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# RESEARCH

# Epoxy Resin Based Composites, Mechanical and Tribological Properties: A Review

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#### ABSTRACT

High fuel consumption by automobile and aerospace vehicles built from legacy alloys has been a great challenge to global design and material engineers. This has called for researches into material development for the production of lighter materials of the same or even superior mechanical properties to the existing materials in this area of applications. This forms a part of efforts to achieve the global vision 2025 i.e to reduce the fuel consumption by automobile and aerospace vehicles by at least 75 %. Many researchers have identified advanced composites as suitable materials in this regard. Among the common matrices used for the development of advanced composites, epoxy resin has attained a dominance among its counterparts because of its excellent properties including chemical, thermal and electrical resistance properties, mechanical properties and dimensional stability. This review is a reflection of the extensive study on the currently ongoing research aimed at development of epoxy resin hybrid nanocomposites for engineering applications. In this paper, brief explanation has been given to different terms related to the research work and also, some previous works (in accordance with materials within authors' reach) in the area of the ongoing research have been reported.

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#### 1. INTRODUCTION

Advanced composite materials (ACMs) are characterized with high strength, high stiffness or modulus of elasticity characteristics, compared to other materials. They are termed advanced composite materials in comparison to the composite materials commonly in use such as reinforced concrete, or even concrete itself [1]. exhibit desirable physical and chemical Thev properties that include light weight coupled with high stiffness, and strength along the direction of the reinforcing fiber, dimensional stability, temperature and chemical resistance, flex performance, and relative ease of processing. However, much of the advanced composites progressively manufacture technology is evolving. Among epoxies, phenolics, polyurethanes and polyimides which are matrix materials commonly used in the development of advanced composite materials, epoxy resins currently dominate due to their superior thermal, mechanical and electrical properties, dimensional stability and chemical resistance [2-3].

Century ago, aluminium has been identified as the most common metal on earth and 8 % abundant on earth crust and normally found in oxide form such as kaolinite, bauxite, nepheline and alunite. In 1808, Sir Humprey Davy discovered the existence of aluminium and its tiny pellet was produced by Oersted in 1825. In 1845, a German scientist, Wohler determined its specific gravity and established the lightness of aluminium and also discovered its ease of deformation, stability in air and its melting with a blow torch. Besides, it is characterised with high corrosion resistance, excellent machining properties, high thermal and electrical properties, high ductility, low strength, hardness and wear resistance [4]. However, because of its lightness and high corrosion resistance, aluminium and its alloy are preferred materials in construction and equipment: panels, roofs and frames, packaging materials for food items and transportation: vehicle and aircraft parts. Researches on aluminium strength and hardness enhancement have been achieved through solid solution hardening. age (precipitation) hardening and work hardening and development of aluminium based metal matrix composites through incorporation of reinforcing fillers in the aluminium matrix [4]. A number of aluminium based alloy and composites have been produced in attempt to provide suitable materials for different applications. For instance in aerospace, cast aluminium engine was used on flier, aluminium 2050 was developed and used in the manufacture of wind ribs. Also, Aluminium 7079 and 7075 were developed for high static strength but their failure to provide adequate toughness and corrosion resistance were reported [5-6].

Many researchers have made efforts for preparing carbon black from agricultural byproducts such as coconut shell, apricot stones, sugarcane, bagasse, nutshells, forest residues and tobacco stems. Coconut shells have little or no economic value and their disposal is not only costly but may also cause environmental problems. Coconut shell is suitable for preparing carbon black due to its excellent natural structure and low ash content through a pyrolysis process (carbonisation of coconut shell) at temperature range from 550 to 900 °C.

Conversion of coconut shells into activated carbons which can be used as filler in composite adsorbents development and in water purification or the treatment of industrial and municipal effluents would add value to these agricultural commodities, help reducing the cost of waste disposal, and provide a potentially cheap alternative to existing commercial carbons [7]. The potential of grain by-product such as barley husk, coconut shell as for thermoplastic reinforcements as an alternative or together with wood fibres was investigated. The thermal degradation characteristics of those fibres were studied to investigate the feasibility of these fibres from the processing point of view. The result revealed that barley husk and coconut shell were thermally stable at temperature as high as 235 and 195 °C respectively which compared with soft wood fibre thermally stable up to 245 °C. The cellulose structural material content in barley is 50 % and in coconut shell is 34 %. Both coconut shell and barley husk have higher carbon rich layer on their surface than soft wood fibre. Barley husk fibre reinforced composite showed 10 % better tensile strength than soft wood fibre reinforced composite, both coconut shell and barley husk reinforced composite showed 80 and 40 % better elongation at break; 20 and 35 % better charpy impact strength than soft wood fibre composite [8].

Manv research citations have confirmed aluminium alloys as dominant structural materials in aerospace applications but their relative high density is a major challenge due to low speed and high fuel consumption of aircraft and other aerospace vehicles built from such alloys [9]. The global objective is to reduce to half the amount of fuel consumption by aerospace and automobile vehicles by 2020 and at least 70 % less by 2025. The weight saving to increase payload and reductions of the cost/time of the production cycles are imperative targets. For these reasons, aerospace and automobile industries which are initially based on relative high weight metallic alloys have been focusing on the advanced composite materials [10-11]. Advanced composite materials are replacing metal components in many uses, particularly in the aerospace and automobile industries and also have numerous, proven applications in off shore racing boats, sport equipment, fishing, building, medical, archery and renewable energy sectors including fuel cell, storage cylinders for compressed natural gas, turbine blades and tidal power sector [12]. The first generation of the advanced composite materials began to appear in civil aviation in 1970s; major changes have taken place in the way they are made in order to enhance their properties. The change was exemplified by the Boeing 787, the first airliner with more than 50 % of its structures composed of the advanced composite materials. Another example is the first business jet (Learjet 85) whose fuselage and wing were built primarily from carbon composites [82].

In the ongoing research work, an advanced composite material will be developed from epoxy resin, and nanoparticle fillers obtained from locally sourced and cheap materials such as aluminium cans and coconut shells.

# 2. EPOXY RESIN OVERVIEW

Epoxy resin belonged to a family of polymeric materials under the aegis of thermoset [13-16]. A polymer can be defined as a giant compound obtained from repeating units of the same or different monomers accompanied with or without any loss of material [15-17]. Such material may be water or ammonia molecule as the case may be. A polymeric material may be thermoplastic or thermoset. A thermoplastic can be reheated, softened and moulded into a new shape while thermoset once moulded into a shape, it cannot be recycled [14-15]. Epoxy resin has been a dominant matrix material used in the development of advanced composite materials because of its following excellent properties: high strength, high adhesion to substrates, high electrical insulation, low toxicity, low shrinkage, low cost and high amenability to various processes and applications [18-19]. It can be used to temperatures as high as 175 °C and are compatible with all common reinforcements. They possess fatigue strength superior to aluminium alloy [20-21]. However, its widespread use for many applications is limited because of inherent brittleness, delamination and low fracture toughness. Epoxy resin properties have been enhanced through several include approaches which chemical modification, increasing the molecular weight, lowering the cross link density and introduction of dispersed toughened phase such as micro

sized particles in the cured polymer matrix [20-21]. Although microsized filler is successfully used in toughening and strengthening the epoxy resin, addition of filler harder than matrix generally leads to an increase in Young's modulus but reduction in the percentage elongation of the matrix [22-23]. A new approach leading to successful result is to reinforce the epoxy resin matrices with nanosized organic and inorganic particles such as carbon nanotubes, nano clays, carbon nanofibres and metal oxide nanoparticles [24].

Epoxy resin normally cures or undergoes a crosslinking reaction on addition of curing agent or hardener to it, leaving no volatiles and byproduct. Basically, epoxy resin originates from a family of ether homologue which contains an oxygen atom attached to two different carbon atoms of two different hydocarbon groups forming its molecular bases [14]. The divergence of molecular bases give rise to various forms of epoxy resins for commercial purposes which include but not limited to the following: diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol- F, tetra glycidyl methylene dianiline and triglycidyl ether of trisphenol methane (Maureen et al.). The productions of epoxy resin classified into two different approaches; both involving transformation of unsaturated carbon-carbon double bond in base molecule into an oxirane ring are dehydrohalogenation of epichlorohydrin (halohydrin intermediate) and direct peracid epoxidation [19]. Another method newly developed is the production of wood based epoxy resin from resorcinol liquefied wood [25].

Two different criteria used in selecting epoxy resin as a matrix for composite application are transition temperature and glass epoxy equivalent weight [3,15]. The glass transition temperature is the primary indicator or criterion. It determines whether a particular epoxy resin is suitable for structural (high temperature) non-structural (low or temperature) applications since the material modulus above glass transition temperature is of several order of magnitude lower than the its value below glass transition temperature. The glass transition temperature of a polymer based composite depends on its curing temperature which in turns depends on structure developed during curing process, curing agent and curing temperature [26]. The temperature at which a thermoset is cured strongly determines its glass transition temperature and the glass transition temperature changes as the curing temperature changes. However every system has ultimate glass transition temperature which is determined by thermoset and hardener formulations such that any increase in cure temperature has no influence on it [27].

Epoxy equivalent weight is the other paramount parameter used to characterise epoxy resin application in composite fabrication. It can be defined as the molecular weight of epoxy resin divided by number of epoxide group per molecule. This estimate is usually supplied by epoxy resin vendors [19].

Curing agent usually react with epoxy resin in order to control or minimise its cross linking reaction, leading to reduction in inherent epoxy resin brittleness, delamination and improved fracture toughness [26]. Different curatives (curing agents) have been incorporated into epoxy resin depending on whether the resinhardener mixtures are to cure at room or elevated temperature. The room temperature curing agents are aliphatic amines which may be primary secondary or tertiary aliphatic amines while high temperature curing agents are aromatic amines e.g 4, 4 diaminodiphenyl sulfone and anhydrides. The ones involving curing at room or elevated temperature includes boron trifluoride amine and substituted imidazoles [16,19]. Generally, high temperature cured resin has superior glass transition temperature and chemical resistance to their cured at lower counterparts or room temperatures. The cured epoxy resin based composites have glass transition temperature ranging from the room temperature to 260 °C and elongation from 1 to 100 %. The uncured resin can be cured from temperature varying from 5 to 260 °C [19].

Superior properties of epoxy resin to other thermosets has attributed to its dominance as a matrix for the development of advanced composites for various engineering applications. In the past decades, a lot of researches have been contributed towards studying of mechanical properties of epoxy resin based composites. However, the search for lighter materials to replace legacy heavy materials in

engineering structures especially in automobile and aerospace industries has made the study of tribological properties of epoxy resin based composites significant. Recently manv researches are now concentrating on studying tribological properties of epoxy resin based composites using parameter such as sliding speed, sliding distance, applied load, specific wear rate and mass loss. Reports from those research works have indicated enhancement of tribological or wear resistance properties of composites epoxy resin based through incorporation of micro and nanofillers which includes both synthetic fillers such as zirconium oxides, titanium oxides, aluminium oxides particles, carbon nanotubes and natural fillers such as coconut shells, palm kernel shell, egg shell particles [28-32]. Optimum combination of excellent specific modulus. lightness, satisfactory thermal and wear resistance of epoxy resin based composites has attributed to their uses in different engineering sectors for instance in building, epoxy resin based composites are used as structural materials for decks, rails, window and building acceptance; in automobiles, bumpers, engine covers, fuel tank and engine bay components are built of epoxy resin based composites while in aerospace industry, airframes, engine nacelles, fan casings, floor boards, fairings, radomes, wing tips, galleys and helicopter rotor blades have been produced from epoxy resin based composites [11, 33-35].

# 3. COMPOSITES

Borode [36] defined composite material as a materials system composed of a combination of two or more micro or macro - constituents that differ in form and chemical composition and which are essentially insoluble in each other and also with resulting properties more superior in some manner to the properties of the individuals constituents. Colton (2011) defined composite as microscopic mixture of two or more different materials. One typically being the continuous phase (matrix), and the other being the discontinuous phase (reinforcement). Composite properties depend strongly on the composite structure i.e matrix and reinforcement/filler. Callister [37] defined composite as artificially produced multiphase materials having a desirable combination of the best properties of the constituent phases. Usually, one phase (the

matrix) is continuous and completely surrounds the other (the dispersed phase). Society of manufacturing engineering (SME) described the composite as follow: Composites consist of two distinct materials, which together improve product performance and/or lower production costs. Composite materials typically include plated, clad, or coated metals, however the term 'composites' has evolved to mean a material containing a matrix, or base substance, and a reinforcement material. Composite materials consist of a combination of materials that are mixed together to achieve specific structural properties. The individual materials do not dissolve or merge completely in the composite, but they act together as one [11]. Valery and Egveny [38] defined composite as any material consisting of two or more components with different properties and distinct boundaries between the components can be referred to as a composite material. Moreover, the idea of combining several components to produce a material with properties that are not attainable with the individual components has been used by man for thousands of years. Examples of naturally occurring composites are trees and bones [37].

They are important engineering materials having higher specific strength i.e the strength per unit volume than that of the known very light metals such as aluminium and titanium. Specific strength of aluminium is greater by a factor of three than that of steel and titanium when mixed silicon carbides in an attempt to produce aluminium-silicon carbide composites, Also that of fiber reinforced polymer matrix composite is greater by a factor of four [39] This gives way for the development of composite structure having the same strength and stiffness as metal structure but with much lighter weight than metal structures. The composites' high specific strength is responsible for replacing of many metallic structures with composites in most of engineering structures especially in automobile, aerospace, shipping, sporting equipment and building construction industries. Replacement of 50 % aluminium alloy structure with carbon fibre reinforced composites has yielded more than 20 % weight reduction of the whole structural weight [40]. Composites are now used as structural materials for antenna dishes, chair, solar collectors, chemical storage tanks, auto body panels, propellers, pipes, wind blades, offshore platform, bath shower units and high performance double core tennis balls [41].

1970s has marked the onset of the use of composites as a metallic structure replacement when Ken Rand made KR-1 and KR-2 kits in his home aircraft construction. Another composites' use is in Burt Rutan's design of Variviggen earned him award of Stan Dzik trophy at Oshkosh [42]. The genesis of material has continued up to date. Currently, Boeing 787 has all its parts being built from composites [40]. Fiber glass reinforced composites are used as fairings, radomes, wing tips, galleys, lavatories and helicopter rotor blades materials; carbon fibre reinforced composites are used as airframes, engine nacelles, fan casings, floor boards and interior parts.

Generally, composite consists of a matrix and a filler or reinforcement. A matrix is a material that behaves as adhesive medium for supports and reinforcements. It bonds reinforcement together and conveys applied load to the reinforcement. Also matrix keeps filler in their position and orientation and offers composite resistance to external attack. Fillers/reinforcements are the loading bearing components of composites. They are in fibrous (carbon and glass fibres) or particulate form (chopped glass and carbon) [37,43]. They offer strength and rigidity and assists composite in bearing structural loads. Commonly used synthetic reinforcements for composite production include carbon, thermoplastics, alumina, boron, silicon carbide, steel and silicon nitride. Currently researchers are now using coconut shells, egg shell, palm kernel shell, periwinkle, Thamocaccus Danielli, bagasse, banana peel and yam peel as natural filler for composite development for use in various engineering applications.

# 3.1 Classification of Composites

Composites can be classified in accordance with matrix and fillers/reinforcements. In accordance with reinforcements, composites are classified as fiber reinforced, particulate reinforced, structural composites and nanocomposites. For matrix classification, composites are grouped into three namely: metal matrix composites (MMC); ceramic matrix composites (CMC) and polymer matrix composites (PMC) [43,44].

In fiber reinforced composites, the load bearing components are fibers which are either continuous or short/discontinuous fibres (see Fig. 1). They are very important composites because of their high specific strength and specific modulus but they are very hard to fabricate [11,43]. A continuous fibers has the same length as the strand while short fibers have smaller length. In this type of composite properties dominate along fiber direction making such composites (unidirectional fibre reinforced composites) anisotropic in natures. Fibre reinforced composites can also attain anisotropy as in titanium and aluminium through proper design such that the fiber orientations offer uniform properties in all directions. This is achieved through weaving or knitting of fibers to give to what is multi directional fibre reinforced composites [11].



**Fig. 1.** Computer image of (a) continuous fibres; (b) short fibres.



Fig. 2. Computer images of reinforcing particles.

In particle reinforced composites, the load bearers are fillers in particulate form (See Fig. 2). Such composites are classified as either large particle reinforced composites e.g concrete or metal matrix composite (SiC/Al composites) or dispersion strengthening composites e.g nanocomposites. The former refers to reinforcement having particle sizes greater than 100 nm while the latter has the particle size less than 100 nm [45-46]. The degree of strengthening depends on bonding strength between matrix and particles. The strengthening mechanism of particle reinforced composites is analogous to but not as high as in precipitation hardening. However, particle reinforced composite strengthening remains at high temperature unlike that of precipitation hardening [45-46]. Strength increases as the particle volume fraction increase due to interaction between particles and dislocation movement within the matrix before the matrix saturation level is reached beyond which the excess filler within the matrix may lead to composite embrittlement and endanger the mechanical properties of the particle reinforced composites [43,47].

#### 3.1.1 Structural Composites

These are composites whose properties depend not only properties of composite components but also on design configuration or geometry of structural layers. They are generally grouped into two, namely: laminated and sandwiched panel composites.

A laminated composites as the name implies contains number of fiber plies or layers that are stacked and cemented together to have a single composite structure having also uniform mechanical properties in all directions unlike in the case of unidirectional fibre reinforced composite that is characterised with high specific strength, modulus or stiffness along a single direction. The structural properties of composite laminates such as stiffness. dimensional stability and strength are determined by fiber ply stacking sequence which in turn characterise the distribution of ply orientation through the composite thickness. However, proper ply orientation selection is very crucial in efficient composite laminate design (see Fig. 3) for targeted engineering applications. Parameters used in strength design for a laminated composites are load direction, ply orientation and stacking sequence which requires 0° plies; 0°, 45 and 90° plies( quasi isotropic lay -up) for axial load; shear and side loads respectively.

Fibers are fillers, reinforcement or load bearer exist in the matrix of fibre reinforced composites/ laminated composites. A single fiber is called a filament, for a glass fibre a strand is used to describe a single fiber. Bundles or packs of filaments are called yarns, roving or tows. A roving contain bundles of filaments, end to end forming straight patterns without being twisted. It exists in 3K, 6K and 12K where K stands for 1000 filaments [11]. Yarns are usually twisted except Kevlar yarns. Tows are nontwisted fibers. Fibers are described as dry or prepreg. A dry fiber needs to be filled with resin before use. A prepreg fiber contains fibers already impregnated with resin.



Fig. 3. Stacking sequence of plies.

In composite laminates, fibres exist in various forms and are generally described under the aegis of fiber ply or layer. Fiber plies are available in three different forms, namely: tape, weaving fabric and knitting or stitching plies.





**Fig. 4.** Form of woven fabrics: (a) plain weave; (b) satin weave [42].

Tape is the unidirectional ply (see Fig. 4a). It has fibres arranged parallel to one another facing a single direction. Such composites produced from a tape fibers have a high specific strength along a single direction and are stronger than woven fabrics. Woven fabrics are the bidirectional fibers (see Fig. 4b). Fibres are weaved both along longitudinal and transverse directions to assume an angle 90° ply. This ply maintains fiber orientation and more flexible for lay up of complex shapes than tape; it gives rise to lighter composites with reduced characteristic resin void size. Woven fabrics are generally of two types, namely; plain and satin fabrics.

Plain fabric are weaved with a transverse fiber intersecting above and below longitudinal fibres one after the other. This weaving type is characterised with a crimp i.e appearance of humps at different points along the ply and much stronger and less distorted than the satin type. In the satin type, intersections of transverse fibres with longitudinal ones are less frequent. Sandwiched panel composites are structural composites (see Fig. 5) having a central core which is adhesively bonded to two outer sheets. The core is a light and strong material which includes rigid polymeric materials/foams (epoxy resin, polyurethane, phenolics), wood and honeycomb. It supports the outer sheets; it must be strong and thick enough to bear the transverse shear stress and give shear stiffness respectively. Outer sheets are very strong and stiff materials. They give strength and stiffness to the composites. They must have enough thickness to withstand compressive and tensile stress from loading. Materials for outer sheets include aluminium, titanium, steel, ply wood and fiber reinforced composites.



**Fig. 5.** Computer image of sandwiched composites: (a) 2D, (b) 3D.

#### 3.1.2 Metal Matrix Composites (MMC)

Metal matrix composites, as the name implies, have a metal matrix. Examples of matrices in such composites include aluminium, magnesium and titanium. The typical fiber includes carbon and silicon carbide.

#### 3.1.3 Ceramic matrix composites (CMC)

Ceramic matrix composites have ceramic matrix such as alumina, alumina silicate reinforced by silicon carbide. The advantages of CMC include high strength, hardness, high service temperature limits for ceramics, chemical inertness and low density. Naturally resistant to high temperature, ceramic materials have a tendency to become brittle and to fracture.

#### 3.1.4 Polymer Matrix Composites (PMCs)

PMCs consist of high strength particles or short/ continuous fibers which are held together by a common organic matrix (polymer). The composite is designed so that the mechanical loads to which the structure is subjected in service are supported by the particle or fiber reinforcement. PMCs are often divided into two categories: reinforced plastics and so-called "advanced composites. The distinction is based on the level of mechanical properties (usually strength and stiffness); however, there is no clear-cut line separating the two [38,44].

#### 3.2 Fabrication of Polymer Matrix Composite

Fabrication of polymer based composites begins with preparation of fillers or reinforcements and then followed with resin impregnation. The common methods employed in the production of polymer (thermoset) matrix composites include the following: hand lay-up, bag molding process, filament winding, pultrusion, bulk molding, sheet molding, resin transfer molding, injection molding.

Hand lay-up method involves the use of flat surface or cavity wood, metal or plastic mold built from inside which reinforcement is put before resin impregnation. It is the oldest, simple and common method for the production both of small and large fibre reinforced products. The resulting laminates is allowed to cure in the mould without further treatment. In bag moulding process, laminated fibers are laid inside a mould, covered with a flexible bag and then cured with heat and pressure. After the calculated curing time, the composites becomes an integrated part formed into a desired shapes. It is divided into three, namely: pressure bag, vacuum bag and autoclave.

Pultrusion is an automated process used for manufacturing continuous cross section profiles. In this products are pulled out of the die instead of being forced by pressure. Pipes, tubes and structural pipes are manufactured from this technique using an appropriate mould.

Filament winding is used for producing revolted surfaces e.g pipes, tubes, cylinders, large and pipe work.

Preformed molding process is divided into three, namely pregreg, sheet and dough moldings. It can done wet or dry.

Resin transfer molding involves application of resin to preform placed in a prepared mould. Resin is introduced into the mould at high pressure from the lowest point and fills the mould in the upward direction in order to reduce entrapped air. Clamping is necessary to prevent resin loss through the trap. Once the mould vent is filled up with resin, resin flow is stopped and the curing begins immediately. This is subdivided into resin transfer infusion (RTI), vacuum air resin transfer mould (vacuum assisted resin transfer mould).

Injection moulding involves heating the polymer matrix and filler in a barrel and the molten blend is fed at high pressure into a cavity of a prepared mould. This method is used for the production of thermoplastic and thermoset based composites [44].

#### 4. INTRODUCTION TO NANOTECHNOLOGY

The development of nanotechnology has led to material restructure which alter the properties of the material. Physics and chemistry of nanostructures are relatively new areas of science arisen in last decade of past century after discovery of fullerenes, nanotubes and graphenes in 1985 leading to introduction into more extent interdisciplinary integrated modern science now known as nanotechnology [48-49].

Although nanotechnology is a new area of research, nanomaterials have been used for centuries. Chinese used gold nanoparticles as an inorganic dye to introduce red colour into their ceramic porcelains more than 1000 years ago. In medivial times, nanoparticles were used for decoration of cathedral windows. Metal nanoparticles contained in Roman glass artifacts provided beautiful colours. [48]. Application of nanoscience in the development of nanostructured material is termed nanotechnology. Nanotechnology is as a unique way in which matter can be rearranged. Through nanotechnology, sophisticated nanoscale tools such as tunneling Junctions were produced [50]. In semiconductor industry, advanced studies on nanotechnology has led to shrinking of devices which is based on famous Moore's law on transistor predicted in 1965 [48,51]. As the particle sizes, fiber diameter or layer thickness of a nanostructured materials changes, the properties of materials also change. This is attributed to the fact that the proportion of atoms at grain boundaries (as size decreases) increases. Furthermore, physical processes such as dislocation creation, ferromagnetism and quantum dot effects are controlled by a characteristic length such that when the physical scale of materials below the length, there is a change in properties [48,52].

# 4.1 Definition of Nanoscience/Nanotechnology

Nanoscience is the study of materials where some critical properties are attributable to an internal structure with at least one dimension less than 100 nanometer [52]. Nanoscience primarily deals with synthesis, characterization, exploration, and exploitation of nanostructured materials [48]. Nanotechnology as building and use of materials, devices and machines at nanometer scale is defined as research and technology development at the atomic. molecular, or macromolecular levels using a length scale of approximately one to one hundred nanometers in any dimension; the creation and use of structures, devices and systems that have novel properties and functions because of their small size; and the ability to control or manipulate matter on an atomic scale [53]. Nanotechnology is the art and science of manipulating matter at nanoscale to create new and unique materials and products with enormous potential to change the society [50]. Nanotechnology is the manipulation of matter for use in particular applications through certain chemical and / or physical processes to create materials with specific properties [54]. Nano in greek simply means dwarf. It can be defined as one-billionth of a meter and 1 nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line [48,52].

### 4.2 Nanostructured Materials

Nanostructured materials (NSMs) are lowdimensional materials comprising building units of a submicron or nanoscale size at least in one direction and exhibiting size effects. They are the products obtained time to time owing to researches into nanotechnology. They exist in different forms. Nanostructured materials are but not limited to nanowear sunblock, I pod memory chip, lacvert nano hydrating cream, Zelen Fullerene face cream, carbon nanotube baseball bat, nanoelectronic power sensor, silicon nanowire solar cell, Boeing 787 [53,54].

Nanostructured materials can be classified based on the extent of nanomaterials, dimensionality, the material of which they are built and mode of synthesis. Under the extent of nanomaterials, nanostructured materials are are divided into three, namely:

- substance containing nanomaterials in the forms of isolated, substrate-supported or embedded nanosized particles, thin films or wires e,g catalyst, semiconductor devices that uses multilayer quantum well structures;
- nanometer sized thin film surface materials which have their surfaces implanted with nanosized thin films especially nanostructured materials for wear resistance applications and;
- the nanometer-scale microstructure bulk solid whose entirety is made of nanomaterials unlike those in the first and second of this classification [48,55,56]. In this the whole volume of the material structure is built of nanomaterials.

Under the aegis of dimension, nanomaterials can be classified as zero, one, two and three dimensional nanostructured materials. This classification is an extension of Gleiter's nanostructured material classification who did not take zero and one dimension nanomaterials into consideration. Zero dimension nanostructured material is the nanostructured material having no dimension e.g nanopores and nanoparticles (fullerene particle, clusters. thoroids and grains); one dimensional nanomaterials having one dimension, e.g. fiber, bundles, ropes corals, bows ; two dimensional nanostructured materials having two dimensions e.g filamentary structure (films) and three dimensional nanostructured materials e.g. crystallites (nanotubes, hetero fibers, hetero layers), see Fig. 6 [48,51,57,58]. Upon the materials of which nanomaterials are built, they can be classified as carbon based materials, metal based materials and dendrimers.

Carbon based nanomaterials are nanomaterials that contain mainly carbon, they normally take the form of a hollow spheres, ellipsoids or tubes. Fullerene is the term given to spherical and ellipsoidal carbon nanomaterials whereas nanotubes are used for carbon nanomaterials having cylindrical shape, see Fig. 7 [54, 49, 58]. Dendrimers are the branched unit nanosized polymers having numerous chain ends which can be made to carry out different roles, see Fig. 8. They are suitable for use as catalyst and drug delivery agents because of interior cavities which other molecules can be placed [54].

Metal-based materials are nanomaterials which are obtained from metals including quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers see Fig. 9 [54].

Nanocomposites are nanostructured materials developed from nanoparticles combined with other nanoparticles or with larger or bulk materials. Nanosized clays have used in the development of nanocomposites with enhanced mechanical, thermal, and flame retardant properties ranging from automobile parts to packaging materials [54,59,60].



**Fig. 6.** Computer image of: (a) spheres and clusters (0D), (b) nano fibers, wires and rods (1D), (c) plates, films and network (2D), (d) crystallites (3D) [58].







Fig. 8. Computer image of a generation of dendrimers [54].



**Fig. 9.** Computer images of: (a) gold nanoparticles, (b) titanium nanoflower, (c) silver nanocubes, (d) tin oxide nanoflower [58].

# 4.3 Nanostructured Materials Based on Mode of Synthesis

Nanostructured materials may be produced intentionally or unintentionally. Unintentionally synthesised nanostructured materials are usually produced through natural occurrences. They are not included in the definition of nanotechnology and are viruses, volcanic ash, friction or airborne combustion by products such as exhaust gases [54].

#### 4.4 Synthesis of Nanostructured Materials

Synthesis of nanomaterials and fabrication of nanostructured materials can generally be classified into two approaches, namely bottom up and top down approaches.

Bottom up otherwise called self-assembly process fabricate nanomaterials from atoms and molecules. It involves the use of chemicals or physical forces operating at nanoscales to combine basic units into larger structures e.g colloidal dispersion whereas the top down process involves synthesis of nanomaterials from macro scale materials e.g mechanical milling, see Fig. 10 [48,51,58].



**Fig. 10.** Computer image illustrating schematic steps in nanostructured material synthesis [58].

Bottom up approach for nanoparticle synthesis is divided into gas phase and liquid phase techniques whereas the top down process is the solid phase/mechanical process. Different methods may be employed in the processing of the same materials in order to enhance specific properties of nanomaterials such as size, symmetry, purity, and size distribution.

Gas phase techniques are employed in the fabrication of thin films, multilayers, nanotubes, nanofilaments and nanoparticles. The techniques are divided into physical and chemical vapour depositions. Physical vapour deposition (PVD) involves the use of physical processes to convert solid materials into a gaseous phase (vapour). The vapour is modified via reaction with gases, then cooled and redeposited on a substrate. Thermal evaporation through resistive, electron beam heating and flame pyrolysis; laser ablation, spark erosion and sputtering are used in PVD conversion processes [48,61]. In chemical vapour deposition, pyrolysis, reduction, oxidation or nitridation is used in a reaction chamber for vapour formation. Then, vapour is deposited on a surface. This is employed in the synthesis of carbon nanotubes

Liquid phase synthesis involves precipitating nanoparticles from a solution of chemical compounds. It is divided into the following methods, namely: polyol, sol-gel, hydrothermal, and water-oil micro emulsion [48,58].

Polyol otherwise called solution precipitation method is the precipitation of nanoparticles within a continuous fluid solvent. It involves dissolving inorganic metal salt such as chlorides and nitrides in water. Hydrated metal cations with basic solution are added into the chloride solution to form hydrolysed species which then condense. The species are washed, filtered, dried and calcined in order to obtain the metallic nanoparticles. Sol gel is a well-established colloidal chemistry technology. Sol is a colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase while the gel is a solid macromolecule immersed in a solvent. Sol gel involves a set of chemical reactions which irreversibly convert a homogeneous solution of molecular reactant precursors (a sol) into a three-dimensional polymer (a gel) forming an elastic solid filling the same volume as the solution.

Hydrothermal/electrodeposition method involves induction of chemical reactions in an aqueous electrolyte solution with the help of applied voltage. It is the process of using electrical current to coat an electrically conductive object with a relatively thin layer of metal. This method is relevant to deposition of nanostructured materials including metal oxides and chalcogenides [62].

synthesis otherwise called Solid phase mechanical process involves disintegration of larger particles of solid materials in grinding mills. When particle size lies in nanometer range, terms ultrafine grinding or nanosizing are often used for the process. Mechanical attrition methods give very high production rates (up to tones per hour) and are widely used for industrial production of clay, coal and metal powders. Mechanical milling nanoparticles productions are top-down process whose products exhibit nanostructural characteristics on atleast two levels. First, the particles themselves can be nanoparticles if their average characteristic dimension is less than 100nm. Second, many materials milled by mechanical attrition equipment are highly crystalline such that the crystallite (grain) size is often between 1 and 100 nm diameter [63-64].

Materials properties change in respect to alteration in their grain, particle size, fiber diameter or layer thickness. This is attributed to the fact that the proportion of atoms at grain boundaries (as size decreases) increases. Furthermore, physical processes such as dislocation creation, ferromagnetism and quantum dot effects are controlled by a characteristic length such that when the physical scale of materials below the length, there is a change in properties [65]. The peculiar properties of nanostructures attributed to the

result of size effects, external and internal, classical and quantum ones, that arise in zerodimensional quantum dots, one-dimensional wires, and two-dimensional layers are as follow: high ductility of nanoceramics at elevated temperature unlike the coarse grained ceramics making them ideal materials for high temperature applications; Luminescence in silicon powder and silicon germanium owing to quantum confinement and nonlinear optical properties, making them suitable as infrared optoelectronic device and window layer in solar cells; high ductility and cold welding properties of metallic nanoparticles making them suitable for metal-metal bonding as applied in electronic industry; single magnetic nanoparticle has a special atomic structure with discrete electronic states, which give rise to special properties in addition to the super paramagnetism behaviour. Magnetic nanocomposites have been used as mechanical force transfer devices for high information storage and magnetic refrigeration. High dielectric constant of polymer based nanocomposites has made them ideal materials in photonic band gap structure [48,50,58,62].

#### **5. REVIEW OF LITERATURE**

Chemical vapour deposition (CVD) grown multi wall carbon nanotubes with weight fractions ranging from as low as 0.001 up to 1 weight were used as fillers in the synthesis of epoxy resin based composites. The electrical properties were analysed using alternating current impedance spectroscopy and the results were compared with spherical carbon particles reinforced epoxy composites. The results revealed that the shear intensive mechanical stirring process adopted caused well dispersed CVD grown multi wall carbon nanotubes in the epoxy resin. Also, there is rapid aggregation of carbon nanotubes in the 0.0025 % weight carbon nanotube epoxy sample processed at low stirring rates whereas in the case of spherical carbon particles epoxy sample, the application of low shear rates and addition of electrolytes improved the network formation of particles [23].

Epoxy resin/Multi walled carbon nanotubes were fabricated using over-aged hardener. Effects of nanotubes additions on mechanical and electrical properties of the composites were evaluated, experimental results revealed that the yield strength and young's modulus were doubled and quadrupled for composites samples with 1 and 4 %wt of carbon nanotubes additions. Also there is a transition from insulator to conductor at nanotube concentration between 0.5 and 1 %wt additions [67].

Thermal analysis and Raman spectroscopy were used to study effects of single walled carbon nanotubes (SWNTs) incorporation onto diglycidyl ether of bisphenol A-based (DGEBA) epoxy resin under isothermal and non-isothermal conditions. Results revealed that presence of SWNTs at lower concentration in DGEBA shifted exothermic reaction peak to lower temperature confirming the saturation of DGEBA with SWNTs at higher concentration [67].

Thermal and mechanical properties of wood based epoxy resin prepared by reaction (through depolymerisation and liquefaction) of wood components with resorcinol and cured with 4-4 diamino diphenyl sulfone (DDS) were studied. Experimental results showed that the mechanical properties of the wood based epoxy resin were superior to those of the petroleumbased bisphenol-A type epoxy resin [25].

MR50/LTM25 and CFS003/LTM25 epoxy resin composites were produced and evaluated mechanically at cold, room and elevated temperatures under wet and dry conditions. Results indicated that each of the composites behave differently in the different conditions and MR50/LTM25 composites showed superior mechanical properties to CFS003/LTM25 composites [3].

Curing process of continuous fiber-reinforced, thermosetting resin matrix prepreg materials were studied using experimental and model approach of which a computer code specifying cure cycles, temperature distribution, degree of cure of the resin, resin viscosity, temperature, pressure inside voids and residual stresses distribution after cure was developed. Results revealed that experimental and model approaches are in good agreements [26].

Epoxy resin SY12 (319)/coconut shell particles composites were produced with coconut shell particle additions increased from 20 to 35 %wt at 5 % interval. Physical properties (density) and tensile properties of the composites were studied. Results showed that there is a linear decreasing relationship among density, tensile strength, modulus of elasticity and %elongation as the %wt of coconut shell particles additions increased. Also, a maximum of 25 and 654 MPa of tensile strength and modulus of elasticity respectively were retained at 35 %wt coconut shell additions and above [68].

Epoxy resin 3554A/50-200µm coconut shell particles composites were developed at 5-15 %wt of coconut shells and the composites were cured at 40 °C for 12 hours. The flexural and tensile properties of the composites were evaluated. Results revealed that an increase in wt% of coconut shell additions increases the tensile stress, flexural stress and modulus of elasticity of the composites. Therefore a linear relationship exists between wt% of coconut shell particles and tensile stress, flexural stress with a correlation factor of 0.9929 and 0.9973 respectively. Also, relationship between %wt of coconut shell additions and modulus of elasticity is quadratic with a unity correlation factor [69].

Sreejarani and Suprakas [70] published a review on Epoxy-based Carbon Nanotubes Reinforced Composites in which he explained various techniques for characteristic features, various techniques for synthesis of carbon nanotubes and their incorporation onto epoxy resin. He emphasised on the fact that carbon nanotubes synthesised so far are in range of particle sizes and production of carbon nanotubes of same/uniform size is still under research.

Physical and mechanical properties of pristine Epoxy resin EA9396 were studied, Different batches of composites were developed from EA9396 as a matrix and graphite and glass fabrics as fillers. Produced composites were cured both at room and elevated temperatures and their physical and mechanical properties were evaluated. Results revealed that the pristine EA9396 resin system absorbed about 9 percent water by weight during humidity aging and that its glass-transition temperature decreased from around 176 °C (349 °F) to around 107 °C (225 °F) as a result of moisture absorption for a 200 °F/45-minute cure. Storage at temperatures ranging from 72 °F to 120 °F for up to 24 months had no adverse effect on interlaminar achievable shear strength. Pot/work life of the resin was only slightly shorter after 18 months than it was for fresh resin and exceeded 90 minutes at 72 °F and 10 minutes at 100 °F. Mechanical properties were very consistent from batch-to-batch.' The absorption of moisture significantly lowered most mechanical properties, particularly with glass reinforcement [71].

Advantages of epoxy resin over polyesters in composite structures were studied. Epoxy resin, polyester and were cured at room temperatures for 7 days and other batches of each of resin and esters were cured at 175 °C and then post cured. Results showed that the tensile strength of epoxy resin is 20-30 % greater than its counterparts. Polyesters cannot withstand natural sun post curing treatment because of its higher volume shrinkage which is up to 7 % whereas that of epoxy resin is less than 2 % within the same period of time. The strength of natural post cured epoxy resin is almost double the strength of cured polyester. Epoxy resin can withstand cyclic loading more than polyester because of its higher adhesive property than that of polyester. Also, epoxy resin has greater resistance to water attack and lower water transmission rate than polyester. Experimental result showed that polyester can only retain a maximum of 65 % of its interlaminar strength after immersion in water for a period of 12 months whereas epoxy resin immersed in water within the same period of time retained up to 90 % of its interlaminar strength [72].

Epoxy resin LY 556 mixed with hardener HY 951 in the ratio 10:1 by weight was reinforced with bagasse at different %wt additions and their micro hardness and erosion wears were studied at different impinging velocities, impact angles and at constant erosion time of 10 minutes using compressed, dried air mixed with silica sand as abrasive surface. Results revealed that there is a slight increase in the hardness of the composites as the %wt of bagasse fibres increased. Also the erosion rate increases as the impact angles increase and attains a peak value at 90° [73].

Thermoplastic poly ether imide (PEI) was incorporated onto epoxy phenol novolac resin at different mixing. The blend of epoxy resin and PEI were used as a matrix for production of glass fibre reinforced composites using diamino diphenyl sulfone as curing agent. Thermal stability and mechanical properties such as tensile, impact, interlaminar shear and flexural strength were evaluated. Results revealed that higher values of heat of reaction were released during DSC composite scan than that of neat epoxy resin. Also, there is a noticeable improvement in mechanical properties of the produced composites due to glass fibre reinforcement; highest tensile and flexural strengths were obtained at 10PEI phr and incorporation of PEI in the epoxy novolac improved on the composite toughness [74].

Polymer/clay nanocomposites were developed from di-functional diglycidyl ether of Bisphenol A (DGEBA) and Tetra glycidyl -4-4-diaminodiphenyl methane (TGDDM) epoxy resin; alkyl ammonium cations organoclays using three different hardeners: tri ethylene teramine (TETA), hexa hydrophtalic anhydride (HHPA) and methyl tetra hydrophtalic anhydride (MTHPA). Effect of surface modification and %weight of nanoclays on morphology, flexural properties and thermal stability properties of the composites were studied. Results revealed that clays added to the epoxy resin act as a physical barrier which prevents resin from reaching full cure. Also reactivity of the hardener towards resin has great impact on the cured nanocomposites morphology; the flexural strength of the produced composites were lower than of the unfilled resins except TGDDM/clay composites cured with HHPA revealing an increase in flexural strength. Moreover, epoxy resin readily intercalate with organoclay on mixing but the effect of hardener varies depending on the system. DGEBA cured HHPA showing largest layer expansion [15].

Composite tubes from west system 105 resin and 3K carbon fibres using 207 special coating hardener were produced using three different approaches through metal tube overlaid with fiberglass, rope/foam and florescent tube mandrels. Results revealed that metal tube/fibreglass and rope/foam mandrels produced perfect composite tubes while in the third approach produced epoxy/carbon fiber tube that is glass lined [75].

Adhesion of multi wall carbon nanotube (MWNTs) to epoxy resin matrix was improved by  $\pi$  stacking involving non covalent functionalization through the use of Kentera, a conjugate rigid polymer. The functionalized

MWNTs were added to epoxy resin through combination of shear and elongation forces. The epoxy resin/MWNTs blend was used as matrix for producing carbon fiber reinforced composites prereg through hand lay-up and autoclave curing approach. Mechanical properties of the epoxy/MWNTs/carbon fibers composites were studied and results indicated about 50, 25 and 24 % improvement in flexural strength, flexural modulus and storage modulus of the composites respectively. Also there is a strong interfacial bonding between the matrix and filler [76].

Uniformly-dispersed nanoclay/epoxy composite samples, based on newly developed tailor-made experiment set up were fabricated. A tensile property test was conducted to examine the mechanical properties of the samples with different nanoclay contents. Result revealed that Young's modulus and tensile strength of a composite with 5 %wt of nanoclay increased up to 34 and 25 % respectively [60]. The effects of processing techniques on morphology. mechanical, thermal and barrier properties of epoxy clay nanocomposites were studied, it was observed based on results that epoxy clay nanocomposites showed remarkable improvement in tensile, flexural and fracture toughness properties. Also thermal stability and barrier properties were significantly improved by incorporation of clay particles to epoxy systems [77].

The epoxy resin (LY 556)/coconut shell and the epoxy resin/wood apple shell composites were produced independently and their physical and mechanical properties were evaluated. The experimental results revealed that density and void content of the wood apple shell particulates composites decrease with increasing the filler the polymer; both content in epoxy resin/coconut shell and apple shell composites possessed the maximum strength at 15 %wt filler content. However, wood apple shell composite showed superior properties than the coconut shell composites. The peak erosion rate occurred at 45 and 60 °C impingement angles for all the composite samples under various experimental conditions irrespective of the filler loading [78].

The tensile and flexural properties of epoxy resin/coconut shell particle composites were

investigated at 5, 10 and 15 %wt filler additions. Two significant aspects of advanced composite materials were examined. The fiber deformation of aligned fiber composites formed to double curvature parts and spring back of woven of woven fiber material-single curvature parts were analysed. Results revealed that 0/90 woven layups and that heating the laminates marginally decrease the spring back experience [79].

Different formulations of cyanate ester and epoxy resin composites were developed at different post curing treatment cycles and characterised. Dynamic Mechanical Analysis result revealed that as the Primaset <sup>™</sup> PT-30 was heated, the storage modulus decreased step-wise by several order of magnitude. Also, superior performance of primaset <sup>™</sup> FR-300 could be observed when added to the multifunctional epoxy resin MY0510 compared to the bisphenol A based epoxy Epikote <sup>™</sup> 828 [80].

Mansour et al. (2013) investigate the efficiency of the nanotube reinforcement on mechanical behaviour of epoxy resin nanotube results nanocomposites. The of their investigation depicted an enhancement in modulus of elasticity at 1 wt% of carbon nanotube and that the experiment result agreed with Halpin-Tsai and Thostenson-Chou models' results [81].

Shakuntala et al., [28] studied effect of wood apple shell particles concentration with different impingement angles (30°, 45°, 60° and 90°) at constant impact velocity 48 m/sec on the erosion rate of epoxy composite. Their results revealed minimum wear by the carbon black filled epoxy resin composites when compared with raw (uncarbonised) apple shell particulate composites.

Veen et al., [29] studied the tribological and electrical properties of epoxy composites filled with nano-sized silica particles. Their result showed that the silica nanoparticle filled epoxy resin developed highest level of wear resistance at 10%wt silica loading such that any further increment in silica loading beyond 10% resulted in particle agglomeration leading to increment in specific wear rate. An indication of reduction in wear resistance.

Bîrsan et al., [30] studied tribological and electrical properties of filled epoxy reinforced

composites using a trial and error approach. Their results revealed an irregular increase in wear resistance as the applied load and sliding distance increased. However, the addition of filler up to 2 %wt enhanced the wear resistance of the filled epoxy resin composites under 1-2 N applied loads.

Chen et al., [31] studied effect of dispersion method on tribological properties of carbon nanotube reinforced epoxy resin composites synthesised asymmetric centrifuge, sonication and hand mixing. It was reported based on the result of their experimental investigation that for the untreated CNTs, it seems that the wear resistance improves with increasing effort put into dispersion: sonication has a positive effect, sonication plus dual asymmetric centrifuge proves even better. A pre-treatment with HNO<sub>3</sub> or a silane-coupling agent can improve the wear resistance of the composite. However, the pretreated CNTs should be dispersed without the use of ultrasound, which seems to damage the pre-treated CNTs. The results showed that the wear resistance in general increases with improved dispersion and integrity of the CNTs.

Zhang et al., [32] studied the novel behaviour of friction and wear of epoxy composites reinforced by carbon nanotubes. Their results shows that surface coverage area of CNTs, carbon nanotube/ matrix ratio (Rc/m), plays a significant role in the wearability of the composites. With Rc/m>25 %, the wear rate can be reduced by a factor of 5.5. It was also reported that based on scanning electron micrograph, the study concluded that the improvement of the wear resistance of a high Rc/m composite was due to the CNTs exposed to the sliding interface which protected the epoxy matrix effectively.

A tribological behaviour of the neat resin, aluminium filled resin and tri phase epoxy, aluminium particles, milled glass and carbon fibres was studied. The study was focused on the role of the particles and fibers in the friction and wear at room temperature and at a typical plastic injection temperature of 160 °C. Results revealed that mixtures of fibres and aluminium particles can be used to optimise mechanical and thermal properties of composite manufactured from rapid tooling applications [83].

Aggarwal, [84] studied sliding wear behavior of glass fibre reinforced  $TiO_2$  filled epoxy resin composite under different loads and sliding velocities using Taguchi experimental design scheme. His result revealed that  $TiO_2$  filled epoxy resin composites exhibit enhanced sliding wear resistance when compared with the unfilled epoxy resin.

Kevlar/alumina/epoxy resin laminated composites were prepared by using low-pressure technique. The single and double layers with thickness of 1mm were prepared. The mechanical properties and densities of the composites were evaluated. Results revealed that density, hardness and impact of the non-vacuum samples are higher than vacuum samples. Also mechanical properties are improved with increased weight percent of  $Al_2O_3$  [85].

In the design of aircraft upper wing, fuselage stiffeners, lower wing and fuselage skins, high strength and damage tolerance is the prime requirement. However, precipitation hardenable alloy such as 2024-T3, 7075-T6 aluminium were employed [86-87]. In response to various challenges which legacy aerospace alloys experienced in service, new derivatives, 2000 and 7000 aluminium series such as 7075-T6, 7055, 7150-T6, 2324, 2524-T3 and 2024-T3 were developed. 7055 aluminium alloy was reported to have a good replacement for 7075 because of its higher strength combined with higher compressive strength, good fracture toughness and corrosion resistance [6].

Gojny et al., [88] studied Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites. It was reported that CNTs in general exhibit a certain potential to improve the mechanical properties of the tested epoxy matrix systems. A functionalization with amino- groups improved the dispersibility in all cases and stabilised the CNT-suspension, thus, reducing the reagglomeration. This effect was attributed to an assimilated polarity of the surface and to a possible reaction between the introduced amino-groups and the epoxy resin, thus, integrating the CNTs into the epoxynetwork structure. The potential of CNTs to improve strength and stiffness can be correlated to the specific mechanical properties, the aspect ratio and the specific surface area.

Aribo et al., [89] worked on High temperature Mechanical Properties of Silicon Carbide Particulate Reinforced Cast Aluminium Alloy Composites. Their result revealed that ultimate tensile strength, yield strength and hardness of composites were enhanced at the elevated temperature.

Multi wall carbon nanotubes (MWCNTs) produced by high-energy ball milling was used as a reinforcement in aluminium for the production of Al-MWCNTs composite by cold compaction, sintering and hot extrusion at 500 °C. It was discovered that there was about 500 % increase in the yield stress after the addition of 1 % MWCNTs in Al-MWCNTs based composite [90].

The effects of particle size and volume fractions of  $Al_2O_3$  on the thermal conductivities properties of  $\alpha$ -  $Al_2O_3$  particulate reinforced aluminium composites (Al/  $Al_2O_3$ -MMC) were investigated and the citations revealed that the thermal conductivities of the composites with an  $Al_2O_3$  particle size of 15 µm is higher than that of composites with a particle size of 30 µm [91].

Al alloy (containing 3.8 %mass Cu, 1.3 %mass Si, 0.5 %mass Mn, balance Al) was melted and injected into the porous carbon (produced by wood pyrolysis at 1400 °C for 2 hours in a vacuum) to produce C/Al composite. The microstructural analysis carried out on the composites revealed that C/Al composites produced from different wood showed similar microstructures and that the size, the shape and the distribution of the Al alloy are controlled by the wood channel structure [92].

Effects of particle size and extrusion on the microstructures and mechanical properties of SiC particle-reinforced pure aluminium composites produced by powder metallurgy were investigated. The results pointed out that both particles size and extrusion process have important effects on the microstructure and mechanical properties of the composites. The SiC particles distribute more uniformly when the ratio of the matrix and SiC particle size approached unity and the smaller –sized SiC particles tend to cluster easily [93].

The foaming behaviour of SiCparticulate/aluminium composite powder compacts containing titanium hydride blowing agent was investigated by heating to 750 °C in a preheated furnace. It was discovered that the increase in the linear expansion of the Al powder compacts was attributable to 10 %wt SiC addition which also increases the surface area and bulk viscosities [94].

An experimental research has been carried out to create finer matrix microstructures and novel interfaces between aluminium matrix (A2014) and carbon fibres using a modified pressure infiltration method. Solidification microstructures show that the dendrite arm spacing in between and around the fibres are much finer than in the region where there is no fibres. This suggests the possibility of refining the matrix microstructures by cooling the fibres extending out of the mould [95].

Nanoparticles of SUS316L stainless steel and commercially pure titanium powder were produced by mechanical milling. The sintered material developed from the particles by hot rolling sintering shows superior strength and good elongation [96].

TiB<sub>2</sub>/TiC nano composite powder was fabricated through high energy ball mills [97]. The microstructural evolution of the ordered L1<sub>2</sub>+D022 multiphase Al<sub>67</sub>Mn<sub>8</sub>Ti<sub>24</sub>Nb<sub>1</sub>allov by mechanical milling and subsequent annealing was investigated. Result revealed that after 15 h milling, the ordered  $L1_2$ +DO22 multiphase Al<sub>67</sub>Mn<sub>8</sub>Ti<sub>24</sub>Nb<sub>1</sub> alloy first transformed into disordered fcc supersaturated solid solution and again into the full amorphous structure as the milling proceeded to 60 hours. The full amorphization of the Al<sub>67</sub>Mn<sub>8</sub>Ti<sub>24</sub>Nb<sub>1</sub> alloy was achieved due to introduction of high dense nanocrystalline grain boundaries and the large internal lattice strain caused by the supersaturated dissolution of the Al<sub>3</sub>(TiNb) second phase particle in fcc solid solution [98].

Amorphous/nanocrystalline Al-based alloys from elemental powder blends with the stoichiometry  $Al_{65}Cu_{35-x}Nb_x(x=/5-25 \text{ at }\% \text{ Nb})$ was synthesised through high energy planetary ball milling. The mechanical alloying of  $Al_{65}Cu_{30}Nb_5$ ,  $Al_{65}Cu_{20}Nb_{15}$  and  $Al_{65}Cu_{10}Nb_{25}$ powder blends for appropriate time (30-/50 h) in a planetary or shaker mill resulted in the formation of a single phase nanocrystalline disordered metallic phase, an amorphous alloy and a nano-aluminide mixture of NbAl<sub>3</sub>, and fcc-Nb solid solution or Nb(CuAl), respectively. Presence of Nb in appropriate amount played a crucial role for introducing adequate disorder and solid state amorphization of this ternary system [99].

The microstructural, compositional evolution and structural applications both at ambient and elevated temperatures of  $Al_{93}Fe_3Ti_2Cr_2$  alloys via mechanical alloying were investigated. The result revealed that Al alloy nanocrystallization proceeded through an initial increase in dislocation density followed by a subsequent decrease to form nanograins with a dislocationfree interior alloy [100].

Al-Zn/Al<sub>2</sub>O<sub>3</sub> and Al-Zn-Cu/Al<sub>2</sub>O<sub>3</sub> were prepared via reaction sintering of partially reacted oxide mixtures derived from a high-energy ball milling process. It was observed that the wear resistance of the milled composites was better than that of the unmilled composites, since  $Al_2O_3$  particle size played important role in bearing the external load, and there was a good interfacial cohesion between Al<sub>2</sub>O<sub>3</sub> particles and the matrix. It was also observed that the wear rate increased linearly with the applied load irrespective of the material and decreased with the increasing sliding distance. The coefficients of friction of the composites against EN32 steel decreased with the decreasing alumina particle size as well as the crystallite size of the matrix [101].

Synthesis of bismuth-ceramic nanocomposite through mechanical milling with MgO/SiO<sub>2</sub>, PH driven chemistries through infusion of ammonia gas and lyotrophic liquid crystal nanoreactors and its possible use as thermoelectric materials were studied. The result revealed that highenergy ball milling of bismuth with a second, insulating ceramic phase yield a composite containing bismuth nanoparticles with sizes ranging down to 5 nm after 24 hours. The morphology of the bismuth in the resulting materials is dependent upon its ability to wet the ceramic, but nanostructure is generated both in wetting and non-wetting systems whereas in the case of chemical synthesis an increase in reducing agent decreased particle size since the greater concentration resulted in faster reactions and thus less diffusion of reactants toward growing particles. Also, nanoparticle size is only weakly dependent on lamellar spacing,

confirming that size control of the nanoparticles comes not through a direct templating, but rather through a control of precursor material available for reaction. The nanocrystalline size of the BiOCl particles produced in the lamellar phase is due to chemical confinement of precursors to the hydrophilic portions of the mesophase. It should be noted that the particle size (~5 nm) is approximately the same size as the lamellar repeat distance of the liquid crystal [102].

The micro sized silicon carbide powder was modified into nanostructured silicon carbide powder via high energy ball milling. The crystal examination at every 5hours of milling revealed that the nanostructured silicon carbide at 26 nm crystallite size was achieved after 50 hours milling. Also, the shape of the 50 h milled particles is irregular and the surface morphology is rough [103].

A plasma sprayed nanoceramic composite with a composition of  $Al_2O_3$ -13Ti $O_2$  exhibited wear resistance, bond strength and toughness unprecedented in a ceramic is now in use in Navy surface ships and submarines, reducing the cost of maintenance due to wear and corrosion [65].

Micro-nanocomposites in which tetragonal zirconia nanograins are embedded into micronsized alumina matrix exhibit improved slow crack growth resistance and stability [104].

The WC- $ZrO_2$  nanoceramic composite developed by spark plasma sintering possesses extremely high hardness. Therefore it is a promising material for wear application [105].

In an attempt to provide a suitable materials for the replacement of lead containing solder, nano scale silver particles were sintered at low pressing pressure both in air and nitrogen environments. Results showed that sintering of the nano-scaled silver in air but under a chip, the case of real interest, is closer to uncovered sintering in nitrogen than in air; densities remain lower and the microstructures more refined, the presence of oxygen eases the sintering of silver [106].

A MnFe<sub>2</sub>O<sub>4</sub> nanoparticle was produced by chemical precipitation method and low temperature combustion method using urea, glycine and glucose as fuel. Result revealed that the size of particles by precipitation method falls below 229 nm and XRD pattern confirmed the presence of cubic phase in all the samples [107].

Ag nano-particle sintering process methodology for die-attach applications was investigated on different test vehicles. The test vehicles include six dies, the die-attach layer and a Cu substrate. The influence of different processing parameters (substrate surface roughness and applied sintering pressure) were evaluated. Result revealed that when the substrate surface roughness decreased, the die-shear strength increased. On the other hand, when the sintering pressure increased the die-shear strength also increased [55].

 $Lu_{2-x}Ho_xO_3$  (x = 50.015-0.211) nanocrystals were synthesized by the modified Pechini method (alternative sol-gel technology). The obtained Lu<sub>2-x</sub>Ho<sub>x</sub>O<sub>3</sub> nanocrystals were used to prepare  $Lu_{2-x}Ho_xO_3$ ceramic and then characterised. Results revealed that the Pechini method was proven to be a suitable method with high crystalline quality to obtain  $Lu_{2-x}Ho_xO_3$  (x = 50.015–0.211) nanocrystals below 20 nm in the cubic crystalline phase and suitable to be used as starting nanopowders to prepare sesquioxide nanoceramics by the high pressure lowtemperature technique (HPLT) [108].

Nanosized tungsten powder was produced by high energy mechanical milling; size dependence of the sintering behaviour, densification and grain growth of nanosized powders during initial and intermediate stages of sintering were investigated. The result revealed that the sinterability of nanosized tungsten powders compared with those of coarser powders is significantly enhanced at lower temperatures. Also there is linear densification behaviour during the initial stage of sintering at low temperatures when density is less than ~50% relative density and grain growth also exhibits a linear behaviour during initial and intermediate stages of sintering [57].

Cu/Nano Ag/Cu sandwhich structures were prepared, annealed under vertical load in air at different temperatures and times ranging from 200 to 400 °C and 0.5 to 6 hrs respectively as an alternative for Pb-Sn solder. The result of Cu/Nano Ag/Cu structure examinations showed that metal nanopowders are promising materials for the preparation of lead-free nanosolders suitable for use at temperatures higher than processing temperature [109].

Nanocrystalline  $Pb_{1-3x}/2Gd_xTiO_3$  (where x = 0.01) abbreviated as PGT was synthesised by high energy ball milling at room temperature. X-ray analysis revealed that single-phase tetragonal structure of nanocrystalline PGT was formed after 15 h milling. The average crystallite size was found to be 17 nm [56].

The La<sub>0.6</sub>Ba<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (LBCF) nano ceramic powders were prepared by Sol-Gel process using nitrate based chemicals for solid oxide fuel cell applications; citric acid was used as a chelant agent and ethylene glycol as a dispersant. Nano powders obtained were calcined at 650 °C/6 h, 900 °C/3 h and then characterized by SEM/EDS, XRD and Porosimetry techniques. Results indicated that the LBCF powders are in the range of 13 - 200 nm [110].

A high gravity reactive precipitation (HGPR) was developed for the massive production of  $CaCO_3$ , aluminium hydroxide and  $SrCO_3$  nanoparticles. The experimental results indicated that the mean size of  $CaCO_3$  ranges from 17-36 nm and depends on operating conditions. 1-10 nm diameter with 50-300 nm length fibers of aluminium hydroxide and 40 nm mean size of  $SrCO_3$  were synthesised (Chen et al., 2000).

Different compositions of  $La_{0.9}Sr_{0.1}CrO_{3-\delta}$  were synthesised by citrate gel combustion method. Effects of Ni substitution on the B site of La<sub>0.9</sub>Sr<sub>0.1</sub>CrO<sub>3</sub> were investigated on phase microstructure and electrical conductivity. Experimental results revealed that the suitable calcination temperature for  $La_{0.9}Sr_{0.1}CrO_{3-\delta}$  to obtain a perovskite phase was 1100 °C with a soaking period for 4 hr; for the compositions with  $x \le 0.5$ , there was a single phase after sintering and conductivity of Ni-doped composition the increased as Ni content increased. The maximum conductivity of 72.76 S cm-1 at 800 °C in air was obtained from  $La0.9Sr_{0.1}Cr_{0.5}Ni_{0.5}O_{3-\delta}$  and its activation energy in the range of 100-800 °C was 0.15 eV. The thermal expansion coefficient in a temperature range of 200 - 800 °C for this composition was 12.5 X 10-6 K<sup>-1</sup> [111].

n]O<sub>3</sub> (PLSZFNT) where n=0, 0.2, 0.4, 0.6, 0.8 and 1 %mol) near morphotrophic phase boundary were fabricated through solid-state reaction method. Effects of grain growth on dielectric and piezoelectric properties were studied. Results revealed that in Nb-modified PLSZFT ceramics, microstructural evolution and nucleation enhanced the crystallization process. The tolerance factor (t=1.00) indicates an ideal and stable tetragonal structure of PLSZFNT lattice. Also, X-ray diffraction results exhibited that Nb modification resulted in chemical homogeneity and diffusivity PLSZFT in nanoceramics supported by tolerance factor [112].

Many works have been devoted to the use of natural fillers in composites in the recent past. Coconut shell filler is a potential candidate for the development of new composites because of their high strength and modulus properties along with the added advantage of high lignin content. The high lignin content and low cellulose content makes the composites made with these filler more weather resistant and hence more suitable for application as construction materials. Composites of high strength coconut filler can be used in the broad range of applications in construction and equipment as, building materials, marine cordage, fishnets, furniture, and other household appliances [113].

#### 6. CONCLUSION

This review has disclosed lengths of work that have been carried out on the improvement of epoxy resin properties both at micro and nanoscale levels. Experimental results in all published papers consulted are in good agreement especially in the case of Sapuan et al, [69] and Baskar and Singh, [68] who studied effects of coconut shell particles additions on epoxy resin up to a maximum of 15 and 35 % respectively [69]. reported an increase in tensile and flexural strength as the %wt of coconut shell addition increased. [68] reported decrease in the measured properties as %wt of coconut shell particle addition increased from 20 to 35 %wt. However, the reversed behaviour of these composites at higher %wt of coconut shell particle addition may be attributed to poor bridging effect between filler and matrix arising from the fact that matrix particle saturation level has been exceeded. Also, this review has exposed the possibility of using mechanical milling for synthesis of nanoparticles from soft and hard material such as tungsten carbide based on the review work of Yadav et al, [114]. Also, this review is aimed at reporting existing work in the area of advanced nanostructured materials development. However, it will serve as a guide for researchers having interest in these field of knowledge to plan their work in order not to duplicate the existing work. Also, it shows the limitations of the existing work in order to give room for further study to provide solutions to the existing limitations. The products of nanotechnology, being described as nanomaterials have special physical and chemical properties, leading to their application in every aspect of human life. However, these materials have been interacted with biological and environmental systems, leading to negative impacts on humans and their natural environment. It is very important to note that as a nanomaterial is being developed to solve a particular problem, there is a need to ensure that the material synthesis path does not lead to new problem or contributing to existing problem. Nevertheless, in every aspect of nanomaterial design, the nanomaterial toxicity must be taken into consideration.

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#### REFERENCES

- [1] M.A. Pilato and M.J. Michno, 'Advanced composite materials', *Polymer International*, vol. 38, pp. 1097-1026, 2003.
- [2] J. Njjuguma, K. Pielichowski and J.R. Alcock, 'Epoxy-Based Fibre Reinforced Nanocomposites', *Advanced Engineering Materials*, vol. 9, pp. 835-847, 2007.
- [3] R.C. Juan, C.H. Shan and A.S. Postyn, Properties of Two Carbon Composite Materials Using LTM25 Epoxy Resin National Aeronautics and Space Administration Langley Research Center, Hampton, Virginia 23681-0001, 1996.
- [4] T. Udomphol, *Aluminium and Its Alloy*, Suranaree University, Lecture 2, pp. 1-112, 2007.

- [5] H. Kroninger and A. Reynolds, 'R-Curve Behavior of Friction Stir Welding in Aluminum-Lithium Alloy 2195', *Fatigue and Fracture of Engineering Materials and Structures*, vol. 25, pp. 283-290, 2002.
- [6] P. Lequeu and R. Maziarz, 'High Performance Friction Stir Welded Structures Using Advanced Alloys', in *ASM International AeroMat Conference*, 2006.
- [7] C. Raul, 'Study of Mechanical and Flexural Properties of Coconut Shell Ash Reinforced Epoxy Composites', *B.Sc. Thesis*, Department of Mechanical Engineering, National Institute of Technology, Rourkella, pp. 1-41, 2012.
- [8] K.B. Andrzej, A.M. Abdullah and V. Jurgen, 'Barley Husk and Coconut Shell Reinforced Polypropylene Composites: the Effect of Fibre Physical, Chemical and Surface Properties', *Composite Science and Technology*, vol. 70, pp. 840-846, 2010.
- [9] R. Fredell, J. Gunnink, R.J. Bucci and J. Hirichsen, 'Carefree Laminate Wing Structures for Aging USAF Transports', in *First International Conference on Damage Tolerance of Aircraft Structures*, TU Delft, Netherlands, 2007.
- [10] S. Laurenzi and M. Marchetti, 'Advanced Composite Materials by Resin Transfer Molding for Aerospace Applications', *INTECH*, 2012.
- [11] Airframe Maintenance Technician Aviation (n,d): Advanced Composite Material, Federal Aviation Authority. Chapter Seven, pp. 1-58.
- [12] S. Faye, S. Graham, H. Alan, K. Ajay and Q. Robert, *Technology Needs to Support Advanced Composite in the United Kingdom*. The Inter-Agency Group Composite, United Kingdom, 2009.
- [13] S.H. Goodman, *Handbook of Thermoset Plastics*. Park Ridge, N.J. U.S.A., Noyes Publications, 15th edition, pp. 133-182, 1986.
- [14] J.A. Brydson, *Plastic Materials*. Heiman Linacre House, Jordan Hill, Oxford, 7<sup>th</sup> edition, pp. 1-916, 1996.
- [15] S. Bradly, 'Epoxy/Clay Nanocomposites: Effect of Clay and Resin Chemistry on Cure and Properties', *M.SC. Thesis*, School of Science and Applied Chemistry, Queensland University of Technology, 2004.
- [16] Crystic, Composites Hand Book. Scott Bader Company Limited Northamptonshire NN29 7RL, pp. 1-100, 2005.
- [17] R.G. Grisky, *Polymer Process Engineering*. Thomson Publishing, 1995.
- [18] Harke, *Epoxy Resin Systems for Composites*. Harke Chemical GmbH, Thailand, pp. 1-20, 2006.

- [19] A.B. Maureen, J.M. Cary and D.N. John, *Epoxy Resin*, Hexcel Corporation.
- [20] S. Dirlikov, I. Frischinger and Z. Chen, 'Phase Separation of Two-Phase Epoxy Thermosets that Contain Epoxidised Triglyceride oils', in Advances in Chemistry Series Toughened Plastics II Novel Approaches in Science and Engineering, Washington DC, American Chemistry Society, pp. 95-103, 1996.
- [21] P.S. Oh, H.S. Kim and P. Ma, 'Effect of Rubber on Stress-Whitening in Epoxies cured with 4, 4 Diamino Diphenyl Sulphone', Advances in Chemistry Series Toughened Platics II Novel Approaches in Science and Engineering. Washington DC: American Chemical society, pp. 111-1119, 1996.
- [22] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer and A.H. Windle, 'Ultra-Low Electrical Percolation Threshold in Carbon-Nanotube-Epoxy Composites', *Polymer*, vol. 44, pp. 5893-5899, 2003.
- [23] K. Supreya, The Fabrication of Kevlar/Al<sub>2</sub>O<sub>3</sub>/Epoxy Resin laminated Composites by Low-Pressure Technique. Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand, 2011.
- [24] M.H. Al-Saleh and U. Sundararaj, 'A Review of Vapour Grown Carbon Nanofiber/Polymer Conductive Composites', *Carbon*, vol. 47, pp. 2-22, 2009.
- [25] H. Kishi and A. Fujita, 'Wood-Based Epoxy Resins and the Ramie Fiber Reinforced Composites', *Environmental Engineering and Management Journal*, vol. 7, no. 5, pp. 517-523, 2008.
- [26] C.A. Loos and G.S. Springer, 'Curing of Epoxy Matrix Composites', Journal of Composite Materials, vol. 17, pp. 135-169, 1983.
- [27] B.S. Hayes, J.C. Seferi, E. Anderson and J. Angal, 'Novel Elastomeric Modification of Epoxy/Carbon Fiber Composite Systems', *Journal of Advanced Materials*, vol. 28, no. 4, pp. 20-25, 1997.
- [28] O. Shakuntala, K.A. Samir and G. Raghavendra, 'Characterization and Wear Behavior of Carbon Black Filled Polymer Composites', *Procedia Materials Science*, vol. 6, pp. 468 – 475, 2014.
- [29] M.G. Veena, N.M. Renukappa, B. Suresha, K.N. Shivakumar, *Tribological and Electrical Properties of Silica-Filled Epoxy Nanocomposites*. Polymer Composites. Society of Plastics Engineers, 2011.
- [30] I.-G. Birsan, A. Circiumaru, V. Bria and V. Ungureanu, 'Tribological and Electrical

Properties of Filled Epoxy Reinforced Composites', *Tribology in Industry*, vol. 31, no. 1-2, pp. 33-36, 2009.

- [31] H. Chen, O. Jacobs, W. Wua, G. Rudiger and B. Schadel, 'Effect of Dispersion Method on Tribological Properties of Carbon Nanotube Reinforced Epoxy Resin Composites', *Polymer Testing*, vol. 26, pp 351–360, 2007.
- [32] L.C. Zhang, I. Zarudi and K.Q. Xiao, 'Novel Behaviour of Friction and Wear of Epoxy Composites Reinforced by Carbon Nanotubes', *Wear*, vol. 261, pp. 806–811, 2006.
- [33] J.W.V. Weil, Future of Automotive Design & Materials Trends and Developments in Design and Materials. Automatic Technology Center, 2012.
- [34] L. Harmeton (n,d), Thermosetting and Thermoplastic Polymer Matrices for Composites. Chemistry Department Faculty of Engineering and Physical Sciences and Surrey Materials Institute, Surrey University.
- [35] M.P. Wollcot and P.M. Smith (n,d), Wood Plastic Composites- Markets and Applications. 39th International Wood Composites Symposium. Washington State University.
- [36] J.O. Borode, Introduction to Composite Materials. Lecture note. Department of Metallurgical and Materials Engineering, Federal University Technology Akure, Ondo State, 2003.
- [37] Colton, Manufacturing Processes and Engineering Georgia Institute of Technology, 2011.
- [38] V.V. Valery and V.M. Evgeny, *Mechanics of Composite Materials*. Elsevier, Science Ltd, The Boulevard, Langford Lane, Kidlinton, Oxford OX5 IGB, UK, pp. 1-27, 2001.
- [39] S.C. Douglas and A. Lysle, *Composite Materials* for Aircraft Structures. Department of Mechanical and Industrial Engineering, Montana State, University, pp. 1-40, 2009.
- [40] Toray, Advanced Materials-Innovation by Chemistry. Toray's Advanced Materials Symposium, pp. 1-42, 2006.
- [41] O. Gabriel, N. Ţăranu, M. Vlad and E. Ioana, Application of Modern Polymeric Composite Materials in Industrial Construction. BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI Universitatea Tehnică "Gheorghe Asachi, 2010.
- [42] Composite Materials (n,d). pp 28-52.
- [43] Pandey, *Composite Materials*. Web Based Course, Department of Civil Engineering IISc Bangalore, 2004.

- [44] P.J. Josmin, K.M.T. Sabu, J. Kuruvilla, G. Koichi and S.S. Meyyarappallil, 'Advances in Polymer Composites: Macro and Micro composites-State of the Art, New Challenges and Opportunities', *Polymer Composites*, vol. 1, First Edition, published Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
- [45] W.D.J. Callister, Materials Science and Engineering An Introduction. (7<sup>th</sup> edition) USA, John Wiley and Sons Inc, 2007.
- [46] R.J. Young, *Polymer Nanocomposites*. School of Materials, University of Manchester, UK, 2011.
- [47] J.O. Agunsoye, V.S. Aigbodion, S.I. Talabi, Y.E. Moses, 'Morphology and Properties of Low Density Polyethylene Reinforced with Thaumococcous danielli Composites', *Journal* of Metallurgical Engineering (ME), vol. 2, no. 3, pp. 107-114, 2013.
- [48] P. Vlamidir, L. Rynno, H. Irina, P. Alex, V. Sergey, *Introduction to Nanomaterials and Technology*. Tartu University Press, 2007.
- [49] S.d. Souza and K.M. Kadish, Hand of Carbon Nanomaterials. vol. 1. World Scientific Publishing Co. Pte. Ltd, Singapore, 2011.
- [50] Masuki (editor), Metallic Micro and Nano Metallic Materials Fabrication with Atomic Diffusion. Springer, Heidelberg Dorrecht London, New York, 2011.
- [51] K. Michael, *Introduction to Nanotechnology*. Veritox Rendmond Washington, 2006.
- [52] S.M. James, 'Special Issue: Nanotechnology', *AMPTIAC Newsletter*, vol. 6, no. 1, pp. 37-42, 2002.
- [53] M. Deal, Nanotechnology, Nanoscale Science Engineering and Technology. Stanford Nanofabrication Facility, Stanford University Ireland, 2012.
- [54] United States Environmental Protection Agency, Nanotechnology White Paper. Science Policy Council, 2007.
- [55] L.A. Navarro, X. Perpina, M. Vellvehi and X. Jorda, 'Silver Nanoparticles Sintering Process for the Die-Attach Power Devices for High Temperature Applications', *INGENIERA MECHANICAL TECHNOLOGIA Y DESARROLLO*, vol. 4, no.3, pp. 097-102, 2012.
- [56] C. Buzea, I.P. Blandino and R. Kevin, 'Nanomaterials and Nanoparticles: Sources and Toxicity', *Biointerphases*, vol. 2, no. 4, pp. 1-103, 2007.
- [57] H. Wang, 'Sintering and Grain Growth of Nanosize Powder', *Ph.D. Dissertation*, Department of Metallurgical Engineering, University of Utah, 2010.

- [58] A. Alagarasi, Introduction to Nanomaterials, Chapter 10, 2011.
- [59] J.M.J. Frechet and D.A. Tomalia, *Dendrimers and Dendritic Polymers*. New York NY: John Wiley, 2001.
- [60] M. Chan, K. Lau, T. Wong, M. Ho and D. Hui, 'Mechanism of Reinforcement in a Nanoclay/Polymer Composite', *Elsevier Composite: Part B*, vol. 42, pp. 1708-1712, 2011.
- [61] http://www.nanohub.org
- [62] G.A. Ozin and A.C. Arsenault, Nanochemistry: A Chemical Approach to Nanomaterials. Royal Society of Chemistry Publishing: Cambridge, UK, 2005.
- [63] C.L. De Castro and B.S. Mitchell (2002). Nanoparticles from Mechanical Attrition, Chapter One, American Scientific Publishers, 2002.
- [64] P. Sks, C. Swarat, N.S. Satyendra and G. Mahmood, 'Electrical Conduction in Nanoceramic PGT Synthesised by High Energy Ball Milling', *Journal of Theoretical and Applied Physics*, vol. 7, pp. 267-276, 2013.
- [65] T.K. Lawrence, *Nano Ceramic Coating Exhibit Much Higher Toughness and Wear Resistance than Conventional Coating*. Advanced Materials and Process Technology Information Analysis Centre, 2010.
- [66] A. Allaoui, S. Baia, H.M. Cheng and J.B. Bai, 'Mechanical and Electrical Properties of a MWNT/Epoxy Composite', *Composite Science and Technology*, vol. 62, pp. 1993-1998, 2002.
- [67] D. Puglia, L. Valentini and J.M. Kenny, 'Analysis of the Cure Reaction of Carbon Nanotubes/Epoxy Resin Composites through Thermal Analysis and Raman Spectroscopy', *Journal of Applied Polymer Science*, vol. 88, pp. 452-458, 2002.
- [68] J. Bhaskar and V.K. Singh, 'Water Absorption and Compressive Properties of Coconut Shell Particle Reinforced-Epoxy Composite', J. Mater. Environ. Sci., vol. 4, no. 1, pp. 113-118, 2013.
- [69] S.M. Sapuan, M. Harimi and M.A. Maleque, 'Mechanical Properties of Epoxy/Coconut Shell Filler Particle Composites', *The Arabian Journal for Science and Engineering*, vol. 28, no. 2B, 2003.
- [70] K.P. Sreejarani and S.R. Suprakas, *Epoxy-based Carbon Nanotubes Reinforced Composites*. Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications, Dr. Boreddy Reddy (Ed.), 2011.
- [71] D.R. Askins, Characterization of EA9396 Epoxy Resin for Composite Repair Applications.

Materials Directorate Wright Laboratory Air Force Systems Command Wright-Patiterson Air Force Base, Ohio 45433-6533, 1991.

- [72] SP Composite, The Advantages of Epoxy Resin versus Pol yester in Marine Composite Structures, SP (Headquarter) St Cross Business Park Newport Isle of Wight, United Kingdom.
- [73] P. Mishra and S.K. Acharya, 'Solid Particle Erosion of Bagasse Fiber Reinforced Epoxy Composite', *International Journal of Physical Sciences*, vol. 5, 2010.
- [74] K. Jagrati, B.Y. Samar and K.N. Arun, Mechanical Properties of Multifunctional Epoxy Resin/ Glass Fiber Reinforced Composites Modified with Poly (Ether-imide). Advanced Material Letters, vol. 4, no. 3, pp. 241-249, 2012.
- [75] J.R.W. Captain, *Building Composite Tubes with West System Epoxy and Braided Fibers*. Epoxy Works Number 26, 2008.
- [76] W. Weijun, M. Fred, W. Yongfeng, M. Greg and P. Srinagesh (n,d), *Carbon Nanotube Enhanced Composite Materials*, Zyvex Performance Materials, 1255 Kinnear Rd., Columbus OH 43212.
- [77] A.A. Azeez, K.Y. Rhee, S.J. Park and D. Hui, 'Epoxy Clay Nanocomposites- Processing, Properties and Applications. A Review', *Composites: Part B*, vol. 45, pp. 308-320, 2012.
- [78] O. Shakuntala, G. Raghavendra, and S.K. Acharya, A Comparative Investigation of Bio Waste Filler (Wood Apple-Coconut) Reinforced Polymer Composites. Department of Mechanical Engineering, NIT, Rourkela, Odisha, India, 2013.
- [79] B. Jarrod, Forming of Advanced Composite Materials. Department of Mechanical Engineering, Massachusetts Institute of Technology, 1998.
- [80] A.D. Lonza, V. Wolfang and A. Magnus, 'High Temperature and Flame Retardant Cyanate Ester Resins for Aerospace Applications', *High Performance Materials, Switzerland*, vol. 15, no. 7, 2010.
- [81] G. Mansour, D. Tzetzis, and K.D. Bouzakis, 'A Nanomechanical Approach on the Measurement of the Elastic Properties of Epoxy Reinforced Carbon Nanotube Nanocomposites', *Tribology in Industry*, vol. 35, pp. 190-199, 2013.
- [82] Technology and Innovation (n,d), 'Challenges in Composites', *Aircraft Technology*, no. 116, pp. 52-56.
- [83] V.V. Pedro, F.J. Lino, M.B. Antonio and J.L.N. Rui, *Tribological of epoxy Resin Based*

*Composites for Rapid Tooling.* Structure 40 Portugal, 2004.

- [84] T. Aggarwal, 'Sliding Wear Behavior of Glass Fibre Reinforced TiO<sub>2</sub> Filled Epoxy Resin Composite', *B.Sc. Thesis*, Department of Mechanical Engineering National Institute of Technology Rourkela-769008, pp. 1-41, 2009.
- [85] K. Supreya, The Fabrication of Kevlar/Al<sub>2</sub>O<sub>3</sub>/Epoxy Resin laminated Composites by Low-Pressure Technique. Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand, 2011.
- [86] J. Staley and J.E.A. Starke, 'Application of Modern Aluminium Alloys to Aircraft', *Journal* of Progress in Aerospace Sciences, vol. 32, no. 2-3, pp. 131-172, 1996.
- [87] J.E.A. Starke and J. Staley, 'Application of Modern Aluminium Alloys to Aircraft', *Journal* of Progress in Aerospace Sciences, vol. 32, no. 2-3, pp. 131-172, 1996.
- [88] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, K. Schulte, 'Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – A comparative study', *Composites Science and Technology*, vol. 65, pp. 2300–2313, 2005.
- [89] S. Aribo, J.A. Omotoyinbo and D.O. Folorunsho, 'High Temperature Mechanical Properties of Silicon Carbide Particulate Reinforced Cast Aluminium Alloy Composite', *Leonardo Electronic Journal of Practices and Technologies*, no. 18, pp 9-16, 2011.
- [90] M. Mortazavi, G. H. Majzoobi, A. N. Golikand, A. Reihani, S. Z. Mortazavi and M. S. Gorji, 'Fabrication and Mechanical Properties of MWCNTs-Reinforced Aluminium Composites by Hot Extrusion', *Rare Metal*, vol. 31, no. 4, pp. 372-380, 2012.
- [91] N. Ozdemir and E. Yakuphanoglu, 'The Effects of Particle Size and Volume Fractions of  $Al_2O_3$ on Electronic Thermal Conductivity of  $\alpha$ -  $Al_2O_3$ Particulate Reinforced Aluminium Composites', *International Journal of Advanced Manufacturing Technology*, vol. 29, pp. 226-229, 2006.
- [92] W. Tian-Chi, F. Tong-Xiang, Z. Di and Z. Guo-Ding, 'Fabrication, Thermal Expansions and Mechanical Properties of Carbon/Aluminum Composites Based on Wood Templates', *Journal of Material Science*, vol. 41, pp. 6095-6099, 2006.
- [93] S. Chao, S. Min, W. Zhangwei and H. Yuechi, 'Effect of Particle Size on the Microstructures and Mechanical Properties of SiC-Reinforced

Pure Aluminum Composites', *Journal of Materials Engineering and Performance*, vol. 20, pp. 1606-1612, 2011.

- [94] M. Guden, S. Yuksel, 'SiC-Particulate Aluminium Composite Foams Produced from Powder Compacts: Foaming and Compression Behaviour', *J Mater Sci*, vol. 41, pp. 4075-4084, 2006.
- [95] L. Eng-Kwong, S.A. Ryoichi and K.R. Pradeep, 'Numerical Simulation and Experimental Study of Solidification of Squeeze Cast Aluminum Composites in the Presence of Cooled Fibers', *Heat Mass Transfer*, vol. 44, pp. 71-84, 2007.
- [96] F. Hiroshi, A. Ryota, N. Atsushi, Y. Yuki and A. Kei, 'Enhanced Mechanical properties of Nano/Meso hybrid Structure Materials Produced by Hot Roll Sintering Process', *Material Transactions*, vol. 49, no. 1 pp. 90-96, 2008.
- [97] J. Li, F. Li, Au and Y. Zhou, 'TiB<sub>2</sub>/TiC Nanocomposite Powder Fabricated through High Energy Ball Milling', *Journal of European Ceramic Society*, vol. 21, no. 16, pp. 2829-2833, 2001.
- [98] J. Sun, J.X. Zhang, Y.Y. Fu and G.X. Hu, 'Microstructural Evolution of an Al<sub>67</sub>Mn<sub>8</sub>Ti<sub>24</sub>Nb<sub>1</sub> Alloy during Mechanical Milling and Subsequent Annealing Process, *Materials Science and Engineering: A.*, vol. 329-331, pp. 703-707, 2004.
- [99] P. Nandi, P.P. Chattopadhyay, S.K. Pabi and I. Manna, 'Solid State Synthesis of Al-Based Amorphous and Nanocrystalline Al-Cu-Nb Alloys', *Materials Science and Engineering: A*, vol. 359, no. 1-2, pp. 11 – 17, 2000.
- [100] M. Zawrah and L. Shaw, 'Microstructure and Hardness of Nanostructured Al-Fe-Cr-Ti Alloys through Mechanical Alloying', *Materials Science and Engineering A*, vol. 355, no. 1-2, pp. 37-49, 2003.
- [101] I. Manna, P.P. Chattopadhyay, F. Banhart and H.J. Fecht, 'Development of Amorphous and Nanocrystalline Al<sub>65</sub>Cu<sub>35-<I>X</sub>Zr<sub>x></sub> Alloys by Mechanical Alloying', *Materials Science and Engineering: A.*, vol. 379, no. 1-2, pp. 360-365, 2004.
- [102] T.M. Dellinger, 'Bismuth-Ceramic Nanocomposites through Ball Milling and Liquid Crystal Synthetic Methods', *Ph.D Dissertation*, Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, 2004.
- [103] B. Basu, J.H. Lee and D.Y. Kim, 'Processing of Nanoceramics and Nanoceramic Composites: New Results', *Key Engineering Materials*, vol. 264-268, pp. 2239-2296, 2004.

- [104] P. Palmero, V. Naglier, M. Azar, V. Garnier, M. Lombardi, L. Joly-Pottus, J. Chevalier and L. Montanaro, 'Nanopowder Engineering. From Synthesis to Sintering. The Case of Aluminium-Based Materials', *Verres and Composites*, vol. 1, no. 1, pp. 62-75, 2011.
- [105] R.J. Babu, G.J. Catherin, I.N. Murthy, D.V. Rao and B.N. Raju, 'Production of Nanostructured Silicon Carbide By High Energy Ball Milling', *International Journal of Engineering, Science* and Technology, vol. 3, no. 4, pp. 82-88, 2011.
- [106] K. Mathias and S. Andreas, 'Power Semiconductors Joining through Sintering of Silver nanoparticles: Evaluation of Influence of parameters Time', Temperature and Pressure on Density. Strength and Reliability, CIPS, pp. 16-18, 2010.
- [107] S. Susan and N. Samson, 'Preparation of MnFe<sub>2</sub>O<sub>4</sub> Nanoceramic Particles by Soft Chemical Routes', *International Journal of Applied Science and Engineering*, vol. 9, no. 4, pp. 223-239, 2011.
- [108] G. Montserrat, C.P. Maria, G. Pawel, S. Wieslaw, J.C. Joan, M. Xavier, A. Magdalena and D. Francesc, 'A Promising Lu2-xHoxO3 Laser Nanoceramic:Synthesis and Characterization', *The American Ceramic Society*, vol. 93, no. 11, pp. 3764–3772, 2010.

- [109] J. Sopousek, J. Bursik, J.V. Zalesak, B.P. Bursikova, 'Interaction of Silver Nanopowders with Copper Substrate', *Science of Sintering*, vol. 43, pp. 33-38, 2011.
- [110] Y.M. Al-Yousef and M. Ghouse, 'Preparation of La<sub>0.6</sub>Ba<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3</sub> (LBCF) Nanoceramic Cathode Powders by Sol-Gel Process for Solid Oxide Fuel Cell (SOFC) Application', *Energy and Power Engineering*, vol. 3, pp. 382-391, 2011.
- [111] A. Ruangvittayanon and S. Kuharuangrong, 'Physical Properties of  $La_{0.9}Sr_{0.1}Cr_{1-X}NixO_{3-\delta}$  (X = 0-0.6) Synthesized Via Citrate Gel Combustion', *Suranaree J. Sci. Technol.* 1, vol. 6, no. 4, pp. 319-323, 2009.
- [112] K.K. Ramama, A.J. Bell, C.R. Bowen and K. Chandramoulid, 'Investigation of Dielectric and Piezoelectric Properties of Niobium-Modified PLSZFT Nanoceramics for Sensor and Actuator Applications', *Journal of Alloys and Compounds*, vol. 473, pp. 330–335, 2009.
- [113] R. Egidija, Applications of Natural Fibers in Composites. Technology Centre KETEK Ltd. pp. 1-27, 2011.
- [114] T.P. Yadav, R.M. Yadav and D.P. Singh, 'Mechanical Milling: a Top Down Approach for the Synthesis of Nanomaterials and Nanocomposites', *Nanoscience and Nanotechnology*, vol. 2, no. 3, pp. 22-48, 2012.