Chapter 1

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Adhesion

Adhesion is the state in which two surfaces are held together by interfacial forces of attraction, owing to the interactions of molecules, atoms and ions on the two surfaces. Adhesion is a branch of Zygology, the science of joining things together; others include welding, riveting and all forms of mechanical joining. The term adhesion is used to describe the common phenomenon or state where two bodies are stuck together. The term adhesion is used both for the fundamental atomic and molecular forces responsible for holding two phases together and for quantities obtained from destructive tests. The science of adhesion, is a many-faceted subject requiring an understanding of interatomic forces, chemical composition and physical properties of materials, and the forces to which a final structure will be subjected. The forces range in magnitude from the strong chemical bonds formed when two atoms share electrons or when electric charges attract each other to comparatively weak attractive forces, known as Van der Waal's interactions, which are formed whenever two substances are placed in intimate contact.

The science of adhesion can be studied in two ways: From the chemistry and physics of surfaces and interfaces and from the fracture mechanics of adhesive joints. Adhesion occurs by physical or chemical bonding. Physical bonding is due to mechanical interlocking and chemical bonding is by covalent or ionic bonds between adhesive and the substrates.

Mechanisms of adhesion are follows:

1) Mechanical interlocking: It occurs when the adhesive flows into pores or adhesive solidify around the projections. Adhesive acts as a mechanical anchor because it flows into the minute openings and crevices on the adherend surfaces. The adhesive diffuses into to the substrates and bonds are formed not just on the surfaces but deeper inside them.
Mechanical interlocking is applicable to porous substrates like wood, paper, textiles etc. There may be hook and eye joints where adhesive molecules seep into the interstices of the two surfaces. This gives fixed joints that cannot be fractured without either physically breaking the adhesive, or the surfaces of one of adhering components 2.

2) Inter diffusion technique: In this adhesive dissolves and diffuses into the substrate material. The extent of diffusion depends upon the affinity of the different types of molecules for one another10. This inter diffused molecules form a layer which may be thin (0.5-10 nm) for high molecular weight adhesives and thick for low molecular weight adhesives. This is different from mechanical interlocking, involving penetration of adhesive at the molecular level whereas in mechanical interlocking adhesive enter into pores which are much larger than molecules.

3) Adsorption: In which adhesive molecules are attracted to a specific site on a solid surface. The attraction may be by Van der Waal's forces or specific donor - acceptor interactions. Chemisorption may occur if the adhesive and substrate molecule have chemical character.

4) Electrostatic attraction: Electrostatic forces develop at the interface between materials and electrostatic attraction takes place11. These forces are attributed to the transfer of electrons across the interface, thus creating positive and negative charges that attract one another12.

Surface and interfacial properties:

The main factor affecting on adhesion are

(a) Surface Topography: - The surface of adherends will be rough even after polishing,13 so when two solids are made to contact, intimate contact will not occur. There will be adsorbed or entrapped gases which may cause the separation of molecules from true molecular contact. For molecules to get attracted less than 0.3 nm distance is required14.

(b) Surface Tension and Energy: - Molecules at surface of a solid or liquid are different from those in the interior. Molecules at the surface are not equally attracted in
all directions so they are attracted inwards by the molecules below the surface. This attraction gives rise to surface tension of liquids.

(c) **Wetting and Setting**: - The adhesive should give intimate contact with the surface and spread freely upon them. So the adhesive must be applied in liquid state and with sufficient pressure in order to flow into the small crevices of the solid surface. It must displace or dissolve the adsorbed impurities such as water or oxygen. The adhesive must be capable of setting to a tough solid. There should be large changes in volume of the adhesive during solidification. The thermal expansion coefficients of the adhesive and adherends must be similar. Setting occurs by cooling, by solvent removal or by chemical reaction. Solvent adhesives have greater shrinkage during solidification. The degree to which liquid wets a solid is measured by the contact angle. When contact angle is zero then liquid spread the surface freely, and it is said to be completely wet. Surface tension is related to contact angle by the equation

\[
V_w = V_d + V_n \cos \theta
\]

\(V_w\) - Surface tension of solid vapour
\(V_d\) - Surface tension of solid liquid
\(V_n\) - Surface tension of liquid vapour.

\(\theta\) - contact angle

\[S_d = \text{spreading coefficient} = \frac{V_w - V_d}{V_n}\]

For measuring surface tension contact angle measurement is widely used. When \(\cos \theta\) against surface tension is plotted and curve extended to \(\cos \theta\) axis then we will get critical surface tension \(V_c\). Any liquid with a surface tension less than \(V_c\) will completely wet the solid surface. Polar solvent gives higher \(V_c\).

**Thermodynamic work of Adhesion:**

If liquid and solid has no interaction then the interfacial tension \(V_d\) will be the sum of surface tensions of liquid \(V_l\) and solid \(V_s\). But there will be interactions, so then \(V_{sl}\) less than \(V_l + V_s\).
The extent of the decrease is a direct measure of the strength of the interfacial attraction, which is the thermodynamic work of adhesion, \( W_a \)

\[
W_a = V_L + V_S - V_{SL}
\]

This expression first given by Dupre states that reversible work \( W_a \) of separating a liquid and a solid in vacuum must be equal to the free energy change of the system \(^{19,20}\).

\[
W_c = \text{Work of cohesion}
\]

\[
W_c = 2V_{LV}
\]

\[
S = W_a - W_c
\]

Higher the value of \( S \) the greater is the thermodynamic work of adhesion compared to the cohesive energy of the adhesive \(^{21,22}\). Even though after solidification of the adhesive these thermodynamic quantities are modified, but the overall features will remain similar.

Weak part of an adhesive bond tends to be interface, a high value of \( S \) will favor cohesive failure within the adhesive rather than interfacial failure and in turn will tend to lead to more reliable junction.

\[
\Phi = \frac{W_a}{(W_{cl} \times W_{cs})^2}
\]

\( W_{cl} \), \( W_{cs} \) - work of cohesion of liquid and solid respectively.

For simple interaction \( \Phi = 1 \). For systems in which there are different types of intermolecular force in the two substances, \( \Phi \) will be less than unity.

\[
V_a = V_S + V_L - 2\Phi(V_S V_L)^{1/2}
\]

\( 2\Phi(V_S V_L)^{1/2} \) is the surface tension owing to molecular attraction between the liquid and solid. The effective adhesion depends critically on the liquid adhesive displacing the third phase and spreading into all the space between the two solid surfaces to be attached to one another. If there is no affinity between the adherends, then there is certainly no mechanical strength for the adhesive bond \(^{23}\). In a good solvent the external layers are oriented and create a certain energetically enhanced surface layer \(^{24-25}\), which will increase wetting and bond strength. The best adhesion characteristics are achieved in bonds obtained from a good solvent, which is due to the energy state of the adhesive surface when formed on appropriate substrates. \(^{26}\)
**Interfacial Chemical Bonding:**

Adhesive joints with chemical bonds between the adherends gives rise to better bonding. The adhesive joints will withstand severe conditions of high temperature and high humidity if coupling agents or adhesion promoters are employed. They have dual chemical functionality, capable of inter linking the two adherends by reacting with the surfaces molecules of both substrates. Specific coupling agents have been developed for bonding specific adherends. The work of adhesion was measured over a wide range of temperatures and rates of separation. The work of detachment was greater for chemically treated than for untreated surfaces. The chemical treatment gives unsaturated groups in the surface, which forms primary chemical bonds during the crosslinking reaction. There is direct ratio between work of detachment and density of chemical bonding at the interface under high temperature and low rates of peeling. The joint strength of a sheet with more crosslinking agents will be lower than those prepared with smaller amount. When the length of molecular strands between crosslinks are long, they contain a large number of bonds that must be highly stressed in order to break or detach one of them. When material is highly crosslinked and molecular strands are short, then it is less extensible and weaker.

Coupling agents are widely used to enhance chemical bonding between different materials. Silane is a good example for coupling agent. The detachment work was found to increase steadily with the amount of interfacial chemical bonding. The adhesion strength is also influenced by the polymeric nature of the adhesive. In high molecular weight elastomeric adhesives, many other bonds must be stressed in order to break the interfacial link.

**Viscoelastic effect in Adhesion:**

The strength of joints made with elastomeric adhesive depends on viscosity, elasticity, yield value and their dependence on shear rate.

\[
F/A = \eta \frac{dv}{dx} \\
\sigma = \eta \gamma^* 
\]

Where \( F \) - Force, \( A \) - Area and \( \eta \) - Viscosity
\[ \gamma = \frac{dv}{dx} \text{- Shear rate} \]

\[ \sigma = \frac{F}{A} \]

The ultimate properties of the adhesive are proportional to the viscous effects. The strength of the adhesive joints increases as the temperature is decreased or as testing rate is increased. Many adhesive joints fail cohesively within the adhesive layer at high temperature or low rate of separation. As temperature is lowered, the cohesive strength of the adhesive increases. When it exceeds the interfacial strength, the path of least resistance to fracture becomes the interface. Test temperature and test rate have opposite effects. The effect caused by test temperature can be overcome by decreasing test rate. This is the principle of rate-temperature equivalence. For amorphous glass forming liquids it is above the glass transition temperature. The WLF equation

\[ \log a_{T_g} = \frac{17.4(T - T_g)}{51.6 + (T - T_g)} \]

\[ a_{T_g} = \text{ratio corresponding test rates at temperature } T \text{ and } T_g \text{ and rates of Brownian motion of molecular segments at } T \text{ and } T_g. \]

From this equations we can predict the rate dependence of the work of detachment over a wide range of peel rates using only limited data obtained at various temperatures over a narrow range of rates. This WLF equation is only applicable to simple viscoelastic substances, not for semi crystalline or glassy adhesives. The shift factor \( a_t \) is determined empirically for each type of adhesive.

**Energy dissipation and Plasticity:**

Energy conservation during steady state peeling requires that work \( \Delta G \) done in detachment = thermodynamic surface detachment energy + energy dissipated within the adhesive + energy dissipated within the stripping member.

Thermodynamic surface detachment energy is the measure of intrinsic bonding across the interface, which is independent of detachment rate and temperature. Adhesive joints tested at normal rates and temperatures deformations are not perfectly elastic, and the detachment energy can be several orders of magnitude larger than the surface energy because of energy dissipation within the adhesive or bonded members or both.
When an adhesive joint is peeled then tensile stress reaches a maximum at the time of detachment and decays rapidly in the direction of the still attached portion of the bond. There will be two curves an extension curve and a retraction curve, which form a hysteresis loop. Retraction curve lies below the extension curve. The area enclosed by the loop defined as hysteresis. The total volume of adhesive that experiences this cycle deformation upon peeling a distance $AC$ is given by $Wt AC$.

$$W = \text{test piece width}$$

$$t = \text{test piece thickness}.$$ 

The energy dissipated within the adhesive on peeling a distance $AC$ is $H WtAC$. This energy provided directly by the peel force. So peel force will be high for adhesives that are capable of dissipating large amounts of energy during detachment, and for thicker adhesive layers, this provides a greater volume of material in which dissipation occurs.

**Adhesives:**

An adhesive is a material that brings two materials together. Adhesives and glues have been used for thousands of years, and up to the early 20th century, the only one of major importance were animal and vegetable origin. Since 1930s the synthetic glues has greatly increased. Their main advantage is their resistance to moisture and mould, and their ability to adhere in extreme temperatures and when structures are continually being flexed or bent. Towards the end of 19th century phenol resins made an appearance and by early 20th century phenol-formaldehyde resins came on the scene. Phenol-formaldehyde resins became the first synthetic resins to be used as adhesives and later on epoxy resins were introduced that were at least as strong as traditional glues.

Today, the number of applications for adhesives is growing fast. They range from industrial processes requiring large quantities of adhesives, to the assembly of components requiring only small amounts. Paper, packaging, footwear and woodworking remain the major applications. The usage has increased significantly in other areas, for construction work to fix window frames into walls, in vehicle manufacture to joint plastic components.
such as dashboards to a metal chassis, in electrical assemblies to fix components to circuit boards and in space to cement solar panels to satellites. The new adhesives have been developed with more efficient way of applying evenly and spreading them on large surfaces. So adhesives are used for joining metal to metal and other materials in load-bearing structures, such as bridges, and for a wide variety of other purposes.

The basic function of an adhesive is to fasten the components of an assembly together and maintain the joined parts under the service conditions specified by the design requirements. Adhesive material provide the answers to many joining problems, simplify and expedite assembly techniques, and reveal opportunities for design in new areas. Following are the advantages of using an adhesive in joining components.

1. Ability to bond a variety of materials, which may be dissimilar and of different modulus and thickness. Thin sheet materials may be bonded where other joining method would cause distortion.

2. Fabrications of complex shapes where other fastening methods are not feasible.

3. Appearance of finished product improved by smooth external joint surfaces and contours eliminate of voids, gaps and protecting fasteners such as rivets, bolts etc.

4. Versatility of adhesive forms and methods of applications permits their adaptation to many production processes.

5. Economic and rapid assembly and possibility of replacing several mechanical fasteners with a single bond, concurrent bonding of may components.

6. Strength of assembly is often higher and cost lower than for joints produced by alternative methods.

7. Uniform distribution of stresses over entire bonded area, stress concentration minimised, and fatigue resistance under alternating loads is improved. Joint continuity allows full use of component strength.

8. Weight reduction can often be effected by the use of adhesives instead of bolts, rivets, use of higher structural materials is allowed with more uniform stress distribution.
9. Elongation qualities of many adhesives allow stress to be absorbed, distributed or transferred; vibration damping and flexibility of properties are good.

10. Ability to join heats sensitive materials which brazing over welding would distort or destroy.

11. Prevention or reduction of galvanic corrosion between dissimilar materials.

12. Good sealing and insulating properties, barrier seal against moisture and chemicals, in many cases adhesive layer insulates against electricity, heat or sound.

The adhesives usually have the following disadvantages too:

1. Process became complicated, by need for surface preparation before joining and maintains clean components, preparation and application of adhesives, processing temperature/pressures and humidity conditions, relatively long curing times, jigs and other equipment.

2. Optimum bond strength usually not realised instantaneously as for spot welding assembly.

3. Difficult to provide enough inspection of adhesive joints.

4. Careful design required minimising peel and cleavage stresses as well as those due to differential thermal expansion.

5. Temperature limitations restrict use of bonded structure to certain service temperatures.

6. Poor electrical and thermal conductivity of many adhesives unless modified by fillers.

7. Possible degradation of bond by heat, cold, biodegradation, chemical agents, plasticisers etc.


9. Assembly hazards such as fire or toxicity are one feature of many solvent-based adhesives.
10. Tendency to creep under sustained loading, low peel strength of many thermosetting adhesives.

11. Some assemblies often joined by conventional methods are more economical.

**Bonding Process:**

Adhesive bonding involves the following interdependent basic steps.

1. Designing the joint specifically for adhesive bonding. The determination of joint stresses, type and size, together with strength requirements, will point to preferred adhesive materials.

2. Selection of adhesives. Take the performance requirements for the bonds.

3. Selection of surface preparation methods. It is necessary to consider suitable adherend pretreatment.

4. Fabrication of the assembly. This is adhesive application and final curing of the bond under controlled conditions.

5. Process control and the establishment of testing procedures to ensure reliability and permanence of the bond.

**Classification of Adhesives:**

There is no single system for the classification of adhesives. The adhesive industry has generally employed classifications based on end-use, such as metal-to-metal adhesives, wood adhesives, general-purpose adhesives etc. Particular end-use adhesives may be useful in several other fields also.

Adhesives can also be classified according to their physical form, chemical compositions, and method of application, various processing factors and their suitability for particular working requirements.

1. Classification based on bonding temperature: Adhesives are classified as cold setting (below 20°C), room temperature setting (20-30°C), intermediate temperature setting (31-100°C) and hot setting (above 100°C).
2. Classification by origin: Adhesives classified as naturally occurring and synthetic type. The naturally occurring are animal, vegetable and mineral adhesives. Synthetic adhesives are elastomeric, thermoplastic and thermosetting.

3. Classification by bonding methods: Adhesive bonding can be done by pressure setting, hot melt, chemical setting, or by solvent release.

4. Classification by bond strength: Adhesives can be structural (higher than 1000N/cm²) and nonstructural (lower than 1000N/cm²).

5. Classification by chemical nature: Thermosets are UF, PF, MF, PU, Epoxides, Polyesters etc. Thermoplastics are EVA, PVC, PVA, Acrylics, Cyanoacrylic etc.

**Surface Treatment:**

In order to obtain a strong and durable adhesive joint, surfaces are pretreated. The surface treatment alter the surface region on either by removal of a weak boundary layer or change in surface topography, change in chemical nature of the surface or modification of the physical structure of the surface.

All adhesives have surface tensions too great to allow them to wet the surfaces of solids with low surface energies. These are the methods to modify surfaces of these materials to get strong bonds.

*(a) Casing or Plasma treatment:* In this method, surface is bombarded with ions of an inert gas at low pressure. This casing causes crosslinking reactions in the surface region of the polymer. When a polymer is cooled from the melt, a low molecular weight fraction is pushed to the surface ahead of growing crystallites nucleated in the interior. This results in weak boundary layer in an adhesive joint. Crosslinking the surfaces increase its strength and can increase joint strength.

*(b) Corona Discharge:* The material is exposed to corona discharge, usually in air and at atmospheric pressure. By this method C=C unsaturated double bonds are introduced
into the surface and the surface get roughened. This indicates that the corona can degrade and remove the portions of the surface material in a non-uniform way. Surface oxidation also occurs during corona discharge.

(c) Acid Etching: Acid etching is usually done by chromic acid. When etching time increases the depth of surface oxidation increases and bond strength improves significantly. Increase in joint strength after acid etching is attributed both introduction of polar groups and increased roughness of the surface. Some etchings make carbonaceous residue resulting in darkening of surfaces. They increase wettability and which leads higher adhesion strength.

(d) Transcrystalline Growth: The ability to bond polyolefins is also improved by moulding them against a high-energy metallic substrate that induces transcrystalline growth in the surface regions. The substrate induce profuse nucleation of crystallalities at the surface and this results in the formation of rod like or columnar spherulites that grow inwards from the interface. This causes the increase in bond strength. The shear strength of the specimens with transcrystalline surfaces is two to ten times higher than those of specimens without transcrystallinity.

(e) Surface Grafting: Surface grafting with suitable chemical species is another technique. Bond strength increases by this pretreatment significantly.

Strength of Adhesives and Joints

Fracture Mechanics: Adhesive joints usually fail by initiation and propagation of flaws. The pressure of flaws governs the strength of most real solids. The strength of adhesive joint is a function of the loading mode, dimensions, elastic properties of the bonded components, and the intrinsic strength of the interface. The aim of fracture mechanics theories is to analyse mathematically the loads, which the flaws propagate and describe the manner in which they grow. The source for naturally occurring flaws, which is termed as intrinsic flaws may be voids, cracks, dirt particles, additive particles in homogenates in adhesives etc., which may be initially present at a critical size or develop
during the fracture test. Fracture mechanics has uses in characterising the toughness of adhesives, identifying mechanisms of failure and estimating service life of structures. The damages may be in form of cracks, air-filled voids, "debonds etc.

One method of analysis uses a simple energy criterion for fracture in terms of a characteristic work of detachment for breaking apart the interface. It is proposed brittle fracture for elastic solids, a energy criterion for fracture has been successfully applied for materials that became locally dissipative, highly elastic materials and to the separation of two adhering solids. Another method consists of evaluating the stresses set up at the site of fracture, and then invoking a characteristic fracture stress as the criterion for rupture.

In applying an energy criterion to adhesive failure, it is necessary to identify an initial site of separation, a flaw or region of high stress concentration at the interface between the two adhering solids. Failure is then assumed to take place by growth of this initially debonded region until the joint is completely broken. An energy balance is taken for a small growth of the debond, changes in the strain energy of the joint and the potential energy of the loading device are equated to the characteristic work of detachment. This energy balance provides the required relation between the breaking load and the properties of the two adhering solids and the dimensions of the joint. Strain energy is supplied by a loading device and started in the deformable material. Failure occurred in two ways by supplying the work of fracture or detachment and by deforming material that was previously deformed. By equating the energy available to that required propagating fracture or detached zone, the magnitude of the stored strain energy at the moment of fractures deduced, and hence the applied stress at break.

The energy criterion arises from Griffith's work, which supposes that fracture occurs when sufficient energy is released by growth of the crack to supply energy requirements of the new fracture surfaces. The energy released came from stored elastic or potential energy of the loading system can be calculated for any type of test piece. Energy required extending a crack over unit area and is termed as fracture energy or critical energy release.
rate is denoted as $G_c$.

$$G_c = \frac{F_e^2}{2b} \frac{dC}{da}$$

$b$ - specimen thickness
$a$ - crack length
$C$ - compliance of the structure
$F_e$ - load at the onset of crack propagation.

This equation is the foundation of many linear-elastic fracture mechanics: $C$ is determined as a function of $a$. If bonded structure does not exhibit bulk linear-elastic behaviour then the fracture energy approach is in a different form of equation \(^{81,82}\).

**Mode of failure:**

(a) **Peeling separation.** The elastic energy of deformation of the adherends changes very little as peeling proceeds. This is because most adhering layers do not stretch significantly under the force of peeling, and the amount of material subjected to bonding does not alter.

For peeling at 90° $P = G_a$

$G_a$ - Work of detachment per unit area.
$P$ - Peel force.

For peeling at 180° $P = \frac{G_a}{2}$

(b) **Lap Shear:** A deformable adhering layer is subjected to a force applied parallel to the bond plane then a layer becomes stretched after detachment \(^{70,77}\).

$$P = 2t \frac{E G_a}{t}$$

The tensile stress $\sigma_b^2 = 2t \frac{E G_a}{t}$

For a bar containing a small circular cavity of radius $r$,

$$\sigma_b^2 = \frac{E G_c}{3r}$$

$G_c$ - work required to propagate a fracture plane \(^{61}\)

As flaw grows and its radius increases, the stress required for fracture is predicated to decrease. If the applied stress is large enough to cause the small initial flaw to grow,
then it will be sufficient to make the process continue. Shearing detachment is therefore predicted to take place continuously at a constant tensile stress in the deformable layer related inversely to its thickness. This theory has been used for unequal adherends and for prestressed layer also.

(c) Pullout test: Pullout force $P$ for a fiber embedded in a cylindrical block of radius $R$ is

$$P^2 = 4\pi^2 R^2 r E G_a$$

$r$: fiber radius

$R$: adherend cylinder radius.

If both radii are same then,

$$P^2 = 4\pi^2 r^1 E G_a$$

The pullout forces increase as radius of the fiber increased. The surface area to be debonded and the energy required to do so are both greater for fibers or cylinders of larger diameter and pullout force increased. For spherical inclusions, the amount of highly stressed material in the vicinity of the debond which provide the energy needed for propagating the debond also increases as the size of inclusion is increased. The highly stressed volume grows in proportion to $r^3$, whereas the area to be debonded only grows in proportion to $r^2$.

When a number $n$ of fibers are embedded in a single block of elastomer and they are all pulled together, then the work required for detachment is larger than for a single fiber by a factor of $n$. The strain energy stored within the block must therefore be larger than before, by a factor of $n$, and the total force applied for pullout must be increased by a factor of $n^{1/2}$. The total force that required to pullout $n$ fibers simultaneously forms a single elastic block until increase in proportions to $n^{3/2}$.

Design of Adhesive bonds.

Bonds are made after considering many important factors. Depending upon the bonding method there are several design factors to be considered.

(a) Uniform stress distribution it is the most important of all of them. The strength
of the joint may affect by the stress concentration over the bonds. In shear stress to a bond, force is directed so as to slide one substrate part another without increasing the bond thickness. Tensile stress tends to increase the bond gap. The optimum directions for these two stresses are perpendicular. The bond will be the combination of shear and tensile stress if the stressing force is not exactly in either the shear or tensile direction. If there is no sharp stress gradients then the bond strength will be the experimental strength on testing.

(b) **Self-Alignment:** The alignment of the substrates should be proper. In mechanical bonding it is essential that ridges, grooves etc. is essential for better alignments.

(c) **Self-Fixturing:** Load should be applied over the bond line to correct for any dimensional shrinkage of the melt or adhesive. Self-fixturing features eliminate the productivity loss caused by the clamping load.

(d) **Ability to Clamp:** Clamping force is applied over the adhesive bonds. So the bonds should have the ability to hold the clamping force.

(e) **Vertical Insertion:** The second substrate must be vertically down upon the first substrate. If more than two joints are made simultaneously in different planes, changes in bond design might be required to satisfy vertical insertion.

(f) **Bond gaps Control:** Bond strength is higher when bond line is thinner. The bond line should be horizontal to avoid flow of adhesive. Adhesive thickness is controlled by any method, which does not affect bonding.

For maximum effectiveness, adhesive bonds should be designed with (a) Stress the adhesive in the direction of maximum strength (b) Provide maximum bond area (c) Make adhesive layer as uniform as possible (d) Maintain thin and continuous adhesive layer (e) Avoid stress concentrations.

**Failure:**

Each polymer material has its own unique set of properties and the exact mode of potential failure is unpredictable. In order to predict the failure one must know the material contributions, temperatures, stress and environmental conditions that cause bond
strength deteriorating effects. When metal is bonded to fiber reinforced plastic (FRP), metal expand quickly and FRP is slow, to catch up and on cooling, metal contracts faster than FRP. Solution for this is to increase the gauge of faster expanding substrate for slowing the rate or using low modulus adhesives or flexible bonding techniques. Chemical reactivity of the substrates may cause problems of failure. Outgassing of unreacted monomer, moisture or chemical fragments of decomposed initiators may lift adhesives from their bond surface. If substrates are exposed to heat, the additives chemically not bound to the substrate polymer will migrate. Thermal and rheological conditions of the adhesives can also alter the adhesive properties. A durable joint will result if the selected adhesive layer is compatible with mobile ingredients and securely bonds to the second substrates.
Wood Adhesives:

Properties of Wood: Wood is naturally occurring, polymeric composite material. The chemical and anatomic structure of wood affects strength properties, appearance, resistance to penetration by water, chemicals and decays, pulp quality and chemical reactivity. Hardwood and softwood forms are the two categories of wood. The principle chemical components of wood are carbohydrates 70-80%, lignin 20-30% and extraneous materials 5-10%. In soft wood lignin content is higher than hardwood. Carbohydrates consist of primarily cellulose (40-50%). The chain length of wood cellulose polymer is between 70,000 and 10,000 glucose units. Wood cellulose is crystalline and resistant to the attack of dilute acids. Lignins are complex phenolic polymers of irregular structure. Extraneous materials in wood are non-polymeric, low molecular weight substances that can be removed by a solvent without being chemically modified.

Physical properties of wood include some that are directly related to water content and movement, such as hygroscopicity, mechanical, electrical and thermal properties, corrosiveness and chemical resistance. Moisture content in wood has great effect on adhesion, so it is dried before use. The amount of moisture absorbed depends on the relative humidity and temperature. Relative humidity changes in atmosphere cause corresponding changes in the moisture content of wood.

The adsorption and desorption of water in wood is accompanied by external volume changes. The volume change or change in shape may occur because of the development of moisture gradients and stresses, and these stresses can be minimised by drying the wood under controlled conditions. The degree of shrinkage is proportional to the specific gravity of wood. Swelling and shrinkage changes with direction. Tangential swelling is greater than radial swelling and tangential shrinkage is higher than radial shrinkage. Longitudinal shrinkage and swelling are smaller in wood.

Permissibility of wood is higher. Wood is a porous material with 60-70% void volume. Permissibility may vary due to the highly anisotropic shape and arrangement of the component cells and the microscopic channels between cells which form a complex capillary network.
Wood consists of a series of tubular fibers or cells cemented together; each fiber is composed of various quantities of polymers. These are the cause for the physical and chemical properties of wood. Wood is an anisotropic material and has mechanical properties in longitudinal, radial and along the tangential axis. Mechanical properties are higher when moisture content is lower and when heated mechanical properties deteriorate. Electrical properties like conductivity will be higher when moisture content is higher. Conductivity increases when temperature increased and is affected by moisture. Dielectric constant is higher when moisture content is higher.

Softwood is chemically more resistant than hard wood. The wood may get corroded depending upon the wood species. Wood is slightly acidic, which may cause corrosion. Corrosion also depends on the external corrosive agents. Some chemically treated wood is usually more corrosive than untreated wood.

**Requirements of Adhesive:**

The adhesive should penetrate into the wood surface and solidly attach the wood fibers. The adhesive should not destroy the continuity of the adhesive remaining in the glue line and one of the adhesive on wood surface should be wetted. The adhesive must be molecularly compatible with the interfaces. The diffusion of solvent or water in the adhesive into the wood is essential for the adhesive. The solvents initially wet the wood surface and pass into the cell walls. The adhesive must migrate sufficiently into the cell walls to form molecular bonds to hold on the wood constituents. To get better adhesion the adhesive must have the properties like physical and chemical characteristics, molecular weight distribution and molecular geometry in balance.

Certain process variables are there for getting good adhesive joints for wood. Assembly time - the time between the adhesive applied and pressure applied. If assembly time is short adhesive could not flow inside the gross capillaries of wood and form better joint. If assembly time is too large then mobility of the adhesive is greatly reduced and
insufficient penetration occur. If the adhesive applied to one surface only then too much solvent will be lost and there will be insufficient adhesive for wetting the unspread surface. Adhesives should spread evenly over the surfaces. The thickness of glue depends on pressure applied time of pressing and compressibility of wood species. Moisture content of the wood is another process variable. Bonding difficulties may arise if moisture content is very high. The quality of bond will reduce if drying temperature goes higher. The adhesive should be applied as soon as the surfaces are prepared. As the time after surfacing increases the bond quality diminishes. The rate of temperature increase on glue line will affect the bond quality. The applied pressure over the bond depends on the relative roughness of the surface and surface area of contact, compressibility of wood, the gap filling capability of the adhesive and amount of glue spread. Small amount of pressure required for smooth surfaces whereas higher pressure is required for rougher surface and larger areas of bonding.

The performance of adhesive in service is dependent on the quality of original bond, the physical and chemical characteristics of the cured adhesive, and the stresses in the adhesive joints. The quality of original bond depends on various factors related to the wood surface. Grain orientation, moisture content, quality of wood surface and species of wood used etc. are the main factors. The physical and chemical characteristics of cured adhesives are its water resistance, heat resistance and resistance to biological attack. The glue line is subjected to shearing stresses across the grain as a result of differential swelling or shrinking of adjacent laminae. This differential swelling or shrinkage occurs due to changes in grain orientation, initial difference in moisture content and due to specific gravity difference. They cause cracking or delamination of wood joints.

Leather Joints

Leather is animal hide or skin that has been processed for use by man. The hide or skin is composed of water and proteins and unless preserved decays quickly.

Leather is made from raw hide in three steps: (1) Removal of undesirable constituents such as hair, flesh, fat and some interfibrillar matters, leaving a concentrated network of
high protein collagen fibers, greatly softened and interspersed with water. (2) Tanning: treating the hide with an agent called tannin that displaces the water and then combines with the coats and the collagen fibers. Tanning increases resistance to heat, hydrolysis and microorganisms. (3) Finishing to obtain proper thickness, moisture, lubrication and aesthetic appeal. The leather is essentially animal skin protein combined with Tannins, small amounts of oils, dyes, finishes, and moisture. The relative properties and distribution of constituents varies with the type of leather 111,112.

The properties that suited for leather footwear are resistance to abrasion, flexing, deforming and stretch, tensile, tear and burst strength, suitability for cementing, vulcanizing, and molding, wearing comfort, permissibility of air and water vapours storage capacity for perspiration, thermal insulation, suppleness, appearance, color fastness, resistance to wet and dry rubbing, easy care etc 111.

Leather is processed either by vegetable tanning or chemical tanning. Leather should be protected against excessive heat, humidity, rain and pests. Raw hides are cured or preserved to prevent decay. Curing consists of dehydration without disturbing skin structure.

Vegetable tanning materials are tannin - complex mixtures of polyphenols and non-tanning materials are carbohydrates, salts and acids. The tanning material is ground, leached with water concentrated into solid or powdered extract. The delimed skins are pickled or preheated with tannin and tanned in paddles or drums, with a blend of tan extracts for three or six months 114.

At present a wide variety of synthetic tannins are available. They are 1) auxiliary tans, strong simple sulfonic acids 2) combination of tans, sulfonic acid of complex phenolic materials used for light tanning and for white leathers, 3) exchange or replacement tans, weak acids containing a large number of phenolic groups to substitute vegetable tans and to produce white, light fast leathers. These leathers then dyed to get colours, and then lubricated. Dyed leathers are treated with oils and fats for lubrication, softness, strength and water proofing 115. The leathers then dried to 14% moisture, and then they are subjected to finishing operation. Some leathers are impregnated with synthetic resins to improve
their properties. Polyurethanes give best scuff resistance. Leather is further finished by coating the grain surface. Water resistance is obtained by treating leather with silicones and waxes.

Leather Adhesives:

Adhesion between two surfaces depends upon the inherent attractions of atoms and molecules when brought close enough together. Even though solid surfaces were smooth enough to achieve molecular contact, layers of gas molecular form a barrier to material contact. Rough surfaces must be wetted to ensure good adhesion. Material must flow to achieve good contact at the interface; the solid surface must be clean of interfering substances.

In most adhesive bonds in leather goods, very high strength is not required. The adhesive must be strong enough to resist tearing, but flexible enough to resist fracture. Adhesive generally must be liquid at the time of application. They clearly undergo a change of state, in converting to the solid. The change of state brought about by a loss of solvent or by a cooling and solidification of a melt adhesive usually involves a change in volume. The adhesive shrinkage causes stress in the joint. The adhesive must be compatible with the surface to which it should stick. The attraction of the solid surface molecules for the adhesive must be at least as great as the adhesive molecules for each other.

Bonding process initially involves the roughening of leather. The grain layer has to be removed completely and on the flesh side all loose fibers have to be removed. The grain layer can also be wiped with a solvent. Next is adhesive application, depending upon the type of adhesive used, different methods of adhesive application is possible. The adhesive must apply within one hour after the preparation of the surfaces to be bonded. The adhesives have to dry after applying. There are wet bonding where, these surfaces are brought together in the wet state. Contact bonding is another type. In this case adhesive applied to both surfaces and after a certain length of time the adhesive layer apparently dry then they are put together under slight pressure. Heat activated bonding in which adhesive is heated sufficiently to get tacky.
Similarly wiping with solvents also activates adhesives. The bonds between two components are pressed by rolling or on a press. There will be failure of adhesive joints when insufficient pressure, if too longer intervals between cementing and assembly, high grease content in the leather, excessive penetration of adhesive, in compatible adhesives on leather, too short drying time of the adhesive etc.\textsuperscript{21}
Rubber to metal bonding:

The technique of rubber-to-metal bonding is utilised by the rubber industry as early as the rubber industry has been using the process of vulcanization. Early bonding techniques include ebonite and brass bonding, which is still used for industrial applications. Many developments have occurred over the years in this field, one of the most significant of which is the introduction of chemical bonding agent systems.

The unique utility of rubber-to-metal assemblies began to be appreciated around the turn of the century through applications that helped cushion motion and deaden noise. The rubber-to-metal composites came to be employed in the mechanical world not only to minimise the damaging effects of vibration and protection against shock, but also to seal against shock, leakage of oil and other fluids, and to simplify assembly by providing a tolerance for misalignment. The automobile industry is by far the biggest user of bonded elastomer components. Applications such as engine mounts, suspension bushing, transmission and axle seals, couplings and body mounts etc. are some of them.

Manufacture involves molding of the elastomer to shape, vulcanization and bonding all in a single-stage press operation. In aerospace sector advanced R-to-M technology has resulted in such highly specialised devices as low maintenance rotor bearings embodying alternating layers of rubber and metal in special geometric configurations. R-to-M assemblies are for non aeronautical vehicles of war-tanks, submarines and for rail and rapid transit rolling stock, as well as for track beds and rail crossings. Bonded parts are essential for materials handling machinery, shipping containers, construction and agricultural equipment, leisure devices, air systems and business machines of various types.

In order to evaluate the performance of rubber-to-metal bonds it is necessary to consider the structure of the surface of the metals. Most of metals form oxide layers on their surfaces, some of which are porous, like iron oxide and this continual oxygen ingress enables the oxide layer to increase continually whilst in aerobic conditions. Metals like aluminum form a dense oxide film, which does not permit oxygen ingress, and this protects the metal underneath from further oxidation.
The bonding mechanisms of the multiphase systems involved in the formation of a rubber to metal component are complex. Bonding incorporates a primer and an adhesive layer, and interactions, which may occur at each interface. In the region of contact with metal, the interactions are a combination of mechanical and chemisorption processes. The primers used in rubber-to-metal bonding contain a variety of halogenated rubber and resins, which have good ability to wet out metal surfaces, thus ensuring the greatest possible degree of interfacial contact. These rubbers and resins act as barriers to the migration of corrosion catalysts. The primers used in rubber-to-metal bonding contain a variety of halogenated rubber and resins, which have good ability to wet out metal surfaces, thus ensuring the greatest possible degree of interfacial contact. These rubbers and resins act as barriers to the migration of corrosion catalysts. The resins and rubbers form interpenetrating network of polymer chains within the adhesive system, thus giving strength and structure of the primer coat. Between the primer and the adhesive there will be adsorption and interdiffusion at the interface. The other ingredients of the bonding agents may form cross bridging reactions between the two parts of the bonding system together into an integral unit. The ingredients in the bonding coat will carry out two related series of reactions, the first to form crossbridging links with the rubber surface during its own and the crosslinking of rubber. There will be interdiffusion of sulfur and accelerator entities between the rubber and the bonding agent; become highly activated by the elevated temperature. The second process will be the vulcanisation reactions within the bonding adhesive. Chemical reactivity at the polymer bonding agent interface includes chemisorption, crossbridging and mechanical interlocking effects. The bond quality greatly depends to a large extent upon the ability of all interfaces to freely exchange chemical entities. Any contamination will upset the surface chemistry at that point and will reduce the bond strength.

Production of bonded parts:

Bonding rubber to metals during the vulcanisation of the rubber makes engineering products for a wide range of applications. The bond achieved must be of sufficient integrity; it should be stronger than the rubber constituent of the component. Components consisting of moulded rubber to metal during high temperature vulcanisation can give rise to inherent stresses, simply due to shrinkage of the rubber when removed from the influence
of vulcanisation temperature and the coefficient of thermal expansion relationship of the rubber to metal combination. The shrinkage of the rubber in the system will vary according to the type of elastomer being used, and is also dependent upon the compound hardness or degree of filler present. Allowances for the mould runner shrinkage must be made in determining the shape of the mould cavity and hence the component's final shape. Some oil and solvent environments will penetrate a bond at the interface and this may weaken or destroy the integrity of the bond until the stress is relieved by failure.

To effect good long lasting bonds between rubber and metals it is essential that both materials presented to the interface be clean and free from dirt and oil. The possibility that compounding ingredients can exude or bloom from the rubber surface, life of the component must also be taken into consideration at the stage of ingredient selection.

The characteristic surface energy of a material controls the contact characteristics of a droplet of liquid at rest on it. A liquid droplet in free space assumes a spherical shape. In contact with the surface of a solid material a liquid will assume a droplet shape characteristic of the relationship between the surface material and the droplet material. When two materials are brought into contact, there will be a change in free energy at the interface which is known as the work of adhesion, and tends to increase the wetting of a solid with a net increase of the surface area of the liquid. Cohesive forces have an opposing effect, which will tend to minimize the surface area of the liquid. By combining the work of adhesion and cohesion one arrives at the spreading coefficient. The spreading coefficient can be either negative in nature, indicating poor wetting of the interface, or can be positive, indicating a good surface wetting. Organic solvents readily wet out the metal surfaces much more than water does.

The choice of rubber and filler are often constrained by end user or customer specification, but other ingredients such as curing systems may often be variable and able to address limitations. Ingredients, which act by causing, surface blooming, such as waxes and antiozonants can be troublesome in bonding applications. Excessive quantities of certain materials such as plasticisers, oils, antidegradants, fatty acids and fatty acids soaps
can bloom to the surface of the rubber and in all probability will also bloom to the interface. Plasticisers can exude, owing to incompatibility with the polymer or simply because they are present in too high a concentration. Some plasticisers can migrate over long periods of time through the bonding agent layers, and cause corrosion or complete bond failure many years after the bond was originally effected.

Curative systems has a very strong influence on the nature of a bond, and often the system required by the compound to meet the specification may result in an adequate ability to bond, for example efficient vulcanisation systems which have low sulfur contents.

Metal preparation:

Metals must be suitably pre-treated for satisfactory bonds to be achieved with rubbers. The significance of the pre-treatment of the metallic surfaces is often underestimated, but it is an important factor in determining quality. Pre-treatment means bringing surfaces to a suitable state for further operational processes without material being removed from the component. The material being subjected to selective attack, without the formation of internal stresses and micro cracking increasing.

There are various types of impurities, which vary greatly in their behavior and consequently cannot be removed by a single universal procedure. The most effective and economically viable pre-treatment method has to be selected individually for each case. The selection of the correct cleaning method should ensure that the surface quality is suitable for the production process. The cleaning must be inexpensive, safe to use and environmentally friendly. According to Sinner's circle, cleaning is influenced by four parameters: (a) Mechanics, (b) chemistry, (c) temperature, (d) duration of the treatment. The cleaning effect of bath cleaning may be increased by moving the bath liquid or the item being treated to a greater or lesser degree. High-pressure injection and ultrasound cleaning intensify mechanical attack of the cleaning media. The choice, composition and concentration of the cleaning chemicals have a decisive effect on the effectiveness of
cleaning with liquids\textsuperscript{157}. Cleaning take place in three stages (1) wetting of impurities (2) detaching from the substrate surface (3) dispersion of impurities. Cleaning requires sufficient time to allow their processes to take place. According to Arrhenius theory, the rate of reaction increases as the temperature rises, in addition the viscosity of the cleaning solution, greases and oil to be removed is reduced, which produces better wetting and finally results in the removal of the impurities and reaction products\textsuperscript{158}. But due to the energy costs and the problems with vapor formation low temperature cleaning are preferentially selected. Cleaning effect is achieved by the interaction of all factors \textsuperscript{159}.

Metal preparation areas, and holding areas for treated metals prior to moulding shop use, must be atmospherically isolated or be protected by a positive air pressure system from any moulding area. The bonding agents must be stirred frequently. Application of primers and bonding agent can be carried out by hand brushing, spraying or dipping. In general conventional moulding methods can be used for the production of rubber to metal components.

\textbf{Metal reinforced rubber products:}

Two major types of materials are used as integral reinforcements for composite rubber structures are textiles, metal fabrics and cords, steel in rod or wire form has been used for many years as reinforcement in composite of various types for a number of industrial products. From 1940s steel or other metal wires replaced the reinforcement by textile. The development of the radial tyre, with its higher running speeds and temperature, led to the progression from textile reinforcements for tyres through nylon, glass and aramid to steel cords\textsuperscript{160}.

Rubber will not bond directly to the surface of steel, requiring chemical treatment of steel surface or chemical modification of the rubber compound to induce adhesion. Steel filaments are drawn from thicker gauge wire being passed through a die or series of dies, with heat treatments to give progressive gauge reduction. Before the final gauge reduction, the wire is coated with brass or zinc \textsuperscript{161}. Wake points out that preferred
composition of brass applied, as die lubricants/rubber adhesion layer, in tyre cord production is 60/40 (copper/zinc). The brass thus deposited into the steel has a crystal form which is much distorted by the drawing process, which enhances the activity of the copper atoms towards that found in an electrolytically deposited 70/30 brass in an undrawn form.

The current accepted brass-coating thickness appears to fall in the range of 5-8 x10^{-4} mm for good adhesion. These type of steel fabric construction can be used in a wide range of applications, including belting and hoses. The brass coating prevent corrosion through water ingress and to facilitate bonding. In common with other types of rubber to metal bonding the choice of rubber compounding ingredients plays a considerable role in the achievement of good adhesion between tyre compounds and cords. Ultra accelerators and low sulphur vulcanising systems cannot be used. Sulphur levels of at least 3 phr must be used and the preferred accelerator system. Delayed action accelerator system is required.

Objectives and scope of the present work

The primary objective of the present study has been to develop novel, low cost adhesives for bonding wood to wood, leather to leather and rubber to metal substrates due their significance. In the rubber to metal bonding field, at present imported varieties such as polylock, chemlock and desmodour predominate, while latex based or solution based adhesives dominate in the wood to wood and polyurethane based adhesives in the leather to leather bonding field. It is proposed to develop novel latex based and solution based adhesives for these substrates. Due to the industrial importance of rubber to metal bonded systems, it is proposed to try novel methods such as rubber strip adhesion in them. This will be more environment friendly than the solution based adhesives available commercially. Adhesive strips based on polymer blends are also proposed to be developed in order to make them more efficient and cost effective. The conventionally used adhesive systems for wood to wood bonding lack water resistance. Hence adhesive systems with improved water resistance are proposed to be developed for wood to wood bonding. Also, in the
case of leather to leather substrates, the conventionally used polyurethane based adhesives lack the necessary strength for critical applications in addition to being expensive. Hence novel adhesives which can contribute to higher strength for these substrates are proposed to be developed. The objectives of the proposed study may be summarised as follows,

1. To develop novel and water resistant systems for wood to wood bonding
2. To develop more efficient and low cost adhesives for leather to leather bonding.
3. To develop a novel strip adhesive system for rubber to metal bonding. It is also proposed to develop novel adhesive systems for steel tire cord/rubber adhesion and bead wire/rubber adhesion replacing the conventional methods.
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