CHARACTERIZATION OF NANO-STRUCTURED OIL PALM ASH AND ITS INFLUENCE AS FILLER IN EPOXY COMPOSITES

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By

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بِسْمِ اللهِ الرَّحْمَنِ الرَّحِيم

“In the name of “Allah, Most Gracious, Most Merciful”

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CMCs	ceramic matrix composites
CNTs	carbon nanotubes
DGEBA	Diglycidyl ether of bisphenol-A
DWCNT	Double-wall carbon nanotubes
EDX	Energy Dispersion of X-Ray
EFB	Empty Fruit Bunches
FT-IR	Fourier Transform Infrared Spectroscopy
GNI	Gross National Income
HEPA	High-Efficiency Particulate Air
LS	Layered Silicate
MF	Mesocarp fibre
MMCs	metal matrix composites
MMT	Montmorillonite
MWCNT	Multi-wall carbon nanotubes
OPA	Oil Palm Ash
OPF	Oil Palm Fronds
OPT	Oil Palm Trunks
PEO	Polyethylene Oxide
PET	Polyethylene terephthalate
PKS	Palm kernel shells

PLA	Poly(lactic acid)
PMCs	Polymer matrix composites
PMMA	Poly(methyl methacrylate)
POME	Palm oil mill effluent
SEM	Scanning Electron Microscopy
SPEEK	Sulfonated poly(ether ether ketone)
SWCNT	Single-wall carbon nanotubes
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
Wt.	Weight
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
°*C*	Degree Celsius
µm	Micrometer
cm	Centimeter
d	Thickness
G	Giga
g	Gram
J	Joule
K	Kelvin
k	Kilo
Kg	Kilogram
L	Span length
M	Mega
m	Mass
m	meter
Ma	Milliampere
mg	Milligram
mm	Millimeter
nm	Nanometer
Pa	Pascal
S	Siemens

T	Tera
$T_{50\%}$	Degradation at 50% weight loss
T_f	Final decomposition temperature
T_g	Glass transition temperature
T_i	Initial decomposition temperature
T_{max}	Decomposition temperature
v	Volume
V	Volt
V_f	Volume fraction
W	Watt
W_f	Weight fraction
X	Magnification
θ	Theta
λ	Lambda
ρ	Density
ρ_c	Composite density
ρ_f	Filler density

LIST OF PUBLICATIONS

		Pages
APPENDIX A	ABDUL KHALIL, H. P. S., FIZREE, H. M., JAWAID, M. & ALATTAS, O. S. 2011. Preparation and characterization of nano-structured materials from oil palm ash: A bio-agricultural waste from oil palm mill. *BioResources*, 6**,** 4537-4546.	108

PENCIRIAN ABU KELAPA SAWIT TERSRUKTUR NANO DAN PENGARUHNYA SEBAGAI PENGISI DALAM KOMPOSIT EPOKSI

ABSTRAK

Penggunaan abu kelapa sawit, sisa bio-pertanian dari kilang kelapa sawit telah dikaji dengan membangunkan ia menjadi bahan terstruktur nano dan sebagai pengisi/penguat ke atas komposit epoksi. Abu kelapa sawit mentah telah dikenakan pengisaran bebola bertenaga tinggi selama 30 jam dan telah ditukar kepada bahan terstruktur nano. Terstruktur nano abu kelapa sawit telah ditentukan ciri-cirinya untuk saiz zarah dan indek penghabluran dengan menggunakan Penghantar Mikroskopi Elektron (TEM) dan analisis Belauan Sinar-X (XRD). Saiz hablur yang diperolehi dari TEM dan XRD telah didapati bersaiz 50 nm dan 54.32 nm masing-masing, dan indek penghabluran terstuktur nano abu kelapa sawit adalah 66,54%. Bentuk dan tekstur abu kelapa sawit mentah dan terstuktur nano abu kelapa sawit telah dikaji menggunakan Mikroskop Pengimbasan Elektron (SEM). Abu kelapa sawit mentah mempunyai bentuk yang tidak teratur dengan struktur seperti span dan berliang, manakala terstuktur nano abu kelapa sawit mempunyai bentuk yang kebanyakannya tidak teratur dan terhancur. Kajian unsur abu kelapa sawit telah menggunakan Tenaga Sebaran Sinar-X (EDX) analisis, XRD dan Spektroskopi Inframerah Transformasi Fourier (FT-IR). Komposisi unsur yang ditemui di abu kelapa sawit adalah silika, kalium oksida, kalsium oksida, magnesium oksida, aluminium oksida, dan ferum oksida. Kesan penambahan pengisi, 0, 1, 2, 3, 4 dan 5% daripada terstuktur nano abu kelapa sawit ke atas sifat-sifat fizikal, mekanik, terma dan morfologi komposit epoksi telah dikaji. Adalah diperhatikan bahawa kesan kemasukkan penambahan pengisi terstuktur nano abu kelapa sawit meningkatkan ketumpatan, kandungan ruang kosong dan penyerapan air komposit selari dengan peningkat penambahan pengisi. Ke atas sifat mekanik, peningkatan dalam kekuatan tensil, modulus tegangan, kekuatan lenturan, modulus lenturan dan kekuatan impak telah diperhatikan selari dengan peningkatan penambahan pengisi sehingga 3% dan kemudiannya berkurang melebihi penambahan pengisi 3%. Walaubagaimanapun, pengecualian untuk pemanjangan pada takat putus, peningkatan pada penambahan pengisi, pengurangan % pemanjangan pada takat putus diperhatikan. Ke atas sifat haba, peningkatan kestabilan terma selari dengan peningkatan penambahan pengisi sehingga 3% dan kemudian berkurang melebihi penambahan pengisi 3%. Pada morfologi permukaan yang telah dikenakan impak, epoksi kosong telah menunjukkan permukaan seakan sungai yang licin dan nipis. Selari dengan peningkatan penambahan pengisi, permukaan yang kasar dengan pemecahan matrik dan permukaan aglomerasi telah diperhatikan. Pada analisis XRD, tiada puncak kristal telah diperhatikan menunjukkan sifat amorfus sampel. Pada analisis TEM, penyerakan dan pengagihan yang baik oleh pengisi terstuktur nano abu kelapa sawit 3% telah diperhatikan

CHARACTERIZATION OF NANO-STRUCTURED OIL PALM ASH AND ITS INFLUENCE AS FILLER IN EPOXY COMPOSITES

ABSTRACT

The utilization of oil palm ash, a bio-agricultural waste from oil palm mills was studied by developing it into nano-structured material and as nanofiller/reinforcement on epoxy composites. The raw oil palm ash was subjected to high-energy ball milling for 30 h and was converted into a nano-structured material. The nano-structured oil palm ash was characterized for its particle size and crystallinity index by using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD) analysis. The crystallite size obtained from TEM and XRD was found to be 50 nm and 54.32 nm respectively, and the crystallinity index of oil palm ash was 66.54%. The shape and texture of raw and nano-structured oil palm ash were studied using scanning electron microscopy. The raw oil palm ash had an irregular shape with spongy and porous structure, while the nano-structured powder had a mostly irregular and crushed shape. The elemental studies of oil palm ash used Energy Dispersive X-ray (EDX) analysis, XRD, and Fourier Transform Infrared Spectroscopy (FT-IR). The elemental compositions found in oil palm ash were silica, potassium oxide, calcium oxide, magnesium oxide, aluminium oxide, and iron oxide. The effect of filler loading, 0, 1, 2, 3, 4 and 5 % of nano-structured oil palm ash on the physical, mechanical, thermal and morphology properties of epoxy composites was studied. It was observed that incorporation filler loading of nano-structured oil palm ash increased the density, void content and water absorption of composites as increased on filler loading. For the mechanical properties, increased in tensile strength, tensile modulus, flexural strength, flexural modulus and impact strength were observed as increased of filler loading up to 3% and then decreased beyond 3% filler loading. But, an exception for elongation at break, as increased on filler loading, decreased on % of elongation at break was observed. For the thermal properties, the thermal stability increased as filler loading increased up to 3% and then decreased beyond 3% filler loading. On morphological of impacted surface, neat epoxy illustrated smooth and thin river surface. As filler loading increased, rougher surface with matrix breakage and aggregated surface was observed. The XRD analysis, no crystalline peaks were observed indicated of amorphous behavior of the samples. The TEM analysis showed good dispersion and distribution of 3% filler loading of nano-structured oil palm ash epoxy composites was observed.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Towards the sustainable economic growth and higher human development, affordable products with advances properties are essential. Thus, the utilization of waste materials which are abundant and cheap, especially from clean resources, has become more pressing than ever especially oil palm biomass. It is estimated that the total potential oil palm biomass from 4.69 million hectares of oil palm planted area in Malaysia in 2009 is 77.24 million tonnes per year comprising 13.97 million tonnes of oil palm trunks (OPT), 44.84 million tonnes of oil palm fronds (OPF), 6.93 million tonnes of empty fruit bunches (EFB), 4.21 million tonnes of palm kernal shell (PKS) and 7.29 million tonnes of mesocarp fiber (MF) (all dry weight) (Foo et al., 2011). Currently, oil palm biomass is mostly used for the purpose of compost and fertiliser, mulching mats, plywood and veneer from OPT. Others than that, oil palm fibre-filled automotive upholstery parts and dampening sheets for automotive industry using oil palm fibres. Furthermore, moulded particleboard, containers, pulp, paper, and moulded pulp products for food packaging from EFB. Moreover, medium density boards, furniture, oil palm lumber, activated carbon, and compostable plastic film also produces using oil palm biomass. But these biomasses are still often used as boiler fuel by palm oil mill plants to produce steam for electricity generation (Hashim and Chu, 2002) and after combustion in the steam boiler, there is approx. 5% of ash being produce (Tay and Show, 1995) and generate another solid waste.

Oil palm ash (OPA) is an abundant agricultural solid waste in Malaysia. This bio agricultural waste ash which the source of siliceous material is produced after the combustion of oil palm fiber, shell, EFB and mesocarp as boiler fuel to produce steam for palm oil mill consumption. Although there are some studies on the utilization of OPA such as a cement replacement material (Tay and Show, 1996), as an adsorbent for the removal of zinc from aqueous solution (Chu and Hashim, 2002) and flue gas desulphurization (Zainudin et al., 2005), most of the ash is still disposed off in landfill that requires a lot of land area and will causing environmental problems. Thus, creating, manipulating and exploring OPA in nanotechnological research as nano structured material will create an advance bio agricultural waste material.

Nanotechnology has become a rapidly growing field with potential applications ranging from advanced application to a daily used product. It include the production and application of biological, chemical and physical systems at scales ranging from individual atoms or molecules to submicrons level as well as integration of the resulting nano-structure to larger systems (Bhushan, 2004). Nanomaterial is defined as the material having dimensions roughly 1 to 100 nanometer (Koo, 2006) or at least one dimension in nanometer range. A variety of ways have been reported to synthesize nanomaterials such as high intensity ball milling, sol-gel synthesis, electro deposition, chemical vapour deposition, plasma arching etc. (Cao, 2004). Among these, high intensity ball milling has the advantage of being simple, reasonably low-cost to conduct, applicable to various class of materials and easily scaled up to large quantities (Baraton, 2003). By this mechanical action, particles are subjected to severe deformation due to repetitive compressive loads arising from impacts between the balls and the particles. This produces crystalline and amorphous material with crystallite sizes at the nanometer scale. (Koch, 2006)

In the last decade, nanocomposite materials consisting of a polymeric matrix materials and nanomaterial/nanofillers have attracted scientific and industrial interest ranging from high barrier packaging for food and electronics (Ahmadi et al., 2004) to automotive and aerospace applications (Njuguna and Pielichowski, 2003) due to their improved properties. At low filler contents as compared with the conventional micro and macro or neat counterparts, they exhibit superior property enhancements. (improved mechanical and thermal properties, gas permeability resistance and fire retardancy is related to the nanostructure achieved in processing these materials) Numerous different types of polymer and fillers have been used so far to prepare nanocomposites. Nylon-6 (Zhang et al., 2011), poly(propylene) (Li et al., 2011), poly(ethylene) (Cheng et al., 2011), rubber (Siqueira et al., 2011) and epoxy (Rafiee et al., 2011) have been used as polymers and reinforced by addition of carbon nanotubes (CNTs), carbon nanostructure, cellulosic nanoparticles and fullerene, respectively. To produce more functional materials, different type of fillers can be used together to obtain diverse favourable properties from the nanocomposites.

1.2 Problem Statement

The aim of this study is to utilize the bio-agricultural waste as filler material on composites production which are abundantly available and low cost compare to the silica, alumina etc. The lacks of sufficient scientific information about the utilization of the OPA on composites production were the driving force for the choice of this work. There are numerous reports on the utilization of OPA as adsorbents, fertilizer, natural rubber production, composites and etc. However, not much effort has been done on the utilization of OPA as filler in polymer matrix. Furthermore, it is a novelty by introducing nanotechnological concept toward the agricultural waste. Thus, creating, manipulating, and exploring OPA in nanotechnological research as nano-structured material has the potential to lead to beneficial uses of this bio-agricultural waste material. In addition, the utilization of this waste will at least give hope on the environment problem regarding the vast production of oil palm production in Malaysia, particularly.

1.3 Objectives of the Study

The objectives of this present study are:

- To explore and to modify the oil palm ash by transforming the macro size into nano-structured material
- To study the characteristic of nano-structured oil palm ash produced.
- To produce nanocomposites with nano-structured oil palm ash as a filler and epoxy resin as the matrix.
- To study the effect of filler loading percentage of filler on physical, mechanical, thermal and morphology properties of the epoxy nanocomposites.

1.4 Organization of Thesis

This thesis has been structured into 5 respective chapters.

Chapter 1-Introduction, focused on introducing and background, problem statement and objectives of study.

Chapter 2- Focussed on literature review of present study. Review of composites, composites constituent, nanomaterial, nanocomposites, oil palm biomass and oil palm ash are given.

Chapter 3-Explains about materials and methodology of production of nanomaterial, fabrication and characterization of nanocomposites.

Chapter 4- Provide the results and discussion of characterization of nano-structured OPA and nano-structured OPA filled epoxy composites.

Chapter 5-Summarizes the overall conclusions and recommendation for future research of this study.

CHAPTER 2

LITRATURE REVIEW

2.1 Composites

Composites are engineered materials made from two or more constituents with significantly different physical or chemical properties from their components, which remain separate and distinct within the finished structure. There are two types of constituent materials, which are known as matrix and reinforcement components. The matrix in the material surrounds and supports the reinforcement component by maintaining their relative positions (Ivan, 2008).

2.1.1 Classification of Composites

Composites are classified based on either matrix or reinforcement material structure. Polymer matrix composites (PMCs), metal matrix composites (MMCs) and ceramic matrix composites (CMCs) are the commonly available in market. Classification in relation to reinforcement is distinguished based on the size and shape of reinforcement, orientations and interlocking mechanisms of it and constituent. They are either fibrous or particulate. Currently, PMCs are most widely used class of composites (Vadlamani and University, 2007). Figure 2.1 represents a commonly accepted classification scheme for composite materials.

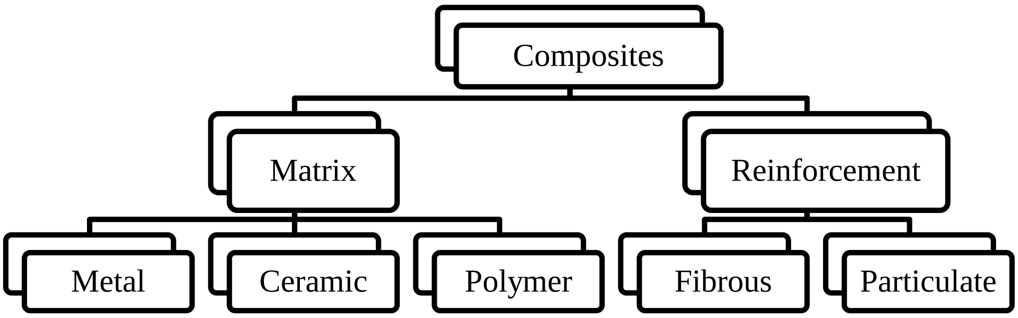


Figure 2.1: Classification of composite materials

2.2 Polymer composites

Polymer composites consist of a polymer matrix strengthened with a reinforcement agent, which may be fibrous or particulate in nature. The matrix binds together and protects the reinforcement, and it transfers any applied load into and out of the composite, and to the reinforcement through friction at the mutual interface. Additional components may include fillers, which can reduce overall composite cost as well as provide specific performance benefits, or additives to enhance processing or modify composite properties (Adams et al., 2000) Polymers, in general, are desirable for use in composite materials because they are conducive to designer materials. In addition, they have a relatively low cost and are often moderately easy to process (Chawla, 1998)

Central to the development of composite materials is the principle that these materials display a combination of the properties of their constituent components; the composite has properties not shown by either ingredient in isolation. Compared to traditional metal or ceramic materials, polymer composite materials have higher strength and stiffness and lower weight and thermal expansion (Chawla, 1998; Adams et al., 2000).

2.2.1 Matrix

The matrix in a polymer composite serves both to maintain the position and orientation of the reinforcement and protects them from adverse environmental effects (Salamone, 1996). In addition, it helps to distribute the applied load by acting as a stress transfer medium (Akovali, 2001). The polymer matrices can be of two types differing in their respective intermolecular structures.

2.2.1.1 Thermoplastic

In a thermoplastic polymer, there is no chemical bond between long chain molecules. They are held by weak intermolecular bonds such as van Der Waals or hydrogen bonds (Muccio, 1994). Thermoplastics are heat softenable, heat meltable and reprocessable (Akovali, 2001). The most important advantages of thermoplastics over thermosets are their high impact strength and fracture resistance which in turn imparts excellent damage tolerance characteristics to the composite material (Schwartz, 1997). It is therefore obvious that in the choice of thermoplastic versus thermoset resin, several trade-offs and compromises must be made considering the application area of the material. Common types of thermoset resin used for manufacturing composite materials are polyethylene, polypropylene, polystyrene and polyvinylchloride.

2.2.1.2 Thermoset

In a thermoset polymer, the molecules are chemically joined together by crosslinks, forming a rigid, three-dimensional network structure. Once these crosslinks are formed during polymerization reaction (curing), the polymer cannot be remelted and reshaped by the application of heat and pressure (Schwartz, 1997). Thermosetting polymers are the most frequently used matrix materials in polymer-based composites production mainly because of the ease of their processing (Akovali, 2001). In the case of thermosets, it is possible to achieve a good wet-out between the fibers and matrices, since the starting materials for the polymerization are low molecular-weight liquid chemicals with very low viscosities (Schwartz, 1997). Thermosets are usually more rigid than thermoplastics and also exhibit generally higher temperature performance, however they usually require much longer processing times (Strong and Ploskonka, 1989). Common types of thermoset resin used for manufacturing composite materials are epoxies, polyesters, vinyl esters and phenolics.

2.2.1.2.1 Epoxy

The word “epoxy” is derived from the Greek prefix “ep,” which means over and between, and “oxy,” the combining form of oxygen (Hartman, 1984). Epoxy resins are an important class of polymeric materials, characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group (Figure 2.2).

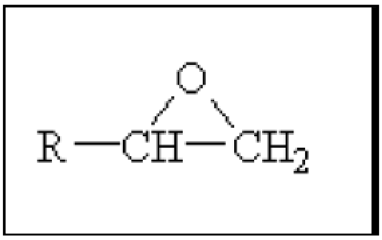


Figure 2.2: Epoxide groups (Pham and Marks, 2002)

Epoxies are one of the most versatile classes of polymers with diverse applications such as metal can coatings, automotive primer, printed circuit boards, semiconductor encapsulants, adhesives, and aerospace composites. Most cured epoxy resins provide amorphous thermosets with excellent mechanical strength and toughness; outstanding chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; no volatiles emission and low shrinkage upon cure; and dimensional stability; a unique combination of properties generally not found in any other plastic material. These superior performance characteristics, coupled with outstanding formulating versatility and reasonable costs, have gained epoxy resins wide acceptance as materials of choice for a multitude of bonding, structural, and protective coatings applications (Pham and Marks, 2002).

The functional group in epoxy resins is called the oxirane, a three-membered strained ring containing oxygen. A wide range of starting materials can be used for the preparation of epoxy resins thereby providing a variety of resins with controllable high performance characteristics. These resins generally are prepared by reacting to a poly-functional amine or phenol with epichlorohydrin in the presence of a strong base. Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesised by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst as shown in Figure 2.3. Chemical structure of diglycidyl ether of Bisphenol A (DGEBA) shown in Figure 2.4. The presence of glycidyl units in these resins enhances the processability but reduces thermal resistance.

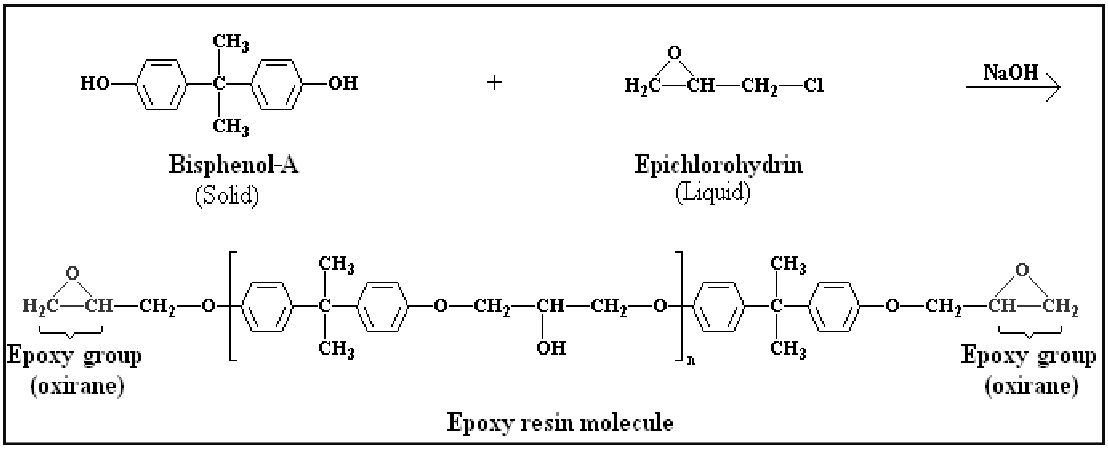


Figure 2.3: Reaction between bisphenol-A and epichlorohydrin to form epoxy resin (Pham and Marks, 2002)

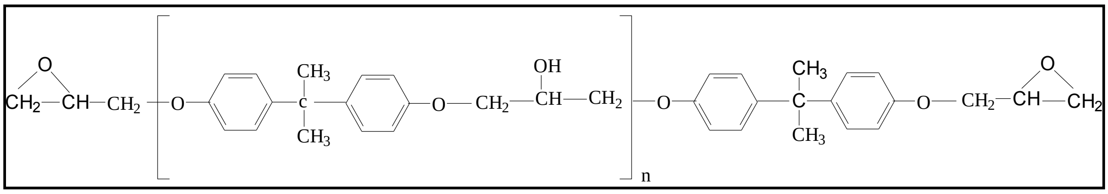


Figure 2.4: Diglycidyl ether of Bisphenol A (Pham and Marks, 2002)

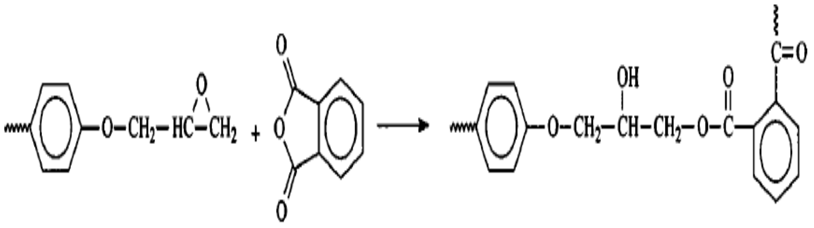
Almost all epoxy resins are converted into solid, infusible, and insoluble three-dimensional thermoset networks for their uses by curing with cross-linkers. Optimum performance properties are obtained by cross-linking the right epoxy resins with the proper cross-linkers, often called hardeners or curing agents. Selecting the proper curing agent is dependent on the requirements of the application process techniques, pot life, cure conditions, and ultimate physical properties. Besides affecting viscosity and reactivity of the formulation, curing agents determine both the types of chemical bonds formed and the degree of crosslinking that will occur. These, in turn, affect the chemical resistance, electrical properties, mechanical properties, and heat resistance of the cured thermosets (Pham and Marks, 2002). The most widely used curing agents for epoxy resins are primary and secondary amines, anhydride, dicyandiamide, polysulfide, and polyamide. Advantages and disadvantages of different types of curing agents for epoxy resin are display in Table 2.1.

The structure of the cured resin depends on the epoxy monomer and curing agent used. Usually, chemical linkages generated by reactions of glycidyl ethers are less stable than other chemical linkages in the epoxy network, and therefore there is justification to discuss here only those structures formed by the glycidyl ethers. Figure 2.5 illustrated the mechanism of cross linking. Carboxylic acids easily react with epoxies; however, generally anhydrides are used for curing (Scheme 1). Anhydrides of dicarboxylic acids produce linear structures with diepoxides, and crosslinking usually occurs due to esterification of the alcohol groups (Scheme 2). Aliphatic and aromatic diamines are the most widely used classes of curing agents. With the proper catalyst, aliphatic diamines cure epoxies at room temperature, whereas elevated temperatures are required for aromatic diamines (Scheme 3).

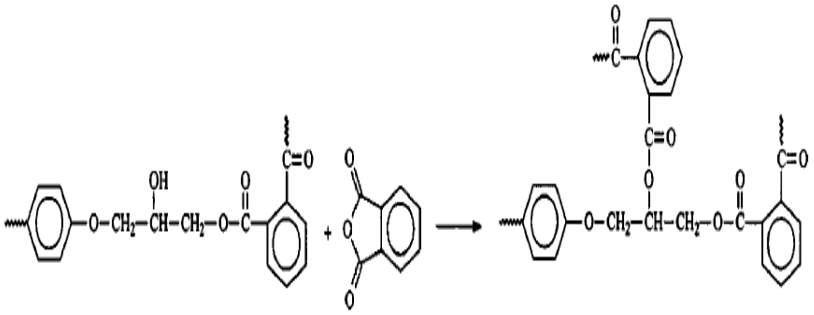
Secondary amines, although more hindered than primary amines, can still react with epoxies and form crosslinks (Sergei and Edward, 2004).

Table 2.1: Comparison of the properties of different types of curing agents for epoxy (Ratna, 2009)

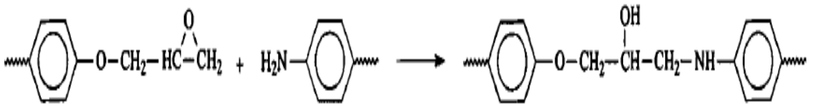
Type	Advantages	Disadvantages
Aliphatic amine	Low cost, low viscosity, easy to mix , room temperature curing, fast reacting	High volatility, toxicity, short pot life, cured network can work up to 80 ^{0}C but not above
Cycloaliphatic amine	Room temperature curing, convenient handling, long pot life, better toughness, and thermal properties of the resulting network compared with aliphatic amine-cured network	High cost, can work at a service temperature < 100 ^{0}C, poor chemical and solvent resistance
Aromatic amine	High T_g, better chemical resistance and thermal properties of the resulting network compared with aliphatic- and cycloaliphatic amine-cured network	Mostly solid, difficult to mix, Curing requires elevated temperature
Anhydride	High network T_g compared with amine curing agent, very good chemical and heat resistance of the resulting network	High temperature curing, long post-curing, necessity of accelerator, sensitive to moisture
Dicyandiamide	Low volatility, improved adhesion, good flexibility and toughness	Difficult to mix, high temperature curing and long post-curing
Polysulfide	Flexibility of the resulting network, fast curing	Poor ageing and thermal properties, odour
Polyamides	Low volatility, low toxicity, room temperature-curing, good adhesion, long pot life, better flexibility and toughness of the resulting network compared with aliphatic amine-cured networks	Low T_g of the resulting network, high cost and high viscosity



Scheme 1.



Scheme 2.



Scheme 3.

Figure 2.5: Cross linking of epoxy resin with hardener (Pham and Marks, 2002)

2.2.2 Reinforcements

Reinforcements for the composites can be fibers, filled, flake, particles or whiskers. Fibers are essentially characterized by one very long axis with other two axes either often circular or near circular. Particles have no preferred orientation and so do their shape. Whiskers have a preferred shape but are small both in diameter and length as compared to fibers. Figure 2.6 shows types of reinforcements in composites. Reinforcing constituents in composites, as the word indicates, provide the strength that makes the composite what it is. But they also serve certain additional purposes of heat resistance or conduction, resistance to corrosion and provide rigidity. Reinforcement can be made to perform all or one of these functions as per requirements. To overcome the strength of the matrix, the reinforcement must be stronger and stiffer than the matrix and capable of changing failure mechanism to the advantage of the composite. This means that the ductility should be minimum or even nil and the composite must behave as brittle as possible (Pandey, 2004)

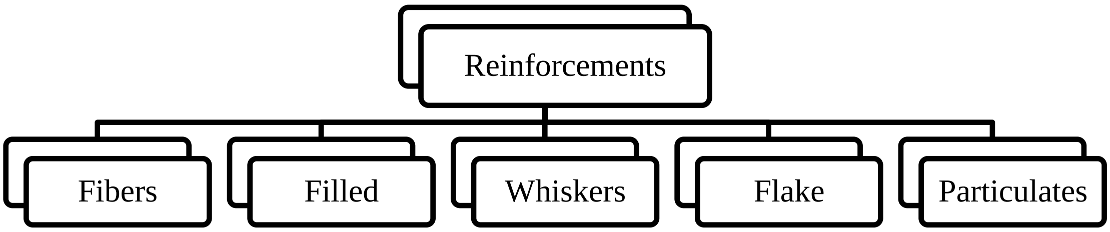


Figure 2.6: Types of reinforcements in composites

2.3 Polymer Nanocomposites

The term polymer nanocomposite broadly describes any number of multicomponent systems, where the primary component is the polymer and the filler material has at least one dimension below 100nm (Koo, 2006). Polymer nanocomposites are generally lightweight, require low filler loading, are often easy to process with good technique, and provide property enhancements extending orders of magnitude beyond those realized with conventional composites or micro-composites (Ng et al., 1999; Chisholm et al., 2005). Rapid advancements in nanocomposite technologies have been realized as new classes of nanoscale fillers continue to emerge. This enhancement of properties can be explained by the fact that the smaller diameter nanofiller has a higher surface-to-volume ratio which accounts for increased interaction between components; the interfacial areas influence the composite properties to a larger extent (Dagani, 1999)

Nanoparticles commonly dispersed in polymer matrices include: Polyoctahedral silsesquioxane (POSS), layered silicate clays, carbon nanofibers, CNTs, graphite nanoflakes and nanocellulose (only name a few). These nano-particles differ in chemistry, morphology, aspect ratio and aggregate size. The nanoparticle chosen for dispersion in a resin is dependent on the intended application. However, realization of significant enhancement in properties with any of the nano-materials requires that the nano-particle is well dispersed throughout the matrix. Effective dispersion is hindered by the tendency of the particulate phase to form clusters or agglomerates. These agglomerates form due to the large surface/volume ratio and inherent surface energy of the primary particles which create dipole-dipole inter-particle forces. The formation of particle clusters can negate any potential benefits of the nanofiller because the reduced surface area of interaction between filler and matrix inhibits effective stress transfer between components. Also, under load, agglomerates can act as defects in the bulk composite (Rodgers et al., 2005), as sites where stress concentrates and fracture is thus initiated (Pervin et al., 2005). In order to overcome the problem of nanoparticle agglomeration and to attain enhanced mechanical properties, an efficient technique must be employed to consistently achieve uniform filler distribution. Surfactants are commonly used for this purpose; however, they can have detrimental effects on the crosslinking of the polymer (Moniruzzaman et al., 2006). In order to avoid this and to still achieve good dispersion, ultrasonic processing technique is required. Furthermore, it is desirable that the particle bond with the matrix. Generally, composite components should interact either chemically or physically, with the matrix to create a strong interface. In all cases, the interface between the composite components plays a defining role in the overall material properties (Yang and Tsai, 2006). This becomes critical as the available interfacial area is increased by the dispersion of nano-sized particles throughout the polymer matrix.

2.3.1 Structure and Morphology of Nanocomposites

Depending on the nature and classification of the nanomaterial with varying level of interactions between nanomaterial and polymer matrix, different types of polymer nanocomposite morphology are observed. In nanoparticle-nanocomposites the degree of dispersion and distribution of particles in a polymer matrix is crucial on its morphology. Homogeneous dispersion and distribution of filler particles in polymer matrix is very important for improvement of mechanical properties of polymer matrix nanocomposites (Hedayati et al., 2011). Figure 2.7 illustrate a schematic representation of the degree of dispersion and distribution of nanoparticles in a polymer matrix.

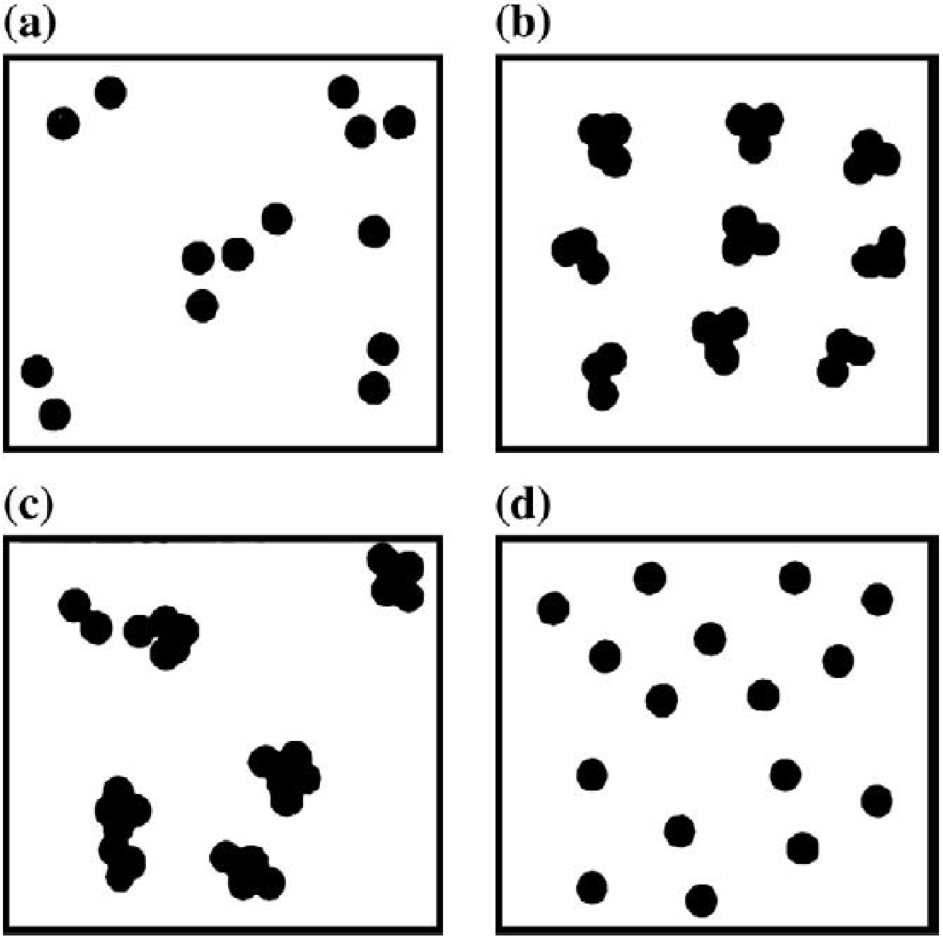


Figure 2.7: Schematic representation of the degree of dispersion and distribution of nanoparticles in a polymer matrix: (a) good dispersion, poor distribution, (b) poor dispersion, good distribution, (c) poor dispersion, poor distribution, (d) good dispersion, good distribution (Hedayati et al., 2011)

While in nanolayers, three different types of polymer nanocomposite morphology are observed. These are: intercalated, exfoliated and phase separated. In intercalated nanocomposites polymer molecules penetrate into the galleries of clay and the interlayer spacing is increased, while clay layers form separate phases in phase separated structures. Exfoliated nanocomposites are obtained when the clay layers are completely delaminated by the polymer matrix and homogenously dispersed in the polymer matrix. Figure 2.8 illustrate the different types of nanocomposites morphology arising from the interaction of layered silicates, and polymers. Due to the homogenous distribution of the layers, exfoliated nanocomposites exhibit superior properties compared to intercalated and phase separated ones (Becker et al., 2002). Moreover, partially intercalated and partially exfoliated nanocomposite morphology also can be observed. In this commonly occurring case, the exfoliated layers and intercalated clusters are randomly distributed in the matrix.

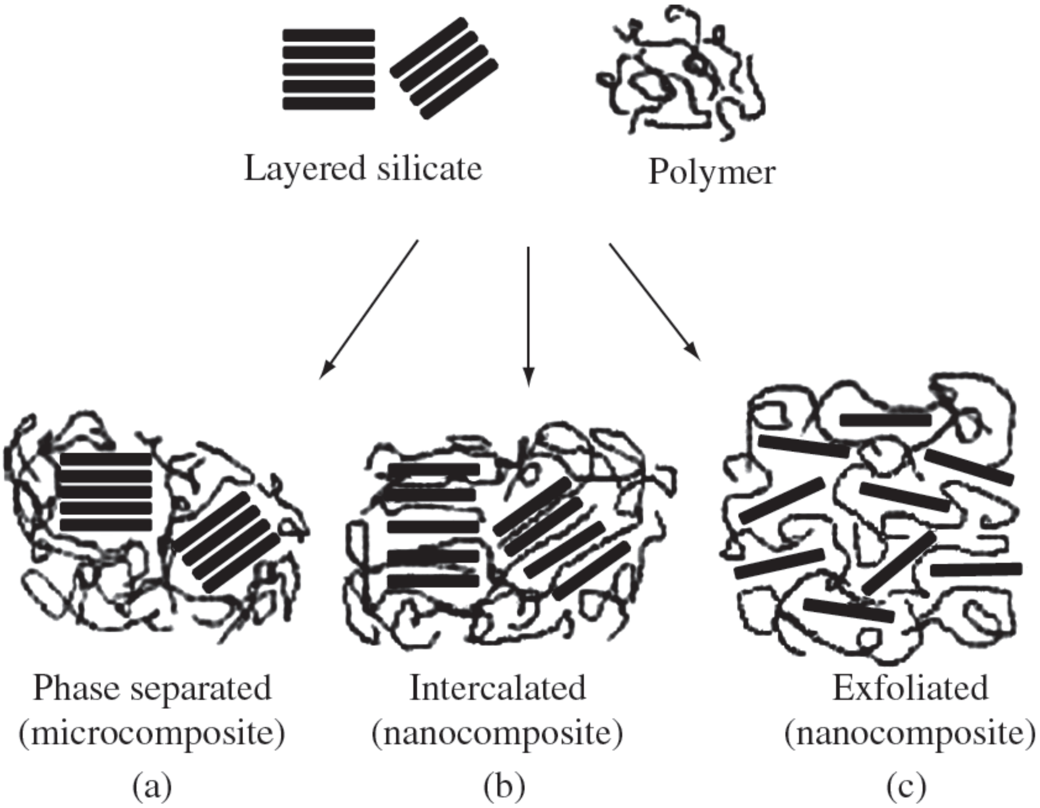


Figure 2.8: Different types of nanocomposites morphology arising from the interaction of layered silicates, polymers: (a) Phase-separated microcomposite; (b) Intercalated nanocomposite, and (c) Exfoliated nanocomposite (Alexandre and Dubois, 2000)

2.3.2 Structure and properties of Nanomaterial

Nanomaterials are classified into three categories depending on the dimensions of the dispersed particles (Alexandre and Dubois, 2000; ISO/TS27687, 2008; Kumar et al., 2009). Figures 2.9 illustrate various types of nanoscale materials. The categories are;

- Nanoparticles: When the three dimensions of particulates are in the order of nanometers, they are called isodimensional nanoparticles. They include spherical nanoparticles, nanogranules and nanocrystals.
- Nanotubes: When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, they are generally called nanotubes or

nanofibers/whiskers/nanorods and they include CNTs, silica and titanium nanotubes, cellulose whiskers, etc.

– Nanolayers: The particulates which are characterized by only one dimension in nanometer scale are nanolayers/nanosheets/nanoplate. In this case the filler is present in the form of sheets of one to a few nanometer thick to hundreds to thousands nanometers long, such as clays (layered silicates), layered double hydroxides, etc.

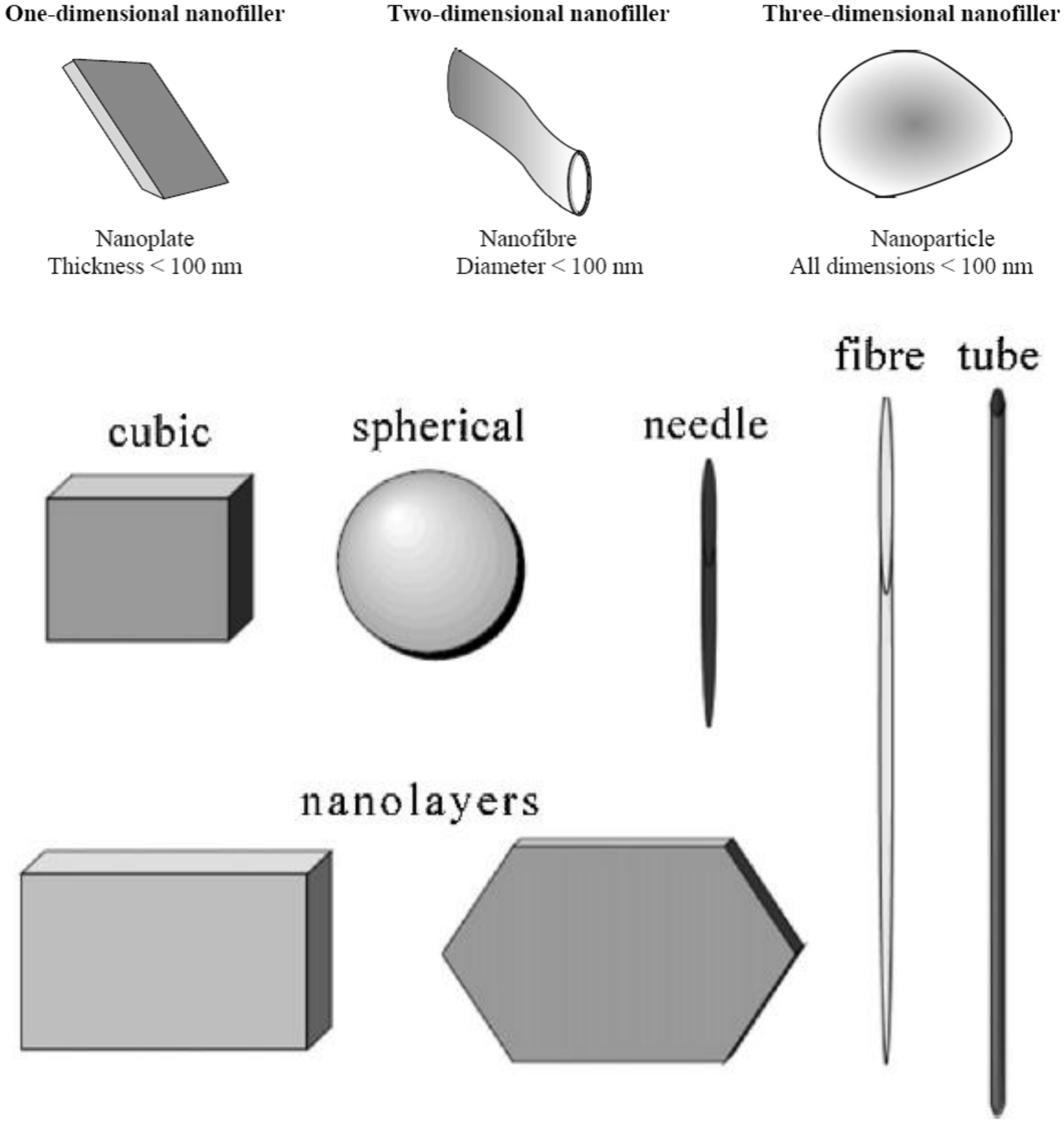


Figure 2.9: Various types of nanoscale materials (Damien et al., 2011),

2.3.2.1 Nanoclays

Nanoplate fillers can be natural or synthetic clays, as well as phosphates of transition metals. The most widely used reinforcement is clay due to its natural abundance and its very high form factor. Clay-based nanocomposites generate an overall improvement in physical performances. The most widely used ones are the phyllosilicates (smectites). They have a shell-shaped crystalline structure with nanometric thickness. Clays are classified according to their crystalline structures and also to the quantity and position of the ions within the elementary mesh. The elementary or primitive mesh is the simplest atomic geometric pattern, which is enough for duplicating the crystalline network, by repeating itself indefinitely in the three directions. (Damien et al., 2011)

2.3.2.2 Nano-oxides

Titanium dioxide: Rutile is commonly used in polymers as a white pigment, as particles from 200 to 300 nm. The nanoparticle of titanium dioxide is not Rutile, but Anastase, and both are tetragonal crystal forms of titaniumdioxide. Anastase is commonly used as spherical particles with diameter around 20 nm. This nanoparticle has photocatalytic properties. Anatase can be converted by hydrothermal synthesis into titanium nanotubes (Mogilevsky et al., 2008). These nanotubes have an outer diameter of 10 to 20 nm, an inner diameter of 5 to 8 nm and a length of 1 μm.

Nanoalumina: Alumina particles are used as fillers in a wide range of size, from 20 nm to micrometric sizes. They are made of spherical crystal particles of Al_2O_3. Nanoparticles of alumina are frequently used as inert fillers in polymers, but highlight catalytic properties in some conditions. (Damien et al., 2011)

Nano antimony-Tin oxide: The raw formula of this nanoparticle is Sb_2O_5/SnO_2. This is a tetragonal crystal particle of a diameter of around 15 nm, commonly used as flame retardant. (Damien et al., 2011)

Nanosilica: Nanosilica corresponds to a large family of nanoparticles from various origins. The most commonly used is a natural one, called diatomite. This filler comes from the skeleton of a unicellular alguea (the diatomea) forming sedimentary layers. It is constituted fromultrafine particles of 750 nm. Two families of widely used synthetic nanosilicas are pyrogenic silica, forming particles from 5 to 100 nm, and silica fume, forming particles of about 100 nm. Precipitate silica historically used in polymers is not a nanoparticle, as its diameter is between 1 and 10 μm when micronized. (Damien et al., 2011)

2.3.2.3 Carbon Nanotubes

CNTs were discovered by Oberlin A., Endo M. and Koyama T. (Oberlin et al., 1976; Endo et al., 1976), without application, and then rediscovered by (Iijima, 1991). The fibre could present a nanometric diameter and length of some orders of magnitude in comparison with its diameter. In general, three kinds of carbon nanotubes are considered:

- Single-wall carbon nanotubes (SWCNT). They present a diameter between 1 and 2 nm;
- Double-wall carbon nanotubes (DWCNT). Diameter is between 2 and 4 *nm*
- Multi-wall carbon nanotubes (MWCNT). They present a diameter between 4 and 150 *nm*.

These nanotubes present a theoretical range of properties incredible (Young modulus up to 1 *TPa*, heat conductivity of 3000 $W.m^{-1}.K^{-1}$, electric conductivity of

107 $S.m^{-1}$, etc.), but considering perfect nanotubes individually makes no sense. They nevertheless provide a wide range of new properties when used in nanocomposites, depending on their purity and dispersion in the matrix. CNTs are produced by two possible ways: a catalytic chemical vapour decomposition process at medium temperatures (600-1000°C) and an electric discharge (arc) process under helium at high temperature (3000 to 4000°C). Both processes produce a mix between SWCNT, DWCNT and MWCNT, with surface defaults (e.g. some pentagonal cycles in place of aromatic rings), and present important catalytic residues. Another important parameter is the chirality of the CNTs (i.e. the direction and deviation in the "roll" process of CNTs), only when they are studied individually, as the processes generate a mix of all possible chiralities. (Damien et al., 2011)

2.3.2.4 Other Nanofillers

Metallic nanoparticles: Most common metallic nanoparticles are nanosilver, nanozinc and nanogold fillers. These particles have a catalytic behaviour, which leads to antibacterial properties at surface. Their electrical and magnetic properties are also used for nanocomposites. (Damien et al., 2011)

Silsesquioxanes: Silsesquioxanes are big synthetic cage macromolecules used as nanofillers in polymers. Their raw formula has been found to be $R - SiO_{3/2}$ with R typically being alkyl or organo-functional groups. The high three-dimensional symmetry and nanometer size make silsesquioxanes building blocks for nanocomposites. The diversity of possible functional groups along with their controlled orientation in $3 - D$ space allows for highly tailored nanometer-by-nanometer construction in all three dimensions.. The most common Silsesquioxanes found are polyhedral oligosilsesquioxanes (POSS), octasilsesquioxanes of the

$[ROSiO_{1.5}]_8$ type and its polymeric derivatives, and $[R - phenylSiO_{1.5}]_8$ type and its polymeric derivatives. They are used to make structured $3-D$ nanocomposites for thin films, monoliths, and fibre reinforced composites. At present time, their expensive price limits their usage in polymers. (Damien et al., 2011)

Boehmite: Boehmite is a mineral aluminium hydroxide orthorhombic dipyramidal cristal used as a nanofiller in nanocomposites. It could be obtained naturally or from chemical synthesis from saturated solutions. Its raw formula is $\gamma-$AlO(OH). (Damien et al., 2011)

2.3.3 Fabrication Method

Several methods have been developed to produce polymer nanocomposites according to the starting materials and processing techniques. However three main methods have been applied widely. These are: in situ polymerization, solution induced intercalation and melt processing methods. Each polymer system requires a special set of processing conditions to be formed, based on the processing efficiency and desired product properties as seen in Table 2.2.

Table.2.2: Processing techniques for nanomaterial/polymer nanocomposites (Zhang et al., 2004)

Processing	Drive Force	Advantages	Disadvantages	Examples
In-situ polymerization	Interaction strength between monomer and nanomaterial surface: enthalpy evolvement during the interlayer polymerization.	Suitable for low or non-soluble polymers: a conventional process for thermoset nanocomposites.	Nanomaterial exfoliation depends on the extent of it swelling and diffusion rate of monomers in the gallery: oligomer may be formed upon incompletely polymerization.	Nylon 6, epoxy, polyurethane, polystyrene, polyethylene oxide, unsaturated polyesters, polyethylene terephthalate.
Solution approach	Entropy gained by desorption of solvent, which compensates for the decrease in conformational entropy of intercalated polymers.	Prefer to watersoluble polymers.	Compatible solvent system is not always available; use of large quantities of solvent; co-intercalation may occur for solvent and polymer	Epoxy, polyimide, polyethylene, polymethylmethacrylate
Melt Intercalation	Enthalpic contribution of the polymer-nanomaterial interactions.	Environmental benign approach -no solvent is required.	Slow penetration of polymer within the confined gallery.	Nylon 6, polystyrene, polyethylene terephthalate

2.3.3.1 In-Situ Polymerization Method

The in-situ polymerization approach was the first strategy used to synthesize polymer-nanomaterial nanocomposites and it is a convenient method for layered silicate/thermoset nanocomposites. This method is capable of producing well-exfoliated nanocomposites and has been applied to a wide range of polymer systems (Fengge, 2004). Example; once the organosilicate has been swollen in the liquid monomer or a monomer solution, the curing agent is added to the system, as shown in Figure 2.10. Upon polymerization, the silicate nanolayers are forced apart and no