). Polymers are insulators, so it is difficult to apply this theory to the adhesives [33].

1.12.5 Weak boundary layer

Adhesive bond Interface has several properties that are different from bulk materials. Therefore, it was thought that failure of adhesive bond will not occur at interface of adhesive and substrate rather because of formation of weak boundary layer will be the cause of bond failure. Adhesives are generally polymeric in nature and a greater force is required for interfacial failure because of cross links and chain entanglements. Bikerman stated that while determining the level of adhesion, a weak boundary layer (WBL) cohesive strength must be considered even if failure is propagated at interface. From this assumption, cohesive energy (WBL) is equal to adhesion energy. The seven classes of WBL considered by Bikerman is illustrated in fig Plasma treatment ensures the formation of weak boundary layer because of polymeric substrates degradation [34].

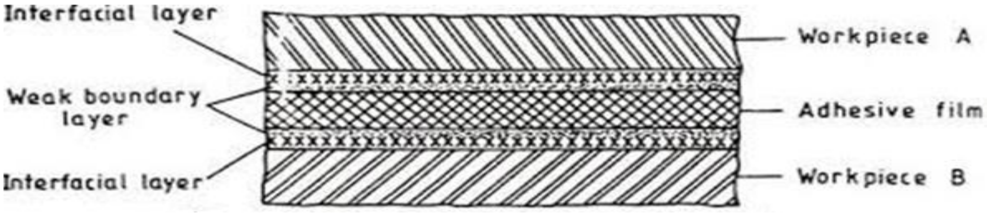

Figure 1.4: Mechanism of boundary layer theory [33]

The weak boundary layer should be removed to achieve a satisfactory bond from an adhesive. Failure in metals take place by formation of scaly oxide layer. However, this problem does not occur in aluminum, because it has coherent layer of oxide on its surface. A low-molecular weight additive is present in polyethylene throughout its surface leading to weak interface. In both cases surface treatments can be performed to remove these weak layers [32],[27].

1.12.6 Adsorption theory

Adsorption theory explains that adhesion between molecules is due to surface and molecular forces, which holds the molecules firmly to make a strong bond. Adhesion is due to interatomic and intermolecular forces that are build up on the surfaces of the material. The van der Waal’s forces and weak hydrogen forces are developed across the interface and chemical bond may be formed. Other than this there might be donor-acceptor interactions occurs at the surfaces and become the medium of strength between primary and secondary bonds [35].

To progress a successful adhesive, it must have the property of wetting the surfaces to be bonded. Many low surface tension materials have been developed after this theory. Epoxy is good example of this theory, as it wets steel providing a strong bond however; it does not wet PP, olefins PE, PTFE and does not form any bond [36].

Figure 1.5: Diffusion theory of adhesion [32]

1.13 Types of contact adhesives

Adhesives can be organized in various categories according to their source, end use, components and choice of solvents etc.

1.14 Classification by source

Adhesive in these categories are either natural or synthetic adhesive.

1.14.1 Natural adhesives

Natural adhesives are also known as bio-adhesives. They are animal or vegetable based. Natural gums include in this category. The simplest form of bio-adhesive is flour paste prepared by wheat and water. Organic resources like starch, resin, bone, blood all these sources belong to this category. These adhesives have no health issues due to their natural resources. They have long shelf life and are easy to apply. They are cheap but have low strength. Mostly water is used as solvent in these adhesives. They are used for bookbinding, lightwood, paper posters etc. [37].

1.14.2 Starch and dextrin adhesives

Various types of starch, corn and potato starch are the raw material for starch adhesives. A very cheap type of adhesive that can work in cool and hot conditions but moisture carrying and low bond strength. In making of books, envelops and paper binding [38].

1.14.3 Synthetic adhesives

Synthetic polymers are not available in nature but they are developed and manufacture by man, we can say synthetic polymers are laboratory made. Synthetic adhesives have an enormous demand due to effective mechanical, physical and chemical properties as compare to natural adhesives [2].

1.15 Classification by forms

1.15.1 Water base adhesives

Mostly known as water borne adhesives. These adhesives are available in the form of solutions and powder. Water borne adhesives applied with water. Water is evaporated or absorbed by substrate and bond strength is achieved. Water borne adhesives have long curing time and lower bond strength as compared to solvent base adhesives. The examples of these adhesives include epoxy resin based, nitrile rubber based, polyvinyl acetate based etc. [39].

1.15.2 Solvent base adhesives

These are the adhesives made by dissolving resin or rubber into a solvent. Mostly, solvent is volatile in nature. Such adhesives are phenol resin, polychloroprene rubber based etc. [40].

1.16 Classification by curing

Curing contact adhesives are very firm in nature, exhibiting great thermal and mechanical properties due to cross-liking 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 [41].

1.16.1 Physical curing adhesives

These adhesives require physical effects like pressure or temperature to produce cohesion and adhesion forces. Contact adhesive solvent-based adhesives pressure sensitive (PSA) are in that list of physical curing adhesives [41].

1.16.2 Chemical curing adhesives

Adhesion forces are built up by chemical reactions. Epoxy, cyanoacrylates and silicone adhesives are in this list [42].

1.17 Classification by chemical composition

All synthetic adhesives can be thermoplastic, thermosetting or elastomeric. All these adhesives are discussed below

1.17.1 Thermosetting adhesives

These materials melt as they are applied onto application and do not require heating to cure. Curing process generally takes place by chemical reaction at temperature depending upon type of the adhesive. One-part system cure at high temperature and their shelf life is limited. While two-part systems have longer shelf life and are cured at room temperature. They can be used as contact adhesive and pressure-based adhesive. Solvent can be added to facilitate their usage [43].

They form highly cross-linked structure when cured because of thermosetting resins which results in their high resistance to heat and solvents. They have low elastic deformation at elevated temperature. Their bonds can withstand temperatures of 93-260^{o}C. They offer good peel strength. Thermosetting adhesives are used to bond most of the materials especially for structural materials. Thermosetting adhesives include epoxy, polyester, acrylic, urea-formaldehyde etc. [44].

1.17.2 Thermoplastic adhesives

These adhesives are melted by high temperature before application and they progress strength upon cooling or evaporation of solvent. No cross-linking takes place during heating and cooling process. They are mostly one-component system. They can be used up to 80^{O} C however, they are not recommended to use at elevated temperatures. They have poor creep resistance and their peel strength is just fair. They are used o bond non-metallic materials like wood, leather etc. They are not generally recommended for structural applications. Some common examples of thermoplastic adhesives are polyvinyl acetate, polyvinyl chloride and acrylics etc. [45].

1.17.3 Elastomeric adhesives

They are based on natural or synthetic polymers. They may be supplied as latex, cements, dispersions, single or two-part systems, solutions in solvents. Curing depends upon form and type of adhesive.

They can be used from 60-204^{o}C. They never melt completely. They have low bond strength but high flexibility. These adhesives are used to join lightweight materials. They are modified with resins to improve bonding for leather, paper, rubber, fabric and plastic films. Examples elastomeric adhesives are natural rubber, butyl rubber, polyurethane, neoprene rubber, nitrile rubber [37].

1.18 Classification based on polymers

1.18.1 Polyurethane

In polyurethane adhesive, the plasticizer is not removed from the bonding surface. Molecules of the bond freely move. It can be adhesive to many substrates. It is not substrate specific. However, 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 [23].

1.18.2 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 [46].

1.18.3 Acrylic copolymers

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

Al 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 [47].

1.19 Polychloroprene adhesive

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. 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. 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 .Crystallization rate can be affected by the choosing of organic solvent [48].

Polychloroprene bonds can also be manufactured by water-dissolved elastomers. The Polychloroprene contact bonds have not replaced the organic solvent-based bonds as it appears in perception. However, water-based rubber takes enough time to get dry. To get drier in short time, a lot of energy will be utilized. Therefore, it will be an expensive process. The initial bond strength is 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 of specific ingredients. However, in this area lot of work has been done. Many developments have been reported until now. In 1931, Du Pont first developed the synthetic polychloroprene and chloroprene rubber replacing the synthetic one. This newly developed synthetic rubber was being given the name of DuPrene [42]. 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. The latest process of converting butadiene to chloroprene is quite fast and economical on industrial bases. 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 [46].

1.20 Motivation

The industrial sector is rising rapidly in Pakistan with every year. Local markets and foreign investment are increasing the development and production of industrial goods. Adhesive products are widely used in manufacturing of many goods and as a single product itself. Packaging, sports, rubber, textile, leather, shoes, furniture, automotive industries have high adhesive requirements for their final assembly. According to power of adhesive strength and quality, adhesive consumption is required. Local industries and small industrial setups, which make substantial income in the economy, are important consumers. Although adhesives are locally manufactured, however high quality and high-strength adhesives are imported from European markets, which contain conditions more expensive and final cost of adhesive is increased. 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 Elephant, Samad Ultra and Camel etc. The demand for adhesives is increasing with increase in local industrial setups and high demand of their products.

Presently, high cost and no standard of adhesion strength of adhesives are available that fulfills market demands. Available products are expensive, imported ones are more expensive. Therefore, a warm need of alternative is mandatory that can satisfy the consumer's need of a high-quality adhesive with reasonable price. 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 products, making them available and affordable for more portion of the population.

The core motivation is to create a high strength and high-quality adhesive with decent price. The formulated adhesive must have high adhesion strength as compared to the commercially available local and imported adhesives. The primarily purpose of developed adhesive is utilization 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, its price also should be reasonable.

1.21 The aim of the study

Aim of this study was to develop a high strength a polychloroprene rubber-based contact adhesive with nanoscale reinforcement. The purpose of research was formulating a high strength adhesive that can resist ageing conditions of extreme environment. Most of the commercially available adhesives have chloroform as the solvent, which makes them unsafe to drug use. Another aim of this study was 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 adhesives available in the market. The set objective was achieved by experimental work done in lab.

CHAPTER 2

Literature Review

2.1 Rubber based polychloroprene adhesives and their constituents

A large-scale variety of rubber-based PCA are available based on cost, range of temperature and end use. Various formulations of rubber based PCA with wide properties have synthesized to join metals, wood, carpet, Formica sheets, plastics and leather. A larger consumer of contact adhesives is shoe industry, which uses 40% of the total product. Several components like magnesium oxide, zinc oxide and mixture of solvents are used to manufacture PCA. The major component of contact adhesive is polychloroprene synthetic rubber and its co polymers. The most common solvents used in rubber based PCA are toluene, ethyl acetate, benzene, xylene, methyl acetate, acetone, amyl acetone, diethyl benzene, methylene, 2,2-dimethylbutane, isooctane, isopentane, isohexane, cylopentane, cyclohexane, naphtha, trichloroethylene, petroleum sprit, methyl ethyl ketone (MEK) and others. Instead of single solvent combination of two or more solvent mixtures can also be used. Mixture of two solvent systems involve like methyl acetate + MEK, ethyl acetate + MEK, acetone + MEK, methyl acetate + toluene and acetone + toluene. Three solvent system also exists which includes methyl acetate + toluene + trichloroethylene, petroleum + toluene + trichloroethylene and methyl acetate + petroleum + toluene solvent [49].

Polychloroprene rubber is the single larger solid component in contact adhesive formulation. There are a large variety of polymers and their co-polymers, which can be used for synthesis of adhesives such as polymers of polychloroprene, homopolymers includes neoprene and copolymers includes isoprene, butadiene or vinyl monomers such as acrylonitrile, acrylates, or methacrylate’s. End use of adhesive application in industries with various rate of crystallization of neoprene rubber are also available which includes neoprene AD , neoprene AC , neoprene blends of polychloroprene and its co-polymers are also use to attain desire properties of adhesive [50].

Accelerates such as polyphenols, hexamethylenetetramines and condensation products of amines with aldehydes, di-phenyl aniline and polyisocyanate can be use be self-curing of adhesives. Hexamethylenetetramine and paraformaldehyde are use as aldehydes. To increase the vulcanization process promoters can be added [51].

Various functional groups are introduced to increase the strength of multilayer resin products of adhesives. Functional groups are in the form of additives to boost the adhesion strength to resins. Many researchers prefer resole phenol resins or resins based on cyclopentadiene to improve the gluing properties of the polychloroprene adhesives [50].The adhesion properties can be improved by introducing minute amount of nanoparticles like multi walled carbon nanotubes, nanoclay and graphene [52].

2.2 Advantages and limitations of adhesive bonding

Shoe, textile, furniture, packaging and metal industries are big consumer of adhesives..Adhesives are considered alternate for mechanical fastening due to their distinguishable advantages over mechanical fastening, welding and brazing process. Beside their promising advantages and use, there are certain limitations too [53].Some of the major advantages and limitations are given below;

2.2.1 Adhesive physical advantages and limitations

Welding is difficult for dissimilar metals which have alternative thermal conductivities. Metals like magnesium, aluminum and titanium have unstable oxides and oxides are distorted due to 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. Polychloroprene rubber based adhesives are viscoelastic with abilities to expand and contract [54]. This property helps in joining the materials having various thermal expansion coefficients. Being viscoelastic the adhesive act as like touch, relatively flexible materials. Adhesives toughness and flexibility shows resistance against crack propagation. Adhesives viscoelasticity and flexibility has ability to with stands against vibration and absorbs shocks [55].

Stress is uniformly distributed from one substrate to other in adhesive joints. In mechanical fastening technique, thickness of the substrates should be reasonable to handle the stress and shocks, thus increasing the overall weight of the product and increase in cost of the final assembly. While in adhesive joint, no need to increase the thickness of the substrates. An adhesive joint is flexible enough to with stands stress and shocks. Therefore, final product is lightweight and low cost [13] .

Polymeric rubber-based adhesives major drawback is their degradation with time due to a number of factors i.e. presence of moisture, high temperature or toxic chemicals. Adhesives mostly can perform at -50^{o} C to 150^{o} C but some can perform even better than these temperature conditions. These temperature limitations restrict the adhesive performance to low temperature and they are not efficient for high temperature operations. The 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 [56].

2.2.2 Structure advantages and limitations

Any solid material can be joined with an adhesive regardless of size and thickness. Sometimes certain materials are too tiny that they cannot be welded well. Adhesives have no limitation according to thickness and size of the material. They can join such materials efficiently and without distortion. Materials such as paper, plastics and elastomers can be joined more economically as compared to other joining techniques [57].

For effective selection and use of 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, they do not work. 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 ageing conditions [58].

2.2.3 Production advantages and limitations

Adhesives are less expensive and faster in joining as compared to other conventional methods. Mechanical fastening demands a lot of labor cost when a large area is joined while with adhesives the whole operation can be performed in one go. In dissimilar metals, galvanic corrosion can happen but in an adhesive joint no fear of galvonic corrosion [59].

A clean surface is necessary for supreme quality 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. The inspection of the finished adhesive joints is also very difficult. Therefore, these production limitations must be considered before selecting adhesive for any substrates [60].

2.3 Adhesives in footwear industry

Adhesive plays very vital role in the joining of footwear’s. It is a key component of manufacturing and transformation of the materials of the shoe. It delivers a shape and structure to the shoe. Number of adhesives used in the footwear industry. However, polychloroprene rubber-based adhesives are particularly used for the shoe industry due to its high strength and high performance. Although the performance of adhesive bond highly depends on substrate, surface preparation and nature of substrate material [61].

Currently adhesive industry has very close relation with footwear industry. It is due to technique involved 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 developing new formulations for better strength and enhanced improvements [23].

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 preferable joining method for shoe parts 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 [62].

Nitrocellulose adhesives are the first adhesives, which were used back in 1496. However, in 1949 adhesive industry reached the new horizon with the introduction of polychloroprene rubber-based adhesive. It is all because of its versatility, durability, and long-lasting effects. Polychloroprene adhesive also provides very good results in leather and textile industry. Although with the introduction of plastic in the shoe industry, the polyurethane based adhesives are also introduced in footwear industry. Both Polychloroprene and PU adhesives are used in footwear industries due to their best and long-lasting results. In footwear industry, polychloroprene adhesives used in the last step due to the requirement of hot melt adhesive for the joining of the shoe sole. Polychloroprene adhesive with the solvent can be applied to any of the substrates depending upon the application technique [63].

2.4 Applying techniques of contact adhesive

One of the most common methods of applying a contact adhesive is brushing. Spraying is the commercial technique used by most local industries as it requires less curing time and forms a smooth uniform layer of contact adhesive. Dry spraying method used for fast curing and quick assembly. This method is so fast that solvents are evaporated as adhesive is sprayed and surfaces of substrates are ready to join after application of contact adhesive.

This method is mostly used in polystyrene foam industry where solvents can harm the surface of polystyrene foam [64].

Hot spraying is other method of fast curing. In that method adhesive passes through a fluid line along with heaters. Due to high-elevated temperature all solvents are evaporated and adhesive with a large volume of air passes through spray gun. Adhesive leaves the spray gun with almost drying condition and is ready to use. Fast curing achieved by hot spraying method [58].

2.4.1 Dispensing methods of adhesives

Dispensing is method of applying an adhesive on the surface of the material. Researchers elaborate various methods of dispensing. Some of them, which are most common in used are:

- Roller transfer
- Pin transfer
- Brushing and troweling

2.4.1.1 Roller transfer

Disc or Wheel coating method is named as roller coating technique. In this method, a storage tank stocks the adhesive. The roller transferred the adhesive to substrate directly or indirectly with the help of another roller. This method is used for large area substrates to be coated like production of conveyer belts and manufacturing of duct tapes [65].

2.4.1.2 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 that 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 vital role in this method. The pins are immersed and wet in adhesive bulk and its successive transfer on substrate surface [56].

2.4.1.3 Brushing and troweling

It is one of the most common techniques used to apply the adhesive coating over the surface of the substrates. Brush, 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 various parameters [1].

2.5 Preparation of surface

Satisfactory bond demands complete wet ability of surfaces of substrate from a good adhesive [66]. Various layers of oxide, dust or paint coating present on surface of substrate that may distress the bonding process. These layers are called “weak boundary layers”. These unwanted layers must be removed before applying the adhesive layers onto substrates. Surface treatment is carried out to clean adherend surface for enhanced adhesion [52].

Since adhesives apply to two surface materials, so proper treatment of surfaces must be implemented on both surfaces. The bond strength and its life mostly dependent on the treatment. According to some investigations, surface treatment is relatively direct to expectations of any adhesive joint life and service. Any layer of containments needs to clean the dirt, grease or oil to develop a satisfactory bond. There are various ways to clean these substrates for better wettability [67].Some surface preparation methods are given below:

1) Passive mechanical treatment
2) Solvent cleaning

2.5.1 Passive mechanical treatment

This method includes abrasive blasting, wire brushing and abrasion with sandpaper, emery cloth or metal wool. Passive mechanical treatment is effective method for the removal of dirt, sand particles and oxide layers from the surface of the substrate. Solid particles from the surface can be detached using blasting and solvent wiping [68].

One of the advantages of blasting treatment is that it supports roughening of the surface. A rough surface has larger specific surface area for adhesion as compared to smooth one [69].

A major drawback of grit blasting is that surfaces are “activated” and it should be coated with adhesive to prevent the oxide layer formation. A Profilometer measures the roughness of the surface. It is a meter with diamond tip that slides over the surface to measure the valleys and peaks of it [69].

2.5.2 Solvent cleaning

Solvent cleaning method is used for the removal of dust pollutants and organic contaminates. There is no modification in physical or chemical properties of surface in this method. Following solvents are used for such purpose:

- Methyl ethyl ketone
- Toluene
- Methyl alkyl alcohol
- Trichloroethylene
- Perchloroethylene

These are the solvents use mostly for cleaning purposes for the surface of the substrates [70].

2.6 Primers for substrate

The adhesion promoters are known as primers, act as bonding layer between substrate and adhesive, and improve the adhesion properties. Polymer chemistry of primers is same as polymer chemistry of adhesives in adhesive technology. A primer improves wettability and provide protection to surface in dry conditions. Primers transforms surface of adherend into polymer surface that is more convenient in adhesive technology than inorganic surfaces [71].

Anti-corrosive primers are used in aircraft industry that have various formulations than normal adhesives. The composition of these primers consists of epoxy resins, resoles, hardening agents and functional component such as strontium chromate [72]. Primers may directly be added in adhesive to improve adhesion properties of those materials that are difficult to join such as nonpolar materials. The adhesion is improved because components in primer etch the adherend and no oxidative pretreatment is required. Adhesive manufacturers do not disclose the chemistry of primers just as they do to adhesives chemistry. It is clear that primer system do affect the surface properties of materials to be joined so, careful consideration should be done while choosing a primer for adhesive applications [73].

2.7 Wetting

Wetting of a material is necessary for a strong bond. Adhesion is not possible without wetting of surface of substrate. Wetting is “Dispersal of a drop of the liquid over the surface[1].

The surface tension force over the drop of liquid is show below.

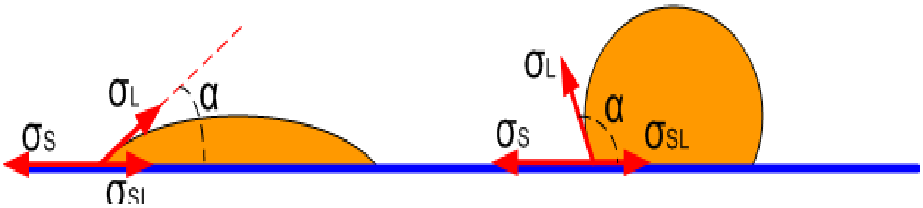

Figure 2.1: Wetting angles for a substrate [75]

$$\alpha_S = \alpha_L \times \cos\alpha + \alpha_{SL}$$

Where:

“α_S” is surface tension of the solid surface of the material, "α_L" is surface tension of the liquid adhesive and "α_{SL}"is interfacial surface tension between the solid surface and liquid adhesive and is wetting angle [13].

Wetting ability is determining by wetting angle. For low value of wetting angle, the wetting ability of the adhesive is superior. Good dispersion of liquid adhesive is possible at lower value of ($\alpha_S < 90^{o}$).The High value of wetting angle gives partial wetting or no wetting at all ($90^{o} < \alpha_S < 180^{o}$) [74].

2.8 Formulation of solvent based adhesive

The solvent based adhesives used in shoe industry are consist of various chemicals according to end use of products. The overall efficiency solely depends on the selection of the components of chemical for the adhesives [49].

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. Various types of elastomers are used in adhesive industry i.e. poly-chloroprene, styrene isoprene, polyurethane, natural rubber etc. The adhesives, which include polychloroprene rubber can easily crystalize. 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. The poly-chloroprene adhesive is bonded to various surfaces due to presence of chlorine atom in every monomer of polymer. Thus, it contains excellent polarity and good physical interactions [71].

2.9 Resins in adhesive formulation

A resin can enhance the tackiness of an adhesive. 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 interaction [75]. The most common resins, which are used in adhesive industries, are as followed:

- Colophony
- Hydrocarbon resin
- Phenolic resins
- Terpene phenolic
- Epoxy resins
- Acrylic resins

Wettability parameter of the adhesive is enhanced by phenolic resin by improving the cohesive interactions between the surfaces of substrate providing the immediate bonding between the surfaces without any of the pressure [76].

2.9.1 Role of 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. These resins increase both the antioxidants resistant and stability of the adhesives. 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 [77].

The ageing particularizations of contact adhesives can be affected using resins. The ageing can be increased and decreased using the resins. The resins must be blended with the antioxidants to get the best mechanical properties of the adhesives. In various regions of the world, shoe industries use various bonds. Like in tropical regions, footwear industries use heat resistant adhesives. The waterborne adhesives have many factors, which make them un-useful are, evaporation of water makes rubber adhesive less effective. 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 [78].

2.10 Nanoscale reinforcement and adhesives

“Nano” is a greek word which means “very small”.The concept of nanoscale reinforcement was introduced by Richard Feynman in 1959 in his talk “there is plenty of room at the bottom”.

Properties of many materials can be changed through nanoscale reinforcement. It has many aspects ranging from magnetic materials, bio medical, structural and coating materials, thermal conductance and corrosion resistance. Researchers have done a lot of work on nanoscale reinforcement and work is still in progress in many fields of science [79].

In medical field nanytechnolgy has progressing results such as photodynamic therapy, drug delivery and tissue scaffolding etc. Research shows that biocompatible nanoparticles are more effective due to their unique properties and high volume to surface ratio [80].

In magnetic materials a lot of work on magnetization, conductance, durability, thermal resistance with impressing results is proceeded [81].

2.11 Potential Advantages of MWCNTs in nano reinforced adhesive

A successful dispersion of nano-fillers (carbon nanotubes, nanoclay, nanofibers, and nanoparticles) into a matrix of a polymer (thermosetting or thermoplastic) is a potential mechanism to develop a nanocomposite. A nanocomposite is a unique combination of improved properties like physical, chemical and mechanical properties. The nano-fillers have exceptionality due to their size and large surface area over traditional fillers [82].

A nanocomposite adhesive is manufactured by a small number of nanoparticles with a large surface area. It exhibits resistance to water absorption and improved ageing properties. A nanocomposite adhesive due to nanofillers reinforcement at resin matrix interface shows the promising results [83]. Some of the properties are discussed below:

1) Mechanical properties
2) Thermal properties and stability
3) Stiffness of adhesive
4) Electrical properties
5) Liquid barrier properties

2.11.1 Mechanical properties

The structural adhesives are applicable to many goods like transportation and aircraft industries such traders require stable and steady materials to resist high temperature environment and resilient to fatigue and loading. The introduction of nano reinforcements to base resin in adhesive matrix increases its adhesion strength. The mechanical properties are improved in terms of peel and shear strength. The main objective for adhesives is creation of a new tough adhesive without loss of inherent properties [84].

A numerous researchers believe that toughness in epoxy resins is due to consumption of fracture energy that is spawned due to collaboration between nanoparticles (MWCNTs) and cracks on the surface of the material [82].

2.11.2 Thermal properties and stability

Thermal stability is an important point of consideration for the adhesive as many adhesives are compromised at elevated temperature, lose their strength and are degraded. The reinforcement of nanofillers in epoxy resins increases the temperature deflection up to crucial value of heat. The addition of nanofillers improves thermal stability and reduces the weight loss during thermal gravimetric analysis. Due to presence of nanofillers, the decomposition temperature of nano adhesive increases with increasing nanoparticles contents [83].

Another property that relates to temperature is coefficient of thermal expansion (CTE). The values coefficient of thermal expansion for nanoparticles are very low as compared to epoxy and adhesive. The high temperature cause residual stresses due to difference of CTE values between substrate and adhesive and micro cracks can propagates causing of cohesion and adhesion failure of adhesive [85]. The values CTE for thermosetting resins changes up to glass transition temperature (T_g). Most of the mechanical properties are degraded as temperature rises above $T_{g,}$ as concern for CNTs; they have negative values for coefficient of thermal expansion. Consequently, it is easier to raise the T_g value to attain the maximum properties from a nanoadhesive. The CETs values for CNTs are calculated which are $-12 \times 10^{-6} K^{-1}$ in case of longitudinal CTE and $-1.5 \times 10^{-6} K^{-1}$ in transverse CTE. Thus, the introduction of CNTs in nanoadhesive give promising results by reducing the coefficient of thermal expansion [82].

The addition of nanoparticles can also enhance thermal conductivity of nanoadhesive composite. The thermal conductivity grows linearly with increasing content of CNTs in polymer matrix [86].

2.11.3 Stiffness of adhesive

The nanoparticles size and functionality are the main factors that change the properties of nanocomposite adhesive. The nanofillers imposed on molecular mobility of polymer chains. As nano particles have greater stiffness than host polymer, therefore when they are incorporated with adhesive. The nanoparticle nested within the spaces that are in between the chains of polymer matrix, causing the reduction of chains flexibility. The nanocomposite has stiffness than its host adhesive due to reduction in molecular mobility of polymer chains and reduction in flexibility of polymer matrix. The stiffness of nanocomposite adhesive can reduce cohesion and adhesion failure of adhesive [85].

2.11.4 Electrical properties

The electrical properties can be improved with the reinforcement of nanofillers. Researchers have developed electrically conductive adhesive known as “conductive nanocomposite”. A percolation behavior can be observed with increasing contents of nanofillers such as CNTs and CNF in the formulation of the adhesive. The enhancement in the conductivity totally depends on the contents being added to the composite [82]. The curve shows better results in case of CNF as compared to CNTs. The dispersion of nanofillers plays a key role in the conductivity of the nana adhesive, both for the efficient dispersion method (ultra-sonication, mechanical stirring, etc.) and efficiency of the dispersion on the nano reinforcement integrity. The percolation behavior is affected High dispersion method can damage the nanoparticles declining their aspect ratio, which affect the performance of the adhesive [83].

2.11.5 Liquid barrier properties

One of the major advantages of the nano reinforcement is enhancement in moisture barrier properties. The measurement of the capability of a material to resist a liquid to penetrate through its layer is known as moisture permeation. The high aspect ratio of the nanofillers provides superior barrier properties according to the equation [82]:

$$\frac{P_c}{p_0} = \frac{1}{1 + \left(\frac{L}{2 \times W}\right) \times V_f}$$

Where;

The “P_c” term stands for the permeability coefficient of the nanoadhesive, “P_0” term stands for the permeability coefficient of the neat polymer, “ $\frac{L}{W}$ ” term stands for the aspect ratio of the nanoparticles and "$1 + (\frac{L}{2 \times W}) \times V_f$" term stands for the tortuosity factor.

Another property that can be improved with nanofillers is water absorption. The rate of water absorption in nanoadhesive can be reduced up to 40% as compared to original polymer .The liquid barrier properties can be enhanced for epoxy resins with the increasing concentration of MWCNTs [83].

2.12 Failure of adhesive

A wide range of adhesives is available in the form of polyimides, polyurethanes; polychloroprene and epoxies. They are in the form of pressure sensitive, contact, thermosetting and hot melt according to their end use. Additionally, they are different in their load carrying ability such as structural, non-structural, or semi-structural.

A failure can happen when substrates are joined with inappropriate adhesive. At broad scope, there is a difference between porous and non-porous substrates to be married with an adhesive. A suitable adhesive is one, which have characteristics of joining regardless of type of substrates whether it may be ceramic, wood, plastic, rubber, metal or leather [87]. Some of the failure modes are discussed below

2.12.1 Adhesion failure

It happens in bonding region between substrate and the adhesive. Adhesive layer is partially or completely removed from the surface of the substrate. Adhesive fracture can occur on both sides and this type of fracture is not required [88].

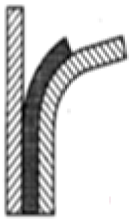

Figure 2.2: Adhesion failue of adhesive [90]

2.12.2 Cohesion failure

Failure of adhesive material itself in adhesive bond. The traces of adhesive can be detected on both of the surfaces of the material [89].

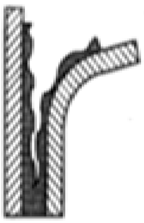

Figure 2.3: Cohesion failue of adhesive [91]

2.13 Reasons for adhesive failure

Various factors influence the adhesive joint. The chemicals can also cause failure of the adhesive and there may be physical factors that can influence an adhesive. Such as:

2.13.1 Selection of adhesive

When choosing an adhesive, it is necessary to take into account (at a minimum) the substrates to be joined, the environment in which it will be used and how long it will work [90].

2.13.2 Environment ageing conditions

Even if the type of adhesive is suitable for the application, an unscheduled or unexpected change in the environment may cause the adhesive layer to fail. Introduction of chemicals, moisture and heat can affect the adhesive layer [91].

2.13.3 Surface preparation

Careful thought should be given to the cleanliness of the two materials. Dust, dirt oil or grease can cause poor adhesion [85].

2.13.4 Crack propagation

The micro cracks are present in voids and spaces of polymer matrix. These cracks can propagate into adhesive layer and cause failure of adhesive. External forces and applied loads can also generate cracks which can cause adhesion and cohesion failure [92].

CHAPTER 3

Materials and Experimental Setup

3.1 Materials

Materials used in the formulation of adhesive.

- Polychloroprene rubber AD-130 grade (Mw. 120000)
- Phenolic Resin (Mw. 700)
- Solvents such as Toluene, Ethyl acetate, Naphtha, *N*, *N*- Dimethylformamide
- Magnesium oxide (MgO) / Zinc Oxide (ZnO)
- Anti-oxidant
- Nanofillers as Multi walled carbon nanotubes (diameter 10-30 nm)

All materials are commercial grade and provided by local industry expect of *N*, *N*-Dimethylformamide and MWCNTs. N, N- Dimethylformamide is supplied by Sigma and is analytical grade with purity of 99.9 %. The MWCNTs are supplied by sun nanotech with a purity > 90%.

3.2 Experimental Work

Experimental work is divided into three steps. First step is the synthesis of PCA. The second step is the preparation of dispersed solution of MWCNTS and third step is the preparation of nanocomposite adhesive.

3.2.1 Preparation of polychloroprene adhesive formulation

To get best performance of adhesive formulation of almost 90 experiments were performed at lab scale. Some of the core experiments are given below:

The formulations are based on permorming a brod range of experiments.To achieve maximum properties of the adhesive optmum amount of materials is selected. Ethyl acetate and toluene based solvent system is used in all experiments. The compatibility of the solvent is based on solubility factor, evaporation rate and final properties of solvents, which is imported in the adhesive system.

Table 3.1 Formulation of experiments

Formulation No	**CR (phr)**	**Resin (phr)**	**MgO (phr)**	**Antioxidant (phr)**	**Ethyl Acetate (phr)**	**Naphtha (phr)**	**Toluene (phr)**
PA-1	100	35	3	6	320	240	190
PA-3	100	40	3	6	420	220	240
PA-4	100	50	3	6	400	280	190
PA-24	100	55	3	6	350	190	240
PA-30	100	65	3	6	420	220	180
PA-32	100	40	3	6	390	250	180
PA-37	100	75	3	6	400	280	180

PA-30 is selected as best formulation to achieve maximum joining strength of polychloroprene adhesive.Its formulation is given below:

Table 3.2 Formulation of PA-30

Sr. No	**Chemicals**	**Parts per rubber**
1.	CR	100
2.	Resin	65
3.	Anti-Oxidant	6
4.	Ethyl Acetate	420
5.	Toluene	180
6.	MgO	3
7.	Naphtha	220
8.	ZnO	3

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.

3.2.2 Preparation of dispersed solution of MWCNTs

- Take a 50 ml of N, N- Dimethylformamide solvent in a beaker
- Add required quantity of MWCNTs in the solvent
- Place the solution in bath sonication for dispersion of nanoparticles up to 1 to 2 hours.
- A uniformly dispersed solution of MWCNTs is obtained after ultra-sonication.

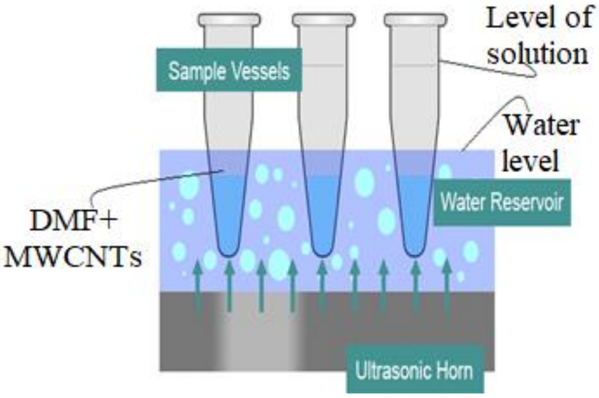

Figure 3.1: Sonication of MWCNTs [93]

3.2.3 Preparation of nanocomposite adhesive

- Prepare polychloroprene adhesive with low bottom mixing of materials.
- Add dispersed solution of MWCNTs in the PCA with continuous mixing of it.
- Mixing of adhesive is done until pale yellow color of the adhesive changes into greenish color and developing a nanocomposite adhesive.

3.3 Description of apparatus

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

- The closed vessel
- Heating element.
- Insulation.
- The impeller is situated at the bottom of the closed vessel.
- Temperature sensor immersed in the vessel.
- The panel consisting of the temperature and motor controller.
- Speed of rotor is set to 135 rpm.

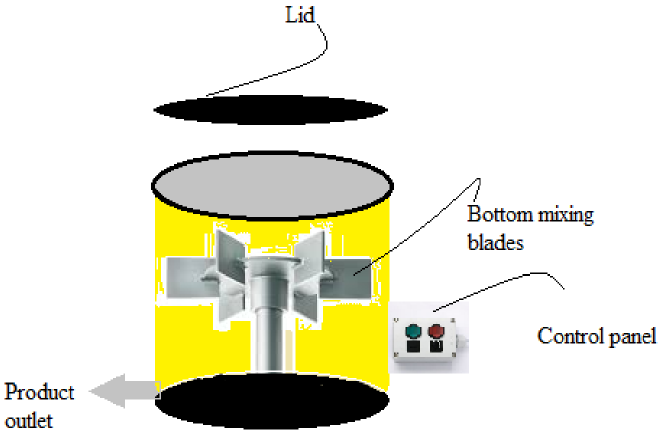

Figure 3.2: Low bottom mixture apparatus

3.4 Procedure for formulation of nanoadhesive

- Bottom impellor machine used to mix all the materials together.
- The quantity of Polychloroprene rubber is 100 phr, dissolved in 180 phr of toluene in round bottom vessel, and leave it for 15 min stirring while applying the constant temperature of 35° C.
- When the chips of the rubber disappear and the uniform slurry mixture is produced, add 65-phr phenolic resin and raise the temperature to 50° C.
- Mix the materials for 40 min.
- Now add the ethyl acetate solvent and stirring it for 60 min at 50° C.
- Adding 4-6 phr of antioxidant while keeping the temperature at 50° C.
- After that add 3 phr MgO and 3 phr ZnO and stir for 30 min while maintaining temperature at 50° C.
- Add required amount of dispersed solution of MWCNTs and mix it for one hour until a uniform slurry mixture formed.
- Add naphtha solvent to lower the viscosity of the prepared solution.

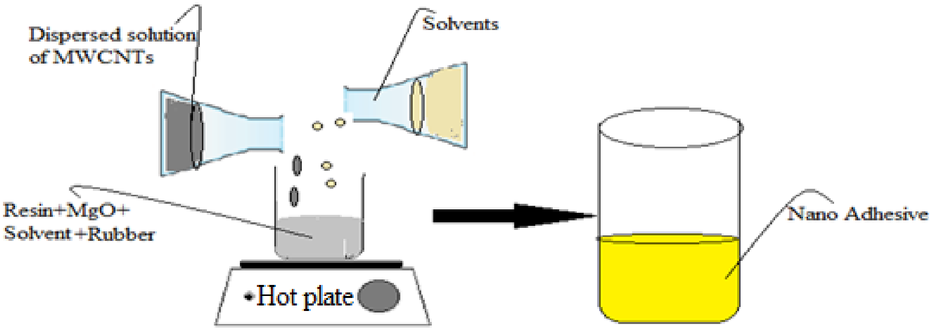

Figure 3.3: Preparation of nanocomposite adhesive

3.5 Preparation of testing sample

Various substrates with different materials were prepared according to ASTM standard D903 (2017) defined in Appendix A for testing the prepared adhesive. Peel test is performed to check the performance of the formulated adhesive. Peel test of 180^o is performed by universal tensile testing machine before and after the addition of MWCNTs in the desired formulation of adhesive.

The substrates used for testing of the adhesive are:

- Canvas-to-Canvas.
- Leather-to-Leather.

Dimensions of the two surfaces of substrates are as follows:

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

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

3.5.1 Applying the adhesive

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

3.5.2 Drying Time

After applying the layers of adhesives over the surfaces of the substrate. The drying time for leather substrate is approximately 20 minutes and for canvas substrate is approximately 25 minutes at room temperature.

3.6 Peel test measurements

A peel test is executed between two materials that are joined together with a layer of an adhesive. Both the materials can be flexible and one may be rigid while the other is flexible. For measuring the value of peel test, a universal tester is used. The tester will describe the strength of the adhesive by drawing a curve. The smoothness of the curve shows the uniformity of the adhesive applied to the surface. The benefit of Shimadzu universal testing machine is that it can also measure the shear strength, applied coating pull-off and tensile strength etc.

3.7 Types of peel tests conducted on adhesive

Many types of peel tests are available to measure the ability and strength of an adhesive. Some of them are T-peel test, peel test at 90^o, peel test at 180^o, floating roller and climbing drum.

3.7.1 T-peel test

This is the test to measure required tensile force to separate two specimens joined with an adhesive. In T-peel, test substrates are prepared with two open ends. Both the end corners are clamped in the grips of the machine. The bonded area is stick horizontally in the form of "T" shape.

One jaw of the machine is moveable while the other one is fixed. When the grip moves upwards, the specimen is peeled off. The force is measured in the form of applied load on the specimens. The ASTM D1876 is the standard method for T-peel test.

3.7.2 Peel test at 90^o

In 90^o Peel test, the applied force is perpendicular to the direction of specimen. A sliding table is used to maintain the 90^o angle during the test. The "L" shape fixture is formed in this type of peel test.

The slider moves away in such a way that two bonded substrates are peeled off from each other. The load unit measures the applied force to the specimen. The standard test method is ASTM D 2862.

3.7.3 Peel test at 180^o

This test is used to measure the maximum strength of the adhesive during the separation of a fixture. The applied force is at 180^o angle, in the parallel line as the direction of peeling of the substrate. A "U" shape is developed in 180^o peel test. This is the most favorable test performed by researchers due to its comfort for flexible fixture. The ASTM D 3330 is followed for this test method.

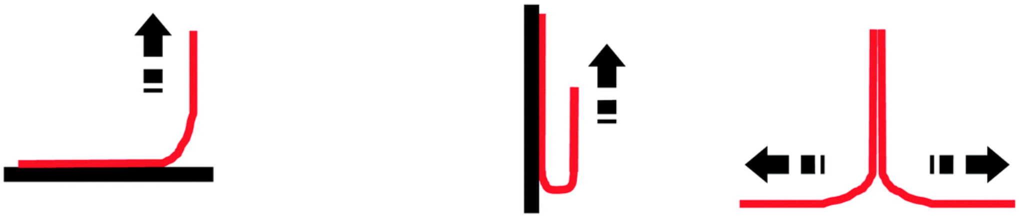

Figure 3.4: Adhesive peel strength at 90^{o}, 180^{o} and” T” peel tests [64]

3.8 Determination of the percentage solids contents

This test is carried out to determine the percentage solids in the adhesive. Percentage 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 flow ability. Higher the number of solids will increase the peel strength but the range for PCA 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 affects the applicability of the adhesive when applied to the substrates. The test is carried out according ASTM D 1582-98(2011) standards explained in appendices.

CHAPTER 4

Results and Discussion

4.1 Effect of raw materials on performance of formulated adhesive

The composition of raw material was most important for high bond strength of polychloroprene adhesive. There were some major components; on changing their small amount, they caused a big change in bond strength of adhesive. To get best results from polychloroprene rubber-based adhesive, the appropriate composition was needed. Different materials had various effects on overall performance of the adhesive bond strength. Some results are discussed below.

4.2 Effect of phenolic resin contents

The amount of phenolic resin in the formulated PCA had an increasing effect in peel strength for canvas-to-canvas and leather-to-leather substrates up to 60-65 phr. Beyond that limit, the overall performance of the adhesive decreased and the peel strength was very poor. The optimum amount of resin contents for adhesive formulation was 65 phr.

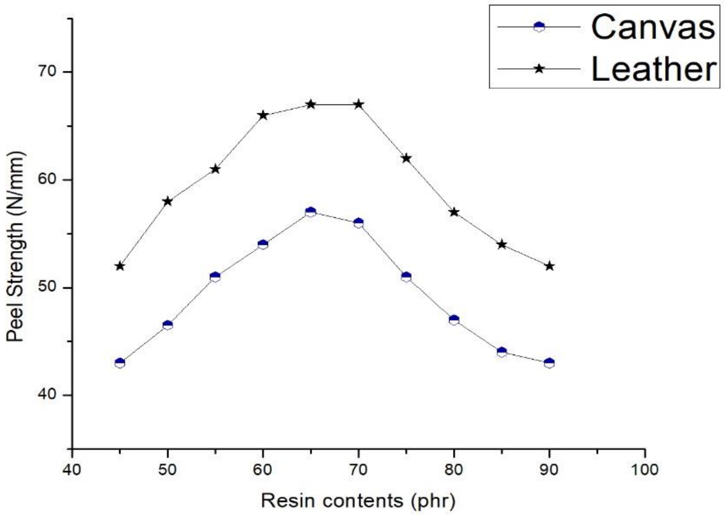

Figure 4.1: Effect of resin contents on peel strength

After the optimized value of resin contents, the adhesion strength starts to decrease. The decrease in the performance of the formulated adhesive was due to decrease in flexibility and poor compatibility with the system. So optimum value for the phenolic resin for maximum bond strength of PCA was 60-65 phr. Higher contents of phenolic resin lead to decrease in peel strength due to reduction in polymer chain and flexibility of the system.

4.3 Crosslinking agent

The optimize value for crosslinking agent was 3-4 phr. Within that limit, the strength of the PCA is good. After that limit, adhesive performance was compromised because of increasing amount of crosslinking agent reduce the flexibility of the system and the layers of the adhesive lose their adhesion with the surface of the substrate. Similarly, adhesive performance was also lower in terms of shear strength as the amount of crosslinking agent increased in the formulation of the adhesive.

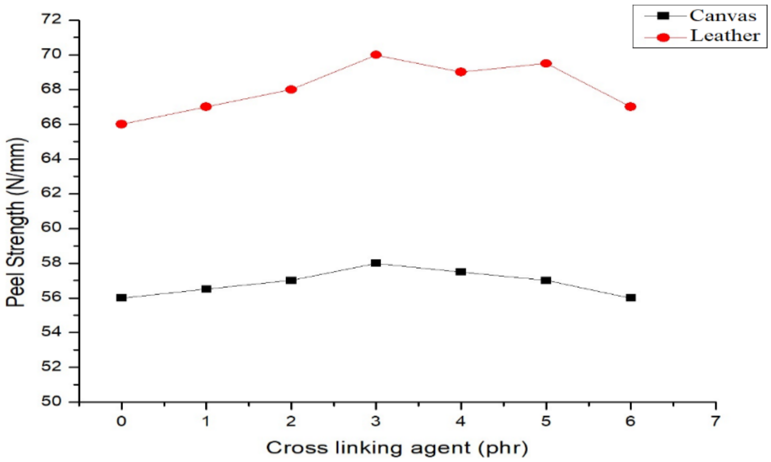

Figure 4.2: Selection of optimized value of cross-linking agent

MgO was used as cross-linking agent for PCA. Fig 4.2 describes that 3-4 phr value of cross-linking agent was the optimize value for the good performance of the PCA. A small quantity was enough to resist the effects of HCl. As HCl produced when the adhesive face heat and hot environment. To minimize the effects of the HCl, MgO was used as the acid scavenger.

4.4 Determination of solids contents in adhesive

The amount of non-volatile components present in the adhesive were calculated by this method. These non-volatile components are responsible for the bond strength in the substrate layers. The standard procedure of ASTM D1582 was performed for the calculation of non-volatile components of the adhesive. First, weight the empty porcelain cup. Then, add 3 to 5 grams of the adhesive. Again, weight the porcelain cup. After that put the cup in the oven for 2 hours at 100^{o} C. After two hours, weight the porcelain cup again. The residue remaining in the cup were solids contents present in the PCA. The formula for percentage of solids content is as follows:

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

Where:

m_0=Weight of the dry empty porcelain cup.

m_1=Weight of porcelain cup containing adhesive.

m_2= Weight of residue in the porcelain cup.

% solids contents = [(40.43-38.92)/ (41.88-38.92)] x 100

% solids contents =51%

The solids contents were in the range of 50 to 60% set by ASTM D1582.This shows more useable solids contents present in the adhesive.

Table 4.1: Solids contents for various adhesives

Adhesive product	**Solids contents (%)**
Dolphin	40-42
Elephant	48-51
Samad ultra	50-54
Camel	40-45
PA-30(SCME)	50-52
PA-N11(SCME)	50-52

4.5 Viscosity measurement

The viscosity affects the flow ability of the adhesive when adhesive is applied to the substrates. It is necessary that a good quality PCA exhibit a reasonable viscosity. Fig 4.3 describes that PA-30 and PA-N11 adhesives viscosities are 2650 cP and 2820 cP respectively.

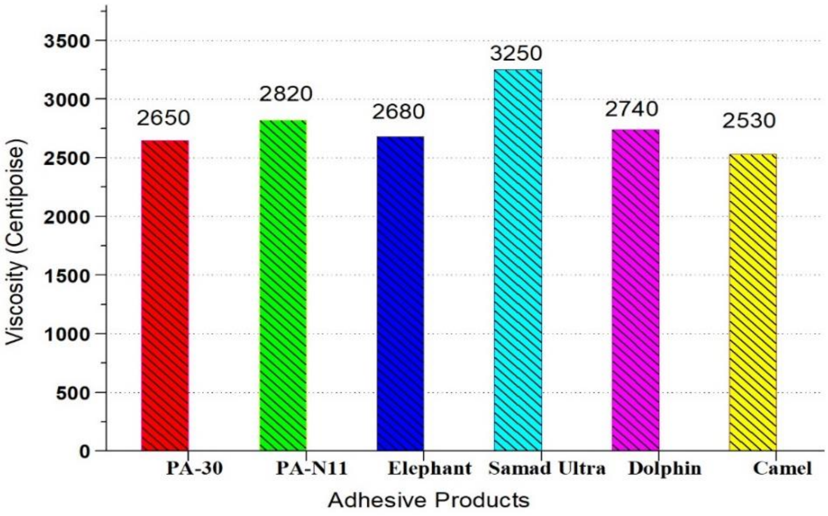

Figure 4.3: Viscosity measurement of various adhesives

4.6 Performance of nanoadhesive in ageing conditions

The PA-30 adhesive formulation showed satisfactory performance in normal environment conditions. However, in ageing environment, its performance was compromised. The PA-30 adhesive bond was not successful due to humidity, temperature, chemicals, seawater and mechanical loading facing during its service life. The MWCNTs were great consideration to overcome these ageing conditions by increasing adhesive stiffness, thermal stability and fracture durability [85]. PA-N11 nanoadhesive was formulated to overcome these conditions. Due to presence of MWCNTs, the adhesive performance was much better in severe environment. The bond strength, thermal stability and liquid barrier properties were improved due to incorporation with MWCNTs [82].

4.7 Effect of MWCNTs on adhesive strength

The increase in peel strength of PA-30 adhesive formulation due to addition of the MWCNTs. The enhancement in peel strength of PA-N11 adhesive was due to improvement in mechanical properties of the adhesive. The enhancement in strength was due to compatibility of the MWCNTs with the resin and the adhesive system. A very small percentage of the MWCNTs showed enormous increase in peel strength of the formulated adhesive. In canvas-to-Canvas substrate, the increase in peel strength was up to 0.6 % incorporation of MWCNTs while in Leather-to-Leather substrate, the increase in peel strength is up to 0.8 % incorporation of MWCNTs in adhesive. Fig 4.4 elaborates the percentage of MWCNTs in adhesive formulation.

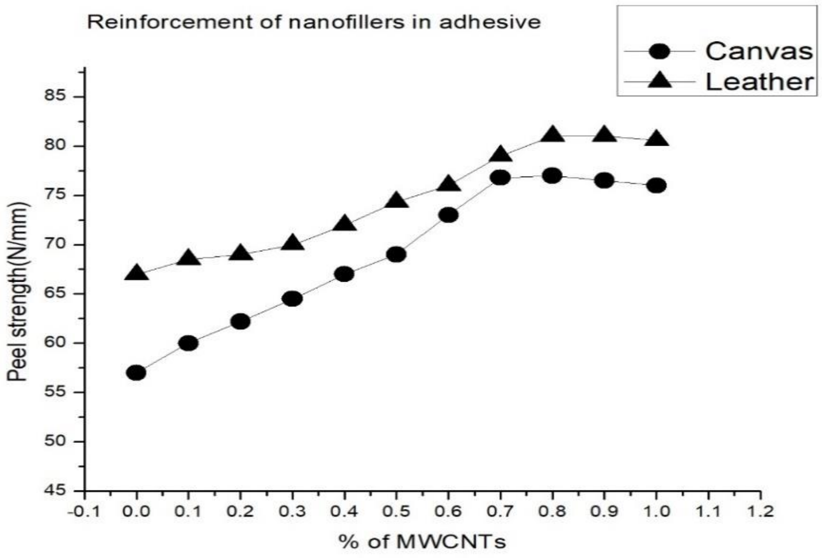

Figure 4.4: Effect of MWCNTs on peel strength of adhesive

After 1 % incorporation of MWCNTs the strength started to decrease, the decrease in strength was due to decrease in cohesive forces between adhesive and substrate [82]. Moreover, the high percentage of MWCNTs in the adhesive bond causes poor wetting of the surface of the substrate and as a result poor performance of the adhesive. The higher contents of MWCNTs cause decrease in peel strength due to agglomeration formation [85].

4.8 Fourier-transform infrared spectroscopy (FTIR)

The C-H bond stretching is normally placed between 3100 and 2800 cm^{-1}in neat adhesive. While in nano adhesive C-H bond stretching is at 2930 cm^{-1} which is more prominent that shows successful reinforcement of MWCNTs in adhesive formulation. The C-C group stretching at 1250 cm^{-1} is more dominant in nano adhesive due to presence of MWCNTs in it. The hydroxyl group (-OH) is present in neat adhesive at 3600 cm^{-1}, while in nano reinforced adhesive no peak is available for –OH group stretching that indicates water repelling property of MWCNTs in adhesive formulation. Due to this nano reinforced adhesive shows better result in water and ageing environment.

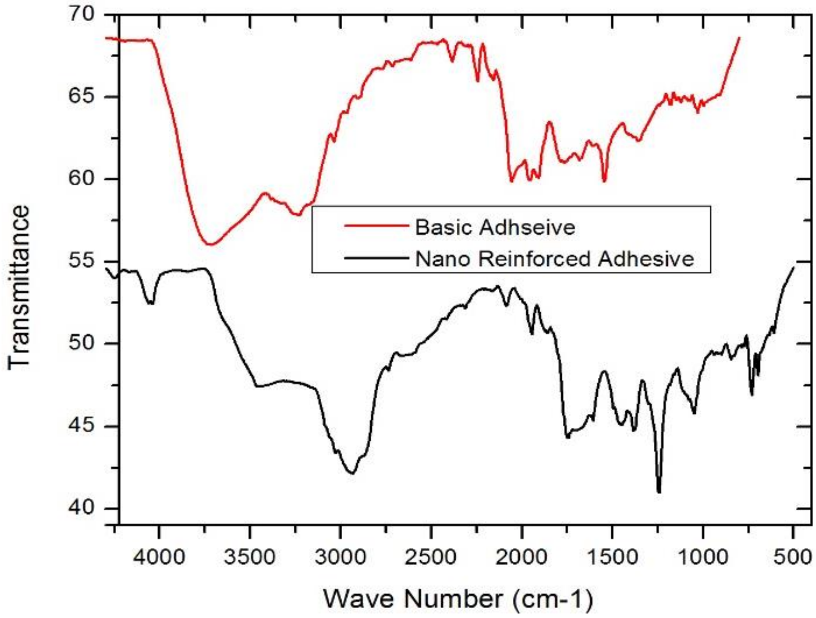

Figure 4.5: FTIR spectra of neat and nano reinforced adhesive

4.9 Thermogravimetric analysis (TGA)

The TGA test is performed to examine the degradation of adhesive formulation. The temperature range for adhesive formulation is 25-220°c.The % of mass loss with increasing temperature is shown in table. As temperature increases, the loss of mass loss also increases. The % mass loss in nano reinforced adhesive is very low due to presence of MWCNTs in adhesive formulation.

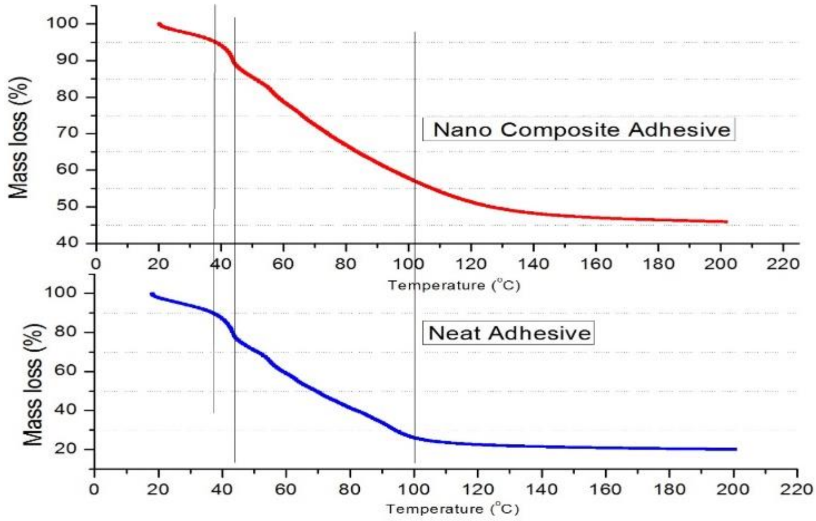

Figure 4.6: TGA for neat and nano reinforced adhesive

Figure 4.6 shows the Thermogravimetric analysis for neat and nano reinforced adhesive formulations in temperature range of 25-220° C.

Table 4.2: % of mass loss in neat and nano reinforced adhesive

Temperature (°C)	**% mass loss in neat adhesive**	**% mass loss in nano reinforced adhesive**
25-45	24 %	11 %
45-100	74 %	43 %
100-200	80 %	54 %

The volatile and organic solvents present in adhesive formulation start to evaporate in temperature range of 25-45° C. After that temperature rises and phenolic groups present in phenolic resin start to degrade in temperature range of 45-100° C. At high temperature of 200° C phenolic groups are degraded and % of mass loss is constant. The % mass loss in neat adhesive is 80% while in nano reinforced adhesive it is 54 % due to presence of MWCNTs in adhesive formulation

4.10 Ageing study of polychloroprene adhesive

The durability of an adhesive joint is affected when it faces environment-exposing conditions. The adhesive is useful when it resist to exposing condition. For a good adhesive, it should not only with stand the mechanical forces, which are acting on it, but also it should with stand the environmental severe conditions. A good bond can resist these environment conditions during its service life

Water is major source of the issue 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-substrate interface. 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 or by changing the system stability. An adhesive is considered good that not only resist mechanical forces it should with stands environment severe conditions. An adhesive bond faces physical, chemical and mechanical factors during his life that produces ageing. The main objective of ageing tests is to understand the behavior of an adhesive and to suggest improvements for long serviceable life of an adhesive bond.

Three main ageing conditions influence an adhesive bond and adhesive itself:

- Physical effects include temperature, heat, light etc.
- Chemical factors involve in water, environment oxygen, saline water, cleaning solvents.
- Mechanical effects include stress, load etc.

For a high-quality adhesive, it should not only resist mechanical forces but also it should resist environmental conditions. A quality adhesive is one, which gives a long lasting and durable joint in working conditions. Every polymeric material has inherent property of decomposition to some degree when it faces a high temperature. High temperature exposure causes polymer's chain scission to decline in weight of bulk polymer and results in the form of poor, shatter and splinted joint.

Environment oxygen is the key to oxidation of adhesives. Oxidation of adhesive not only decline in shelf life of it but also decrease in peel strength and results in the form of weak bond of layers of substrates. The adhesives oxidation can be minimized by using anti-oxidants. To face elevated temperatures, crosslinking agents and resins play an important role. Their ratios in adhesive formulation is vital role to resist oxidation and elevated temperatures.

Water is a disturbing concern to stability of adhesive joint in environment. Water can enter in adhesive joint by:

a) Capillary action
b) Diffusion through substrate and adhesive
c) Transport through interface

Whatever the source of entry of water, it is the fact that water changes the properties of the adhesive. It affects the adhesive/adherend interface by displacing the adhesive film.High temperature stability of adhesive bond is an other quality of a good adhesive.Exposure to heat and high temperaure environment, causes the degradation of polymer chian and as a result poor performance of the adhesive.

4.11 Ageing under ambient environment conditions for 4 months

Ageing has been studied for various surfaces of canvas-to-canvas and leather-to-leather substrates and results are discussed below:

4.11.1 Canvas-to-canvas substrate

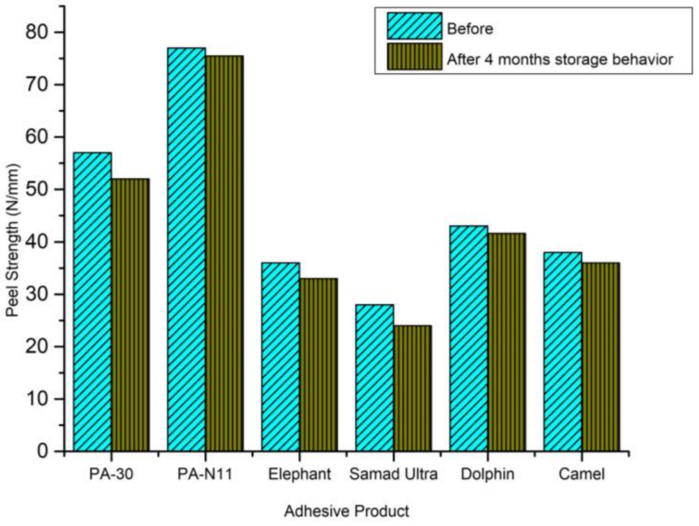

Figure 4.7: Ageing under ambient environment canvas substrate

4.11.2 Leather-to-Leather substrate

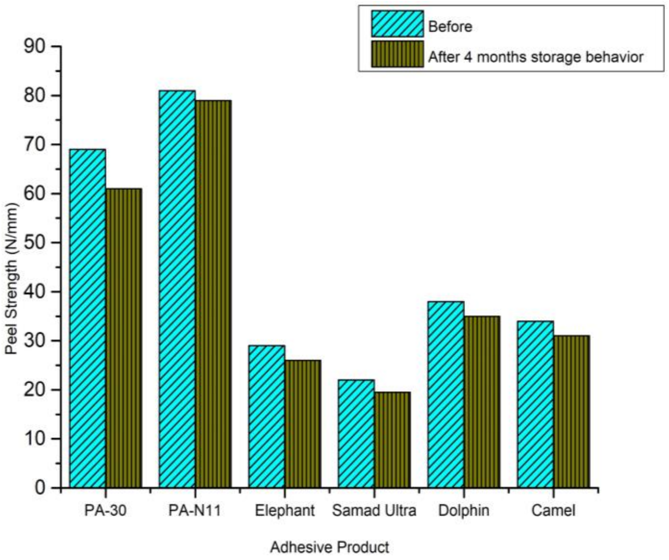

Figure 4.8: Ageing under ambient environment leather substrate

Table 4.3: Characteristics of various adhesives under ambient condition

Ageing condition	**Type of adhesive**	**Canvas-to-Canvas**	**Leather-to-Leather**
Ambient conditions for 4 months	------	**% Fall in peel strength**	**% Fall in peel strength**
	PA-30	8.77	11.59
	PA-N11	1.95	2.47
	Elephant	8.33	10.34
	Samad ultra	14.29	11.36
	Dolphin	3.26	7.89
	Camel	5.26	8.82

Table 4.3 illustrates that PA-30 and commercial adhesives loses their adhesion strength due to harsh environment conditions. The PA-N11 nanoadhesive was synthesized to overcome these loses. The PA-N11 performed much better due to presence of nanofillers. The mechanical properties were enhanced due to MWCNTs in adhesive formulation. As a result, PA-N11 can with stand ambient ageing conditions better than all commercial adhesives.

4.12 Ageing results at 100° C

4.12.1 Canvas-to-canvas substrate

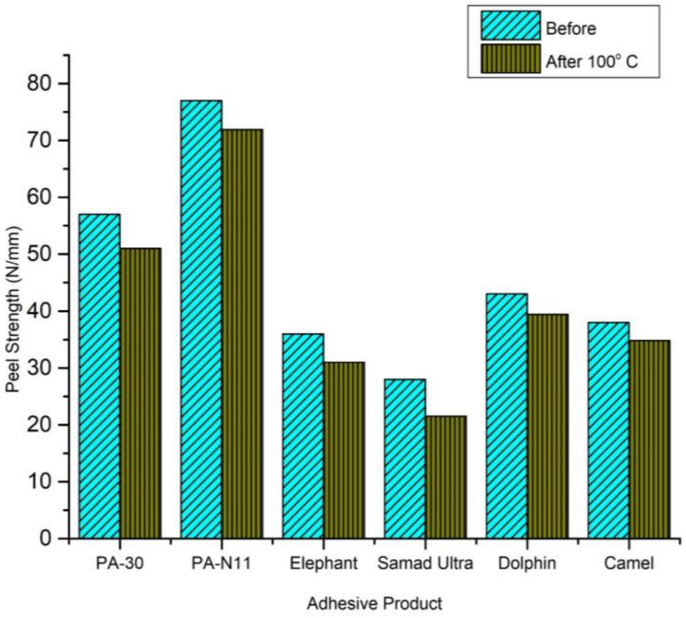

Figure 4.9: Ageing at 100 ° C canvas substrate

4.12.2 Leather-to-Leather substrate

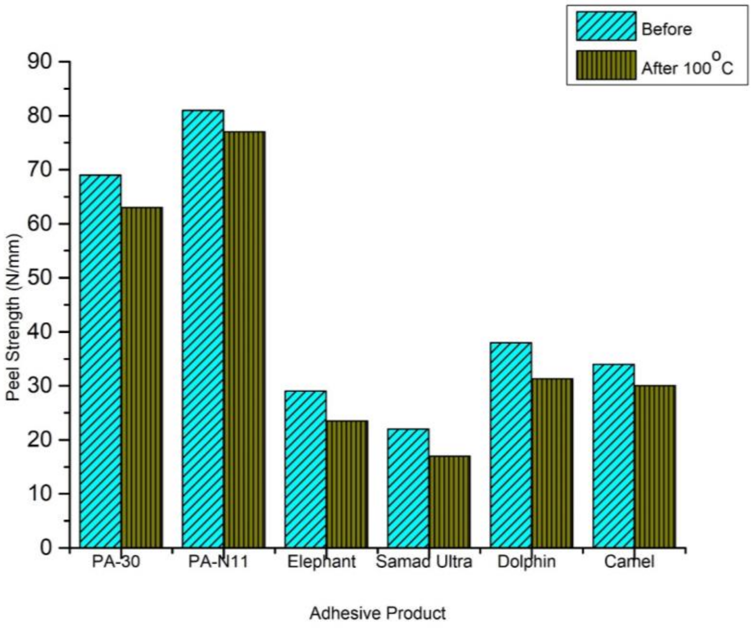

Figure 4.10: Ageing at 100 ° C leather substrate

Table 4.4:Characteristics of various adhesives under ageing at 100° C

Ageing condition	**Type of adhesive**	**Canvas-to-Canvas**	**Leather-to-Leather**
Ageing at 100° C	-----	**% Fall in peel strength**	**% Fall in peel strength**
	PA-30	5.26	8.7
	PA-N11	6.62	4.94
	Elephant	13.88	17.24
	Samad ultra	23.21	22.73
	Dolphin	8.37	13.89
	Camel	8.42	11.76

Table 4.4 describes the behavior of various adhesives at different substrates when they were exposed 100° C temperature. A network of crosslinking of phenolic resin is present in adhesive which is affected by high temperature.PA-N11 thermal stability is enhanced due to presence of nanoparticles to resist high temperature environment [85]. The flexibility of adhesive system is important to operate at high temperature environment.PA-N11 has better flexibility at high temperature environment. PA-N11 has very small amount of CNTs that provide a better crosslinking network to surfaces of substrate [82]. Mismatch of properties leads to failure of adhesive bond strength even at low loads and temperature. PA-N11 shows excellent thermal stability in ageing conditions due to existence of MWCNTs crosslinking network.

4.13 Ageing results in hot water

4.13.1 Canvas-to-canvas substrate

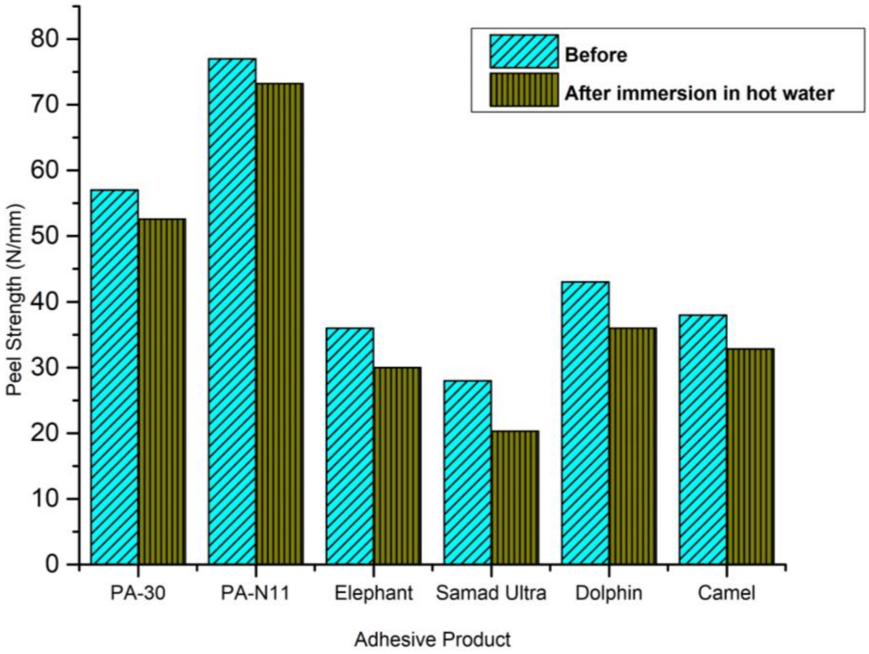

Figure 4.11: Ageing in hot water canvas substrate

4.13.2 Leather-to-Leather substrate

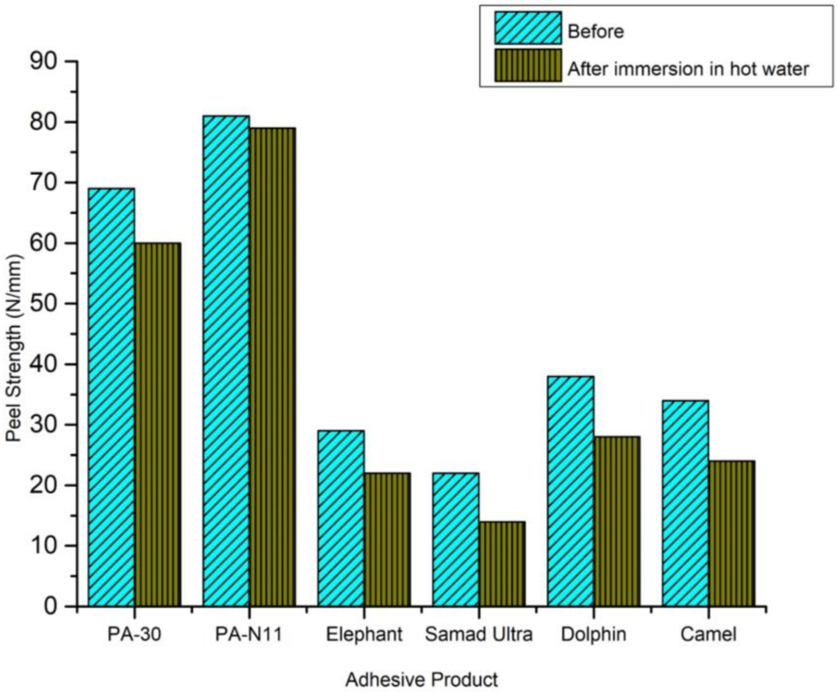

Figure 4.12: Ageing in hot water leather substrate

Table 4.5:Characteristics of various adhesives under ageing in hot water

Ageing condition	**Type of adhesive**	**Canvas-to-Canvas**	**Leather-to-Leather**
Ageing in hot water	-----	**% Fall in peel strength**	**% Fall in peel strength**
	PA-30	10.53	13.04
	PA-N11	4.94	2.47
	Elephant	16.67	24.14
	Samad ultra	27.5	36.36
	Dolphin	16.28	22.22
	Camel	13.68	29.41

Table 4.5 demonstrates that water is a major concern for the performance of the adhesive bond. The PA-30 and commercial adhesives performance is compromised due to permeation of water in adhesive-adherend interface. However, PA-N11 shows great resistance against water and severe environment. The resistance to liquid is due to enhancement in liquid barrier properties. Adhesive stiffness and fracture toughness is increased to resist hot liquid environment [85]. These properties are increased due to presence of MWCNTs in adhesive formulation [82].

4.14 Ageing results in salt water

4.14.1 Canvas-to-canvas substrate

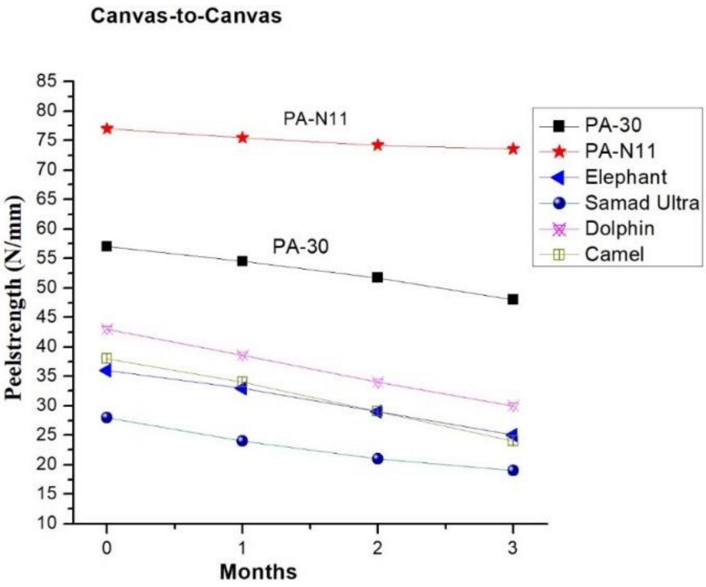

Figure 4.13: Ageing in salt water for canvas substrate

4.14.2 Leather-to-Leather substrate

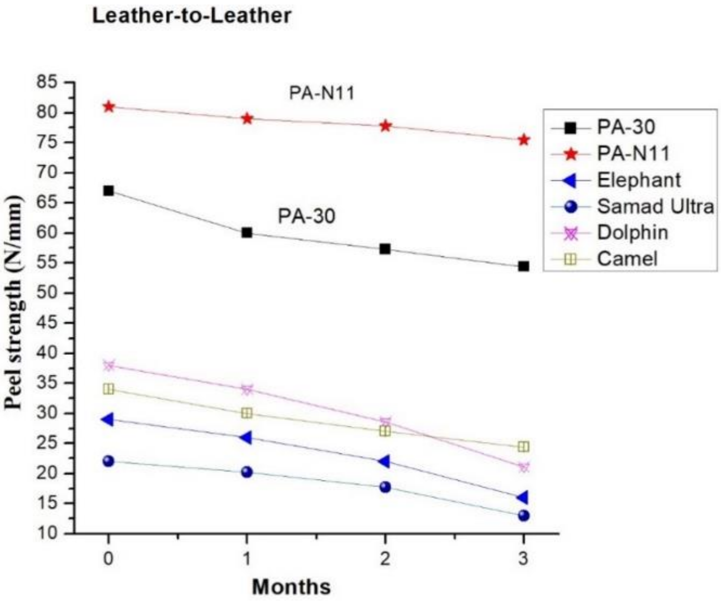

Figure 4.14: Ageing in salt water for leather substrate

Table 4.6 Characteristics of adhesives under ageing in salt water

Ageing Condition	**Type of Adhesive**	**Canvas-to-Canvas**			**Leather-to-Leather**		
Ageing results in salt water	-----	**% Fall in peel strength**			**% Fall in peel strength**		
	PA-30	4.39	9.30	15.79	10.14	14.35	18.12
	PA-N11	3.9	6.49	9.74	2.47	3.95	6.79
	Elephant	8.33	19.44	30.55	10.34	24.14	44.83
	Samad ultra	14.29	25	36.84	8.38	19.37	36.11
	Dolphin	10.23	20.93	30.23	10.34	24.13	44.82
	Camel	10.53	23.68	38.84	11.76	20.59	38.23

Table 4.6 demonstrates that presence of salt has drastic results on the performance of adhesive. It is because of corrosive nature of salt with water. The salt water diffuses through layers of substrates and attacks the bond between layers of substrates. The formulated PA-N11 shows resistance against salty solution and its performance salt water is comparatively better against all commercial adhesives. The ability against corrosive nature of water is due to crosslinking network of MWCNTs present in the adhesive. The crosslinking network withstands corrosive nature of salt present in the water because of MWCNTs resistance against it [83]. All other adhesive do not have ability against salt water and adhesive breaks out due to diffusivity of salt solution but PA-N11 shows impressing results in salt water due to presence of MWCNTs in formulation [85].

4.15 Percentage of improvement in peel strength

4.15.1 Canvas-to-canvas and Leather-to-leather substrates

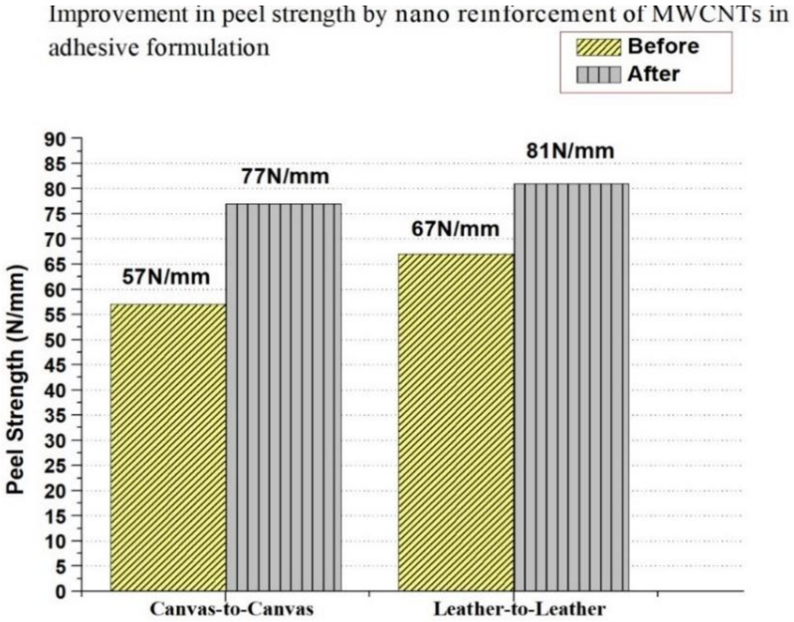

Figure 4.15: Improvement in peel strength by adding MWCNTs

Fig 4.15 describes the enhancement in peel strength of the polychloroprene adhesive. PA-N11 nanoadhesive gives better results for canvas-to-canvas and leather-to-leather substrates. In canvas-to-canvas substrate, peel strength was improved up to 35 % while in leather –to-leather substrate it was 21 %. The nano reinforcement of MWCNTs was up to 1% in adhesive formulation [82].

Conclusions

- The formulations PA-30 (unreinforced) exhibited peel strengths up to 57 N/mm and 67 N/mm 180^o on canvas and leather substrates, respectively.
- The formulation PA-N11 (reinforced by 1 % MWCNTs), displayed enhancement in peel strength up to 77 N/mm on canvas and 81 N/mm on leather substrates respectively. The enhancement in peel strength was 35 % on canvas and 21 % on leather substrates.
- PA-N11 showed <2 % decrease in peel strength after 4 months shelving at ambient environment; this decrease was the lowest compared with the investigated commercial adhesives.
- PA-N11 showed <7 % decrease in peel strength when exposed at 100^{o}C for one hour in air; it was also the lowest compared with the commercial adhesives.
- PA-N11 showed <5 % decrease in peel strength when exposed to hot water (50-60^{o}C); it was also the lowest compared with the commercial adhesives.
- PA-N11 showed <10 % decrease in peel strength after exposure in 3.5% salt water at room temperature; it was also the lowest compared with the commercial adhesives.

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