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M. Sc. in Mechanical Engineering

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UNIVERSITY OF GAZİANTEP

GRADUATE SCHOOL OF

NATURAL & APPLIED SCIENCES

INVESTIGATION OF THE EFFECT OF NANOPARTICLES ON ADHESION OF SINGLE LAP JOINTS IN COMPOSITES

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BILAL FAAEK AHMED AHMED

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Supervisor

Assoc. Prof. Dr. Ahmet ERKLİĞ

by

Bilal Faaek Ahmed AHMED

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This is to certify that we have read this thesis and that in our consensus opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Bilal Faaek Ahmed AHMED

ABSTRACT

INVESTIGATION OF THE EFFECT OF NANOPARTICLES ON ADHESION OF SINGLE LAP JOINTS IN COMPOSITES

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Adhesively bonded joints of fiber-reinforced polymer structural components offer numerous advantages, including high strength and high stiffness-to-weight ratios, good fatigue and corrosion resistance, and high-energy absorption capacity, all of which make them more efficient compared to mechanical fasteners. Many techniques have been used to strengthen ABJs such as use of fillers, hybrid joints, and co-cured joints. The vast majority of studies have been focused on using filler materials for technical and economical reasons. In this study, three types of Nano-fillers (Nano-clay, Nano-silica and Nano-graphene) were used to reinforce epoxy resin. Based on weight content of epoxy; clay, silica, and graphene were added by (1, 2, 3, and 5 %), (1, 2, and 3 %), and (0.1, 0.2, 0.3, 0.4, and 0.5 %), respectively. Glass fiber reinforced polymer plates produced commercially were used as adherends. The experimental results obtained from lap shear test and 3-point bending test, have demonstrated that the three types of Nano-fillers positively affected the joint strength. The highest improvement in shear and flexural strength was obtained by adding graphene particles as 145% and 100%, respectively. As the joint strength increased with the Nano-particle inclusion, the adhesive failure mode of the neat epoxy joints was changing to more and more progressive mode. The most important failure mode was observed in the fracture surfaces of the joints prepared with graphene particles.

Keywords: Nano-particle, bonded joints, nano-clay, nano-silica, nano-graphene, epoxy, single lap joint

ÖZET

KOMPOZİTLERDEKİ TEK BİNDİRMELİ YAPIŞTIRMA BAĞLANTILARINDA NANO PARÇACIKLARIN ETKİSİNİN ARAŞTIRILMASI

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Haziran 2018
89 sayfa

Fiberle güçlendirilmiş polimer yapısal bileşenlerin yapıştırılma bağlantıları, yüksek mukavemet ve yüksek sertlik-ağırlık oranları, iyi yorulma ve korozyon direnci ve yüksek darbe enerji emme kapasitesi olmak üzere, bunların hepsinin mekanik tutturucularla karşılaştırıldığında daha verimli olmasını sağlayan çok sayıda avantaj sunar. Dolgu maddeleri, hibrit eklemler ve yardımcı kür eklemleri gibi yapıştırma bağlantılarını güçlendirmek için birçok teknik kullanılmaktadır. Çalışmaların büyük çoğunluğu, teknik ve ekonomik nedenlerle dolgu malzemelerini kullanmaya odaklanmıştır. Bu çalışmada, epoksi reçinesini güçlendirmek için üç tip Nano dolgu maddesi (Nano-kil, Nano-silis ve Nano-grafen) kullanılmıştır. Epoksi ağırlığına göre içeriğine; kil, silika ve grafen sırasıyla 1, 2, 3 ve 5%, 1, 2 ve 3% ve 0.1, 0.2, 0.3, 0.4 ve 0.5% oranlarında eklenmiştir. Ticari olarak üretilen cam elyaf takviyeli polimer plakalar yapışma yüzeyi olarak kullanıldı. Lap makaslama testi ve 3 nokta bükme testinden elde edilen deneysel sonuçlar, üç tip Nano dolgu maddesinin yapışma gücünü olumlu yönde etkilediğini göstermiştir. Kesme ve eğilme mukavemetinde en yüksek gelişme, sırasıyla,% 145 ve % 100 olarak grafen parçacıkları ilave edilerek elde edildi. Nano-parçacık eklenmesiyle yapıştırma mukavemeti arttıkça, saf epoksili yapıtırıcıya göre kırılma modunun değiştiriği görülmüştür. Grafen parçacıkları ile hazırlanan numunlerin kırılma yüzeylerinde en önemli kırılma modu gözlenmiştir.

Anahtar Kelimeler: Nano-parçacık, yapıştırma bağlantıları, nano-kil, nano-silika, nano-grafen, tek bindirmeli bağlantı

This Thesis Is Dedicated To ….

My parents, my brothers, my sisters, my family, and my friends for their continuous support and never ending love and encouragement ….

WITH GREAT LOVE

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CHAPTER 1

INTRODUCTION

1.1 Introduction to Adhesive Bonding

Materials joining approach in which an adhesive, positioned between the substrates surfaces, solidifies to present an adhesively bond is known as "Adhesive Bonding". The application of these bonds in structures made of fiber reinforced polymers has increased considerably in the last some years. The conventional fasteners often result in permanent damage for fibers, and hence introduce stress concentration points, both of which reduce the structure integrity [1].

Adhesive bonding approach offers many advantages compared to other joining techniques. These advantages include smaller weight, tightness, avoidance of drilled holes, ability to bind thin and dissimilar sheets, elimination of the galvanic corrosion, good sealing, good vibration and damping properties, low manufacturing cost and energy, and uniform distribution of stress or reduced concentrations of stress (Figure 1.1). These features are reasons of longer fatigue life and higher fatigue resistance than traditional joining techniques [2-4].

Adhesively bonds have continuous bond areas than localized areas of contact emerging in mechanical fasteners and hence they offer better stiffness when compared to mechanical fasteners [5]. However, once a crack is started in the bond line under mechanical loading, the crack may propagate so readily depending on the nature of adhesive material, whether it is brittle/ductile or not. In a brittle material crack propagation is very quick and once crack is started it will take very short time for the whole material to fail. In ductile materials the crack propagation is comparatively slow and may take longer period than brittle material to fail depending on the applied load. Once a crack has initiated in the adhesive layer it is so hard to repair it. Then the entire structure or at least the adhesively bonded components will have to be replaced [6].

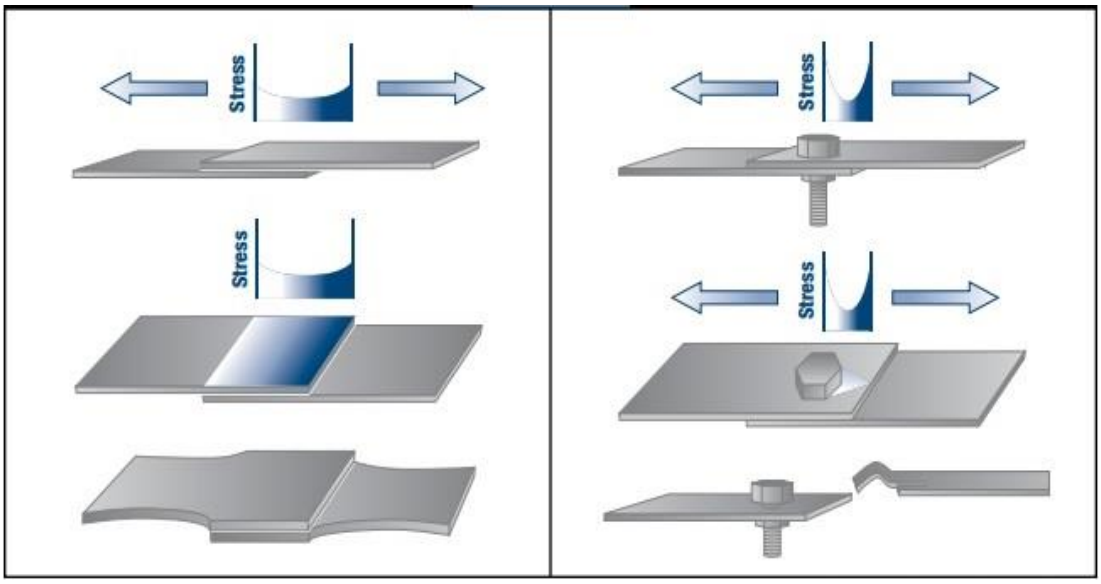


Figure 1.1 Stress Distribution Through, (a) Adhesive Joint, (b) Bolted Joint

1.2 Adhesive Bonding vs. Mechanical Fastening

There are some ways for joining dissimilar or similar materials. The first way which is extensively used in metallic structures is mechanical fastening where rivets or bolts are utilized. It is simple way, and possible to obtain high strength of joining with small scatters [7]. Traditional mechanical joints are preferable due to its simplicity and ease of destruction required to join metals or composite materials [4]. However, it has disadvantages of low sealing performance and an increase in weight of the structure [7]. Also, when a high load is given to the mechanical joint, the local damage will take place at bolt/rivet holes due to stress concentration. This fact damages the structural integrity of the joint and leads to the degradation of structural links [4]. In addition, presence of the bolt/rivet holes in mechanical fastening reduces the cross-sectional area of structural components, and increases the stress concentration [7].

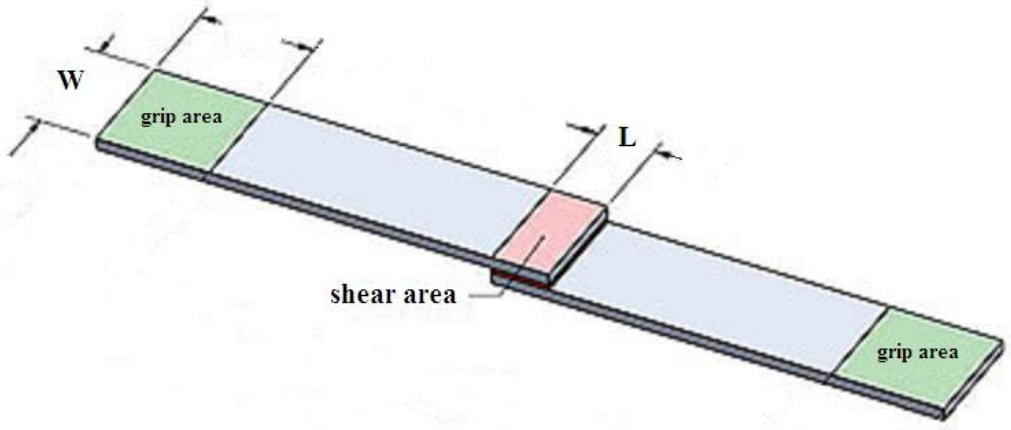
Generally, the failure of a large structure returns to minor damages at the points where components are linked. As a result, it has been affirmed that effective joint design and decreasing the number of joints are of utmost importance. The most popular joining way is the mechanical joining, such as pinned, riveted, or bolted joints, in both metals and composite materials. Mechanical joints are very simple to produce and are proper choice where structure disassemble is required. The fastener holes of mechanical joints result in micro and local damage to the composite laminate during the manufacturing process [8]. However, Demands for producing light-weight structures with keeping

stiffness and strength have encouraged many designers and researchers to look for an alternative joining way (i.e. using adhesives) [4].

With regard to this context adhesively bonded joints are increasing alternatives to mechanical joints in engineering applications and provide many advantages over traditional mechanical fasteners [1].

1.3 Single Lap Joint

Single lap joint is the most popular configuration used in engineering applications and has been extensively studied. The single lap configuration (Figure 1.2) has been increasingly used in the automotive, wood and plastic, and aerospace industries. Single lap samples are practical, economical and easy to produce. Single lap joints can improve joining efficiency of dissimilar materials. The single lap joint is vastly utilized in adhesive bonding and has been the subject of significant research in the last decades. It also allows easy control and measure of the bond thickness. The simple and efficient design of a single lap joint often enables to evaluate the mechanical properties of the adhesively bonded joints [9].



(**Figure 1.2** Single lap Joint Configuration)

1.4 Types of Adhesives

According to Baldan [10], adhesives can be classified into high temperature adhesives, epoxy adhesives, hot melts adhesives, cyanoacrylates adhesives, acrylics (based thermoplastic adhesives), anaerobic acrylic adhesives, silicone adhesives, urethane adhesives, pressure-sensitive adhesives, latex adhesives, addition-reaction to polyamide adhesives, reactive adhesives, solvent-based adhesives and bismaleimide

adhesives. Adhesives can also be categorized majorly into very brittle adhesive, an intermediate adhesive, and a very ductile adhesive. Brittle adhesive with no plasticity should increases the joint strength with the increase in adhesive bond line thickness while ductile adhesives should increase the joint strength with the decrease in adhesive thickness [11].

1.5 Epoxy as Adhesive

The most popular type of adhesives that are being utilized recently is epoxy based adhesive. The epoxy adhesives are being developed and being fabricated according to the requirement of application in which they are applied. For example, epoxy is being extensively utilized as a structural adhesive with high performance in aerospace, aircraft, and automotive applications. Epoxy resins are of high attraction for adhesive bonding of metal systems because of their low shrinkage during curing (less than 0.5%) and for their capacity to cure without producing volatile by-products [12]. Epoxy adhesives are relatively stuck well to a vast range of metal surfaces even if they are not previously untreated [13]. The essential feature of the two-component epoxy adhesive is that it is suitable for binding almost all substrates types such as plastics, metals, wood products, glass, ceramic, and many kinds of rubber. In addition, epoxy adhesive can offer plentiful beneficial properties such as high failure strength, high modulus, high stiffness, high shear and tensile strength, low shrinkage upon curing, low creep, good thermal and electrical insulation, high resistance to chemicals, good damping properties, good performance at raised temperature, and prevent corrosion between dissimilar metals in bonded joints. On the other hand there are also several influential disadvantages such as high sensitivity to moisture and surface contaminants, low peel strength, the slowness of some curing systems, brittle behavior at low temperatures, poor resistance to crack starting and growth, and high costs [10].

In industrial applications surface preparation, although it has many benefits, is often not implemented accurately for safety and economic reasons. Efficient surface preparation requires a lot of processing time as well as more labor and it is usually done with the help of dangerous tools. Thus, it can be said that structural adhesive properties industrially produced are suitable for use on surfaces of less idealism [14].

1.6 Introduction to Nano-Composite Polymers

In the last two decades, great efforts have been made by the researcher community to evolve Nano-composite polymers. Nano-composite polymers are such defined due to the dimensions of the filler material, which is in the scale of nanometers. In general, the unique combination of specific mechanical properties of Nano-fillers (e.g. strength, stiffness, etc.) and low concentration required to affect the overall properties of the polymers, places Nano-composite polymers among the set of the most advanced materials [15]. The transition of particles from micro-scale to Nano-scale is accompanied by significant changes in the physical properties of the material under consideration. Nano-scale particles are considered superior filler materials due to a large surface area for the given volume [16]. Final properties of the modified polymer depend on the size of the Nano-particles and the degree of dispersing within the polymer.

As the Nano-fillers are usually free of defects, their usage in the area of polymers are considered new trends of possibility to overcome the constraints of conventional micro-fillers. Homogeneous and uniform distribution of Nano-particles in the polymers is responsible for altering relaxation behavior, as well the harmonious mechanical and molecular mobility. Generally, Nano-fillers present in the minor-zone whilst only few of the micro-fillers participate in the plastic-zone deformation. This gives a way for the Nano-fillers to enhance mechanical and fracture properties of the polymer matrix of brittle nature. Nano-fillers having higher aspect ratio (ratio of largest to smallest dimension) are of utmost importance because they present better reinforcement for the Nano-composite polymer production. Their high specific surface area is beneficial to overcome restrictions such as the weak interfacial attractions between matrix polymer and the substrates [17].

1.7 Nano-Platelets

Clay, graphene and silicate based Nano-particles fall under the classification of Nano-platelets. In general Clay Nano-particles has a layered structure consisting of aluminum silicate or hydrous magnesium [18]. Clay type Montmorillonite (MMT) is the most popular filler material used for reinforcing polymers due to its high surface area and low cost as well as surface reactivity. Similar to Nano-clays, natural graphene flakes have a layered structure [19]. In graphene flakes each layer of carbon atoms is

covalently bonded to the other carbon atoms, and these covalent bonds are responsible for providing the overall structural strength. Interlayer spacing between different graphene layers is kept by weaker van der Waals forces. The weak inter-planar forces allow for certain ions, atoms and molecules to intercalate into the inter-planar spaces of graphite.

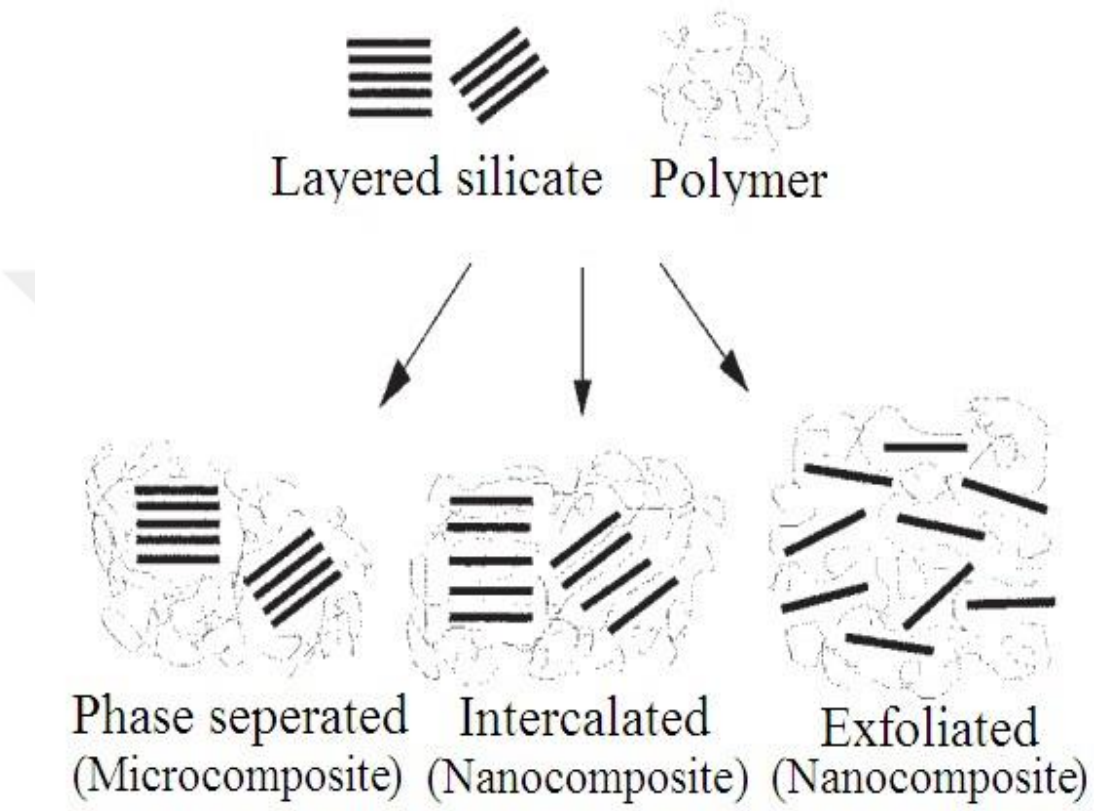


Figure 1.3 Nano-platelets (Nano-composite polymer) [16].

1.8 Objectives of Study

The objectives of this study are as follows:

1. Investigate the effect of various contents of three different Nano-fillers (Nano-silica, Nano-clay, and graphene Nano-platelets) in epoxy adhesive on the shear and bending strength of GFRP bonded joints.
2. Compare the shear and bending strength of the Nano-composite adhesive with the shear strength of the neat epoxy
3. Develop stronger adhesive than epoxy for engineering applications.

4. Recommend the best type of filler among the above three ones which would be given maximum strength.

1.9 Assumptions of Study

1. The dispersion of Nano-filler particles in the epoxy adhesive layer was assumed to be homogenous.
2. The average particle size in the adhesive layer was assumed to be constant for all samples.
3. The surfaces of all adherends were assumed to have the same properties.

1.10 Outline of Thesis

This thesis consists of 5 chapters. Chapter one involves general introduction about adhesive bonding, single lap joint configuration, types of adhesives, epoxy adhesives, and Nano-fillers, objectives of study and assumptions of Study. In chapter two, a literature review about theories of adhesion, adhesive bonding of composite structures, adhesive joints, surface preparation, adhesives, Nano-particles, graphene Nano-platelets, Nano-clay, Nano-silica, and fillers will be given. Chapter three will be concerned with materials and tools, preparation of adhesive material, preparation of single lap joint samples, and mechanical tests. Chapter four presents the results of tensile and three point bending tests to show the effect of Nano-fillers on the shear and bending strength with discussions. Chapter 5 involves a conclusion on experimental study.

CHAPTER 2

LITERATURE REVIEW

2.1 Adhesives

As stated earlier, adhesives in various formats have been utilized for bonding purposes since the dawn of recorded history. However, highly effective methods of bonding have only been developed since the mid-1940s as a result of the evolvement of synthetic polymers as a precursor for technological applications. Synthetic polymers are capable of adhering most materials and enable the transfer of considerable magnitudes of load. The oldest definition of adhesives is attributed to Kinloch, who defined adhesives as a material that joins adherends and resists the dismantling of the adherends [20]. Among adhesives, those that can carry significant loads and in some cases improve the stiffness and strength of the structures are referred to as structural adhesives [21]. Adhesives are available in a wide range of strengths, from 5 MPa to 50 MPa, and in a variety of materials, from polyurethane to epoxy. Prior to being bonded, surfaces are called substrates; after bonding, they are referred to as adherends. Both sealants and adhesives are based on the concept of adhesion. More specifically, while cohesion describes the intermolecular forces inside one material, adhesion involves intermolecular forces established between the interfaces of two substances. These intermolecular and cohesion forces are mainly Van der Waals-type forces [22]. Substances bonded with adhesives or sealants work through either interface or cohesion, or a combination of them. The interphase refers to the zone enclosed by the adhesive and the adherend in general, whereas the interface refers to the contact surface of the adhesive and adherend within the interphase. Mechanical and chemical properties of the interphase differ from those of the adherend or neat adhesive and thus play a significant role in determining the adhesive bond's strength [20].

2.2 Adhesive Joints

Adhesive joints take-on many different classifications depending on their configuration of materials and adhesive. There are many examples of such joints,

including single-lap, double-lap, scarf, bevel, butt strap, and double butt strap as shown in Figure 2.1.

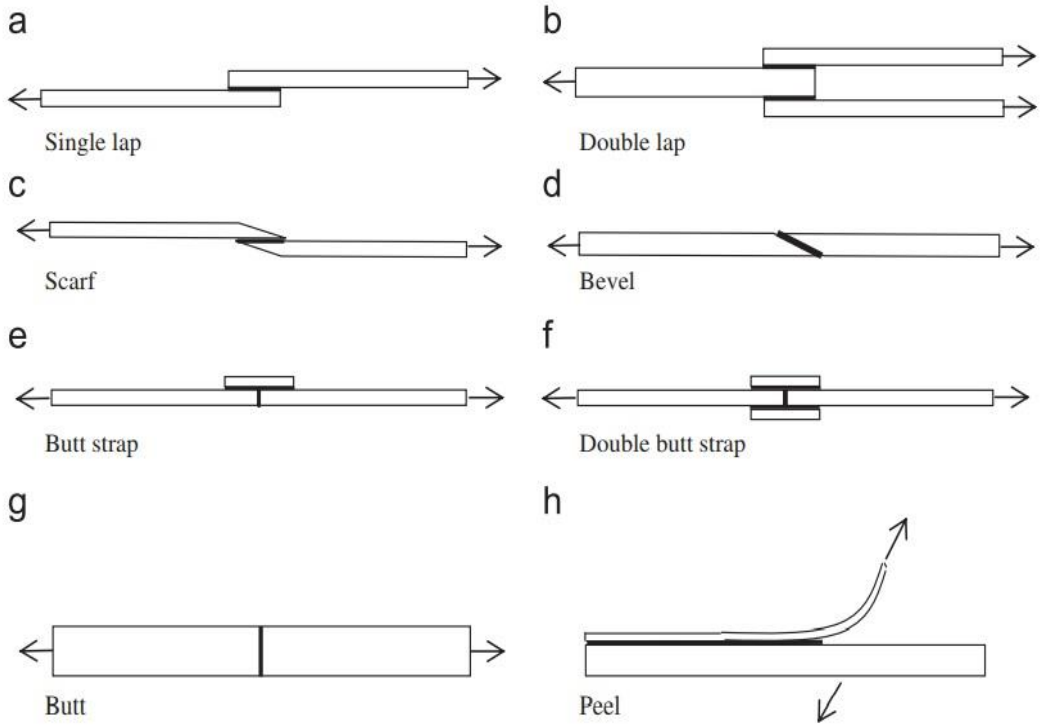


Figure 2.1 Adhesively bonded joint examples [23].

Of these, the single-lap joint (SLJ) has been widely used for investigations of adhesive joints for its simple geometry. A SLJ requires only two materials referred to as adherends to be overlapped and bonded in the overlap system with an adhesive. However, despite the simplistic geometry, SLJs experience complex stress states due to the eccentricity of the load path during tensile loading [23]. In adhesive joint systems, several different forms of failure can occur, each indicating a different cause. For simple cases with uniform materials such as metals, failure occurs either in the adherend, in the adhesive, or in the bond between the adhesive and the adherend. For composite structures, the failure principles are the same, but can be more complex with more modes. The American Society for Testing and Materials (ASTM) identifies seven different identifiable failure modes for fiber-reinforced-plastic joints which are adhesively bonded in their standard ASTM D5573. These include adhesive failure, cohesive failure, thin-layer cohesive failure, fiber-tear failure, light-fiber-tear failure, stock-break failure, and mixed failure (defined as any two or more of the primary six forms of failure) as shown in Figure 2.2 [24].

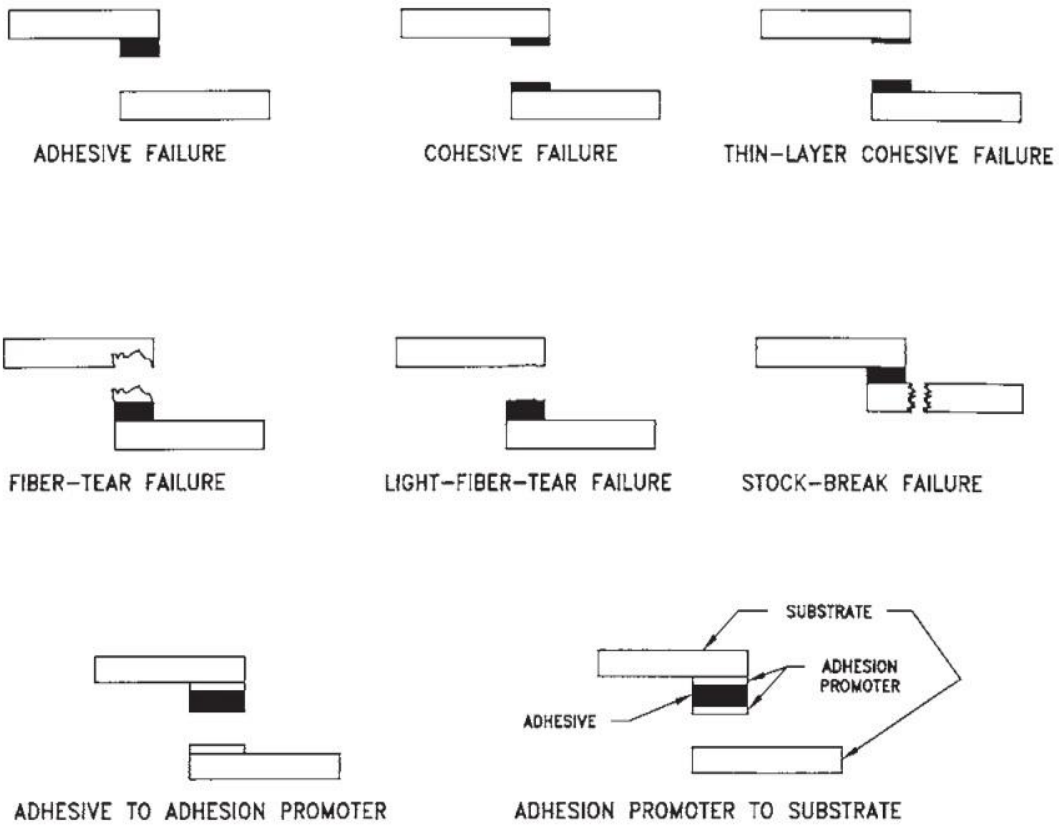


Figure 2.2 Representations of adhesive joint failure modes [24].

Hart-Smith [25] made large contributions to our understanding of the mechanics of adhesive joints, expanding greatly on the previous works of Vokersen's [26] shear-lag model and theories created by Goland and Reissner [27]. Hart-Smith's work in a NASA study evaluated the effects of many factors on SLJ strength and created closed-form solutions for both balanced and unbalanced joints. In balanced SLJs, both adherends are the same thickness and have the same material properties, whereas in unbalanced joints, each adherend may have a different thickness and/or different material properties [25]. According to a study by Moura et al. [28], damage initiation for single lap joints between the adherend and the adhesive occurs in the form shown in Figure 2.3.

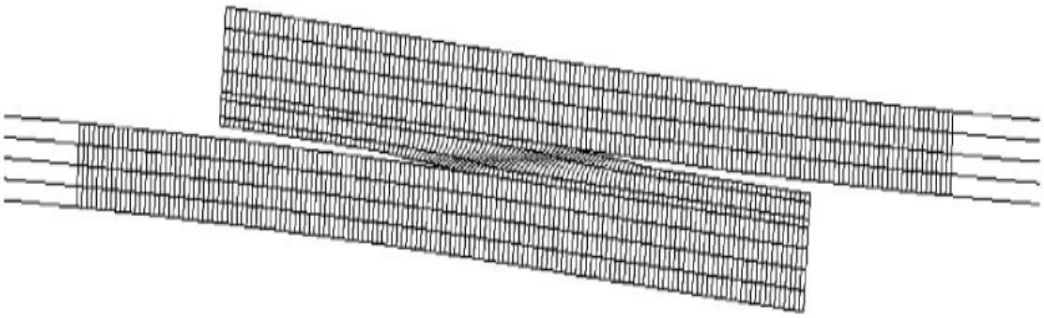


Figure 2.3 SLJ damage initiation mode [28].

In this failure mode, the adhesive begins to peel away from each end of the joint between the adhesive and adherend, in the form of cohesive failure. The study identified that the softening at the ends of the overlap starts to occur at 20% of the maximum load. Then, damage initiation occurs at the critical points at each end of the bond-line between 85% and 90% of the maximum load. It was found that when the maximum load is reached just before the joint ultimately fails, the peeling damage in the bond-line had propagated between 10% and 20% the length of the overlap. Moura et al. made the important conclusion from the study that joint failure at the joint's maximum load does not occur immediately upon the initiation of damage propagation, but instead, occurs during the process of the cohesive failure of the joint. As a result, it was also concluded from the study that bond-line defects nearest an end of the bond-line more greatly reduce the strength of the joint than similarly sized defects nearer the center of the bond-line [28]. Seong et al. [8] conducted a study in which single lap joints of dissimilar materials were evaluated and compared to joints fabricated from metal alone. Their experiments evaluated the joints by means of tensile tests in which the use of strain gauges for data collection were implemented. The study explored the effects of overlap length, curing pressure, adherend thickness, and adherend material types, comparing the strengths of each joint.

2.3 Adhesive Joining Technique in Composite Materials

Composite plates made of fiber reinforced polymer have been widely used since four decades ago for major and minor structures in many engineering applications, because they offer significant features over conventional structures made of metals only. These

features include considerable reduction in weight, low maintenance and manufacturing costs and hence improving performance [29]. Joining composite materials by adhesives is preferable due to absence of stress concentration emerging in bolted and riveted joints as well as lack of defects induced by machining. The adhesive bonding offers excellent sealing, superior fatigue strength and good performance in raised temperature [1]. Adhesive bonded joint is often composed of adhesive and two adherends. Prior adhesive bonding process, the adherend surface preparation is a crucial issue to insure reliability of the adhesively bonded joints. The adherend-adhesive interface is considered the most weakened region in adhesive assembly of the composite structures. It was reported that about 70% of the adhesively joint failures were started at the adhesive layer [30]. It is necessary to have a substantial understanding to the role of environmental degradation and its influence on the adhesive bonded joint components and their response to the applied load. This interaction is unique to adherent-adhesive couple. It is necessary to study this interaction in order to ensure reliability of the composite structures in-service in different environmental conditions [31].

2.4 Adhesion Theories

There are five fundamental theories of adhesion which can be listed as: 1. Theory of adsorption, 2. Mechanical interlocking, 3. Theory of diffusion, 4. Electrostatic and 5. Chemical bonding. Several theories were proposed for explaining the adhesion phenomenon but these five were majorly qualified. Wake [32] and Kinloch [33] also proposed theories which were widely recognized. Contact between the adhesive and the adherend is necessary for the adhesion forces to be working [20]. The above theories are briefly explained below.

2.4.1 Theory of Adsorption

This theory is the most acceptable theory of all the five theories [33]. It can be said that this theory is widely credited to Sharpe and Schonhorn [34]. This theory proposes that when there is a contact between both the adherend and adhesive, the intermolecular and interatomic forces at the interface results in the adhesive strength that are more powerful with closeness depending on distance of separation according to the Lennard-Jones model [35]. The emerging forces between the substrate and the adhesive are usually divided into two groups: a) primary forces and b) secondary

forces. The primary forces involve ionic forces which range from 600-1100 kJ/mole, covalent forces from 60-700 kJ/mole and metallic bonds can range in between 110-350 kJ/mole. Van der Waal's forces or secondary forces are most common forces lead to adsorption, i.e. dipole interactions and induced dipole interactions which can be accredited to attract the electrically neutral elements to each another. Some researchers [36-37] have showed through experiments that the adhesion mechanism in numerous joints includes secondary forces. They calculated the attraction forces between two surfaces which were found to be much greater than the joint strength measured experimentally. These variations from theory may be the result of defects, voids or other geometric irregularities within the adhesive, which may cause stress concentration points during loading.

2.4.2 Mechanical Interlocking

As explained by McBain [38], the adhesion occurs when an adhesive flows into a rough surface and results in interlocking. The most important feature that influences the strength of the interlocking is the degree of roughness of the substrate being considered. As the degree of roughness of the substrate in contact increases, the area for intimate contact with the adhesive also increases [39]. Depending on the pore size of the surface of the substrate and roughness produced during surface treatments, these treatments have been grouped by Venables et al. [40] as follows:

Group I: Surface treatments that neither produces micro roughness nor macro roughness,

Group II: Surface treatments that produce macro roughness.

Group III: The treatments that produce micro roughness as a result of a porous oxide layer.

Here micro roughness is one with a pore size less that 0.1 µm and macro roughness pore size more than 0.1µm. The theory of mechanical interlocking states that typical adhesion takes place only when adhesive molecules permeate into the holes, pores, crevices, and any other irregularities on the substrate surface, and mechanically locks to the substrate surface. The permeation of adhesive into the pores must be in reasonable time [41]. The mechanical interlocking gives powerful bonds in adhesively joining that are resistant to thermal and hydrolytic degradation [20]. Several

researchers [42, 43] have increased the joint strength through factors such as increased surface area, enhanced wetting kinetics, or an increase in the plastic deformation zone.

2.4.3 Theory of Diffusion

The diffusion theory was first suggested by Russian scientists. This theory states that adhesion between polymers results from reciprocal diffusion of molecules across the interfacial layer. When it cannot be reached to satisfying explanations by applying other existent theories dealing with adhesion between dissimilar polymers, theory of diffusion is suggested to interpret the experimental results [44]. This theory is quite applicable to adhesion between polymer systems where adhesion takes place at the separation of two polymer surfaces due to the intermixing at a molecular level for polymer chains. This requires that the chain segments or macromolecules of polymers have adequate mobility and are reciprocally soluble and compatible so that diffusion can take place [45]. Effects of contact time, influence of temperature and time on bonding level, and the influences of polymer structure and polymer molecular weight are the major factors involved in this theory [39]. The inter-diffusion between two compatible polymer systems, the thickness of the inter-diffused area, is proportional to the square root of time and inversely proportional to the number of monomers per chain [46]. The theory of inter-diffusion is not applicable to all adhesive bonding systems and only limited to polymer-polymer bonds, therefore, it has been found limited application for systems where the adherend and adhesive are not soluble or the polymer chain movement is constrained by crystalline structures, highly cross-linked polymers, or for polymers below their glass transition temperature [41].

2.4.4 Electrostatic

Electrostatic theory was suggested by Derjaguin et al. [47]. The electrostatic theory proposed that if one metallic substrate makes a contact with another one, electrons will be transferred between each other, forming a dual electrical layer which gives the attraction force. The difference in electro-negativities of materials that are coming in contact with each other plays a main role on the resulting force of attraction. As a result of the difference in electro-negativities, there is a transfer of electrons at the interface of the substrate and the adhesive creating a negative and a positive charge which leads to attraction. The basic theory is that the electropositive material donates charge to the

electronegative material, which results in the electrostatic forces and hence creating an adhesive bond.

The electrostatic theory has not been put into use widely because there are a lot of controversies around it. There were few positive points which could explain certain set of adhesive properties, and also a few negative aspects which were not explained by this theory. When the temperature of a system is decreased the electrostatic forces become weak due to smaller charge densities, but the adhesive strength increased when the systems temperature was decreased for many systems including electrostatic bonding. Also, the adhesive bonding performance did not change much when the adhesives were varied by electronic character [39].

2.4.5 Chemical Bonding

This theory is valid only when there is an intimate contact between the adhesive and substrate in consideration. The theory states that a chemical reaction between two substances having an intimate contact is responsible for adhesive properties [48]. A covalent bond is formed at the interface of two contacting surfaces as a result of a chemical reaction. For proper chemical bonding to take place at the interface, the substrates have to undergo proper surface treatment so that fresh layer of substrate is exposed for better reaction and not an oxide layer or impurities that cover the substrate [41]. Proper contact also can be achieved by utilizing conjugation agents that require reciprocal reacting chemical groups attached very tightly at the adherend surface and coating surface. This process of chemical reaction by the use of coupling agents in holding the adhesive at the surface is very frequent. Chemical bonds are usually strong and primary chemical forces might range form 60-1100 kJ/mol [20].

2.5 Surface Preparation

During production and transport, the adherend surfaces usually become covered with oils, drawing compounds, press lubricants, mold release agents, and anti-corrosive coatings [8]. This layer of contaminants will decrease the critical surface tension of the surface and also prevent close contact between the adhesive and the adherend surface. As a result, the strength and durability of the bonded joint will decrease. It is thus necessary to remove the contaminants prior to bonding. In addition, most native adherend surfaces are not suitable for bonding. This can be due to a low critical surface

tension of the adherend materials themselves or to the presence of loose porous oxide layers formed under atmospheric conditions. To obtain a strong and durable bond, it is usually essential to modify the native surface topography of the adherends [28]. The process of removing contaminants and modifying the adherend surfaces, involves under the name of "surface preparation".

Surface preparation of the substrates which have to be bonded is a very important step in the sample preparation as it directly affects the bond strength of the adhesive and indirectly affects the failure mode. The surface preparation also influences the mode of adhesion that is going to occur within the substrate and adhesive interface. For better binding and longer life of the bonds, rougher adherend surfaces are prepared by various methods such as sand blasting, peel ply, grit blasting etc. This increase in surface roughness is helpful in mechanical interlocking of the adhesive with the substrate. Also in the case of chemical bonding or electrostatic adhesion, a virgin layer of the adherend is preferred to be attached with the adhesive to prevent any oxide layer or impurities to weaken the adhesive bond strength. By preparing a bonding surface to specifications the bond strength can be at its full potential and hence resulting in a longer structural life. The major role of surface preparation in sample preparation is to first remove the macro and microscopic impurities from the surface of the adherend, increase the surface area of the adherend and improves the surface roughness which is the key factor [49].

The objective of the surface preparation is to ensure complete wetting of the adherends by the adhesive and to increase the interfacial joint strength. The surface preparation usually involves the removal of surface contaminants, and the replacement of the native surface layers with a new, continuous, solid layer which bonds better to the adhesive [50]. The types of surface preparations required depend on the type of adherends and on the particular adhesive, the history of the adherends before bonding, and the service conditions [51-52].

Smooth surfaces of composite plate obtained from molding process, have low surface energy which results in weaker interfacial bonds with adhesives. On the other hand, contaminants reduce the surface energy and could be another reason of failure. These contaminants include: fingerprints, grease and oils, release agents, etc. Adequate treatment and cleaning are essential for surfaces prior adhesive bonding process to

improve the surface energy or the chemical surface properties. These treatments can be classified into three sorts, chemical, energetic and mechanical treatments [53]. Since the early application of composites in industrials, a wide range of energetic, chemical and mechanical surface treatments have been examined intensively [54]. The surface treatment efficiency is based on the composite material type. For example, plasma treatments could raise temperature and cause specific change in surface energy of composites. Solvents could remove a particular sort of contaminants or change the surface properties for particular sort of bulk composites. An appropriate selection of surface treatment type is essential to ensure the reliability of adhesive bonding in composite materials. Mechanical abrasion is the most common type of surface treatment in adhesive bonding for composite materials. The objective of mechanical abrasion is to increase the surface roughness. The increase in surface roughness can change the failure mode from adhesive failure, for example, to more progressive type of failure, which results in improving toughness of the bond-line [55-56]. As mentioned above, appropriate selection for the surface treatment method depends on the composite material type. There is no international standard of surface treatment for general composite materials.

2.6 Nano-Particles

Particles that having one or more dimension in Nano-size scale are called Nano-particles. There are three categories of Nano-particles depending on the number of Nano-size dimensions. The first category is called particulates and have three Nano-size dimensions. The second one is called fibrous and have two Nano-size dimensions. And the third is called layered and have one Nano-size dimension [57]. The most important physical property of particles is surface to volume ratio (S/V). For Nano-particles, S/V ratio is three times higher, in magnitude, than that one of micro-particles. This considerably affects the extent of interaction between the system phases of a composite polymer. Physiochemical interaction becomes the dominant factor on effectiveness of bulk composite and hence control the local loads transfer within the composite structure. S/V ratio is proportional to van der Waal's attraction forces arising between each of the Nano-particles. Fully interfering between polymer molecules and Nano-particle is difficult to obtain with increased S/V ratio due to the higher surface attraction which leads to particles agglomeration [58-59]. Nano-particles have superior properties and good dispersion into polymers is the responsible to benefit these

properties. However, strong attraction forces arising between the Nano-particles have prevented shifting these properties to polymers especially in case of Layered silicate, graphene Nano-platelets and silica [60]. Dispersion of Nano-particles can be achieved by different techniques such as shear mixing, mechanical stirring, surfactants, sonication, and in situ [61].

2.7 Graphene Nano-Platelets

Graphene Nano-platelets (GNPs) are a category of two dimensional graphitic Nano-fillers. GNPs are composed of stacks of graphitic layers bonded to each other by attraction of Van der Waals forces [62]. Graphite exists as multi layered structure in the bulk graphite. These layers should be exfoliated and dispersed into the polymeric matrix such that they form an interconnected network that makes the bulk material conductive [63]. In 2004, Novoselov et al. [63] managed to extract one-layer crystalline graphene from bulk graphite. This two dimentional graphite has been studied for past 60 years. The basic unit graphene Nano-platelets were obtained by exfoliation of natural graphite. To make GNPs, the graphite is intercalated by a special acid treatment process, followed by exfoliation prompted by a thermal shock applied at a temperature of around 600°C. The thickness of the platelets ranged from 0.34 to 100 nm and this material was found to be alternative to metal because of light weight and low cost [64]. GNPs possess superior thermal and mechanical properties just like the other classical two dimensional Nano-fillers do, such as Nano-clays. However, GNPs offer impressive electrical properties. Therefore, they can be used with polymers to improve both the electrical and mechanical properties and that make them distinct Nano-fillers [65-66].

GNPs are recently developed Nano-particles. They cost considerably less than their carbon nanotubes (CNTs) counterparts, which their production requires complicated manufacturing operations and hence make them cost much. However, there are many significant differences in structure between CNTs and GNPs [67]. Graphene platelets of high purity can be derived from different sources of natural graphite, which are plentiful and available, using the traditional methods. GNPs can be effectively used to produce multi-functional filler systems [68]. Thereby, the use of GNPs in diverse engineering applications can be considered as more cost-effective than higher cost materials.

Several attempts have been implemented to assess diverse beneficial influences of GNPs experimentally when added to different polymers [69-70]. As a result, some semi experiential and theoretical models have been evolved to predict the electrical conductivity and elastic modulus of GNP Nano-composite polymers [71]. In a majority of Nano-graphene addition cases, the results have showed that the elastic modulus of polymers could be increased. As well as, the ultimate strength of Nano-composite polymers have improved with the inclusion of GNPs while their fracture strain could be decreased [70]. The thermal conductivity of Nano-composite polymers has also been found to increase considerably even with the addition of small quantity of GNPs into resins [72]. In addition, it has found that the flexural modulus and fracture toughness of Nano-composite polymers would impressively be increased with low concentrations of GNPs in the resins [70-71].

2.8 Nano-Clay

The term Nano-clay is adopted by material scientists in the late 1980's due to the thickness of the clay layers that are in the order of a nanometer. Although a number of layered silicates are available for use by material scientists, montmorillonite, a member of smectite group of clay mineral, is often utilized. Moreover, the term Nano-clay refers to montmorillonite, in the context of materials science, unless specified otherwise [73].

Montmorillonite, sometimes abbreviated as MMT, has a 2:1 layered structure consisting of two silica tetrahedral layers sandwiching an octahedral sheet of alumina. Individual layers with typical thickness of 1 nm and 0.1-2μm in width and length, have interlayer spaces of 2-3nm between each other. These layers are bonded with one another by weak van der Waals forces [74]. Montmorillonite layers have a net negative charge caused by isomorphic substitutions within the crystal structure. This net negative layer charge is balanced by exchangeable cations, such as Na^+. Highly hydrophilic Nano-clay can effectively be dispersed in water down to the individual layer scale [75]. This clay is existing in nature as stacks of plentiful platelets. Single Nano-clay layer was suggested to be a typical reinforcing factor in 1974 due to possessing high aspect ratio as well as due to their thickness of nanometer scale compared to the scale of polymer chain structure [76].

The properties of a Nano-clay-polymer system are greatly affected by the size scale of Nano-clay phases and the mixing degree between these phases. Figure 2.4 presents the three main types of the Nano-clay reinforced polymer. A phase-separated composite is obtained, when the polymer can not be intercalated between the silicate sheets. The properties still stay in the traditional micro-composite. In the intercalated structure, a single extended polymer chain can penetrated between the silicate layers. When the silicate layers are completely and well dispersed in the polymer matrix, an exfoliated structure is obtained [77].

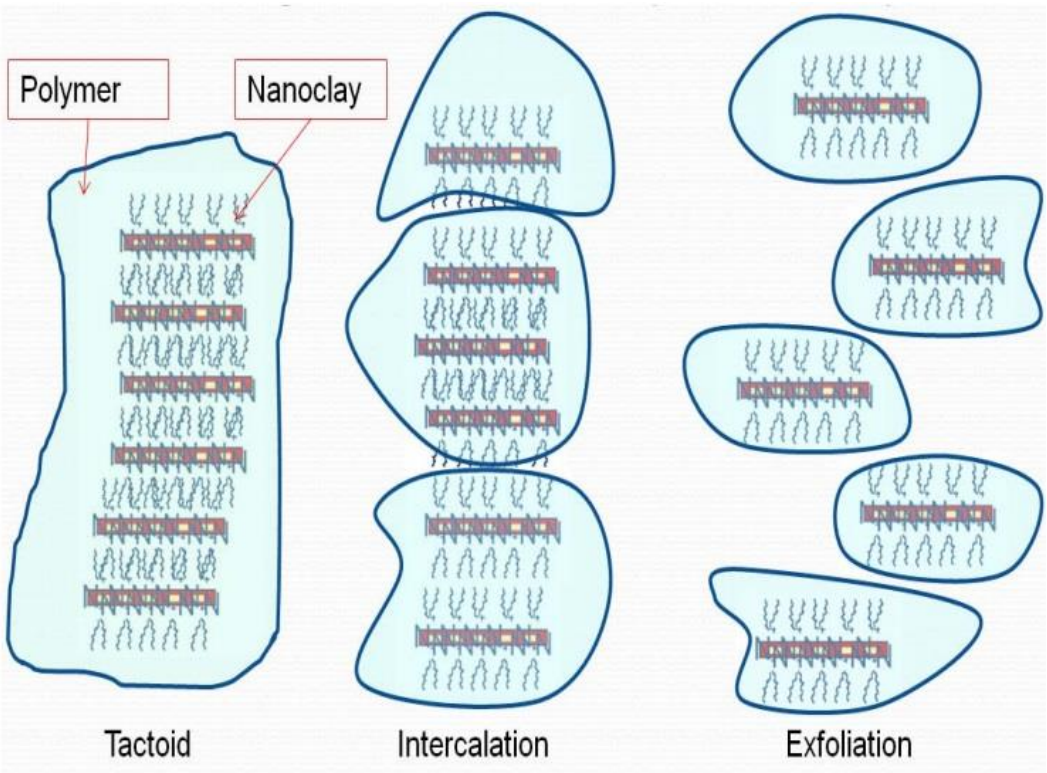


Figure 2.4 Three morphology stages of MMT Nano-clay-polymer [78]

It has been approved that the Nano-clay will not present improvements to mechanical properties if it is without appropriate dispersion. In fact, a random dispersion of Nano-clay may negatively affect the mechanical properties of polymers [15]. While a good dispersion leads to better adhesion at the interface which results in improved properties such as corrosion resistance, delamination resistance and fatigue. However, the hardest mission is breaking down the tactoids to the exfoliated and well dispersed individual clay layers in the mixing process to form ideal Nano-clay/polymer system. It was a crucial issue in research in many literatures [79].

According to many previous of studies [80-81], less than 5 wt. % Nano-clay added into the polymer system and could get best result in dispersion, mechanical and thermal properties. Increasing the amount of Nano-clay will also increase the viscosity of the reinforced polymer system, and higher viscosity polymer will cause higher temperature during the sample fabricating.

2.9 Nano-Silica

In nature silicon can be never found free. It is always oxygen compound and primarily its coordinate number is 4. Basic group of these materials is SiO2 and in the structure it could be found isolated, connected into chains, cycles, layers or three-dimensional structures. Silicon dioxide (silica) is maybe the most investigated chemical compound, anyway after water [82]. There are 22 known crystalline phases of silica and over a dozen polymorphs of "pure" SiO_2. Silica is found in nature; the most frequent as quartz. It is the major mineral in granite and sandstone and also occurs as a multitude of different rock crystal. In addition to natural silica, there is some techniques used to produce silica such as plasma arc, carbon arc, carbon electrode fusion or gas fired continual extrusion, and the product is called synthetic silica. By these techniques, extremely high purity degree of silica can be produced with silica content of 99.4 to 99.9% [83].

Sol-gel is another common process for producing silica. This process allows to produce ceramic with high degree of homogeneity and purity. The process takes place in liquid solution for precursors of organometallic. The standard precursors used in this process to produce silica are tetraethyl orthosilicate (TEOS) and tetramethyl orthosilicate (TMOS). The process is performed through condensation and hydrolysis of silicon alkoxide at a low temperature with the existence of alcohol and water [84].

The silicate monomer nucleates in extreme-saturated solution during the condensation and hydrolysis processes and grows to cyclic, dimeric, gel networks or spherical particles. In comparison with other oxides, One substantial feature of silica is that the condensation of silicic acid [$Si(OH)_4$] composes a so stable amorphous SiO_2 instead of a crystalline SiO_2 [85]. Therefore, SiO_2 particles, with a fixed chemical composition, can be produced in diverse shapes and sizes by controlling some parameters like the amount of water, concentration of catalyst, concentration of alkoxide, electrolyte additive, solvents and aging time [86].

The manufacturing processes of ceramics and silicate glasses require presence of silica as starting material. Silica can be existed in a crystalline form or in an amorphous form which known as vitreous silica. There are three forms of crystalline silica; cristobalite, tridymite and quartz. Each of these specific crystalline forms can be divided into two distinct forms depending on the treating temperature: low temperature form and high temperature form. The high temperature form comprises of various arrangements of non-deformed tetrahedral silicate (SiO4) connected to each other by shared corners. The low temperature form has an identical structure but is deformed [87]. Industrially, silica is used as high purity quartz, silica gel, diatomaceous earth, vitreous silica, and fumed silica. It is used in the microelectronics industry as quartz. Quartz is a piezoelectric material and finds excellent uses in crystal oscillators and as filters for modulation and frequency control. In the plastics industry, ultrafine powered SiC (fumed silica, bulk density is 0.03 to 0.06 g/cm^3 and surface area of 150-500m2 /g) is used as a thixotropic thickening factor in treating polyester and epoxy and a filler in silicone rubbers. Because of its chemical inertness, silica does not disrupt the peroxide started cure of the silicone [83].

2.10 Fillers

Mechanical and thermal properties of polymers can be altered by the addition of nano and/or micron-scale particles called filler materials [88]. Fillers are the most common ingredient employed in the majority of epoxy formulations. They are relatively non-adhesive substances added to an epoxy resin to modify density, improve heat resistance, and reduce the coefficient of thermal expansion. Fillers are also used to modify viscosity, increase pot life, and improve adhesion. In addition, they can be employed to improve machinability, increase hardness and wear resistance, increase chemical and solvent resistance, modify friction characteristics, and improve thermal shock resistance [85].

Traditional fillers, such as micron-scale aluminum particles, are shown to significantly improve stiffness while resulting in reductions in strength [88]. However, Nano-scale particulates such as Nano-clay and carbon nanotubes are proven to be capable of improving strength and stiffness as well as thermal and barrier properties simultaneously, even with small inclusions [84]. Especially Nano-clay has gained wide

acceptance as a reinforcing agent in various polymer systems, owing to its low-cost and accessibility [89-90].

The addition of good dielectric fillers, such as mica, asbestos, and powdered glass can improve the electrical properties. Fillers are particularly effective in decreasing curing shrinkage due to the reduced peak temperature and to bulk replacement. Typical fillers include silica, calcium carbonate and metal powders. Before being added into the resins, fillers should be heated to drive off moisture and absorbed gases to prevent volatilization during curing. Many fillers are in the form of powders, fibers, or flakes. It has been found that the incorporation of particulate fillers such as silica, glass spheres, and aluminium trihydrate can increase the toughness of epoxy resins. This is due to an energy absorption mechanism caused by the crack pinning effect. The crack pinning mechanism was first proposed by Lange [91], and was extended and modified by Evans [92] and Green [93]. When a propagating crack front encounters particulate fillers, the crack front bows out between the particles while remaining pinned at the particles. To release the crack front, an increase of applied load is required to create the new fracture surface and increase the crack front length. This leads to an increase in toughness. The degree of improvement depends on the particle size, particle size distribution and surface chemistry of the fillers.

The filler material types used in different applications extend to a vast range of morphologies, materials, and size scales. Now-a-days, Nano-particles have been examined extensively because they are able to cause true improvements to diverse properties exceed those improvements obtained from using micro-particle and conventional models [94]. This may return to the reality that Nano-particles, in comparison to the other filler materials, have high surface area and aspect ratio. Nano-particles contain a numerous number of surface atoms and these atoms behave at the surface in a totally different way compared to the bulk state. So, even low concentrations of Nano-particles can make true changes in material properties like toughness and strength [95].

The greatest trouble with Nano-particles is their tendency to form agglomerates [96]. Non homogeneous distribution of Nano-particles is the determinist result of agglomerations and insufficient particle dispersion in the polymer can present negative influences on final properties. Having good polymer-particle interface can limit

particle chances to agglomerate which results in better adhesion. The powerful bonds between the particles can be broken by polymer intercalation and this is achieved through proper selection of dispersing technique. The resulting adhesion between the polymer and the particles offers great probabilities for the final properties to be well established [97-98].

While several researches have proven the possibility to obtain adequate dispersion of particles by conventional mechanical blending [99], many researchers have recommended the particle surface modification [95, 100]. The researchers have demonstrated that particles with modified surface are dispersed more effectively within the polymer than unmodified ones, and the resulting Nano-reinforced polymers present better improvements in different characteristics. This promotes the need of well dispersed particles for improved characteristics [101]. The degradation in properties at a specific content of Nano-particles is greatly attributed to insufficient dispersion. In order to hinder Nano-particles from forming agglomerations, the amount of Nano-particles in polymers can be kept as low as possible or particles can be modified where surface chemical properties can be changed to modify polymer-particle adhesion [98].

Many researches have stated that the inclusion of Nano-particles into adhesives like epoxies has improved the adhesive characteristics by higher than 50% [102-104]. Most researchers have demonstrated that this improving is limited, and that beyond a certain loading of particles these characteristics start to decrease [98, 103]. In addition, characteristics that often have inverse relationship between each other, such as lap shear strength and peel strength, are found to increase simultaneously with the inclusion of Nano-fillers [103]. Enhancements to adhesion can be attributed to the mechanical and chemical interactions between the adhesive and filler material [96, 102]. Nano-particles have the ability to fill in any micro-gaps in the adhesive and establish numerous points of contact within the adhesive as well as at the interfacial layer of substrate-adhesive link [96]. The particles also help in blunting the crack tip and cracks would be compelled to create a more tortuous path to enhance toughness [97]. Furthermore, chemical bonds were found to be created of substrate-particle interactions such as the bonds between the hydroxyl groups of silica particles or alumina and aluminum substrates [100].

Since the adherends are often more powerful than the adhesives used to bond them, one of the choices for toughening the adhesive joints is to reinforce the adhesives. Several researchers have tried to improve the mechanical properties of adhesives by incorporating fillers in them. Kahraman et.al [15] tried to introduce aluminum filler content into the adhesive layer in order to try and improve the mechanical properties of adhesive. They used the single-lap shear test as standard test for comparison [13, 105]. One of the reasons to use aluminum fillers was to improve the electrical conductivity and study the role of these aluminum fillers in influencing the mechanical properties of the adhesive. Aluminum and silver flakes were used as fillers to improve electrical and thermal conductivity, also, adhesives with aluminum and other metal fillers were commercially available but their role was in mechanical performance of adhesive was studied by Kahraman. He used 10%, 25% and 50% wt. of aluminum powder with epoxy adhesive for study. From his results, he concluded that addition of aluminum filler into epoxy adhesive increases mechanical strength of the bond. Cohesive failure occurred even with 50% wt. aluminum filler [15].

Gilbert et al. [106] also had worked with alumina Nan-sized particles of various shape and size and added them to the epoxy adhesive. These Nano-particles were included at 5 and 10% of weight into the adhesive. For fracture tests composite substrates were used and for lap shear and peel tests aluminum substrates were used. The peel and shear strength of the modified adhesives with Nano-fillers were said to have improved in the case of aluminum substrates. But the fracture toughness of the unreinforced adhesive was said to be greater than the fracture toughness of Nano-particle reinforced adhesive in the case of CFRP joints. Also, these Nano-particles did not help with the low electrical conductivity issue of epoxy adhesives.

Another study which involved the use of fillers in adhesives was done by Darwish et al. [107]. The main objective of his research was to improve the electrical properties of structural epoxy resin adhesive, therefore only metallic fillers were used for this study. Powdered metallic fillers in the form of alumina powder were used in the adhesive and from the results obtained they concluded that powdered fillers are better at improving the mechanical properties of the adhesive rather than improving its electrical conductivity. Fibrous metallic fillers possibly in the form of copper wires were incorporated in two different ways; one is randomly chopped fibers and the other in effectively oriented fibers. From the results they concluded that randomly chopped

fibers were more effective in improving the electrical conductivity of the epoxy resin adhesive and the powdered fillers were better in increasing the mechanical strength of the adhesive.

Another study which was based on inclusion of fillers in adhesive to study their effect was done by Gude et al. [108] who used carbon nanotubes and carbon Nano-fibers as fillers with epoxy adhesive and with carbon fiber reinforced composite as substrate. Lap shear tests and double cantilever beam tests were performed to analyze the mechanical properties of these reinforced adhesives. The inclusion of carbon nanotubes or Nano-fibers in epoxy resin to improve the mechanical strength, electrical and thermal properties was already reported [109-111]. Processing of carbon nanotubes into the epoxy matrix was always a matter of concern which dealt with a great deal of time and labor, to eliminate this Gude et al. [108] used a solvent for better dispersion of Nano-particles into the matrix. The electrical resistivity of epoxy was reported to decrease 13 times with the inclusion of 0.1% carbon nanotubes and 10 times with the inclusion of 0.25% carbon Nano-fibers within epoxy. But this inclusion of Nano-particles did not influence the lap shear strength of single lap joints [112]. This study also included the use of substances like chloroform which were used for better immiscibility of Nano-particles with epoxy. The epoxy adhesive with carbon Nano-fibers had increased the fracture energy of mode I tests by 10% as compared to the neat epoxy and 23.5% increase in fracture energy with the addition of carbon nanotubes. However, from the graphs it could be said that even though the fracture energy of the reinforced adhesives were more compared to pure epoxy, the peak load of the reinforced epoxy with carbon nanotubes dropped considerably [108].

Experimental work of Rafiee et al. [113] further justified the selection of graphene as a Nano-filler for their research project. In their experimental work with graphene reinforced polymer, an improvement of 60% in fracture toughness was reported for polymer material reinforced with 0.125%wt of graphene. Similar improvements in fracture toughness of epoxy-based polymer was achieved with different weight fractions of Nano-clay.

2.11 Conclusion

From the above literature review concerning to adhesive bonding technique, it can be said that adhesively lap joints are a progressing method in the area of fiber reinforced

polymers. In the light of progress made in joining technologies, adhesive bonding of composite materials has been become simpler in terms of alignment and consuming time. Many studies have been pointed out the significance of toughening and strengthening adhesives. In order to enhance the mechanical properties of the adhesives, the use of fillers have been proposed by several researchers. Fillers have been showed positive influence on the mechanical properties of adhesives in most experiments. Carbon and its counterparts have been affected the adhesive joints positively. Clay and silica have demonstrated great influence on the mechanical properties of polymers and their composites. Thus, three kinds of filler materials (GNPs, clay Nano-particles, silica Nano-particles) were proposed to reinforced epoxy based adhesive in SLJs of composite plates.These fillers were separately added into epoxy resin to study their contribution in adhesion characteristics, lap shear strength and bending strength of adhesive SLJs joints.

CHAPTER 3

EXPERIMENTAL STUDIES

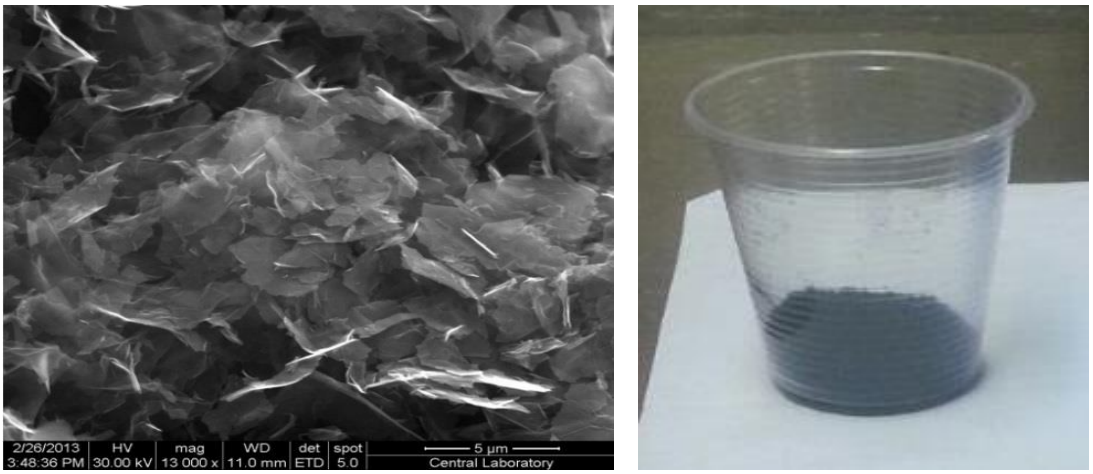
This chapter is concerned with the experimental work carried out to determine the influence of the Nano-fillers dispersion in epoxy adhesive upon the strength of adhesive bond. The following sections describe the materials used for making the interface layer, specimen preparation and details of the experimental approach adopted.

3.1 Materials

3.1.1 Graphene Nano-Platelets

Graphene has emerged as an alternative to carbon nanotubes with comparable mechanical properties. Stankovich et al. [114] recently introduced a unique technique to mass-produce graphene sheets. Relatively low cost of graphene offers the opportunity to reinforce polymers for a variety of applications. Many contributions have been made by researchers to explore the unique properties of graphene and related Nano-composites [115-116].

Graphene Nano-platelets (GNPs) used in the present work were supplied from Grafen Chemical Industries, Turkey. It looks like a black and grey powder, and has bulk density of about 0.05 g/cm^3, purity of 99.5%, particle diameter of 5 μm, specific surface area of 150 m^2/g, and thickness of 5-8 nm, as well as Raman Spectra ID/IG Ratio of 0.08 and XRD 2-theta of 26 ºC peak. Figure 3.1 (a) and (b) show SEM image of GNPs and its powder.



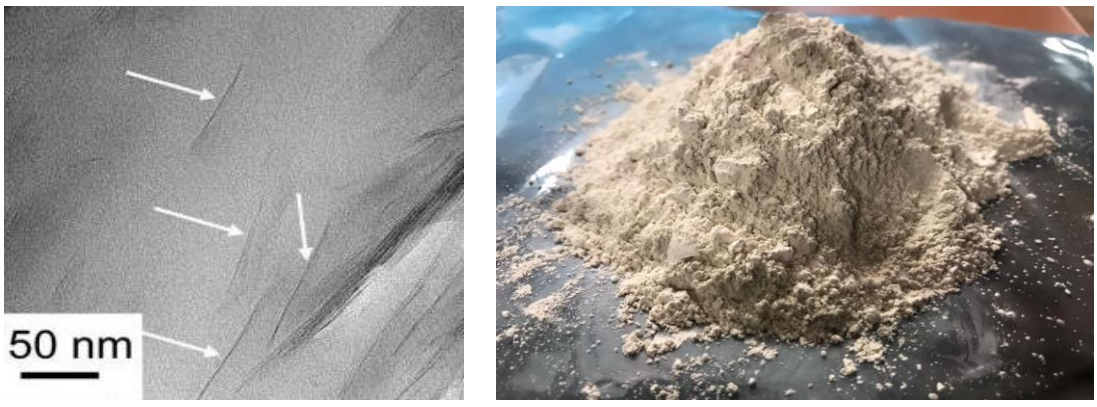
(a) (b)

Figure 3.1 GNPs; (a) SEM image [117], (b) Nano-Graphene as received

3.1.2 Clay Nano-Particles

Clay is known to scientist for centuries; however its application as a reinforcing agent in polymers is relatively recent. Although a number of researchers have mentioned the idea of subjecting the Nano-clay to cation exchange reaction to make them compatible reinforcements for polymers, Toyota Research Labs was reported the utilization and characterization of Nano-clay reinforced polymers for the first time [118-120].

Nano-clay type Montmorillonite (MMT) was used as a Nano-filler in this study to reinforce epoxy resin. MMT Nano clay with 35-45 wt. % dimethyl dialkyl (C14-C18) amine was obtained from Grafen Chemical Industries, Turkey. The density of MMT Nano clay is 200-500 kg/m^3 and the Nano particles are in size of 1-10 nm. Figure 3.2 shows MMT clay Nano-particles.



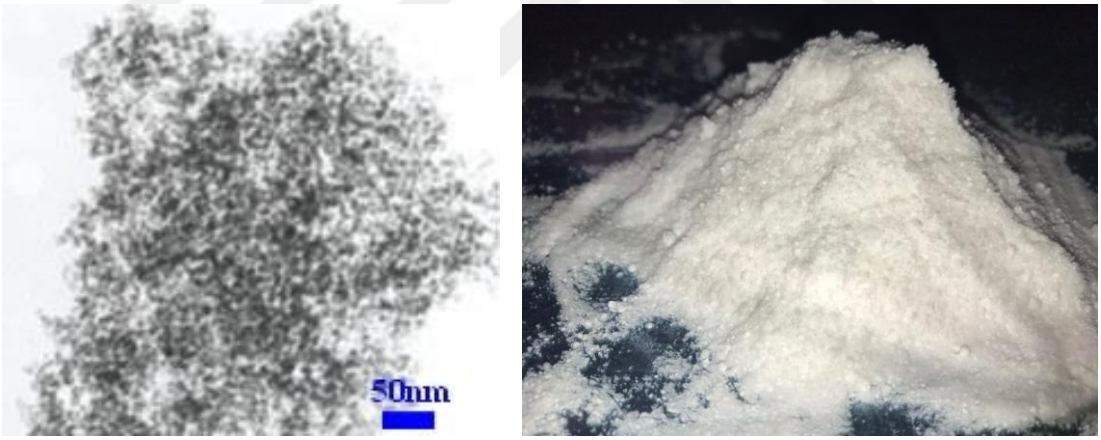
(a) (b)

Figure 3.2 MMT clay Nano-particles; (a) SEM image [117], (b) Received Nano-clay

3.1.3 Silica Nano-Particles

Silica is one of the most abundant oxide materials in the earth's crust. It is commonly found naturally in sandstone, silica sand and quartzite. Besides the silica occurring in nature, synthetic silica can be produced by a carbon arc, plasma arc, gas fired continual extrusion or carbon electrode fusion. By these methods, a high purity grade of silica with silica content of 99.4-99.9% can be produced. Fused silica is primarily used in the electronics industry where its good dielectric and insulating properties are exploited; it may, however, also be used as a refractory material or in investment casting [121].

Silica oxide (SiO2) nanoparticles were another filler material used to reinforce epoxy in order to strengthen adhesively joints of epoxy based adhesive. Nano-silica particles having average particular dimension of 15 nm, specific surface area of 300 m^2/g, mass density of about 0.05 g/cm^3 and high purity as 99.5%, were provided from Grafen Chemical Industries, Turkey. Figure 3.3 (b) illustrates the silica Nano-fillers as received.



(a) (b)

Figure 3.3 Silica Nano-particles; (a) SEM image [117], (b) Received Nano-silica

3.1.4 Composite Plates

Fiber reinforced polymer (FRP) composite materials are widely used in aerospace, civil and structural industries because of several favorable properties such as low density, high specific strength and stiffness. In addition, the fatigue strength to weight ratios as well as fatigue damage tolerances of many composite laminates are excellent. Thus, FRP composites have emerged as a major class of light-weight structural

material. These materials are used as substitutions for metals in many weight critical components.

Industrial glass fiber reinforced polymer (GFRP) composite laminates made of epoxy resin-bonded continuous filament glass fiber material (G10-FR-4) were chosen as adherends in this experimental work. GFRP plates commercially produced were bought from Kupar Pompa, Küçükparmak Mühendislik San. Tic. Ltd. Şti. The considered GFRP plates were 2 mm in thickness and the important technical features are shown in Table 3.1. Figure 3.4 shows used GFRP composite plates.

Table 3.1 Technical Properties of GFRP Plates

Properties	Value
Density (g/cm^3)	1.7101
Flexural Strength (MPa)	357
Tensile Modulus of Elasticity (MPa)	23752
Compressive Strength (MPa)	371.2
Charpy Impact Strength Parallel to Lamination (kJ/m^2)	117.79

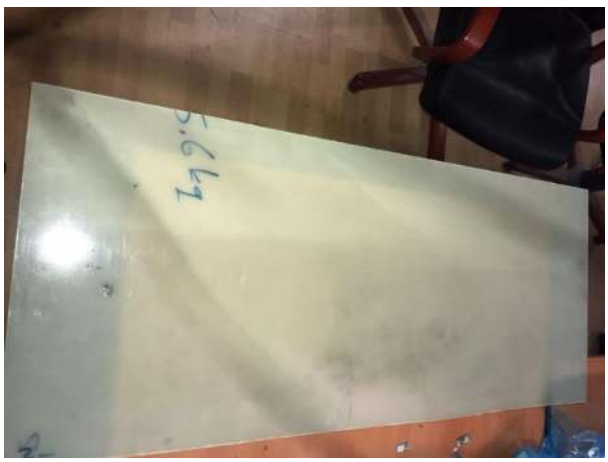


Figure 3.4 Used GFRP composite plate

3.1.5 Epoxy Resin and Hardener

Epoxy resins have good mechanical properties, superior dimensional stability and good resistance to heat and chemical attack. Because no small molecules, such as water, or volatile liquid is liberated during the curing of epoxy resin, they exhibit low shrinkage, and they can be formed and cured under contact or low pressure [122].

In this study, we used an epoxy type MOMENTIVE-MGS L160 produced by DOST Chemical Industrial Raw Materials Industry, Turkey. It is a two-component adhesive, with a conjugated hardener type (MOMENTIVE-MGS H260S), which is easily mixed at room temperature and has high adhesion strength. Resin and hardener mixing ratios are 100:36±2 in weight and 100:43±2 in volume. This adhesive system has an excellent environmental resistance and bonds to a variety of substrates. The original properties, as provided by the manufacturer, are summarized in Table 3.2, Table 3.3 and Table 3.4. Figure 3.5 shows epoxy and hardener vessels.

Table 3.2 General features of epoxy MGS L160 [123]

Certificate	German Federal Aviation
Application area	Gliders, motor gliders, motorized aircraft, boats, ships, sports equipment, model aircraft, molds and general applications
Operating temperature	-60 ° C / + 50 ° C Without heat treatment -60 ° C / + 80 ° C By heat treatment
Process Temperature	+10 °C / +50 °C
Features	Very high level compatibility Very good mechanical and thermal properties 45 min. to 4-5 hours work time
Storage	24 months in unopened package

Table 3.3 Physical Properties of Laminating Resin MGS L160 (Measuring Conditions: 25 ° C) [123]

Properties	**Value**
Density g/cm³	1.13-1.17
Viscosity MPa	700-900
Epoxy equivalent gr/equivalent	166-182
Epoxy value equivalent/100gr	0.55-0.60
Refractor index	1.5480-1.5530

Table 3.4 Physical Properties of Hardener MGS H260 (Measuring Conditions: 25 ° C) [123]

Density g/cm³	0.93-0.97
Viscosity MPa	80-100
Amine value (mgr. KOH / gr)	450-500
Refractor index	1.4980-1.4985

Figure 3.5 Epoxy and hardener used through the study

3.1.6 Release Agent

Release agent type (RENLEASE QZ 5111) was used to coat aluminum mold surface before preparing the lap joint samples. As described by the supplier "It is a liquid form mold release agent which can be applied to all types of mold surfaces with brush. It should be expected to dry in 15 minutes between coatings. It should be shaken before every use. It is an ideal choice for room temperature applications". Figure 3.6 shows the release agent container.

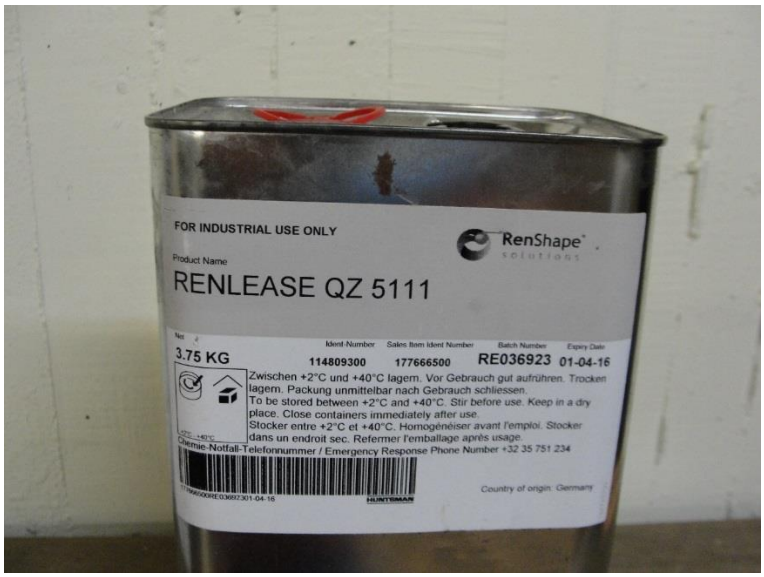


Figure 3.6 Release agent used through the study

3.1.7 Acetone

To obtain higher adhesion between substrate surfaces and adhesive, a solvent must be used to treat the bonding areas in order to remove oils, greases, environment contaminants and finger prints which negatively affect the bonds strength. A commercial acetone (Figure 3.7), an organic solvent, was purchased from markets and used for this purpose.

Figure 3.7 Commercial acetone used to clean bonding areas

3.2 Tools

Figure 3.8 shows used tools in the experimental studies as follows:

- Abrasive paper: used to prepare the composite substrate surfaces to adhesive bonding.

- Digital scale: used to measure weight for epoxy, hardener and Nano-fillers.
- Geotine machine: used to cut the composite plates to appropriate dimensions.
- Aluminum mold: used to fabricate SLJs samples.
- Universal tensile machine: used to perform mechanical tests on SLJs samples.

(a)

(b)

(c)

(d)

(e)

Figure 3.8 Equipments and tools used through the experiments, (a) Abrasive paper, (b) Digital scale, (c) Geotine machine, (d) Aluminum mold, (e) Universal tensile machine

3.3 Preparation of Nano-Reinforced Epoxy Based Adhesive

To economically enhance the mechanical properties of the epoxy resins, attempts were made to use various types of fillers. It is clear that fillers are able to affect a variety of properties and that the use of Nano-sized fillers can give rise to unique properties from conventional fillers. Three different types of Nano-particles (GNPs, clay Nano-particles and silica Nano-particles) were selected to be dispersed into the epoxy resin. The epoxy resin was modified by different weight ratios of those Nano-particles. For lap shear test, GNPs was added by 0.1, 0.2, 0.3, 0.4, 0.5 % wt. and clay Nano-particles was added by 1, 2, 3 and 5 % wt. while silica Nano-particles was added by 1, 2 and 3% wt. For three point bending test, weight ratios of 1, 2 and 3 % wt. were implemented for clay and silica Nano-fillers and 0.1, 0.2, and 0.3 wt. % for graphene Nano-filler.

However, the uniform dispersion of Nano-particles in the resin is quite challenging, time-consuming and thus an added cost. Not only because the dispersion is directly govern the mechanical properties of the adhesive, but more importantly, the Nano-particles agglomeration causes severe statistical inconsistencies in the strength and performance of adhesives. Therefore, the Nano-particles were first dispersed in the resin and stirred for 10 minutes and then the curing agent or hardener was added to the mixture and further stirred for 2 minutes as shown in Figure 3.9. This ensures the homogeneous dispersion of the Nano-fillers into the adhesive and prevents temperature rising of the adhesive.

Figure 3.9 Preparation method of Nano-particles/epoxy adhesive

3.4 Surface Treatment of Composite Substrates

Surface treatment is a crucial issue in the adhesive bonding technology. Very smooth surfaces are not preferable due to adhesive escaping while rough surfaces prevent the adhesive to spread homogenously through the bonding region. Suitable surface roughness should be obtained for good wetting of substrate surfaces by the adhesive. The degree of surface roughness is the material property. For example, adhesive bonding of aluminum substrates requires surface roughness different to that required for plastic substrates. Environmental contaminants such as oils, grease and dust atoms are considered main factors for weak bonding strength. On the other hand, mold release or oxide layers negatively affect the adhesion strength due to the ease separation of these layer under moderate loads. The proper surface treatment presents higher adhesion in adhesive-substrate interference in comparison with the case of raw surfaces.

According to ASTM D2093-03 standard, only a mechanical abrasion is needed to treat the substrate surfaces of composite plates prior to adhesive bonding process. GFRP composite plates, used in this study, were wiped with acetone, abraded with an abrasive paper, wiped with a dry cloth to remove released atoms, and then wiped again with acetone. Water proof silicon carbide abrasive paper grade P120D was used to prepare the bonding areas for adhesive bonding. Figure 3.10 shows the surface treatment procedure of the composite plates.

Figure 3.10 Surface treatment procedure used to prepare substrate surfaces

3.5 Fabrication of Adhesively Joint Samples

For the purposes of this work, the single-lap joint (SLJ) configuration was selected to bind the composite plates. The single-lap joint is a common method of joining two plates in-plane. It is easy to produce and inspect. Its geometry seems simple enough, but the state of stress developed in the joint makes it one of the weakest ones. However, the use of SLJ allows for simple tensile testing of bond-line for the measurement of shear strength. In this work, the adherends were prepared from GFRP composite plates by geotine machine as rectangular pieces with appropriate dimensions according to ASTM D5868 – 01 as shown in Figure 3.11. SLJs were created using two thin adherends, each one is 25 mm in wide and 100 mm in long. They were bonded with a 25 mm overlap length, resulting in an overall sample that is 25 mm wide by 175 mm long. The two adherends were of same material. The thickness of the adherends was 2 mm. The adhesive bond-line thickness was 0.1 mm.

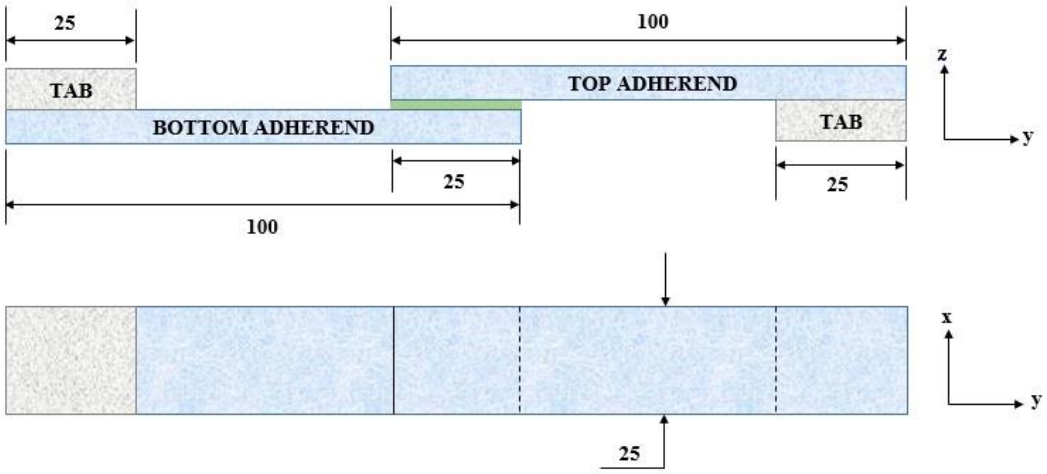


Figure 3.11 Dimensions of single lap joint according to ASTM D5868 – 01

To prepare SLJs, a commonly used epoxy resin (i.e., MGS L160 resin and MGS H260 hardener) was used as the adhesive, mainly due to its common use and relatively low cost. Neat epoxy and Nano-reinforced epoxy were used to prepare SLJs. Nano-reinforced epoxy was designed with the considered Nano-particle weight ratios (see section 3.3). Five samples for each epoxy mixture design were prepared and tested.

An aluminum mold was also designed and fabricated to make SLJs consistent and accurately aligned, as shown in Figure 3.12. The mold was machined as stepped base

to obtain the required thickness of the bond-line (i.e., 0.1 mm). The aluminum mold was previously coated by release agent to prevent samples from attaching to its surface.

SLJs samples were prepared first by applying the adhesive onto one substrate. The second substrate was then placed accordingly to obtain the desired overlap length and excess resin was wiped from the edges. The substrates were then bonded together and carefully cured at a room temperature for 7 days.

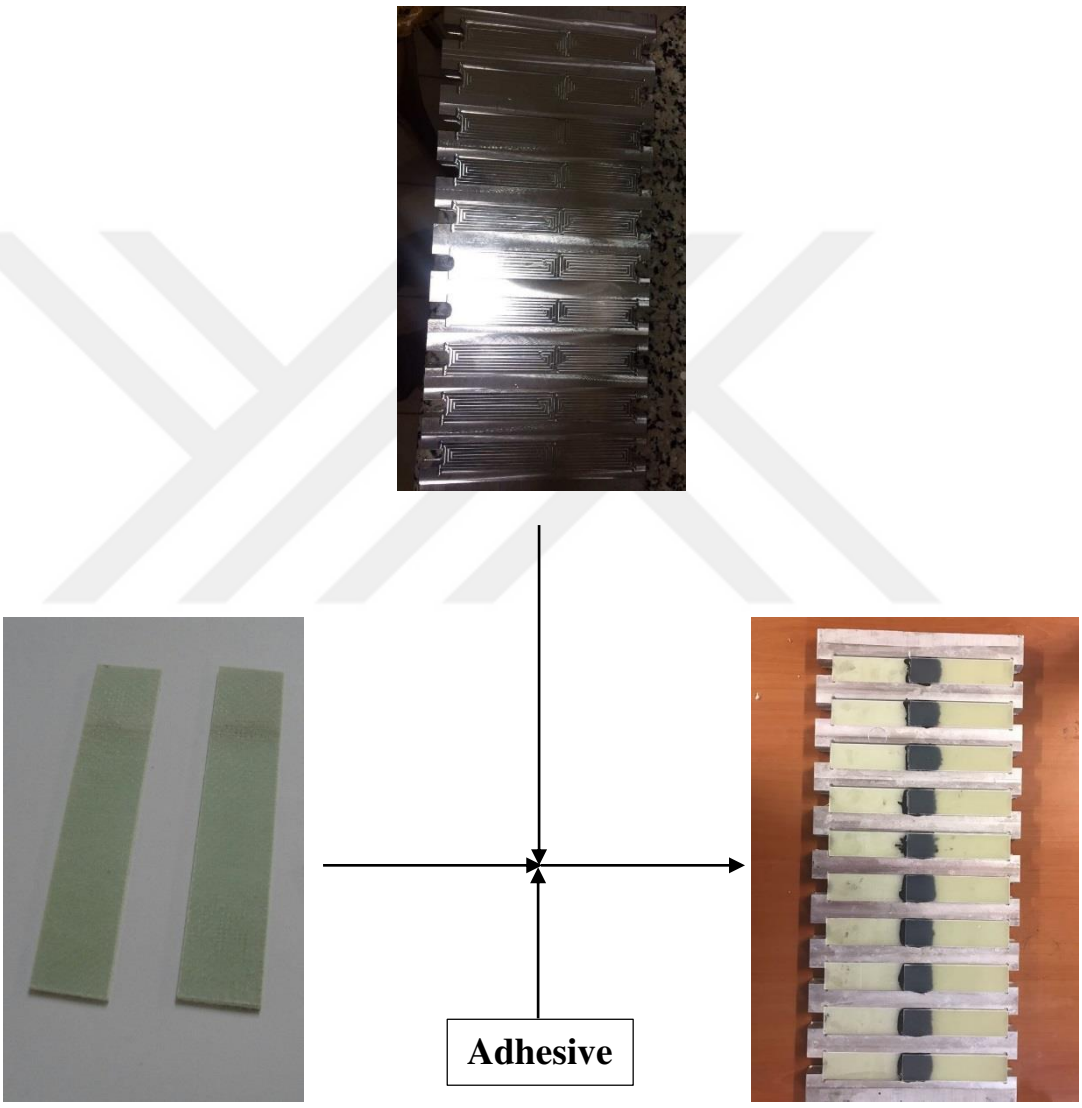
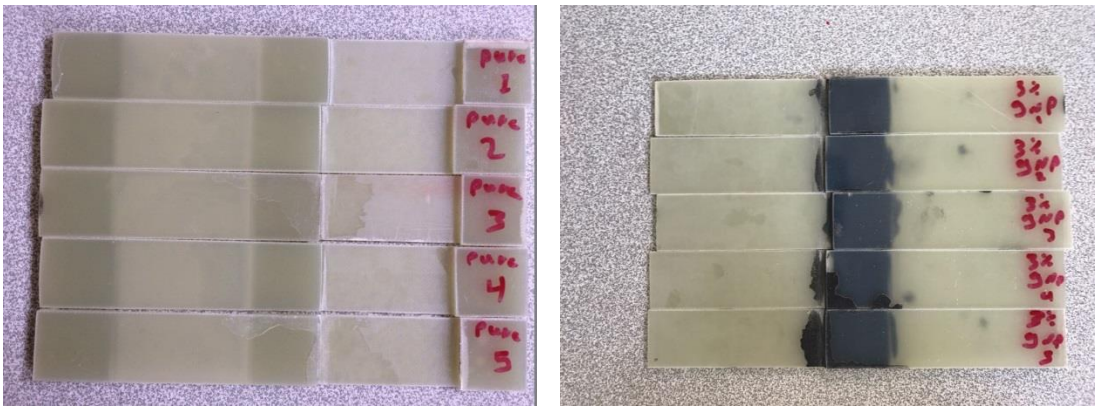
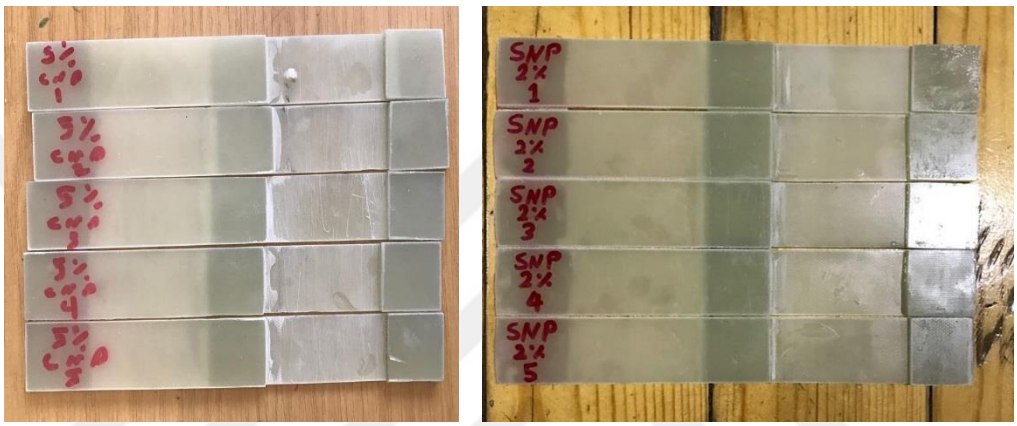


Figure 3.12 Production of single lap joint samples with the help of aluminum mold

To ensure that the adhesive in ABJs would be subjected to concentric load, tabs made of GFRP with appropriate thickness were used for this purpose. 25 mm by 25 mm tabs were added to the ends of the adherends to minimize the bending moment created by the tensile load applied to offset adherends, matching the overall thickness of the single lap joint (see Figure 3.11). Some typical SLJ samples are illustrated in Figure 3.13.



(a) (b)



(c) (d)

Figure 3.13 Some SLJ samples prepared for mechanical tests, (a) Neat epoxy samples, (b) Graphene samples, (c) Nano-clay samples, (d) Nano-silica samples

3.6 Experimental Tests

3.6.1 Lap Shear Test

Because many adhesive joints are subjected to shear stresses [124], it is logical to examine shear strengths. Lap shear tests are a quick and inexpensive method to assess shear strengths, and in fact, lap shear strength is the most commonly reported adhesive property [125-126].

SHIMADZU universal tensile testing machine (Figure 3.8 (e)) with 300 kN loading capacity was used to perform lap shear tests. This machine has two heads move relatively to each other. The lower head is fixed while the upper head moves with selected constant speed. The adherends were securely tightened to the head jaws of test machine by gripping areas of 25 × 25 mm. This arrangement ensured that no slip

would take place during testing. Analogous to the tensile test, the loading path was vertically aligned prior to testing. Samples were pulled at extension rates of 1.0 mm/min until failure, based on ASTM D3165 – 07 standard. Controlling, data acquisition and processing were performed by Trapezium software installed in a computer (control unit) connected to the testing machine. Force values and corresponded displacements were also recorded through the control unit of test system. These values used to establish stress-strain curves for the studied adhesively joints. According to principles of the strength of materials, stress and strain values were calculated as follows:

$$\tau = \frac{w}{\ell \times b}$$

$$\varepsilon = \frac{\Delta\ell}{\ell}$$

Where;

τ: is the shear stress

w: is the tensile load,

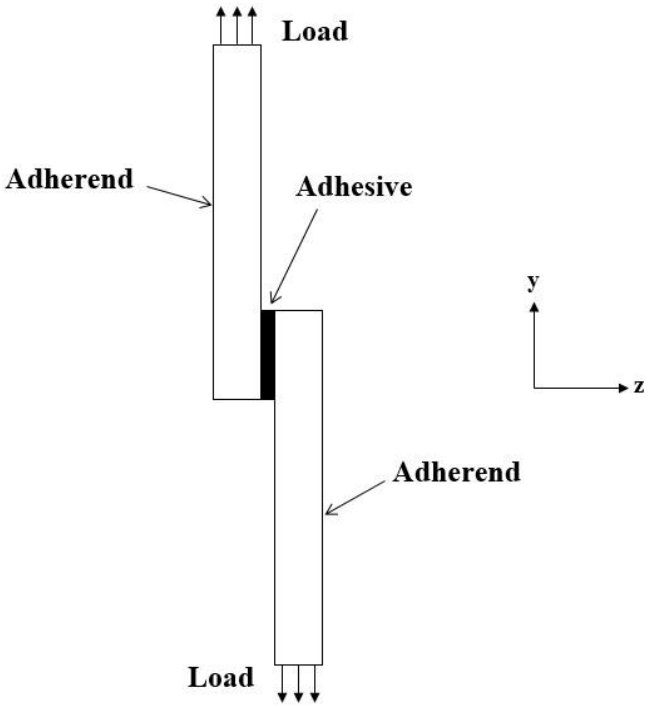
ℓ: is the overlap length,

b: is the width of adhesive joint.

ε: is the shear strain

$\Delta\ell$: is the measured displacement

All lap shear tests were conducted at standard conditions. Figure 3.14 (a) shows schematics of the test set-up used for the testing of the interface layer. Figure 3.14 (b) shows test sample under lap shear loading till fracture.



(a)

(b)

Figure 3.14 Lap shear test, (a) Schematics of the test set-up, (b) test sample under lap shear loading till fracture

3.6.2 Bending Test

In this part of the study, the strength of adhesively bonded joints was investigated by three point bending test. This test was performed using SHIMADZU universal tensile testing machine (Figure 3.8) with 300 kN loading capacity. The tensile test heads were replaced by other heads fit the three point bending test as shown in Figure 3.8. The influence of the considered Nano-particles on the flexural strength of adhesively joints was investigated with the help of this type of mechanical test.

The test samples was put onto two fixed supports while loading force was applied at the mid-point of span length as shown in Figure 3.16. The cross head speed was 2 mm/min according to ASTM D 790 – 07 standard. Because of the bonded connection, left and right side of the sample do not position horizontally on the test supports. To prevent this, additional plates having appropriate thickness were inserted under either the right side or the left side of the test sample. Three point bending test equipment and sample positioning are shown in Figure 3.15.

As a result of the bending loading, the sample bends, causing formation of tensile stress in its convex side and compressive stress in the concave side (Figure 3.15). The flexural stress and corresponding flexural strain are calculated for each load value as follows:

$$\sigma_f = \frac{3PL}{2bd^2}$$

$$\varepsilon_f = \frac{6Dd}{L^2}$$

Where:

σ_f = flexural stress at midpoint (MPa),

P = load at a given point on the load-displacement curve (N),

L = support span (mm),

b = width of joint tested (mm), and

d = depth of joint tested (mm),

ε_f = flexural strain at midpoint (mm/mm).

D = maximum displacement at the center of the joint (mm)

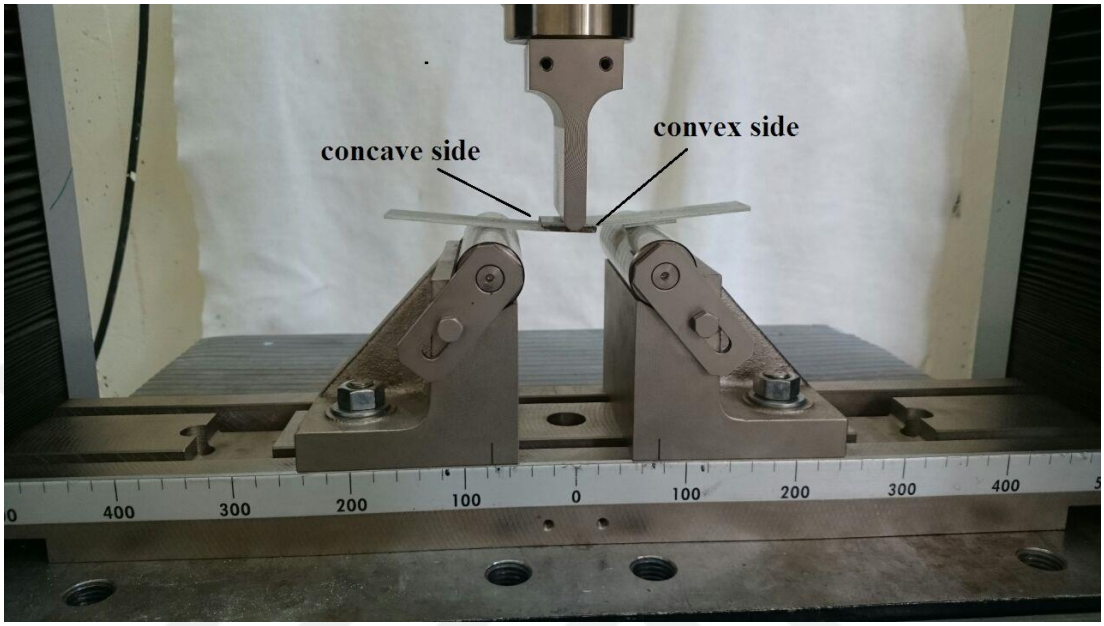


Figure 3.15 Test sample position and loading conditions through the bending test

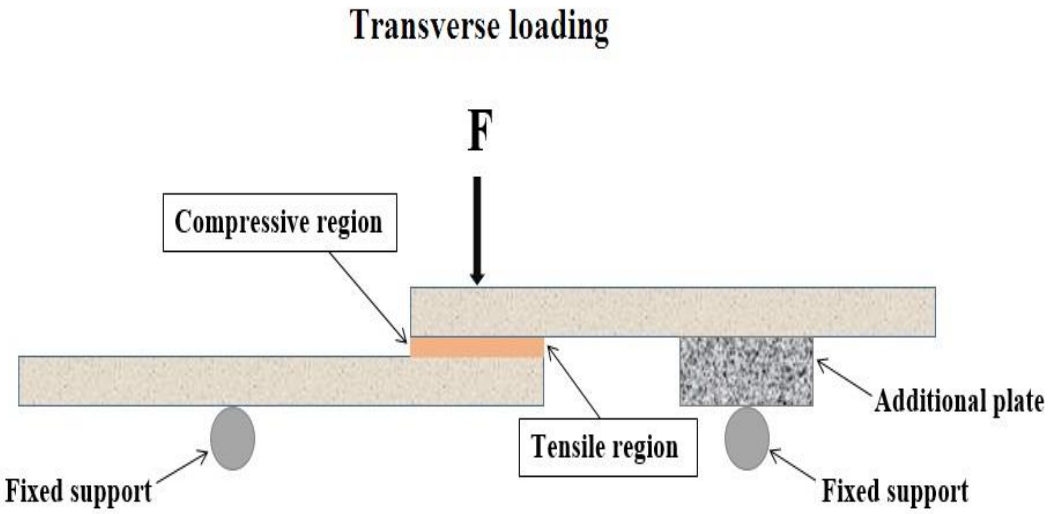


Figure 3.16 Schematics of the three point bending test set-up

CHAPTER 4

RESULTS AND DISCUSSIONS

In chapter three, materials and tools used in this work were briefly described. Preparation method of neat and Nano-reinforced adhesive, surface treatment of bonding areas and production procedure of single lap joint (SLJ) were given. As well as, mechanical tests with loading conditions were clarified. In this chapter, results of the mechanical tests are presented with discussion.

4.1 Effect of Nano-particles on Mechanical Response of Adhesive Joints

In this study, the effects of Nano-reinforcements on the mechanical response (lap shear and bending) of adhesively bonded single lap joints with composite adherends are systematically investigated. Lap shear test and three point bending test on SLJs were conducted in mechanics laboratory of the Mechanical Engineering Department at Gaziantep University. The reinforced adhesives were prepared from different weight ratios of Nano-particles within epoxy resin. The dispersion of nanoparticles was accomplished using a mechanical stirrer. Five samples of bonded joint for each type of adhesive were produced.

The samples were subjected to controlled displacement loading to establish the load-displacement curve for each adhesive type. First, mechanical tests were performed on the neat epoxy at room temperature. Subsequently, the reinforced epoxy samples underwent similar tests. Compared to neat epoxy resin, the results of the mechanical tests revealed the positive influence of Nano-reinforcements on the load carrying capacity of the joints.

Using the recorded values of load and displacement, the stress-strain curve of each adhesive type was constructed. In all tests, the strength of the joints increased as the Nano-reinforcement was increased till the maximum strength obtained from optimal additive rate and then started to trend inversely with more addition of Nano-particle weight content.

4.2 Effect of Clay Nano-Particles (CNPs)

4.2.1 Lap Shear Test Results

Single lap adhesive bonded joints were prepared with epoxy/CNP composite adhesives and tested under lap shear loading in tension. The joints based on different weight ratios of CNP were tested and compared with control samples of neat epoxy. Two parameters fundamentally dominate the adhesive strength: (a) mechanical characteristics of the epoxy resin and CNP and (b) adhesion properties and viscoelastic behavior of epoxy resin. In previous researches on adhesively joints of epoxy [127], it was noticed that the mechanical properties of the joints increased with the increase of Nano particle content, but, at the same time, their viscoelastic behavior has been changed from liquid-like to solid-like. Thus, it was likely that epoxy containing high weight content of CNP will not have good adhesion properties. The results of lap shear tests in tension on the adhesive joints prepared with epoxy containing different amounts of CNP were obtained and presented in load-displacement diagrams (Figure 4.1) and shear stress–shear strain diagrams (Figure 4.2). The shear stress was calculated from tensile load applied on adhesive joints divided by overlap bonding area, and the shear strain was obtained from joint displacement divided by overlap length. The maximum shear strength of SLJs (Figure 4.3) is estimated using the average maximum shear stress shown in Figure 4.2. The variations of standard deviation for the results shown in Figure 4.3 were 0.276 to 0.661 MPa for composite epoxy.

The influence of CNP incorporation into the adhesive layer on the shear strength of SLJs was studied comparatively by the results of adhesive joints reinforced and unreinforced with CNP. It can be seen that the shear strength of adhesive joints increased with the addition of CNP, but above 2 wt. % of CNP, the shear strength decreased. The shear strength values for pure epoxy and epoxy reinforced with 1, 2, 3, and 5 wt. % of CNP were 4.532, 6.187, 8.653, 7.417, and 6.026 MPa, respectively. The results obtained from the lap shear test can be given in Table 4.1.

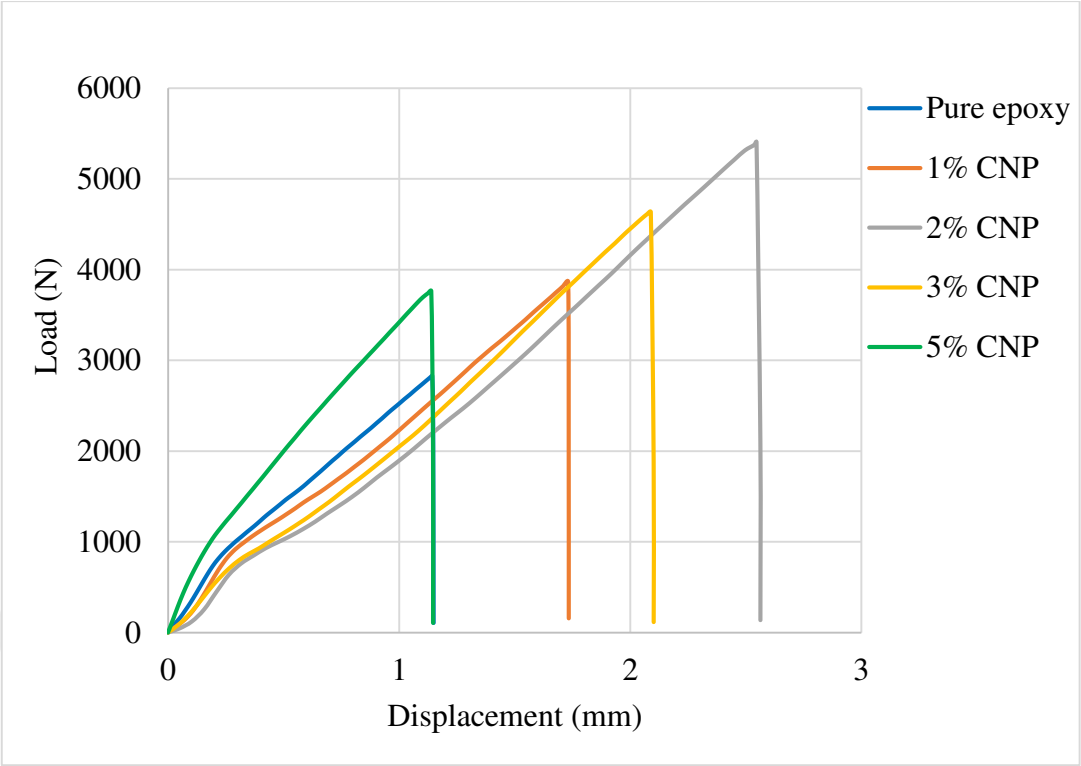


Figure 4.1 Load-displacement curves for SLJs reinforced with different amounts of CNP and subjected to tensile loading

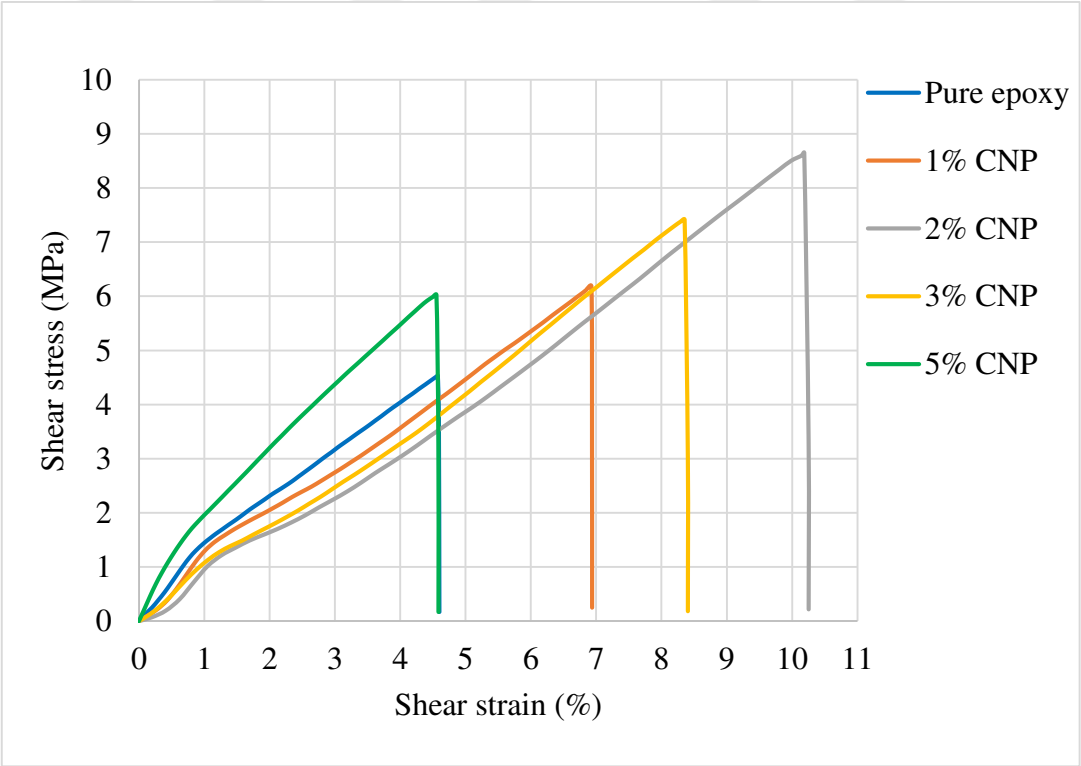


Figure 4.2 Shear stress-shear strain curves for SLJs reinforced with different amounts of CNP and subjected to tensile loading

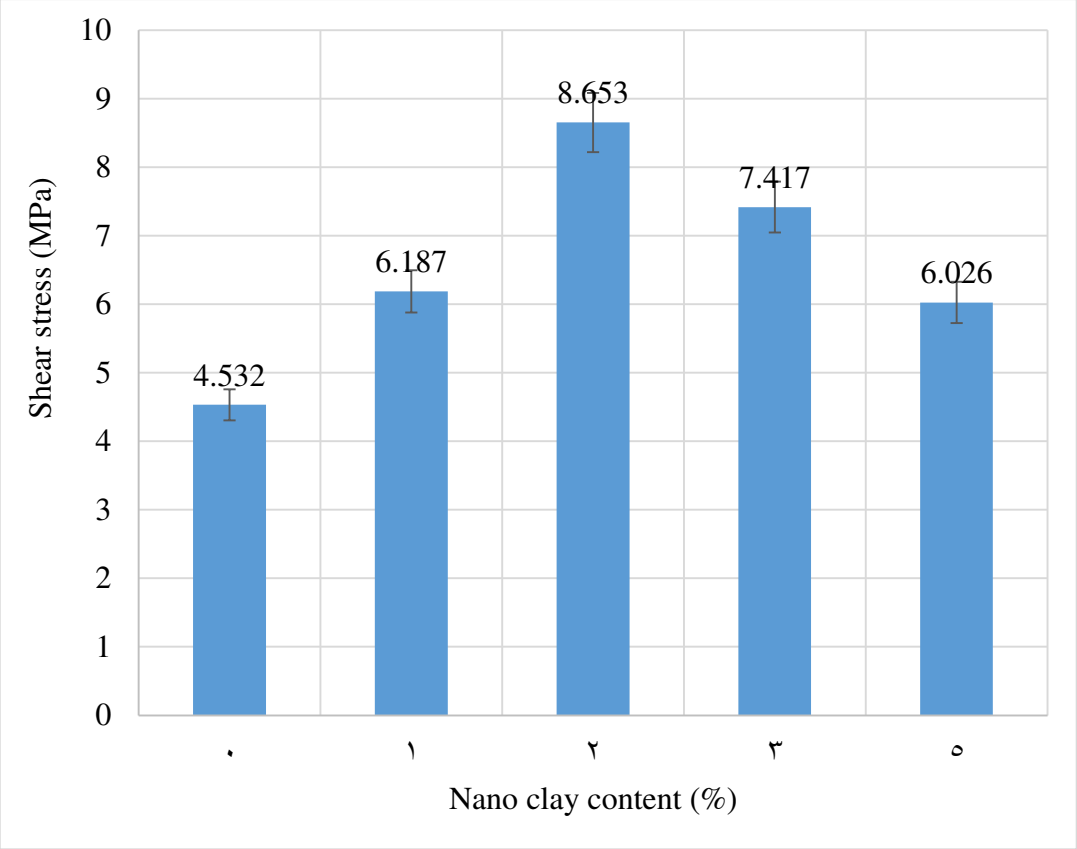


Figure 4.3 Maximum shear strength of SLJs versus CNP weight content

Table 4.1 Lap shear test results of SLJs with various amounts of CNP

Sample code	Epoxy + Hardener (%)	Clay (wt. %)	Max. Force (kN)	Max. Shear stress (MPa)	Max. Shear strain (%)
T_0	100	0	2832.472	4.532	4.573
T_1	99	1	3867.078	6.187	6.927
T_2	98	2	5408.394	8.653	10.187
T_3	97	3	4635.823	7.417	8.355
T_5	95	5	3766.573	6.026	4.554

The shear strength increased by about 36% and 91% with the addition of 1 and 2 wt. % CNP in the epoxy resin. When CNP content exceeded 2 wt. %, the shear strength of Nano-composite adhesive joints decreased with the increase of Nano clay amount. This can be attributed to the aggregation of particles which causes stress concentration and crack growth in the adhesive layer and lead to sudden failure under lower stresses. However, the results stated that the adhesive joints of Nano composite adhesive, for all epoxy/Nano clay designs considered in this study, have shear strength higher than that of control samples. The increase in shear strength was about 36, 91, 63, and 33% for 1, 2, 3, and 5 wt. % of CNP. Much change was noticed in shear strain with the addition of CNP content. The shear strain increased as the CNP increased up to 2 wt. % which resulted in highest shear strain. After that a reduction trend was observed in the shear strain with more addition of CNP than 2 wt. % and the strain value at 5 wt. % was very close to that of neat epoxy. However, for high content ratios, CNP prevent the formation of a homogeneous network in the adhesive layer.

4.2.2 Three Point Bending Test Results

The experimental results obtained from the bending tests for the samples with neat epoxy and CNP reinforced epoxy can be seen in Table 4.2. This table shows the load carrying capacity and flexural strength of the adhesive joint samples. The flexural strength increased with CNP content up to 2 wt. % and decreased for 3 wt. % CNP. The addition of 2 wt. % CNP into the epoxy led to an increase in flexural strength by about 1.85 times (increase percentage is 85%) when compared with flexural strength of neat epoxy joints. Bending load results in higher peel stress concentration in the adhesive layer as compared to shear loading. The increase in peel stress is due to considerable deflection of the joint under transverse normal load [128]. However, it seems that CNPs improve the shear strength and flexural strength of the adhesive joint in the same manner (similar optimum weight content and convergent improvements). The high strength of reinforced joint is basically return to the high tensile properties of adhesive and Nano-particles and the aspect ratio of the CNPs and the interfacial behavior between the CNP and the adhesive matrix [128].

Table 4.2 Three point bending test results of SLJs with various amounts of CNP

Sample code	Epoxy + Hardener (%)	Clay (wt. %)	Max. Force (kN)	Max. Flexural stress (MPa)	Max. Flexural strain (%)
B_0	100	0	171.597	39.222	0.549
B_1	99	1	265.487	60.682	0.859
B_2	98	2	316.890	72.432	1.002
B_3	97	3	274.165	62.666	0.942

The exfoliated clay Nano-platelets were re-aggregated into clay Nano-particles during the mixing process. When the clay weight concentration is higher, thicker particles can be found and the CNPs dispersion is less uniform with a further increase in clay content. The high clay concentration in the matrix as well as the large aspect ratio and high surface to volume ratio of the clay Nano-platelets make it difficult to obtain a uniform dispersion in the epoxy [129]. Furthermore, the number of micro-bubbles is increased with higher CNP content [128]. Therefore, the flexural strength is reduced for reinforced epoxy with high weight content of CNPs for bending loadings.

The three point bending test results were plotted in load-displacement diagram (Figure 4.4) and stress-strain diagram (Figure 4.5). Figure 4.6 shows the maximum flexural strength of joints at different weight ratios of CNP. The results show an increase in flexural strength with the addition of CNP as about 55, 85 and 60% for 1, 2 and 3 wt. %. On the other side, the inclusion of CNP made the epoxy more flexible and hence more strength compared to neat epoxy. The flexural strain increased as CNP content increased up to 2 wt. % and then more addition was resulted in reduced flexural strain.

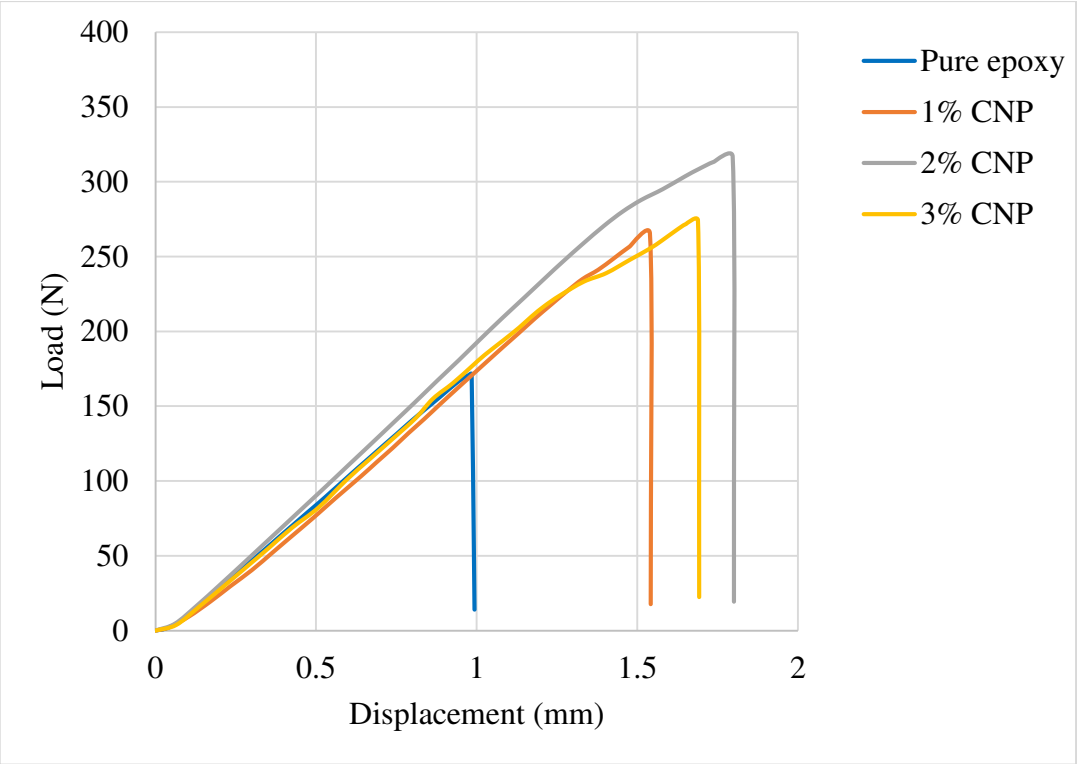


Figure 4.4 Load-displacement curves for SLJs reinforced with different amounts of CNP and subjected to bending loading

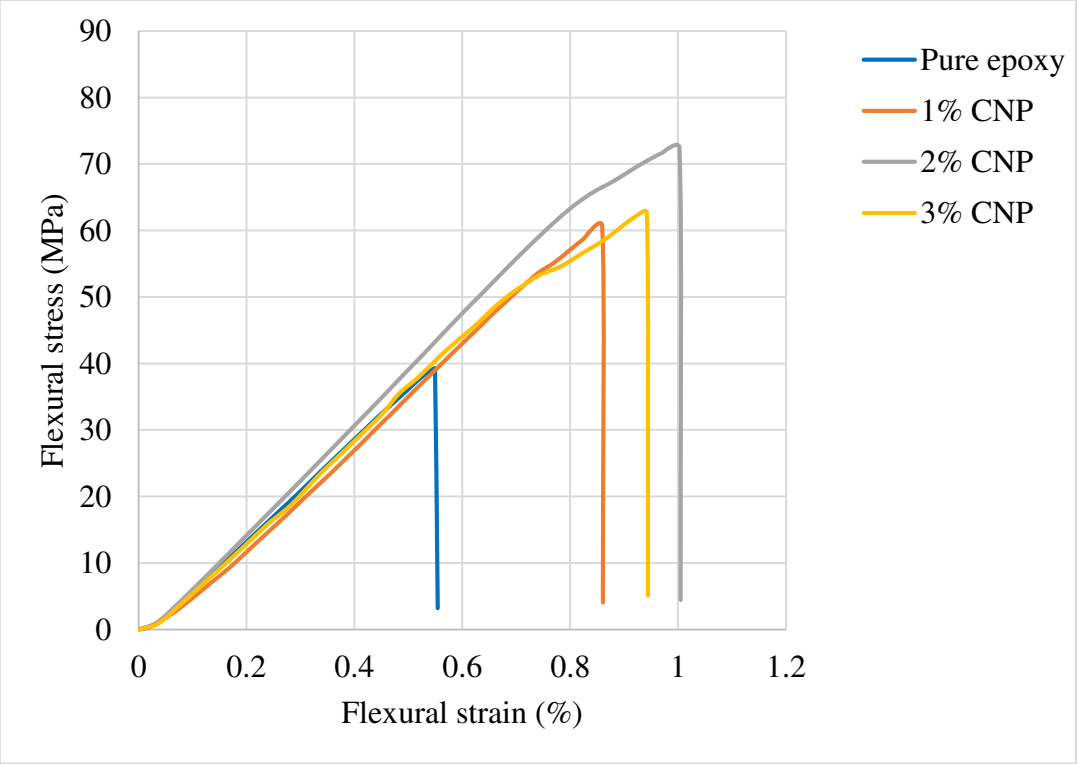


Figure 4.5 Flexural stress-shear strain curves for SLJs reinforced with different amounts of CNP and subjected to bending loading

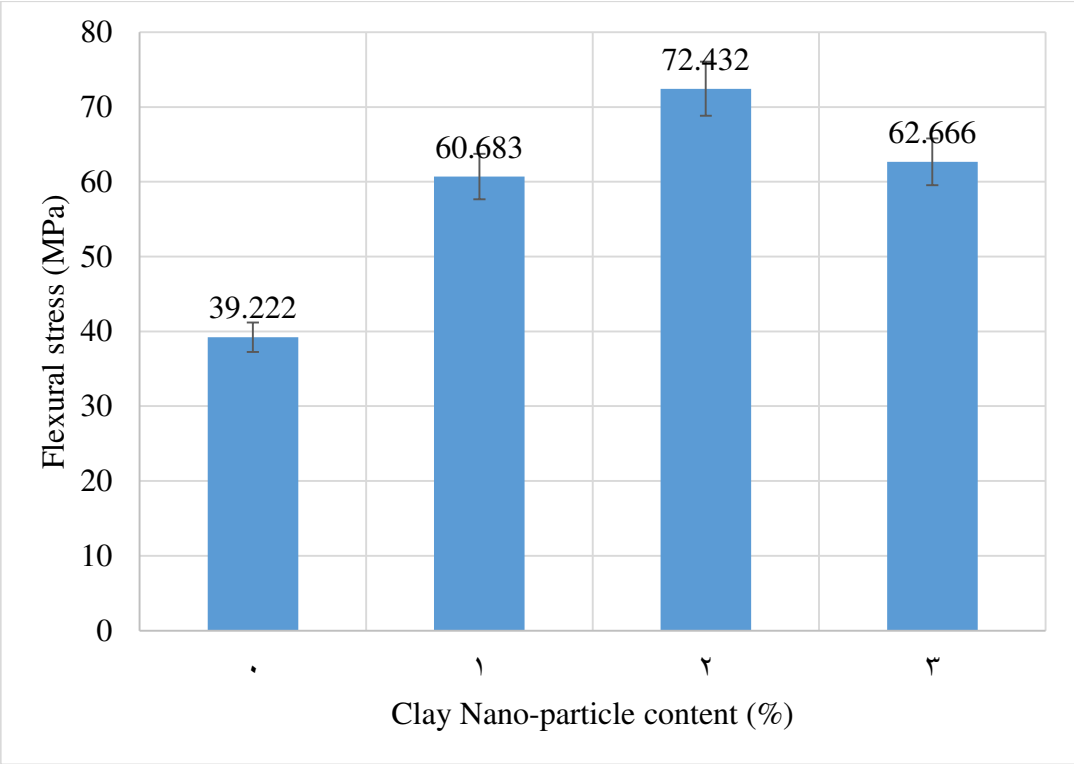


Figure 4.6 Maximum flexural strength of SLJs versus CNP weight content

4.3 Effect of Graphene Nano-Platelets (GNPs)

4.3.1 Lap Shear Test Results

In addition to clay Nano-particles, graphene Nano-platelets were implemented to reinforce epoxy and prepare single lap joints. These joints were tested by tensile loads in shear mode. The lap shear test results of neat and Nano-reinforced epoxy were studied comparatively. During the test, the applied load was increasing gradually till reaches the highest value which can be carried by the joint and then drop suddenly indicating the fracture point. At each load point applied, there was recording for displacement taken place in overlap length. The load-displacement values were plotted and presented in Figure 4.7 while the standard values of shear stress/strain can be seen in Figure 4.8. Each shear strength reported in Figure 4.9 is an average of five samples with the error bars corresponding to standard deviation. The standard deviation was in range of 0.037 to 0.639 MPa.

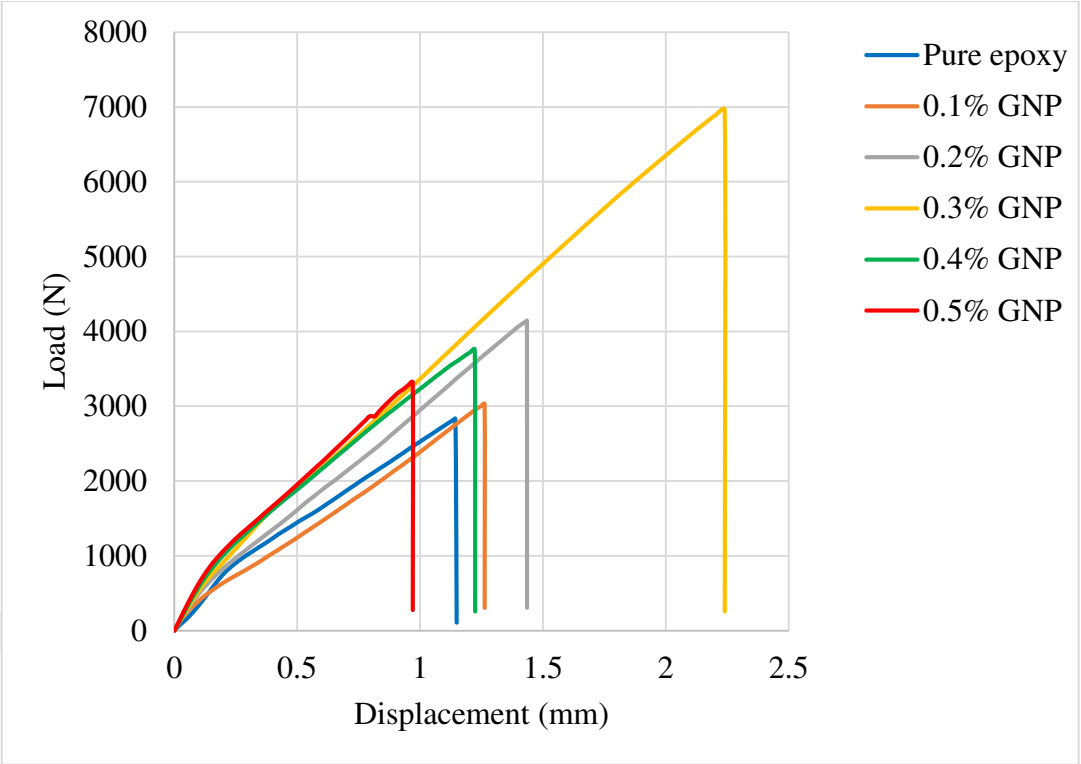


Figure 4.7 Load-displacement curves for SLJs reinforced with different amounts of GNP and subjected to tensile loading

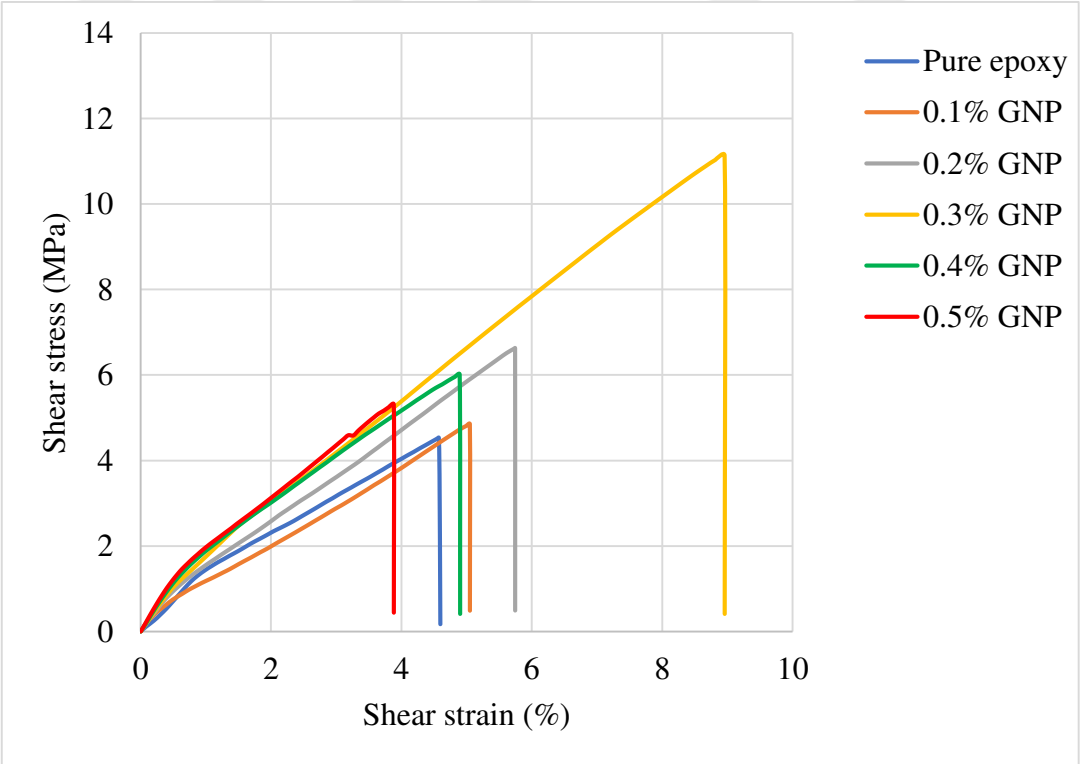


Figure 4.8 Shear stress-shear strain curves for SLJs reinforced with different amounts of GNP and subjected to tensile loading

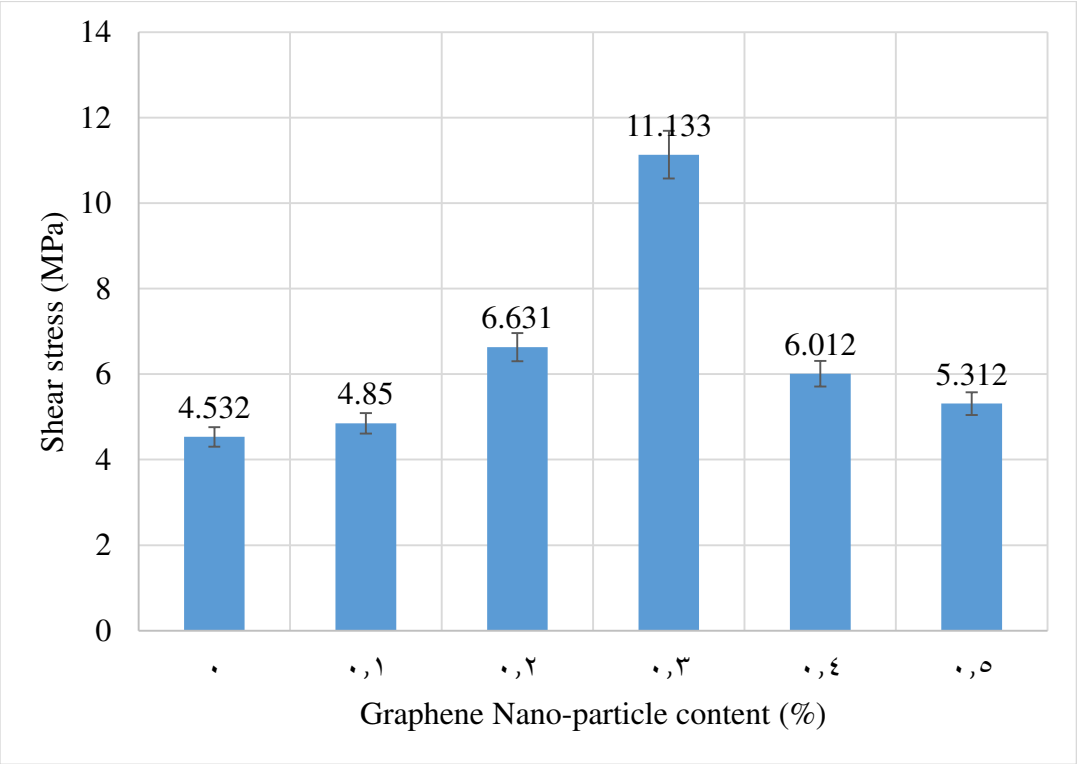


Figure 4.9 Maximum shear strength of SLJs versus GNP weight content

The results showed that GNP was found to be the most effective filler among the three Nano-fillers in shear property. Also the results demonstrated that there is a significant difference between the joint strength of neat epoxy and that of Nano-reinforced epoxy. As the amount of GNPs in the epoxy increases, the joint strength increased and reached the highest value of 11.133 MPa for 0.3 wt. %, which corresponds to a 145% increase in the strength compared to the neat epoxy joint. After that, more addition of GNPs was resulted in reducing the strength of epoxy joints. The high tensile strength and modulus of GNPs contributed to the enhanced shear strength of the adhesive joints. At lower fractions, GNPs were dispersed uniformly and there was a strong interfacial bonding between the matrix and the particles which enabled effective load transfer between them. At higher fractions of the GNPs, the strengthening effect started to reduce due to the formation of agglomerates which are expected to have a weak interface with epoxy [130]. From Figure 4.9, the lap shear strength of the adhesive joints prepared with 0.4 wt. % GNPs was observed to be much lower than that of the adhesive joints prepared with 0.3 wt. % GNPs. This can be attributed to the severe agglomeration of GNPs and the network structure of GNPs which may not get infiltrated properly with epoxy [130]. The joint strength of neat epoxy was 4.532 MPa while the joint strength of GNP/epoxy was 4.850, 6.631, 11.133, 6.012 and 5.312 MPa

for graphene content of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %, respectively. The experimental results of lap shear test can be seen in Table 4.3. These results show an increase in joint strength for all additive ratios of GNPs, considered in this work, in comparison with the joint strength of pure epoxy. These increases were about 7, 46, 145, 32 and 17% for graphene additive ratio of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %.

Table 4.3 Lap shear test results of SLJs with various amounts of GNP

Sample code	Epoxy + Hardener (%)	Graphene (wt. %)	Max. Force (kN)	Max. Shear stress (MPa)	Max. Shear strain (%)
T_0	100	0	2832.472	4.532	4.573
T_1	99.9	0.1	3031.047	4.850	5.051
T_2	99.8	0.2	4144.795	6.631	5.741
T_3	99.7	0.3	6958.293	11.133	8.957
T_4	99.6	0.4	3757.651	6.012	4.890
T_5	99.5	0.5	3320.233	5.312	3.881

Shear strain also has changed in the presence of Nano-graphene and increased as graphene content increased up to 0.3 wt. %, indicating the highest value of shear strain at 0.3 wt. %. More addition of graphene was resulted in decreasing the shear strain significantly. At 0.4 wt. % of GNPs, the shear strain value was higher than that of neat epoxy and less than that of 0.1% GNP-reinforced epoxy. The lowest value of shear strain was obtained in the case of 0.5 wt. % GNP compared to neat epoxy and other cases of graphene additives.

4.3.2 Three Point Bending Test Results

Transverse normal loading of the joint causes considerable deflection of the adherend, which leads to a higher peel stress concentration as compared to the in-plane loading.

There were several important observations for symmetrical transverse normal loading of the joint. First, the peel stress changes from tensile at one edge of the joint to compressive at the other. The magnitude of the maximum peel stress was found to be higher than for in-plane loading of the joint. Second, the crack always initiates from the edge of the lower adherend where the peel stress is tensile in nature. Third, the stress distribution around the crack tip changes as the crack propagates through the adhesive. Fourth, the toughness of the adhesive was found to have a great influence on the load carrying capacity of the joint. The toughness of the adhesive becomes more critical when the loading is transverse normal to the plane of the joint. In transverse normal loading, the joint and the adhesive undergo considerable deflection. Therefore, decrease in the toughness of the adhesive could be expected to have a pronounced effect on the load carrying capacity of the bonded joint [131].

Graphene Nano-platelets was used as an attempt to toughen epoxy joints subjected to transverse loading. Three point bending test was conducted on single lap adhesive joints of neat and graphene reinforced epoxy for that purpose. The addition of GNPs to epoxy was found to increase the failure strain and failure stress. In terms of performance, the energies to failure of the joint with GNPs-reinforced epoxy were found to be much higher than that of joint with neat epoxy. It was found that flexural strength increased as GNP content increased up to 0.2 wt. %. The maximum increase in flexural strength was about 100% and determined at 0.2 wt. % of GNP. Addition of 0.3 wt. % GNP was resulted in reduced strength compared to 0.2 wt. %. At high fractions of Nano-particles, poor adhesive wetting ability occurs due to increased viscosity which resulted in poor adhesion. Also, agglomeration possibilities of Nano-particles due to high surface area could be a reason for reduced strength as a result to stress concentration at particle aggregates.

The results of bending tests are given in Table 4.4 in terms of failure load and stress. Applied load values with corresponded displacements were plotted as shown in Figure 4.10 while the standard values of stress and strain can be seen in Figure 4.11. Figure 4.12 shows the flexural strength of adhesive joints at fracture for neat and reinforced epoxy. The energy to failure increased as a result to increase in flexural strain of the joints with the inclusion of GNP. The flexural strain increased in low graphene content cases (0.1 and 0.2 wt. %). High graphene content (0.3 wt. %) was resulted in reduced strain and hence reduced energy to failure as shown in Figure 4.11.

Table 4.4 Three point bending test results of SLJs with various amounts of GNP

Sample code	Epoxy + Hardener (%)	Graphene (wt. %)	Max. Force (kN)	Max. Flexural stress (MPa)	Max. Flexural strain (%)
B_0	100	0	171.597	39.222	0.549
B_1	99.9	0.1	236.352	54.023	0.738
B_2	99.8	0.2	346.374	79.171	1.125
B_3	99.7	0.3	233.475	53.366	0.714

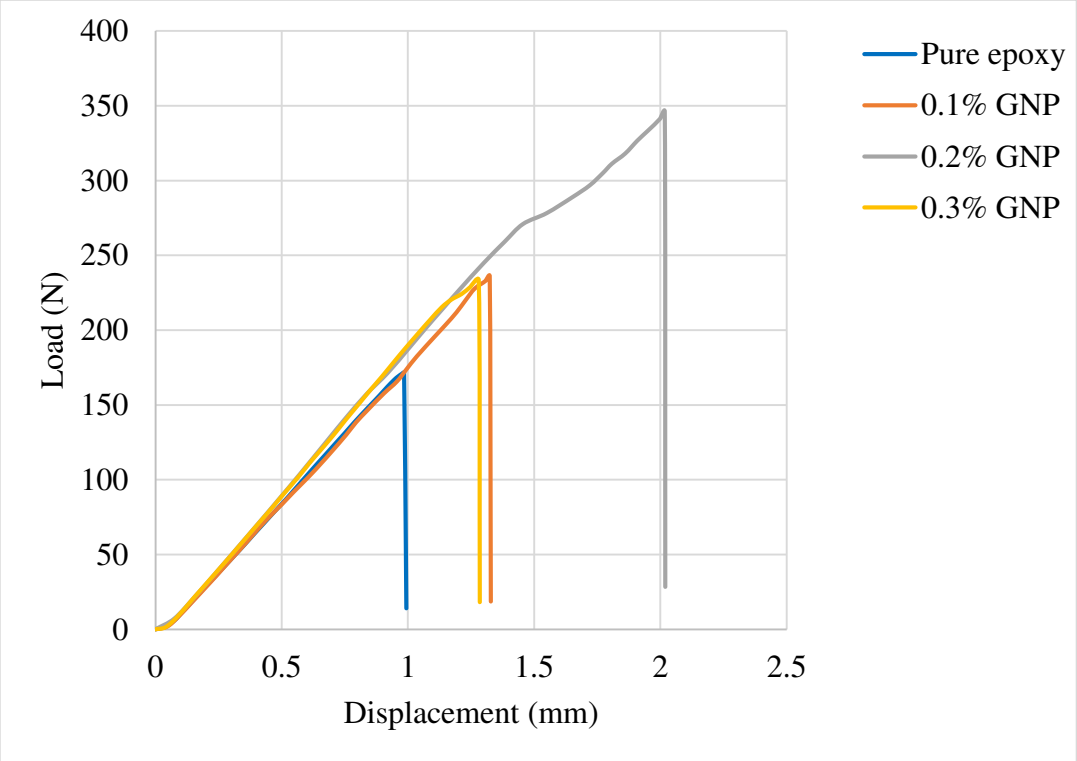


Figure 4.10 Load-displacement curves for SLJs reinforced with different amounts of GNP and subjected to bending loading

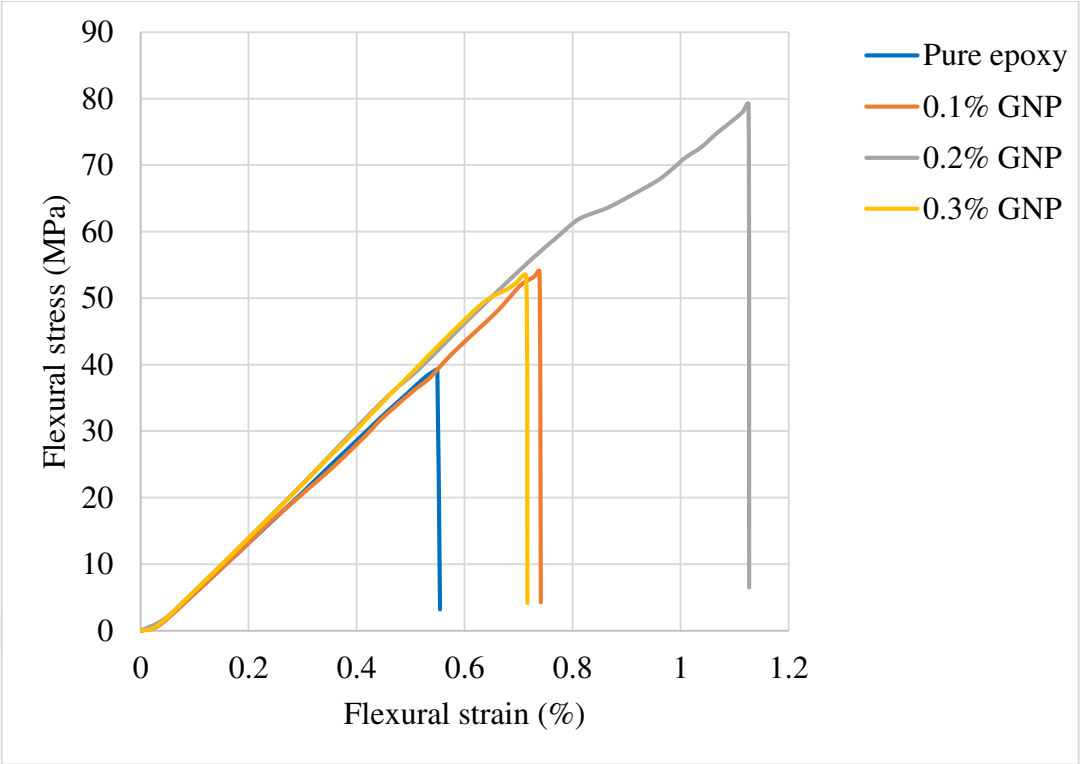


Figure 4.11 Flexural stress-shear strain curves for SLJs reinforced with different amounts of GNP and subjected to bending loading

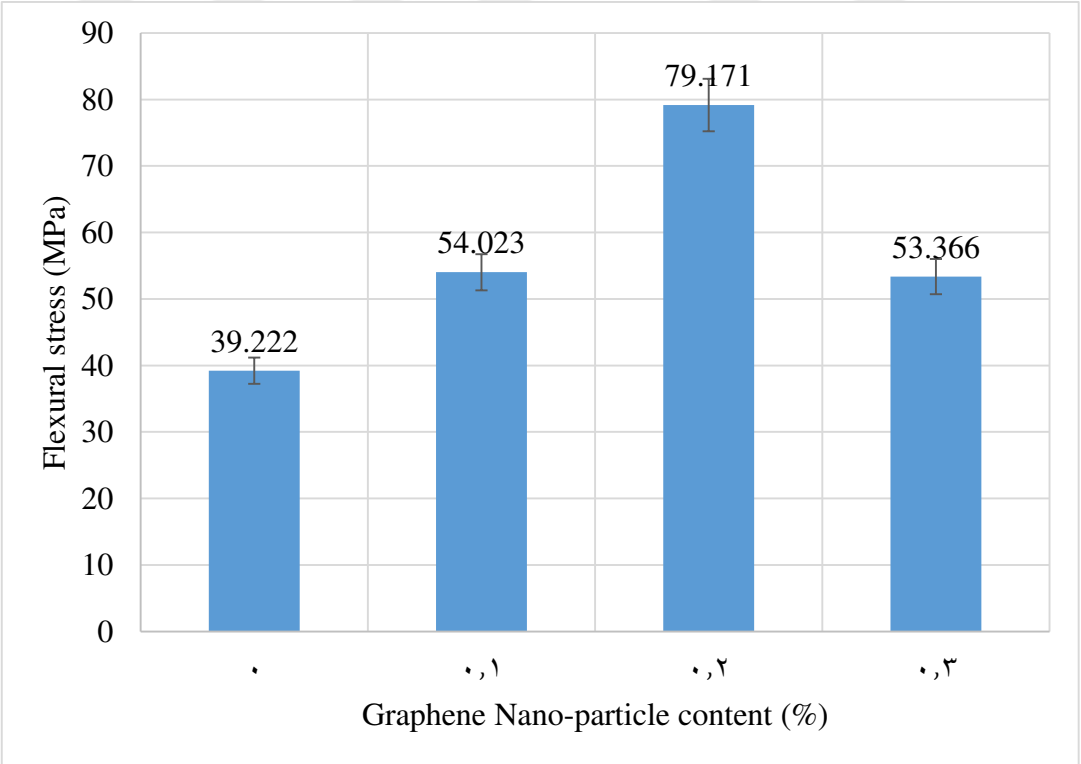


Figure 4.12 Maximum flexural strength of SLJs versus GNP weight content

4.4 Effect of Silica Nano-Particles (SNPs)

4.4.1 Lap Shear Test Results

The lap shear behavior of SNPs reinforced epoxy joints was studied by different weight ratios (0, 1, 2, and 3%) within epoxy resin and the results can be seen in Figures 4.13 and 4.14. The results showed that the shear strength (Figure 4.15) at fracture increased with increasing fraction of SNPs, indicating that the incorporation of SNPs in the epoxy resin has improved mechanical properties of the epoxy resin. The maximum increase in shear strength with the dispersion of Nano-sized SiO2 particles is about 19 % for 1 wt. % of SNPs as compared with neat epoxy. The decrease in shear strength at the higher weight percentage of nano-sized SiO2 particles is due to agglomeration of particles at percentages higher than 1 wt. %. The decrease in strength with further increase in filler percentage is due to the increase in the constraint between polymer chains and thereby decreasing the length of chains over certain critical length [132]. Initially, with the increase in particles concentration, shear strength increases up to a critical value of strength, beyond which it starts decreasing with further increase in concentration. With the increase of SNPs dispersion, there is an increase in disturbance of bonding between molecular chains due to excessive proximity among particles which may lead to build stress concentration and finally the shear strength decreases. Because of the high surface area, the interaction of nanoparticles with epoxy matrix will be efficient. Thus, much nanoparticles may be added to the epoxy matrix to reach to a level where it will start disturbing molecular chains (due to excessive proximity among particles) [133]. Since the increased amount of Nano-sized particles beyond critical value makes it difficult to disperse in matrix, it starts agglomerating leading to decreasing shear strength of the Nano-composite adhesive. Nano SiO2 reinforced epoxy joints have showed the lower amount of strain at fracture as compared with neat epoxy joints at all concentrations studied. When bonding between matrix and Nano-filler is strong, then the ultimate shear strength and toughness of the Nano-composite adhesive increases. The strength depends weakly on the size of the cluster and depends strongly on the number of separated particles or fine clusters which might restrain the mobility of polymer chain more effectively. Increased connectivity of yielded micro-zones around individual particles is expected to result in superior reinforcing effect generated by the SiO2 nanoparticles compared to that provided by conventional particles or nanoparticle clusters in the size range of microns [134]. The enhancement

of toughness may also be contributed by the change in the morphological architecture which increases the interaction between the nanoparticle and the matrix at the particle-matrix interface [135]. However, further increase of nanoparticle loading in the epoxy matrix results in increase in cluster size and thereby the loosely bound clusters may easily lead to cracking and reducing the toughness of the Nano-composite adhesive. The results obtained from the lap shear test are shown in Table 4.5. The variations of standard deviation for the shear stress values shown in Table 4.5 were 0.038 to 0.281 MPa for SNP/ epoxy.

It is worth mentioning that the reinforced adhesives showed brittle behavior compared to un-reinforced adhesive. Joint displacement decreased as the particle content increased.

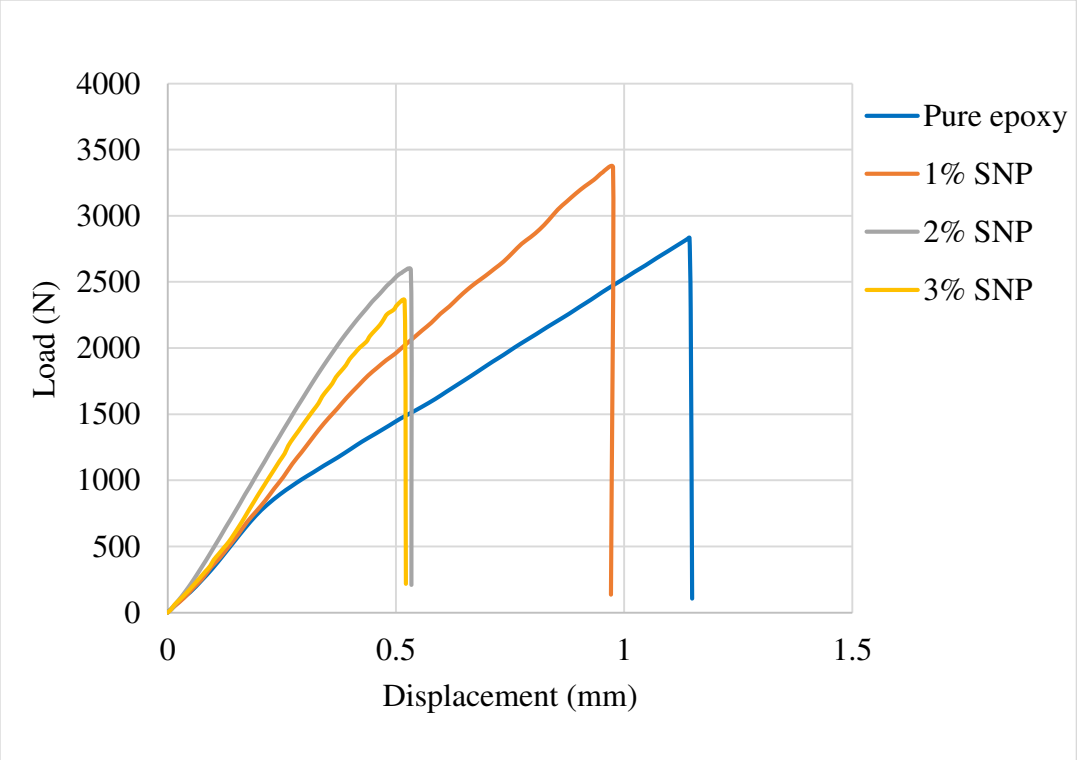


Figure 4.13 Load-displacement curves for SLJs reinforced with different amounts of SNP and subjected to tensile loading

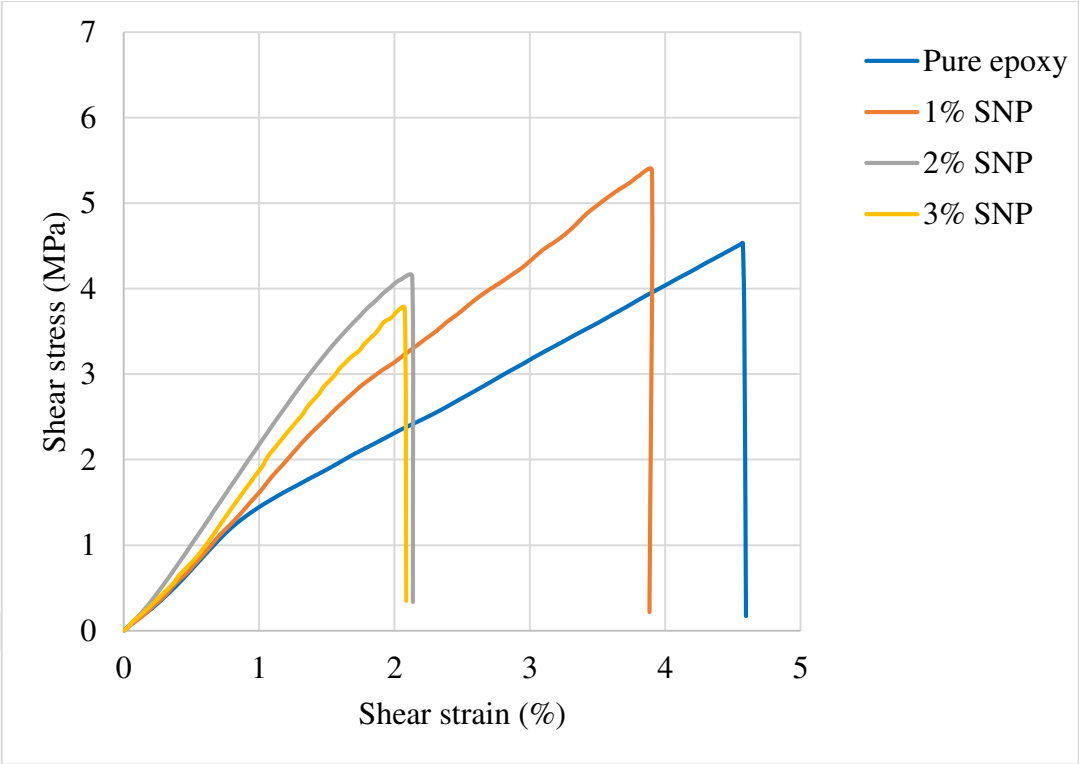


Figure 4.14 Shear stress-shear strain curves for SLJs reinforced with different amounts of SNP and subjected to tensile loading

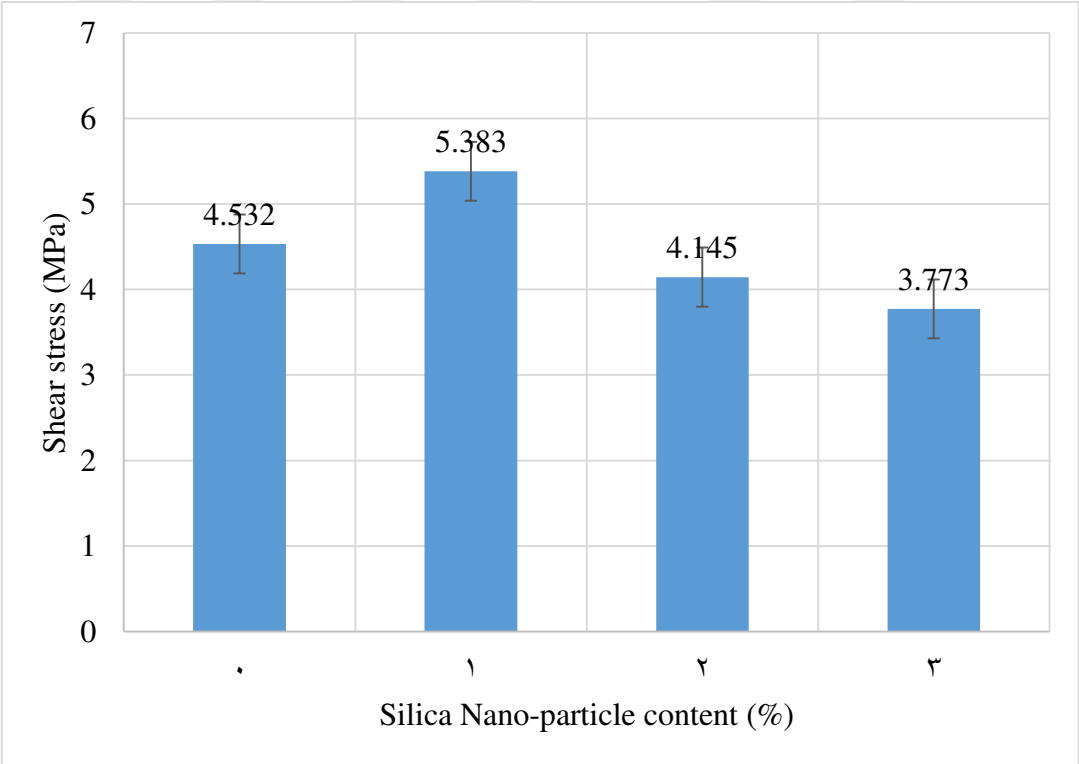


Figure 4.15 Maximum shear strength of SLJs versus SNP weight content

Table 4.5 Lap shear test results of SLJs with various amounts of SNP

Sample code	Epoxy + Hardener (%)	Silica (wt. %)	Max. Force (kN)	Max. Shear stress (MPa)	Max. Shear strain (%)
T_0	100	0	2832.472	4.532	4.573
T_1	99	1	3364.705	5.383	3.902
T_2	98	2	2590.592	4.145	2.130
T_3	97	3	2358.436	3.773	2.076

4.4.2 Three Point Bending Test Results

The failure behavior of the joint in bending test is due to the increase in stress concentration at the tensile end edge. The crack initiates and propagates towards the other end edge. The bending loading was continuing with constant cross head speed till the failure occurs [136]. Adding silica Nano-particles (SNPs) into epoxy was another attempt to strengthen the adhesive joint and increase its resistance to bend loads. The experiments have demonstrated the excellent influence of silica on the bending strength. The effectiveness of Nano-silica reinforcements is quite obvious in increasing the strength and displacement of the joint together and hence the toughness of the joint. Increases in joint strength and load carrying capacity have obtained with all weight contents of silica selected in this work. For comparison purposes all test data, that is, the average ultimate failure loads, displacement and stresses of all the joint samples are summarized in Table 4.6. Figure 4.16 shows the load-displacement curves for samples of reinforced adhesive along with the sample of the neat adhesive for comparison purposes. Figures 4.17 and 4.18 indicate that reinforcing the adhesive by SNP enhances the flexural strength of the joints. Figure 4.18 indicates that the highest ultimate strength was presented by the joint reinforced with 2 wt. % SNP, whereas the joint reinforced with neat adhesive displayed the lowest one. However, the behavior of the joint reinforced with 3 wt. % is better than that one reinforced with 1 wt. %. As can be seen, the maximum increase in the joint strength was 94% for the joint in which the adhesive layer reinforced with 2 wt. % SNP.

On the contrary of lap shear test, the bending test results show that the epoxy reinforced with SNP are more ductile than pure state. Much change was observed in the strain to failure of the reinforced joints compared to the neat adhesive. The strain increase was not continued with the addition of SNPs. The flexural strain increased as SNP content increased till optimum rate (2 wt. %). Then, reducing was observed in the flexural strain with more addition of SNP resulting in reduced strength.

Table 4.6 Three point bending test results of SLJs with various amounts of SNP

Sample code	Epoxy + Hardener (%)	Silica (wt. %)	Max. Force (kN)	Max. Flexural stress (MPa)	Max. Flexural strain (%)
B_0	100	0	171.597	39.222	0.549
B_1	99	1	214.004	48.915	0.720
B_2	98	2	332.943	76.101	0.933
B_3	97	3	265.375	60.657	0.776

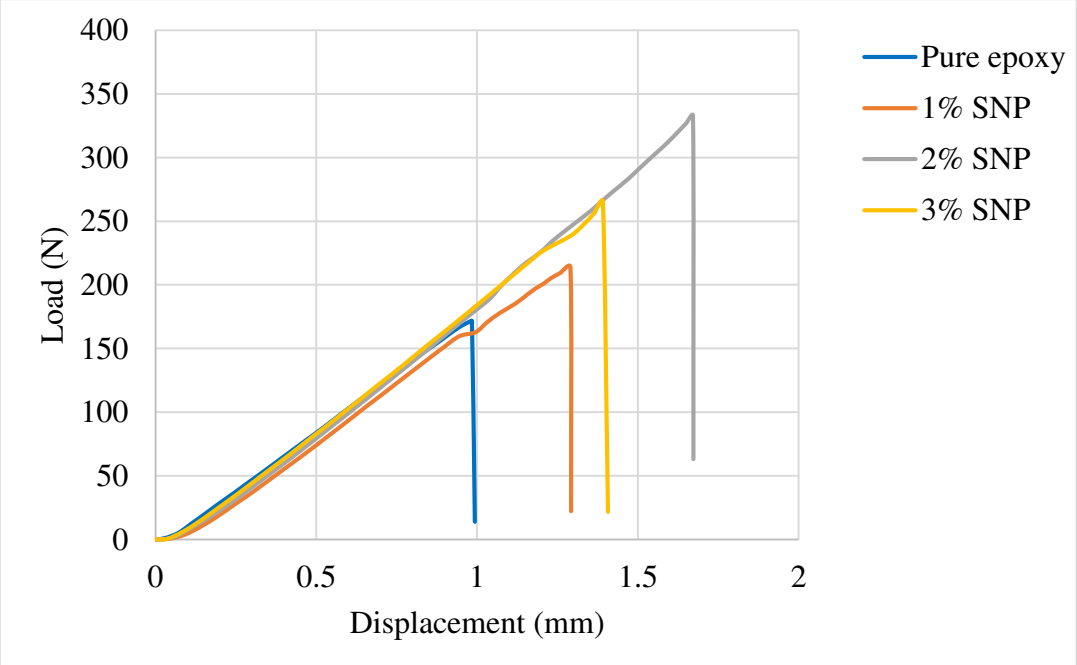


Figure 4.16 Load-displacement curves for SLJs reinforced with different amounts of SNP and subjected to bending loading

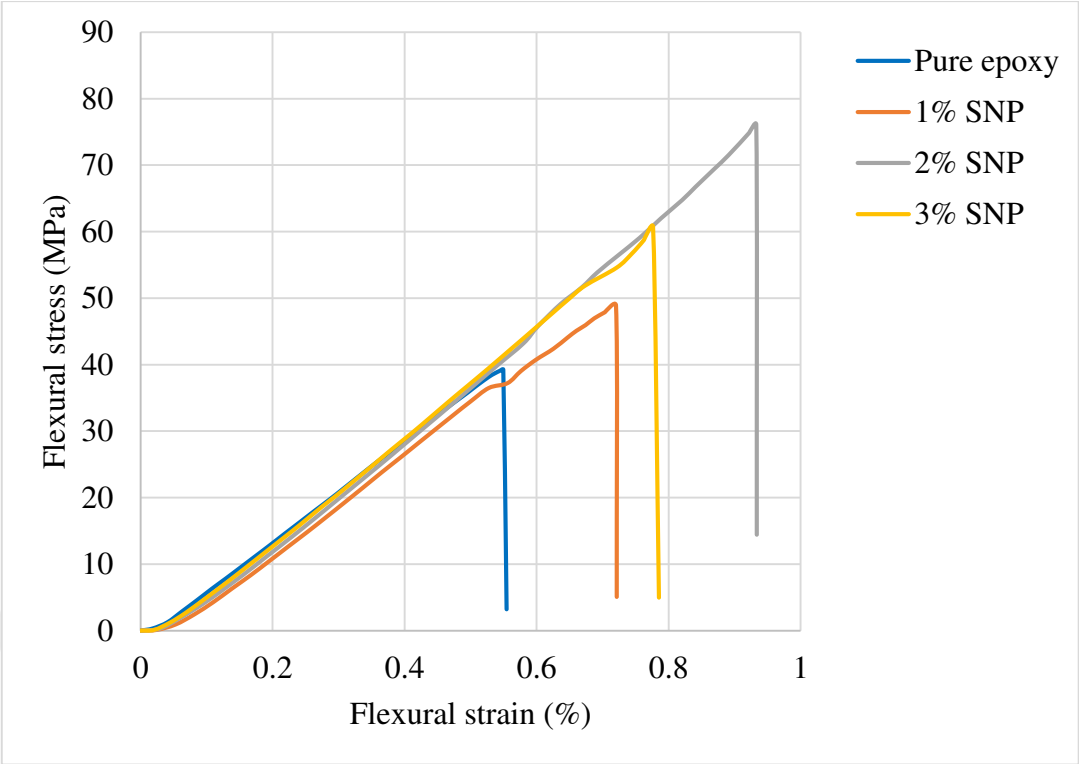


Figure 4.17 Flexural stress-shear strain curves for SLJs reinforced with different amounts of CNP and subjected to bending loading

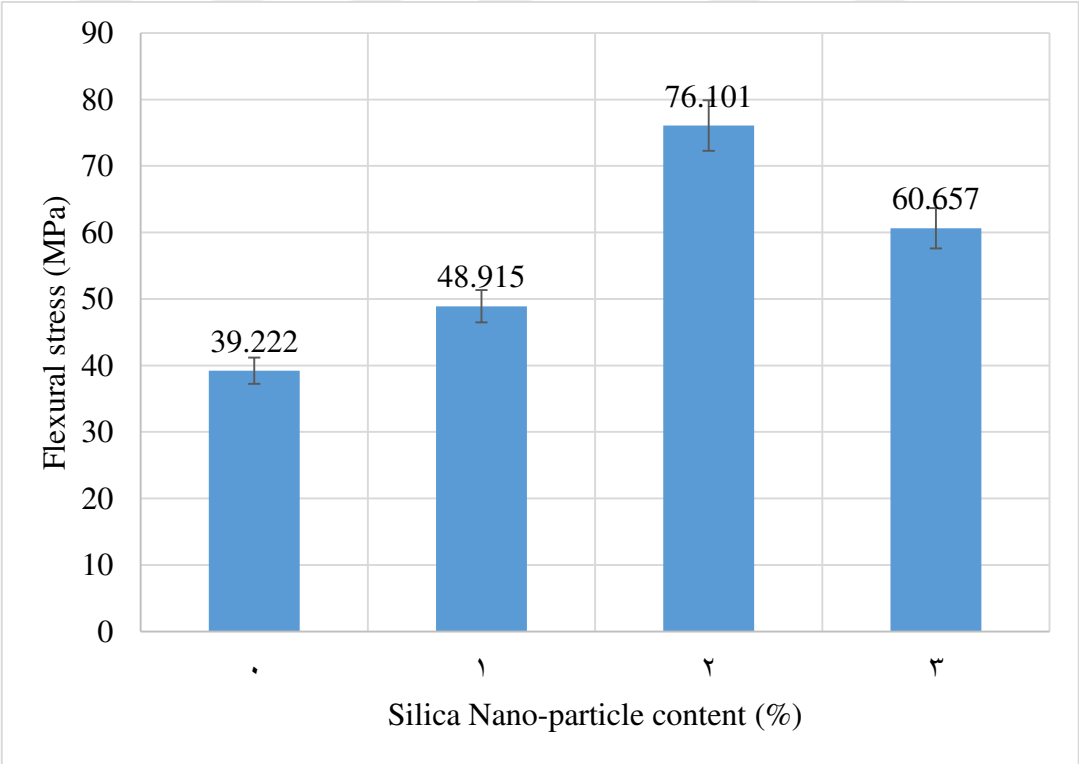


Figure 4.18 Maximum flexural strength of SLJs versus SNP weight content

4.5 Failure Modes of Adhesively Single Lap Joints

Causes of a certain mode of bond failure can be detected by observing and studying the fracture surfaces. Since single lap joints are not subjected to co-linear loads through in-plane loading, bending moment can be occurred leading joints to rotate. As a result, peel stresses arise at overlap tips. Failure initiation is taken place at the free ends of bonded joint due to these stresses (beside basic loads) [137].

There are two fundamental failure modes in adhesive bonded joints: adhesive failure and cohesive failure. Adhesive failure is an interfacial failure caused by complete separation between the adhesive and the adherend at one side. Cohesive failure is taken place in the adhesive layer only when a thin layer of adhesive still stuck on both sides. A combination between the two modes of failure can be obtained if the joint is neither strong enough to fail cohesively nor very weak to fail adhesively [138]. Nano-particles have the ability to fill micro voids of the substrate surfaces, emerging new points of contact and hence great opportunity to improve the adhesion strength is offered. On the other side, Nano-particles can fill in the inner-spaces between adhesion molecules which results in improved cohesion. Through many studies, it was proved that Nano-composite adhesives can give higher surface wetting capability than pure adhesives resulting in higher adhesion strength of joints. Some researchers have attributed the improvement in joint strength to the forming of chemical bonds between the Nano-composite adhesive and the adherend surfaces. Others have justified the strength increment of the joints by the improvement of adhesive mechanical properties [139].

Incorporating the Nano-particles at low concentrations within epoxy resins was found to have a significant influence on the mechanical properties and particularly the epoxy toughness and lap shear strength. Many researches and documented reports have been stated the increases in the adhesive properties with addition of low content of Nano-particles. These increases are directly related to the improved plastic deformation of the adhesive layer due to the formation of new toughness mechanisms, such as crack deviation and crack twisting around the Nano-particles [140]. The particles also help in blunting the crack tip and cracks would be compelled to create a more tortuous path to enhance toughness [97]. Collision between cracks and the Nano-particles deviates the crack path to a longer path and thus resulting in larger fracture surface [141]. However, at relatively high concentrations of the Nano-particles, the adhesive

mechanical properties fall because of the adhesive disability to wet surfaces due to its increased viscosity. The reduced mechanical properties of the adhesively joints can be interpreted by another mechanisms, such as increased viscosity of the adhesive or the formation of particle agglomerations of micro-sized because of inefficient dispersion [139].

For this study, the test samples have showed different failure mechanisms depending on the Nano-filler type and loading type. However, the basic modes of failure observed were adhesive, cohesive and mixed mode. Neither fiber imprints nor other types of failure (like fiber tear failure, adherend failure, etc.) were seen during the experiments. After conducting the lap shear test the fracture surfaces of neat epoxy joints showed an adhesive failure only. This type of failure had been changing gradually to more developed failure (i.e. higher failure load) with the addition of Nano-fillers up to a certain content. For the case of CNP, adhesive failure was the only mode of failure observed at particle loading of 1, 3 and 5 wt. % (Figure 4.19a). While addition of CNP by 2 wt. % presented a mixed mode failure with apparent adhesive layers at both side of fracture surfaces (Figure 4.19a). This content of CNP was resulted in the highest joint strength compared with the other particle loadings and this type of failure was an inevitable result for the increased strength. Sever particle agglomeration can be seen at the adherend-adhesive interface for the case of incorporating 5 wt. % CNP which resulted in the lowest joint strength value compared to other addition cases of CNP (Figure 4.19a). Nano-silica had almost similar failure behavior to that of the CNP. For this type of Nano-filler, the maximum joint strength was obtained by adding 1 wt. % of silica into the epoxy and the joint of this epoxy composition was failed with mixed mode of failure (Figure 4.19b). Adhesive failure mode is quite obvious for silica addition cases of 2 and 3 wt. % (Figure 4.19b).

The third type of Nano-fillers (GNPs) has presented different failure modes than those observed in samples of CNP/epoxy and SNP/epoxy. No ideal separation has taken place at the joint components interface in all addition cases of GNP. Small portion of the adhesive layer had tended to separate from one side of fracture surfaces and stick on the other side representing the mixed mode failure for graphene addition cases of 0.2, 0.4 and 0.5 wt. % (Figure 4.19c). This small portion was missed on both sides at 0.1 wt. % of GNP which resulted in the lowest joint strength value in comparison with the other cases of GNP addition (Figure 4.19c). Separating of part of the adhesive from

both side of surfaces may had ruptured the bond and prevented it from carrying more loads. The most interesting failure mode in the lap shear test can be seen in the joint of GNP/epoxy with 0.3 % weight content. This joint has given the highest shear strength compared to all joints reinforced with different Nano-fillers and weight contents. Adhesive and cohesive failures with different proportions can be clearly observed on fracture surfaces of this joint (Figure 4.19c). This unique combination of failure modes is rare occurrence and may be attributed to the high improving percentage (145%) in the shear strength.

0% CNP

1% CNP

2% CNP

3% CNP

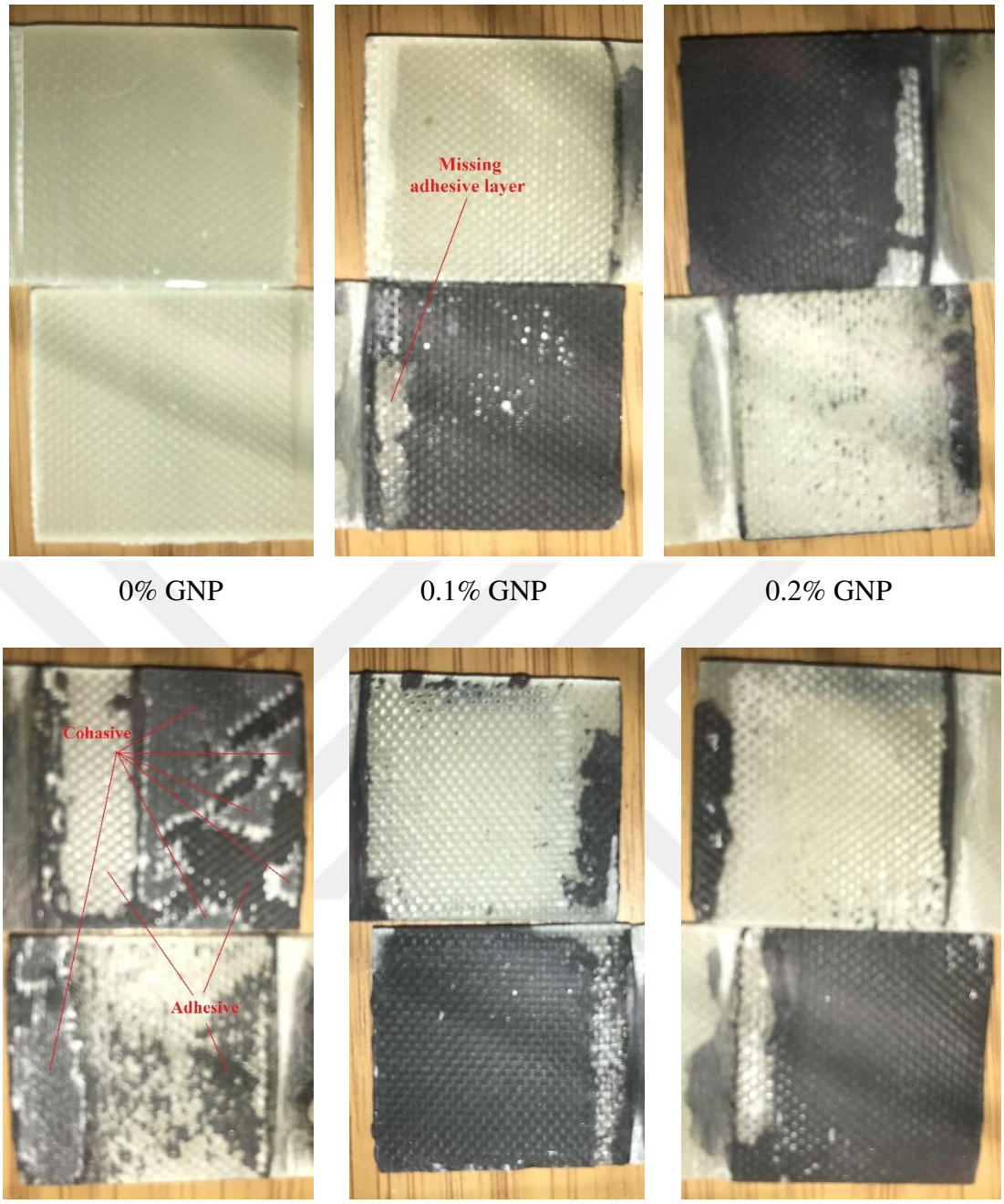
5% CNP

(a)

0% SNP

1% SNP 2% SNP 3% SNP

(b)



0% GNP 0.1% GNP 0.2% GNP

0.3% GNP 0.4% GNP 0.5% GNP

(c)

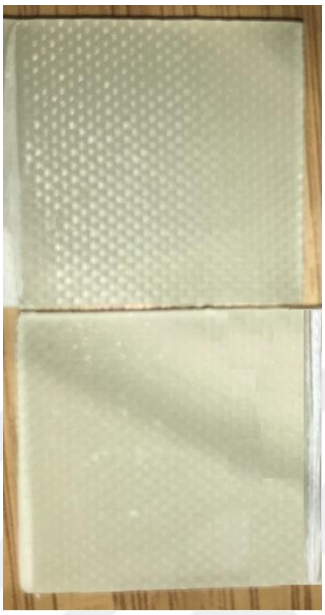
Figure 4.19 Fracture surfaces of SLJs prepared with different weight contents of Nano-fillers and tested under lap shear loads; (a) CNP, (b) SNP, and (c) GNP

In the case of out-of plane loading, the adhesive joints are subjected to tension action at one free end while the other free end is exposed to compression action. These two reverse actions produce positive peel stress at tension region and negative peel stress at compression region. As a result, crack starts at the joint tip exposed to positive peel

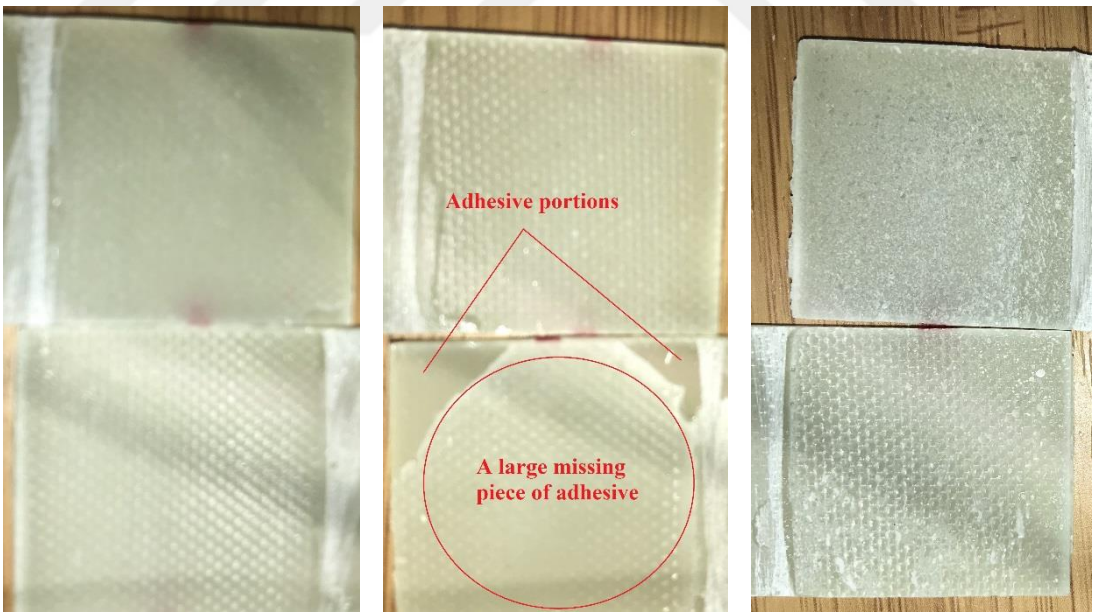
(crack opening) and propagates towards the other tip (crack closing) and then an inevitable and fast failure will be occurred [142].

The fracture surfaces of the adhesive joints subjected to three point bending loading (out-of plane loading) have been studied and several observations can be reported. The joints of neat epoxy were failed with adhesive failure mode only and the surfaces were left intact. This type of failure was a result of the lowest flexural strength obtained from the bending test. The addition of 1 and 3 wt. % of CNP into the epoxy, has improved the joint strength considerably but the failure mode was kept without any change (adhesive mode). The mixed mode of failure is quite apparent in fracture surfaces of the joints reinforced with 2 wt. % CNP. A large area of adhesive layer was separated from both side of adherends while small portions were stuck on each sides (Figure 4.20a). As a result, this joint has given the maximum strength among the joints reinforced with different contents of CNP. The joints reinforced by 1 and 3 wt. % of SNP were failed in same manner of their counterparts of CNP. Adhesive failure is clearly seen with intact surfaces at both adherend sides. Whereas, a small part of adhesive was separated from one side and stuck on the other side of fracture surfaces (Figure 4.20b) for the case of addition 2 wt. % SNP. This kind of rupture in the adhesive layer changes the failure mode to more advanced one (mixed mode) leading to increased strength. It is worth mentioning that severe particle agglomerations can be shown at relatively high particle concentrations (3 wt. %) for both types of Nano-fillers (clay and silica). They might be the main reason of premature failure and reduced strength. The graphene comes again, but this time in the bending test, to present the best improvements in strength and more advanced failure compared to the other Nano-fillers. Addition of 0.1 wt. % of GNP enhanced the flexural strength of the adhesive joint and presented mixed mode of failure. The fracture surfaces obviously show this type of failure where small piece of adhesive were found to be stuck on one surface individually, leaving the remaining adhesive on the opposite side. The adhesive joints reinforced with 0.3 wt. % GNP have exhibited adhesive failure with very little proportion of cohesive failure (Figure 4.20c). The most important failure mode obtained from the bending test is shown in samples prepared with 0.2 wt. % GNP/epoxy. This failure is somewhat similar to the failure of the joint prepared with 0.3 wt. % GNP/epoxy and subjected to shear loading. Different areas of the adhesive layer failed cohesively, while other larger areas clearly showed adhesive failure. This

failure is caused by high joint strength where the highest flexural strength was obtained by reinforcing the adhesive joint with 0.2 wt. % GNP. Finally, the experiments have demonstrated that there is a strong correlation between the joint strength and the fracture pattern that the joint presents.

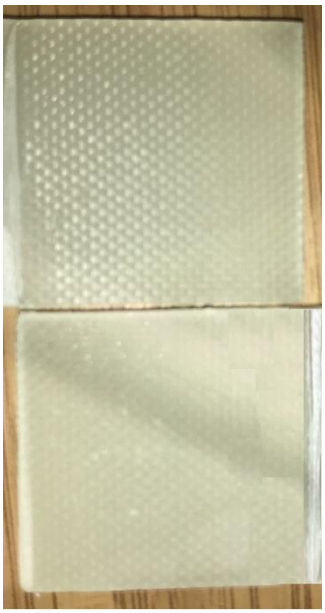


0% CNP



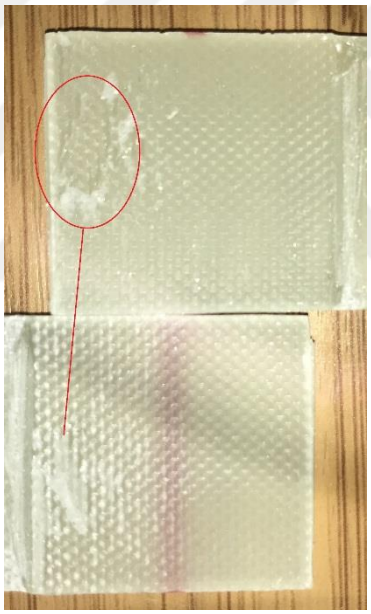
1% CNP 2% CNP 3% CNP

(a)



0% SNP

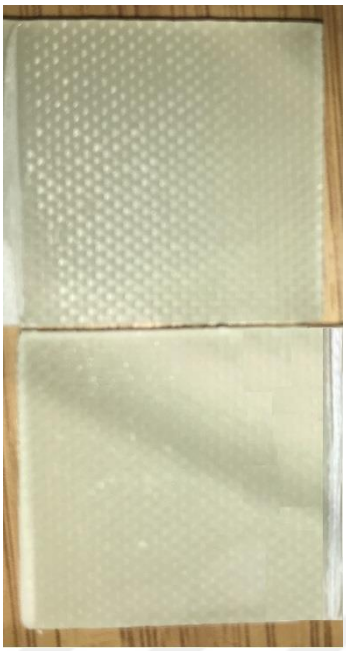
1% SNP



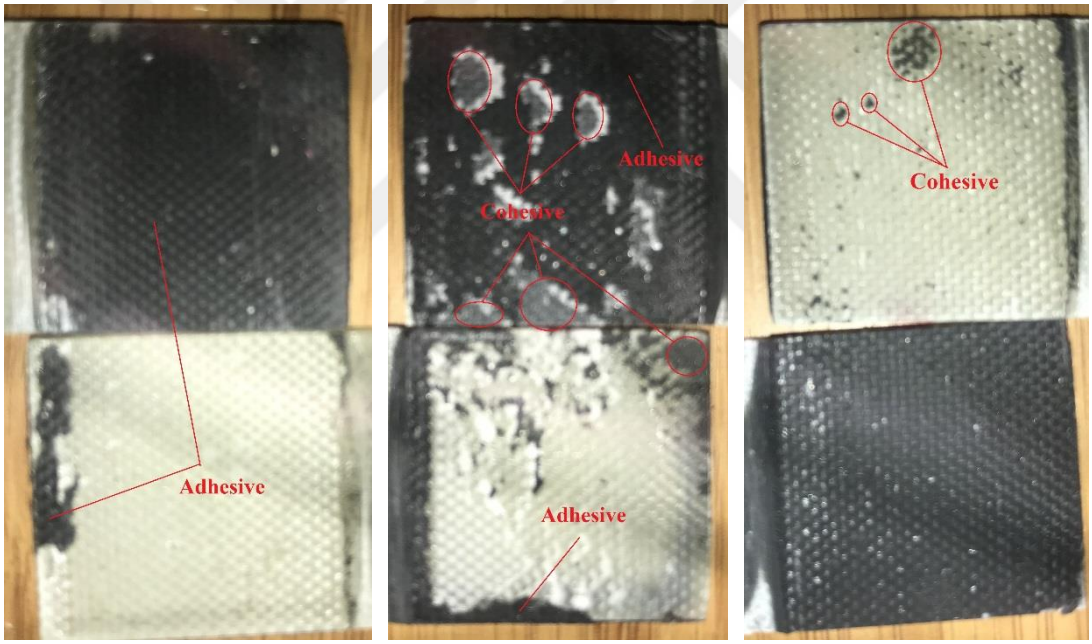
2% SNP

3% SNP

(b)



0% GNP



0.1% GNP 0.2% GNP 0.3% GNP

(c)

Figure 4.20 Fracture surfaces of SLJs prepared with different weight contents of Nano-fillers and tested under 3-point bending loads; (a) CNP, (b) SNP, and (c) GNP

CHAPTER 5

CONCLUSION

In this thesis, the mechanical response of adhesively bonded joints (ABJs) formed by epoxy adhesive reinforced with various type of Nano-particles were systematically investigated. ABJs made by glass fiber/epoxy adherends were considered. The study was performed through experimental investigation to verify the effect of Nano-particles weight fraction on the mechanical response of ABJs. This work was undertaken primarily to determine the influence of various weight percentages of clay Nano-particles, graphene Nano-platelets and silica Nano-particles utilized to reinforced ABJs under two different loading sorts (shear and bending). The overall aim of this thesis was to develop a relatively inexpensive and strong adhesive for common engineering applications. The experimental results showed excellent improvements in the mechanical properties with addition of the three Nano-fillers. Based on those results, it can be concluded the following:

- The mechanical response of the epoxy adhesive increased with the addition of Nano-fillers. The addition of graphene at lower concentrations showed better properties than the other Nano-fillers. The uniform distribution of Nano-fillers as well as the high aspect ratio and high specific surface area of Nano-particles were found to be most important parameters for achieving superior Nano-composite adhesive mechanical properties.
- The addition of Nano-fillers efficiently improves the chemical compatibility between epoxy adhesive and composite substrate surfaces and hence more efficient wetting of surface occurs which resulting in increasing the joint shear and flexural strength.
- The inclusion of Nano-fillers into the epoxy resulted in more flexible behavior and this means more uniform stress distribution across the joint which results in higher strength. However, the results showed that the inclusion of silica increased the epoxy brittleness beside the increased shear strength.

- The lap shear test results showed that the joint strength enhanced with the addition of Nano-fillers. The increase was high for GNP and CNP addition while it was small for SNP. The joint strength increased with increase of CNP, GNP and SNP weight content up to 2, 0.3, and 1 wt. %, respectively.
- The maximum shear stresses values of 8.653, 11.133 and 5.383 MPa were obtained with the optimum addition of CNP, GNP and SNP, respectively, resulting in percentage increase in shear stress of about 91%, 145% and 19% compared to the neat epoxy adhesive joints.
- The bending strength of adhesive joints has improved with the Nano-fillers inclusion. The highest strengthening efficiency was observed for GNP among the three Nano-fillers. The bending strength increased as the Nano-fillers weight content increased up to an optimum addition rate and then more addition was resulted in reversely effect on the bending strength.
- Addition of 2 wt. % CNP, 0.2 wt. % GNP and 2 wt. % SNP resulted in an increase of flexural strength by 85%, 100% and 94%, respectively. The highest calculated flexural stress at fracture was 72.432, 79.171 and 76.101 MPa for CNP, GNP and SNP, respectively.
- Due to higher mechanical properties of joints, low weight fractions and relatively low cost of Nano-fillers, it can be said that the use of graphene, clay and silica Nano-fillers is considered a way to toughen adhesives technically and economically.
- The experiments have shown that there is a powerful correlation between the joints strength and the failure mode. As the joint strength increased the failure mode was changing to more and more progressive mode.
- Adhesive failure was presented by joints reinforced with relatively lower and higher concentrations of clay and silica Nano-particles. The optimum particle content results in the highest improvements for shear and flexural strengths which was reflected on the fracture pattern giving mixed mode of failure.
- Adhesive failure was absent in the fracture surfaces of joints reinforced by GNP where the mixed mode of failure was the dominant failure mode in those joints. However, a unique and rare combination of adhesive and cohesive failures was observed for the joints reinforced with the optimum addition of graphene resulting in the highest strength of joints compared to all studied samples.

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