

Adhesion Theories and Effect of Surface Roughness on Energy Estimation and Wettability of Polymeric Composites Bonded Joints: A-Review

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Abstract: Adhesive bonding is getting more attention for research and considered as most promising and well-known technique for joining the two materials which may be similar or dissimilar naturally polymers, metals etc. and to be utilized in light weight structures for reduced stress distribution. Adhesion bonding consisting on intrinsic bonding force which plays vital role to make the joint withstand more strength. To fabricate an effective gripped joint between the components, good adhesion strength is compulsory attainment factor for long life of structures. Recently, along with metallic materials polymers and their composites are also trending in multiple industries. All materials always have forces of attraction between their atoms/molecules which extremely crucial role to ensure stronger bond strength and often dependent on roughness of surface of material which are taking part to fabricate the joint. Consequently, surface roughness and surface morphology are most important parameters to decide the joint strength and life of bonded joints of polymeric composites. In this review article, mechanical interlocking mechanism, surface roughness effects on wettability, surface energy estimation and various bonding theories including adsorption theory, diffusion theory, boundary layer theory and chemical theory are discussed briefly to emphasize the various technological & industrial developments

Keywords: Mechanical interlock model, Adhesion theories, Surface energy estimation, Surface roughness

1. Introduction

Adhesion is a process that is used to join two solid materials either similar or dissimilar when they come in a close contact with each other. Mainly adhesion is used in multilayer sandwiches, polymer blends, filled polymers, coating paints, composite materials and adhesive joints. Across the interface there is a need to generate intrinsic adhesion forces to make adhesion possible because the mostly significant performance of these multi component materials depends on the interface quality that is usually formed between the polymers. If we would have a good knowledge about the phenomena of adhesion, then it would help for the practical application. The study of adhesion and adhesion mechanism is going to start back to 1930s, but the fields of adhesion become really interested in scientist circles about 60 years ago.

The research about the mechanism of adhesion is carried out throughout these years but researcher are working in this are still unable to find out the absolute

principal or mechanism of adhesion, just because the fact that adhesion is really a complex phenomenon and it involves multiple knowledge branches related to mechanics of material, fracture mechanics, polymer and surface chemistry and others. Although Fourche [1] has already been describe some of the importance of adhesion models with considerable details and it could take help from these models to better understand the working of the adhesion between two substrate, therefore adhesion become a complex subject to study about the exact phenomenon, although we have some scientific work but still improvement in working on practical grounds are required.

The term of Molecular forces of attraction then it directly relates to “Intrinsic adhesion” as it happens between the molecules of same body or material. Intrinsic adhesion is a very important as it is used to find the toughness or strength of the joint. Now the forces that basically act of the adhesion on the surface of the material and within the adhesion are called “Adhesion

forces” and “Cohesion forces”. Adhesion forces generate a strong contact with the molecules of substrate and the adhesive on the surface as the particles in the adhesive are attracted by the particles of solid material and as a result it makes a strong bonding which causes a good joining strength.

Cohesion forces are those that are between the adhesive and it helps to make a strong and effective strength between the particles of adhesive. Adhesion is the interaction between two surfaces which include interatomic and intermolecular interactions[2]. Since the beginning of both aerospace and automobile industries surface characteristics of the polymer are dependant on the surface properties of the material, mostly in previous 30 years it is to be observed that understanding and investigation of adhesion mechanism has surprisingly increased in these both aerospace and automobile industries due to their special properties of light weight, cheaper and most suitable alternative to the metal[3].

Adhesion is not a simple mechanism as it includes a number of parameters that directly or indirectly effects the understanding and the working of adhesion, these parameters are polymer surface chemistry, polymer physics, mechanics of material, fracture mechanics analysis and other subjects[4]. The main purpose of all this is to obtain a mechanism or process that simply used to understand and explain the adhesion phenomenon [2, 5, 6]. A debate on adhesion mechanism that consists of many molecular, mechanical, diffusion, thermodynamics and chemical adhesion phenomena are being carried out in a wide range of literature[3]. Adhesion mechanism study start in 1920s when Hopkins and MacBain introduced the mechanical interlocking model[7]. Although a lot of paper work is reported on the adhesive but still there is a need to develop fundamental knowledge about adhesion process, further more till now no theory or any global approach explain all mechanics and adhesion phenomena in details[8, 9]. Adhesives are widely used but the bond nature of adhesive is still having some confusions and problems. To cover all the aspects of adhesive bonding there are six main theories or mechanism which includes (1) Mechanical Interlocking Model (2) Adsorption Theory (3) Diffusion Theory (4) Electronics Theory (5) Weak Boundary layer Theory (6) Chemical Bonding Theory that are used to explain the phenomena that associate with adhesive bonding[10] [1, 9, 11, 12] which are explained below. Mechanical interlock model and joint failure modes have been briefly described and compressive review of theories is explained in this article.

2. Mechanical Interlocking Model and joint failure modes:

McBain introduced the most earliest theory known as mechanical interlocking model [7]. The Awaja and George stated that Intrinsic adhesion occurs due to the irregular surface of the adherend that help the adhesive to make a strong grip [1, 3]. It was presented by a graphical image as shown in fig.1 [12]. Yang Shu stated that adhesion basically occurs in mechanical interlocking due to pores and other aspects of a substrate [9]. Mechanical interlocking theory mostly depends on the roughness of the substrate and porosity of the polymer as far as wettability by adhesion is sufficient. Mechanical Interlocking mostly used to be expected as to make a good and enough in bonding strength and it helps to increase the effective surface area for adhesion. Although crevice angles help to increase the tensile strength of the bond in lap shear joint, but these joints significantly depend on the roughness of substrate or adhered surface, joint strength increase due to change in roughness of the substrate until optimum level of roughness is achieved. Surface roughness is only a method that tends to regulate and increase the spreading of adhesion on the required surface of the substrate. Figure 1 represents a mechanical interlocking model which illustrates the mechanical coupling between the substrate that had irregular notches and it helps to make the surface rough for good adhesion strength.

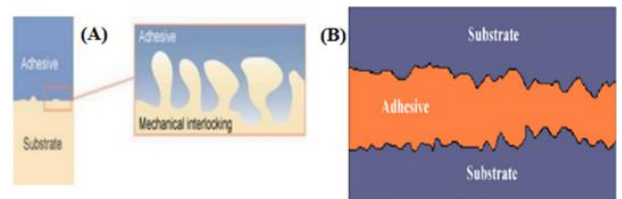


Figure 1: Mechanical coupling between two substrate [12]

In parallel, van Leeden and Frens [12] reported that mainly three types of irregularities are used to be assumed as illustrated in fig.2. However type (b) usually based on mechanical interlocking and in the case of type (a) or (b) the strength of adhesive mainly depends on applied force direction just because only mechanical hooking is acting on that points[12]

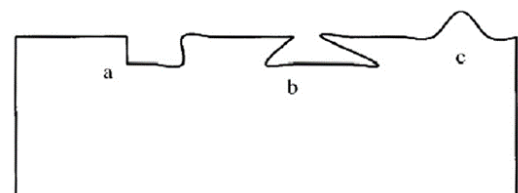


Figure 2: Three types of surface deformities [12]

Along with these three types of surface deformities, sufficient wetting also plays an important role in making a strong grip between substrate and adhesive. Main factors that usually affect the mechanical interlocking

model are irregularities of surface, roughness, porosity but it happens only under sufficient wetting condition as show in figure 3.

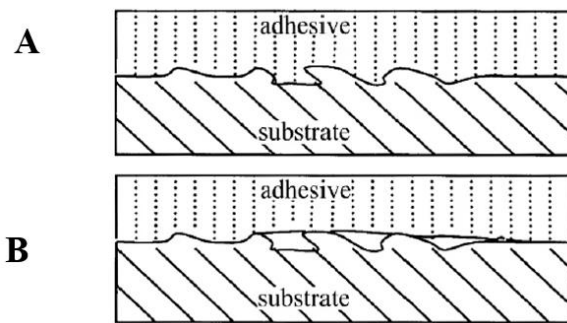


Figure 3: (A) Sufficient wetting (B) poor wetting [1]

In case of not complete wetting given factors would not be able to achieve. Maeva group [11] reported that for making a strong grip it is necessary to make a good wettability on the surface and adhesive should reached into the pores of the surface for making the proper mechanical characteristics in the pores of the substrate. Mechanical interlocking model is considered only where the substrate are suitable for adhesion mechanism and sufficient surface roughness is available[11].

Furthermore, in order to make the bonded joints more reliable, selection of adhesive and surface enhancement technique plays important role for joint strength and life. Table 1 (see appendix I) summarizes the reported results of bonded joints of metals and polymers by application of numerous adhesives.

2.1 Adhesive Bond Failure Modes

Adhesive failure is defined as the failure occurs within the adhesive layer and between the adhesive and the adherend interface. Cohesive failure occurs when the separation between adhesive and the adherend interface occurs in certain manner that both adherend/substrates surfaces must be covered with adhesive layer. In some cases adhesive joint fails in such a way that one of the adherend covers the entire layer of adhesive after the lap shear joint strength test of the adhesively bonded specimen. Failures of adhesively bonded joints often subjected to more than one mode of failure and are defined as a percentage to adhesive failure or cohesive failure and are presented in figure 4. This percentage can be easily calculated on the basis of fraction of surface contact area that subjected to cohesive or adhesive failure [23, 24].

2.2 Lap Shear Joint Test

Now a days, automotive industry is also trying to implement the adhesive based metal joints technology that is used by the aerospace industry from decades and

has gain better results with the use of adhesive for joining load-bearing components [26].

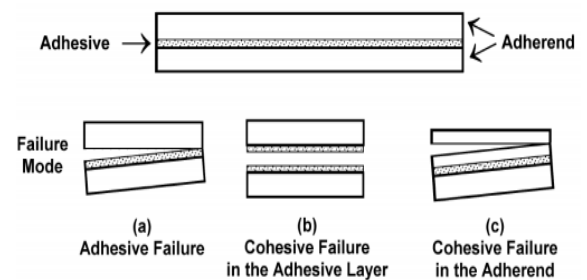


Figure 4: Various modes of adhesive bond failure [25]

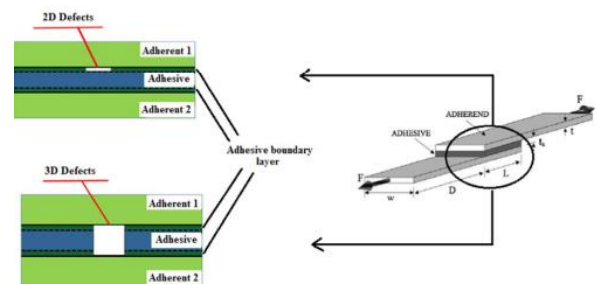


Figure 4: Joint Configuration [29]

At present, the structural adhesives present for adhesively bonded metal joints are very little. For the greater and wiser use of this technology and to improve adhesive joint behavior, a handsome data is required. Single-lap joint strength test is most common and widely known test used to study bond strength of adhesively bonded metal joints. Adherend/substrates are taken to make adhesively bonded single lap joint and these joints can be subjected to bending or in tension (In some cases both together). The two defined loading conditions are used to study the joint strength of these bonded joints. ASTM D1002 standard is used for the making of adhesively bonded metal joints specimens for testing [27]. This test is designed to determine adhesive durability related to given environment, adhesive strength and adherend surface preparation. Two metal specimens are taken as adherend. With the use of adhesive, these metal specimens are bonded together to form a lap joint and cured as per specified time. The specimens with adhesively bonded lap joint are then subjection to lap shear test using universal testing machine (UTM) and are pulled at a rate of 1.3 mm/min until rupture of joint occurs. The grips of UTM are used to secure the alignment of the test specimens, so that load must act across the centerline of the specimen joint. Failure of the joint can be both adhesive (separation of adhesive from any of the substrate) and cohesive (adhesive fall apart from itself). Joint configuration of lap shear specimen is presented in figure 5. The

recommended wide of lap shear specimen is (1") 25.4 mm, with an overlap length of (0.5") 12.7 mm. The recommended specimen metal thickness must be 1.62 mm (0.064"). The overall length of adhesively bonded metal specimen should be (7") 177.8 mm. It is recommended that specimen failure must occur within the adhesive but not at the adhesive, substrate interface [27, 28].

3 Theories of adhesion:

There are numerous theories of adhesion which are discussed below

3.1. Adsorption Theory:

Adsorption theory was introduced by Schonhorn & Sharpe [30]. The most extensively used theory in adhesion science. The theory consider that adhesion will dependent on the substrate because of intermolecular/interatomic forces are entrenched at the interface and provided close contact is obtained [9, 30, 31]. Most common interfacial forces result from Lewis Acid-Base interactions and Vander wall forces. The adsorption theory called thermodynamics theory (also known as Acid-Base and wettability theory). As a result of the magnitude that created by using these forces can mostly be linked to thermodynamics quantities (e.g. surface free energies) of both adherend and adhesive. Usually when a strong joint is formed it comes as result of the combination of liquid and solid contact and for that purpose a good wetting on the surface of the substrate is very essential. Adsorption theory includes a bundle of models that are conceive as separate theories (chemical adhesion model) rheological and wetting. In epilogue of this theory states that adhesive must be able enough in making a sufficient wettability to make a strong bond between the substrate and adhesive [32].

3.2. Diffusion Theory:

Diffusion theory illustrate that adhesion strength of polymer to themselves (autohesion) or with one another is the fact due to mutual diffusion (interdiffusion) of macro molecules all over the interface and it creates an interphase. Diffusion theory was proposed by Voyutski [33] and describe that when both adhesive and substrate are polymer in nature than it will be more compatible [34]. In inter-diffusion phenomena adhesion strength mostly depend on following factors including temperature, molecular weight, contact time and nature of polymer. Figure 4 is classical representation of diffusion theory.

Vasenin [36] develop a quantitative model from Fick's first law that is used for theory of diffusion and it correlate with the amount of material w , diffusion in a specific direction x and across in a unit area to the gradient concentration $\partial c/\partial x$ and at time

$$\partial w = -D_i \partial t \frac{\partial c}{\partial x} \quad (1)$$

Where D_i is used as a diffusion coefficient.



Figure 5: Schematic Illustration of Diffusion theory [35]

To calculate the penetration depth of the molecule that are inter diffused into the region of junction during a constant time t , it was supposed that variation of time with D_i was make a form $D_i t^\beta$ where D_i is the constant characterizing the mobile chain mobility and the order of β is 0.5. While seeing all these it could be possible to reduce the penetration depth LP as well as number of N_c of the chain crossing the interface as described in equations (2) and (3).

$$LP \approx k (\pi D_i t^{1/2})^{1/2} \quad (2)$$

$$N_c = \left(\frac{2Np}{M}\right)^{2/3} \quad (3)$$

Where "k" is known a constant, "N" is known as an Avogadro's number, p is density, M is the molecular weight of the polymer. After that finally Vasenin work on the measured peel energy and it conclude that G was proportional to both the penetration depth and number of chains that are crossing the interface between two polymers. Comparing equation 2 and 3, Finally G becomes

$$G \cong K \left(\frac{2Np}{M}\right)^{2/3} D_i^{1/2} t^{1/4} \quad (4)$$

where in equation K is used as a constant depends on the molecular characteristics of polymer in constant. Eq.(4) found very good agreement in junction of polyisobutylenes of different molecular weight[36]

3.3 Electronics/ Electrostatic Theory:

Electronics theory of adhesion is mostly known by using different names e.g. electrostatic theory of attraction, electrical adhesion theory mechanism, parallel plate capacitor theory and it was proposed by Deryaguin and their Coworkers in 1948 [37, 38] as shown in figure 5.

Scientists suggests that two material when join at the interface, then mechanism of electron transfer between the substrate and adhesive which have difference in electron bond structure could be helpful in equalizing the Fermi levels [9]. Deryaguin and their co-workers

proposed that when electrostatic force would act as a resultant then it will significantly contribute in the strength of the adhesion.



Figure 6: Working principle of electrostatic theory.

In other words, when one surface carries a net +ve charge and other carries a net -ve charge then the force of attraction between two surfaces will increase in case of ionic bonding and acid base interaction. It is to be assumed that due to change in electrostatic charge between different surfaces may cause a reason to enhance the force of attraction bonding, as attraction is definitely very helpful in increasing the bond strength of the interface. G Von Harrach and Chapman showed that contribution of electrostatic force in peel strength that is estimated from the measurement of charge densities could be negligible[39]. Finally, strength of the interface mostly depends on the density of charges and this attraction is unlikely to contribute in the bond strength of the interface[40, 41].

3.4. Weak boundary Layer Theory:

Weak boundary layer theory is important as know it is observed that modification and alteration of adherend and adhesive can play an important role in the scenery of the interface that helps in the making of an interfacial zone which exhibit properties that are different from bulk materials. Bikerman [42] said that the important factor to measure the level of adhesion would always be cohesive strength of a weak boundary layer even if the failure or crack appears in the interfacial zone. According to Bikerman the measured adhesive energy “G” that is taken as equal to cohesive energy G_c of weak interfacial layer. Good and Bascom [43, 44] were two researchers who stated that the stress concentration and stress distribution in the material near tip of crack shows that the failure must disseminate very near to the interface but it also imply that failure is not at the interface. After that much attention was thrown on in the formation of interfacial layer and it starts a new concept of “thick interface” or “interphase” in adhesion science [45]. Surface morphology which include plasma treatment can mostly degrade polymeric substrate and as a result it makes a weak boundary layer and this weak boundary layer should be eliminate for an adhesive to make a strong grip[3, 46, 47]. Bikerman [42] shows that mostly separation and failure of structure take place at

interface (see figure 6), although mechanism effects the strength of joint but assembly strength only depends on the majority properties of the substrate Figure 7 graphically represent seven classes of weak boundary layer that cause failure.



Figure 7: Weak bonding interface [48]

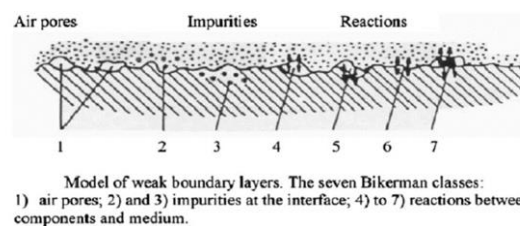


Figure 8: Seven classifications of weak boundary layer [42]

3.5 Chemical Bonding Theory

Chemical bonding theory is known as the oldest theory. It is clearly understandable that the formation of chemical bond across the adhesive substrate interface can increase the adhesion level between two different materials [49-52]. In general, these bonds are considered as primary bonds if come in examination with the physical interaction, on the other side van der Waals is known as secondary force interactions. Secondary and primary term is from the relative strength of bond energy of each interaction type. Strength of covalent bond is from 100-1000 KJ/mol and strength of hydrogen and van der Waals interaction bond do not exceed from 50 KJ/mol. Formation of bond that is chemical in nature mostly depends on the reactivity of the substrate and adhesive [53]. Chemical and physical behavior of matter depends on the nature of chemical bonding. Molecular bonding is a mechanism that is famous for briefly explain the adhesion between different surfaces that are in close contact [3].

Another important area of adhesion that involve interfacial chemical bond is the use of adhesion promoter molecules known as “Coupling agent” and is used to enhance the joint strength between substrate and adhesive. Coupling agent has ability to react chemically with one side of the substrate and on the other side of the polymer as result it creates a chemical bridge at the interface. Silane molecules in coupling agent are a common type of adhesion promoter[54, 55]. Rider et al [56] stated that silane coupling agent usually perform two major functions to improve the durability of a joint

strength, first it will help in increasing the strong bond density that occurs between adhesive and oxide, second it will increase the hydrolytic stability of inorganic surface[57-59]. Reactive molecules such as organo-functional silanes RSi(OR)_3 are used as cross linkers for moisture curing silicone elastomers[60]. Adhesion includes the directly interaction of the solid surface and polymer caused by van der Waals forces to chemical forces. Covalent forces are effective when the distance between molecules and atoms do not exceed 0.5 nm, van der Waals and ionic forces become active at distances of from 1nm to 10 nm. The adhesion process completes with the inter-atomic interaction of contacting phases that complies minimum surface (interphase) energy. Primarily, polymer interacts by van der Waals and electrostatic interaction with contacting surface by electrostatic and van der Waals interaction as represented in Fig. 8. Owing to these forces, the bonds developed between these contact surfaces are accompanied by junctions (chemisorption or physisorption) established on the contact spots. Polymer chains adsorptions proceeds with assumption of molecular bonds formation between polymer solids due to the occurrence of instability of the energy at the interface. In such case, induction, dispersion, ionic, orientation and hydrogen inter-molecular bonds could be involved. Polymer chains chemisorption describes the adhesion phenomena from the perspective of the strong chemical bond's appearance between the contacting points of mostly ionic or covalent type. Chemical bonds become active generally 1-1.5 Å and, thus, substantially stronger than the inter-molecular bonds. The adhesive constituent of friction is controlled by the development and rupture of the junctions[61]. Hydrogen bonds and van der Waals are common for the bulk of polymers[62]. Hydrogen bonds in polymer consisting COOH, NHCO and OH develop at short distances, wherein hydrogen atom is connected with the electronegative part. Under favorable circumstances, two nearing atoms are bonded/joined by electron providing a stable and strong compound. Owing to the application of tangential force; sheared junctions induce the frictional force. In other words, the work carried out by the frictional force emerges from the interfacial bonds' breakdown. Generally, the growth, formation and fracture of the interfacial junctions are affected by the surface chemistry, surface nature and the loading conditions (surface layer stresses). The junctions between the interfaces collectively with their fracture products and localized deformed layers, are named as "third body"[63].

3.6 Wetting Theory

Wetting theory is schematically presented in figure 9 which illustrates that adhesion derives from the

molecular contact of two materials and developed surface forces between them. The first step in forming bonds is the development of interfacial forces between the adhesive-substrates interface. The process of continuous contact formation between the adhesive-substrate interfaces is called wetting. For an adhesive to completely wet a solid surface, the surface tension of adhesive should be lower than the critical surface tension of the solid, which is considered as reason for treatment of the plastic surface.

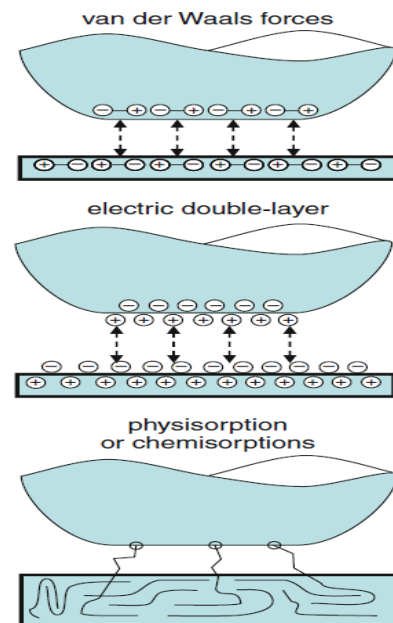


Figure 9: Schematic illustration of adhesive interaction between polymers[64]

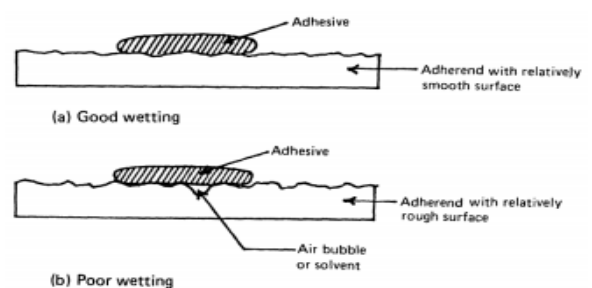


Figure 10: Working principle of wetting Theory [48]

4. Surface energy Estimation

Several theories have been proposed to measure the surface tension of different material by utilization of polymer. Sample surface energy is a consideration of sample surface tension. A list of methods for the calculation of surface energy of solids are available and they directly depends upon the selected liquid to be tested and the surface to be examined[65, 66]. Some of these approaches are (a) The Owens Wendt method [67] (b) Zisman plot approach [68] (c) Good-Girifalco

interaction approach[69, 70] (d) A method proposed by Schultz[71] (e) van Oss, Good, and Chaudhury approach [72] (f) Good and van Oss approach [73] (g) Fowke's and co-workers[74-76]. The Owens Wendt introduced a new and advance method of the analysis of differences in the surface free energy values of a given solid and calculated it by using the Owens-Wendt and Neumann method and two measuring liquids, water and diiodomethane.

The main concept of the analysis bases on the differences in surface free energies, which occur under a specific condition and nevertheless of both the accuracy and the performing conditions of the contact angle and the given measurements. These differences result for the use in different relationship in mathematical formulation between contact angle and surface free energies in each of the methods[77]. Fox and Zisman stated that $\cos \theta$ is a linear function of γ_l . Plotting the points that is used for many liquids and fitting a line in them, we can obtain a critical surface tension γ_c by compute the line to $\cos \theta = 1$. γ_c is closely related to Surface free energies of a solid[78]. γ_s (Surface free energy of solid) can be calculated by using the exact measurement of equilibrium contact angle on a solid surface and by using a series of tests liquid while providing the relationship between solid γ_s , γ_a and liquid γ_l . Girifalco and Good introduced the exact equation to find a relationship between surface free energies as:

$$\gamma_a = \gamma_s + \gamma_l - 2\gamma_s \gamma_l \gamma_l \quad (5)$$

$$\gamma_s = \gamma_{sv} + \pi_e \quad (6)$$

where π_e is known as equilibrium spreading pressure and ϕ is the Good- Girifalco interaction parameter. Mostly π_e is difficult to exactly measure and usually used to neglect π_e [79]. Another effective method is also proposed by Owen-Wendth to show a relationship of work of adhesion(W_a) [67]. The equation is:

$$W_a = W_a^d + W_a^p \quad (7)$$

where W_a^d is derived from London dispersion forces and W_a^p is derived from non-dispersive e.g. acid base interaction. Initially Fowkers take that dispersion forces interaction is only applicable by using solid liquid interface but after further study the equation developed for the dispersion component of geometric means in both liquids

$$\gamma_a = \gamma_s + \gamma_l - 2\gamma_s \gamma_l \gamma_l^d \quad (8)$$

by using Youngs's equation, we can change the Fowker's equation

$$\gamma_l (1 + \cos \theta) = 2\gamma_s \gamma_l^d \quad (9)$$

By using above equation we can calculate the surface free energies of the dispersive interaction of system and for the calculation of complex system this equation is not reliable but still we can get some useful approximates[80]. The work of adhesion can easily be represented by geometric mean of dispersion where only dispersion forces are involved

$$W_a^d = 2\gamma_s \gamma_l^d \quad (10)$$

Kin and Lee were the scientists who worked and calculated the dispersion component γ_s^d and polar component γ_s^p of the surface free energy of epoxy/carbon composite and for that purpose they use equation of geometric mean to make a combination of dispersive and polar component together by using the measurement of contact angle of glycerol drop and water. Glycerol drop and contact angle of water are inversely proportional to the surface free energies as show in figure 12.

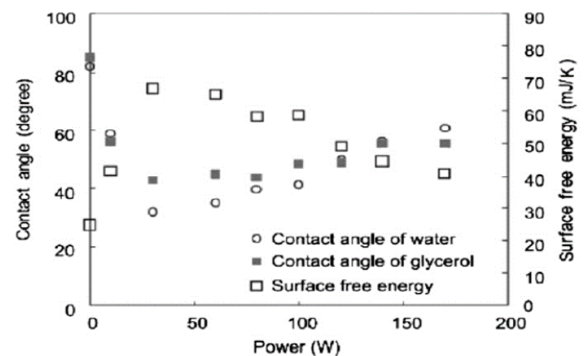


Figure 11 : Contact angle of water and glycerol drop and the surface free energies of epoxy/carbon composite calculated from the contact angle [81]

Further study was also been developed to show the behavior of the contact angle of water drop on the surfaces that are treated as plasma surface treated epoxy/carbon composite and the other one is not treated. The results shows that there is a decrease in the contact angle of liquid drop on the epoxy/carbon composite when it is treated by plasma surface because there is a rapid increase in the surface free energies of epoxy/carbon composite[81]

5. Effect of Surface roughness on the wettability

To make a good and strong adhesive joint a very major role plays by the design parameter and that design parameter mostly used as the roughness of adherend surface [82]. Many scientists and researchers have been tested and examined the effect of surface roughness to the durability and strength of adhesive joints by using different adhesives and adherends but till now there is no satisfactory data that relates and linked the strength of joint to the surface parameters[83-88]. An experiment is performed by using profilometry and scanning electron

microscopy (SEM) on the adherend surface and it discover that all the material surfaces are always rough when molecule scale is approached. Further studies developed a concept that there is always a change in the surfaces of engineering materials, which effects the differences in the composition or structure of the surfaces as initially they were seemed to be examined. In adhesion both physical and chemical nature of surfaces are very much important and can alter the strength of adhesive joint. Chemical nature can increase or decrease the reactivity of adherend surface toward the adhesive[13]. Fundamental characteristics of wetting and surface free energies affect the stability and strength of adhesion. Sancaktar et al said that adhesion process can be strong by surface treatment and it could be possible by doing surface pretreatment e.g. by removing of etching and abrasion.

If we remove weak boundary layer and improve the wetting behavior, then effective bonding will be occurred by complete spreading the adhesive over the surface and as a result effective bonding will help to make an effective and strong joint of the polymer. Capillary forces and viscosity of adhesive also effects the penetration of adhesive into the surface crevices, but penetration and spreading do not ensure the removal of air from the cavity on the surfaces. To ensure a satisfactory level of bond strength surface pretreatment is very necessary for some surfaces [89]. Shahid et al [82] believe that although many methods used to increase or decrease the roughness of surfaces but the most effective method for control and to achieve the optimum surface roughness is grit-blasting. Grit-blasting is the method that can remove the weak boundary layer and could also change the chemical characteristics of the required adherends [88]e.g. work on steel cleavage specimen showed that grit-blasting is more effective to achieve required cleavage strength than diamond polishing[90]. Adhesion and roughness are not very simple in relationship, and to attain optimum surface profile there are any other factors e.g. types of applied stress, types of adhesive etc. that directly or indirectly affects the making of a strong joint[91]. Bikerman [42] reported that when a liquid spread into the surface of topographical valley then the air that is already present in the tiny holes of surface could effects the strength of the joint and the air pockets are not good in making a strong bonding strength of the material, so care must be taken in making an intimate contact with the adherend surface.

Many Scientists and researchers use powder to alter the surface roughness [92]. Contact angle could possibly play a vital role in making a strong grip between substrate and adhesive[93]. Wenzel

introduced a parameter “R” to explain the behavior of surface:

$$R = \frac{\text{Total surface area}}{\text{Apparent geometric area}} \quad (11)$$

Wenzel assumed that roughness decreases as the value of “r” increase, generally it is believed that with the increase in roughness value the apparent contact angle decreases. However, wetting of a surface is a kinetic process and initially the liquid must advance on the surface. It is noticed that if the ultimate equilibrium contact angle is zero, the advancing contact angle is never be zero but it is only a part of the rate of movement of the liquid [94]. Polymer matrix composites are used to meet non-structural and structural functional requirements in the large-volume applications namely, agricultural equipment, automotive, rail cars, civil infrastructure, sporting goods, in-shore and offshore marine and bridge rehabilitation. An important factor, polymer-polymer interface performs a critical role in the economic competitiveness of composite manufacturing. Ten prime polymer-polymer interfaces have been tabulated in figure 13 [95].



	Liquid B (L)	Solid with As-Cast Surface (S _v)	Solid with Fractured Surface (S _f)	Solid with Fractured and Treated Surface (S _{fc})
Liquid A (L)	L-L Virgin (Control)	L-S _v Repair/recycling	L-S _f Repair/recycling	L-S _{fc} Repair/recycling
Solid with as-cast surface (S _v)		S _v -S _v Welding	S _v -S _f Welding/repair	S _v -S _{fc} Welding/repair
Solid with fractured surface (S _f)			S _f -S _f Crack healing	S _f -S _{fc} Wear/repair
Solid with fractured and treated surface (S _{fc})				S _{fc} -S _{fc} Wear/repair

Figure 13: Table of important interfaces confronted during recycling, joining, repairing and manufacturing of Polymeric composites[95]

The interfaces mentioned in the table studied by a simple experiment shown in figure 14 which involves compact-tension (CT) samples with A and B halves. In the A-B contact plane, an interface can be formed by assembling two halves of CT specimen. The A-half might be only Liquid (L), a solid having as-cast surface (S_v), a fractured solid surface (S_f) and either fractured chemically treated surface (S_{fc}). Correspondingly, B-half can also be the one among the four. Consequently, there are ten interfaces with six interfaces of solid-solid and three liquid-solid interfaces and one virgin (control) liquid-liquid interface, including joining, recycling, repair, crack healing, welding and wear. Damage can occur in the operational life of the structural composite component and economically it is more practical to repair the damage than the complete replacement. Repairing may include different processes in the following ways: (a) a fresh mixture of the liquid polymer can be poured at the surface of fracture solid and cured in-situ. This technique includes L-S_v interfaces.

(b) The damaged portions can be kept together and annealed above T_g temperature in order to heal the crack. This methodology would include S_i-S_i interfaces and (c) The damaged pieces can be bond together with an adhesive. Whichsoever technique is employed, it is anticipated that the virginal strength of the repaired material is restored. Bonding/joining is another vital fabrication procedure that has significant potential in the advanced applications like agricultural equipment, composite armored vehicle, whereby composites of different kinds are bonded together utilizing thermoset adhesives. Additional applications include adhesion bonding of cross-linked dental teeth with denture-based resin[96], fabrication of electronic materials, net shaping utilizing thermosets, etc. The bonding/joining technique would include interfaces of $L-S_i$ and bonded strength of the material is dependent on the $L-S_i$ interface strength.

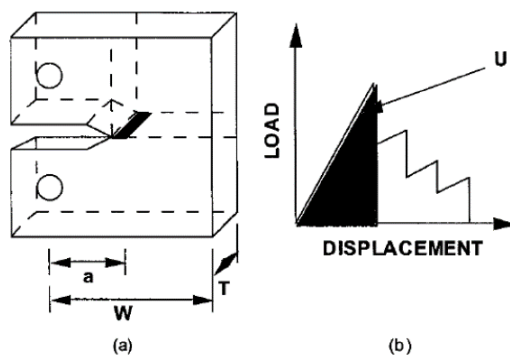


Figure 12: Illustration of (a) CT specimen and (b) Load-displacement curve

6. Summary and Outlook

The scientific world is facing a serious problem of developing advance techniques and methods to optimize the joint strength of polymeric materials, as a number of factors affect the phenomena of adhesion which include surface pre-treatment, type of adherend and adhesive, adhesive thickness, adhesive bonding and test conditions. Adhesion bonding contain a delirious interdisciplinary because it always involves different interpretations in a same circumstance by the researchers of different disciplines. Prime aim of the study of adhesion bonding technique is to understand the behavior of mechanical properties and to estimate the durability of the adhesive polymeric joint on different surface roughness. Adhesion is purely a surface physico-chemical phenomena and character of the surface of the substrate depends on the physically properties of the adhesive joint and the adhesive that interact with the substrate. Physical bond of wander waals category is mainly responsible for showing the liquid interfacial tension and surface tension. Acid base interaction, Hydrogen bonding interaction, polar interaction, Universal wan der Waal interaction and intermolecular interaction

generates when two smooth polymeric surfaces met each other while having few nanometers. The strength of the joint depends on the quality of the contact angle between the substrate and adhesive. Many surface characterization techniques are used to investigate the chemical and physical properties of the joined surfaces related to adhesion strength and adhesion mechanism (a) X-ray photoelectron spectroscopy (XPS), (b) Atomic force microscopy (AFM), (c) Scanning electron microscopy (SEM), (d) Time of flight secondary ion mass spectroscopy (ToF-SIMS), (e) Attenuated total reflectance infrared spectroscopy (ATR-IR). An adhesion phenomenon requires the knowledge of many disciplines include mechanics, material and chemistry to make a good grip on the adhesion bonding techniques. As conclusion, in order to fabricate outstanding firmad adhesive bonded joint with comprehensive understanding have brighter future in the field of polymeric structure with high strength and light weight.

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APPENDIX - I

Table 1: Comparison of various adhesives reported so far

	Adhesive	Surface Enhancement Technique	Results	Reference
1	Epon 815 and 830	Sand blasting at 552 KPa and Etching for 2 to 10 minutes with chromic acid	Specimens were prepared by maintaining average surface roughness value from 7 μm to 17 μm . These specimens were tested under two loading conditions (100 mm/min and 1 mm/min). It was concluded that the failure occur more rapidly during 100 mm/min loading rate and the cold rolled specimen in comparison with hot rolled specimens showed higher reduction in failure load values.	[13]
2	Diglycidyl epoxy called bisphenol A	1-Mechanical abrasion (abraded with scotchbrite and alkaline cleaning was done) 2-Free-chromium etching pretreatment, based on a sulphuric acid-ferric sulphate solution	Reports shows that Free-chromium etching pretreatment, based on a sulphuric acid-ferric sulphate solution provides higher strength values than the common abraded treatment.	[14]
3	Resin PE A, PE B (catalyst butanox M50) and EPO (catalyst SD 8822)	Mechanical abrasion with P 180 and P 40 grade grinding paper	It was illustrated that PE A and PE B resin showed less effect of roughness on joint strength but EPO showed greater effect of roughness on joint strength.	[15]
4	Araldite 420 A/B	AP abrasive polishing, CE (caustic etch), TR Tucker's reagent, CSA CSA etch:	It was seen that abrasive polishing and CSA pretreatment techniques provide more joint strength then the other one.	[16]
5	Bi-component Epoxy	At room temperature, specimens undergo ultrasonic treatment in 0.1 M NaOH solution for varying times of immersion, namely, 5, 30 and 60 min.	Aluminum adherends with dilute NaOH treatment showed more 20 percent increase in joint strength than the specimens tested just after decreasing.	[17, 18]
6	C45 steel	Grinding with silicon carbide sheet and lapping	The highest repeatability of results and shear strength was obtained when specimens undergo lapping III surface pretreatment and tested under tensile test which was upto 26.7 MPa.	[18]
7	Araldite GZ7 7071X75	zirconium-based conversion coating	Surface treatment of aluminum by Zr conversion coating caused to increase in surface roughness and surface free energy. The adhesion of the epoxy coating to the aluminum surface increased significantly after Zr treatment of the aluminum surface.	[19]
8	Polyurethane	Abraded with three grades of silicon carbide sheet (1000, 180, 50)	Results witnessed that not only surface roughness greatly alter the bond strength but the contact angle also alter the bond strength of adhesively bonded joints.	[20]
9	Epoxy resin supplied by M/s.Hunts-man India pvt. ltd.,	solvent decreasing and FPL etching	It was observed that the shear strength obtained after FPL etching was up to 20 MPA and shear strength obtained after solvent decreasing was upto 13 MPA.	[21]
10	Aluminum 2024 T3	Chromic acid anodizing and sulphuric acid	The specimens those were pre-treated with SAA showed 8 percent better results than the other one.	[22]