UNIVERSITY OF TURKISH AERNAUTICAL ASSOCIATION
INSTITUTE OF SCIENCE AND TECHNOLOGY

STRUCTURAL AND MECHANICAL CHARACTERIZATION OF HYBRID NANOCOMPOSITE MATERIAL

MASTER THESIS
HALA M. KADHIM
ID: 1406080022

Institute of Science and Technology
Mechanical and Aeronautical Engineering Department
Master Thesis Program

MAY 2017

UNIVERSITY OF TURKISH AERNAUTICAL ASSOCIATION
INSTITUTE OF SINENCE AND TECHNLOGY

STRUCTURAL AND MECHANICAL CHARACTERIZATION OF HYBRID NANOCOMPOSITE MATERIAL

MASTER THESIS
HALA M. KADHIM
Ref. NO: 10148971

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF SCIENCE IN MECHANICAL AND AERONAUTICAL ENGINEERING

Supervisor: Assist. Prof. Dr. Murat Demiral

بسم الله الرحمن الرحيم

(ربي اشرح لي صدري۞ويسر لي امري۞واحلل عقدة من لساني۞يفقهوا قولي)

سورة طه (صدق الله العظيم)

Türk Hava Kurumu Üniversitesi Fen Bilimleri Enstitüsü'nün 1406080022 numaralı Yüksek Lisans öğrencisi "**HALA M. KADHIM**" ilgili yönetmeliklerin belirlediği gerekli tüm şartları yerine getirdikten sonra hazırladığı "STRUCTURAL AND MECHANICAL CHARACTERIZATION OF HYBRID NANOCOMPOSITE MATERIAL" başlıklı tezini, aşağıda imzaları bulunan jüri önünde başarı ile sunmuştur.

Tez Danışmanı **: Doç. Dr. Murat Demiral**
Cankaya Üniversitesi …………………..

Jüri Üyeleri **: Yrd. Doç. Dr. Baris Sabuncuoglu**
Türk Hava Kurumu Üniversitesi …………………..

: Yrd. Doç. Dr. Durmuş Sinan Körpe
Türk Hava Kurumu Üniversitesi ………………….

Tez Savunma Tarihi: 29.5.2017

STATEMENT OF NON-PLAGIARISM PAGE

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

HALA M. KADHIM
29.5.2017

Acknowledgment

Before anything, thanks to God Almighty for the blessing and giving me the health and strength to complete my thesis successfully. Hopefully, God will always help and blessing me in future.

I would like to express my grateful and my sincere appreciation to my kind supervisor Prof. Dr. Murat DEMIRAL and Prof. Dr. Adel K. Mahmoud for the continuous support and valuable guidance in the preparation of this study. Without them continued support and encouragement, this thesis would not have been the same as presented here.

I wish to express my sincere thanks and love to my parents specially my mother, I hope to God has mercy on here. And to my sisters specially (Zainab) for supporting me throughout my academic career.

I place on record, my sincere gratitude to my husband who support and help me in every step of life.

I also place record, to the staff of the University of Turkish Aeronautical Association, Institute of Science and Technology and mechanical Department.

I also extend my thanks and appreciation to the University of Technology –Material Engineering Department for help me opportunity to do all experimental work, so my University (Diyala)-Mechanical Engineering Department.

May 2017 HALA M. KADHIM

Contents

List of tables

List of Figures

Abstract

STRUCTURAL AND MECHANICAL CHARACTERIZATION OF HYBRID NANOCOMPOSITE MATERIAL

Hala M. Kadhim
Master. Department of Aeronautics and Mechanical Engineering
Supervisor: Assist. Prof. Dr. Murat Demiral
May 2017, 83 Pages

Abstract

Hybrid nanocomposite materials do not represent only a creative alternative to design new materials and compounds for academic research, but their improved or unusual features allow the development of innovative industrial applications. Nowadays, most of the hybrid materials that have already entered the market are synthesized and processed by using conventional soft chemistry based routes developed in the eighties. Looking to the future, there is no doubt that these new generations of hybrid materials, born from the very fruitful activities in this research field, will open a land of promising applications in many areas: optics, electronics, ionics, mechanics, energy, environment, biology, medicine for example as membranes and separation devices, functional smart coatings, fuel and solar cells, catalysts, sensors, ……..etc.

In this work synthesized new hybrid nanocomposite materials by using mechanical stirring method through combination of different types of material; epoxy based matrix and nanofiller (TiO_2& SiO_2 nanoparticles) as a reinforcement material. Studied the effect of TiO_2& SiO_2 nanoparticles percentage 2-8 wt% and 2-6 wt% respectively added to epoxy based matrix on the morphology, bonding type and mechanical properties using atomic force microscope (AFM), Fourier transforms infrared spectroscopy (FTIR), tensile test and micro hardness test. The results show tensile strength of Nano composite material increased gradually with increasing the weight percentage of TiO_2 nanoparticles from 2 wt% to 8 wt % TiO_2, while the best tensile strength was at 8 wt % TiO_2. The increase percentage of tensile strength was 270% higher than the neat epoxy matrix.

The micro hardness increase gradually with increase percentage of TiO_2 nanoparticles from 2wt% TiO_2 up to 8wt% TiO_2, the maximum value of micro hardness was at 8wt % TiO_2 , so the hardness of nanocomposite is around 86% higher than the neat epoxy matrix. The addition of SiO_2 nanoparticles to the nanocomposite material in order to synthesize new hybrid nanocomposite material resulted in decrease in tensile strength from 2wt % to 6wt % SiO_2, also, that the micro hardness value decrease from 2wt % to 6wt % SiO_2 . FTIR confirmed the formation of a charge transfer complex between the TiO_2 and SiO_2 nanoparticles 900→450 cm-1 and 952 cm-1 respectively. Atomic Force Microscope images have been showed that the SiO_2 – TiO_2 particles size was about 20 – 50 nm, this indicates that TiO_2 – SiO_2 hybrid nanocomposite particles are homogenously and well disperse in the epoxy matrix.

Özet

HİBRİT NANOKOMPOZİT MALZEMENİN YAPISAL VE MEKANİK KARAKTERİZASYONU

Hala M. Kadhim
Yüksek Lisans Tezi, Makine Mühendisliği Anabilim Dalı
Danışman: Doç. Dr. Murat Demiral
Mayıs 2017, 83 Sayfa

Özet

Hibrit nanokompozit malzemeler, yalnızca akademik araştırmalar için yeni malzemeler ve bileşikler tasarlamak amacıyla yaratıcı bir alternatif olmayıp aynı zamanda geliştirilmiş veya alışılmadık özellikleri, yenilikçi endüstriyel uygulamaların geliştirilmesini sağlamaktadır. Günümüzde, piyasaya henüz giren hibrit malzemeler, seksenlerde geliştirilen geleneksel yumuşak kimya tabanlı yönlendirmeler kullanılarak sentezlenmekte ve işlenmektedir. Geleceğe baktığımızda, bu araştırma alanında verimli faaliyetler sonucu ortaya çıkan bu yeni nesil hibrit malzemelerin, örneğin membranlar ve ayırma cihazları, fonksiyonel akıllı kaplamalar, yakıt ve güneş pilleri, katalizörler, sensörler, vb. gibi optik, elektronik, iyon, mekanik, enerji, çevre biyoloji, tıp gibi pek çok alanda hedef uygulamalar açacağı kuşkusuzdur.

Bu çalışmada, mekanik karıştırma metodu kullanılarak takviye malzemesi olarak Epoksi esaslı bir matris ve nano-dolgu (TiO_2 ve $Si0_2$ nanopartikülleri) gibi farklı türdeki malzemelerin kombinasyonu ile yeni hibrit nanokompozit malzemeler sentezlenmiştir. Ayrıca, atomik kuvvet mikroskopu (AFM), Fourier transform infrared spektroskopi (FTIR), çekme testi ve mikro sertlik testi kullanılarak, epoksi esaslı matrise % ağırlık olarak sırasıyla % 2-8 ila % 2-6 oranında eklenen TiO_2 ve $Si0_2$ nanopartiküllerinin morfoloji, bağlanma tipi ve mekanik özellikler üzerindeki etkileri araştırılmıştır. Sonuçlar, Nanokompozit malzemenin çekme mukavemetinin, TiO_2'nin ağırlıkça %2'den % 8'e çıkarılmasıyla TiO_2 nanopartiküllerinin arttığı ve en iyi çekme mukavemetinin ağırlıkça % 8 $Ti0_2$'de elde edildiğini göstermektedir. Çekme mukavemetinin artış yüzdesi, saf epoksi matrisinden % 270 daha yüksek olmuştur.

TiO_2’nin ağırlıkça %2'den % 8'e çıkarılmasıyla artan TiO_2 nanopartiküllerinin yüzdesi ile kademeli olarak mikro sertlik de artarken, mikro sertliğin maksimum değeri % 8 TiO_2 olmuş dolayısıyla da nanokompozitin sertliği saf epoksi matrisinden % 86 daha yüksek olmuştur. Yeni hibrit nanokompozit malzemeyi sentezlemek için nanokompozit malzemeye SiO_2 nanopartiküllerinin ilave edilmesi, SiO_2’nin ağırlıkça %2 ’den % 6'e kadar çıkarılmasıyla çekme mukavemetinde azalma ve ayrıca SiO_2’nin ağırlıkça %2 ’den % 6'e kadar çıkarılmasıyla mikro sertlik değerinde de azalma ile sonuçlanmıştır. FTIR, TiO_2 ve $Si0_2$ nanopartikülleri arasında bir yük transfer kompleksi oluşumunun sırasıyla 900 → 450 cm-1 ve 952 cm-1 şeklinde olduğunu doğrulamıştır. Atomik Kuvvet Mikroskop görüntüleri, TiO_2 - $Si0_2$ partikül boyutunun yaklaşık 20-50 nm olduğunu göstermiş olup bu da TiO_2 - $Si0_2$ hibrit nanokompozit partiküllerinin, epoksi matriste homojen ve iyi bir şekilde dağılmış olduğunu göstermektedir.

List of Symbols and Abbreviation

Symbols	**Meaning**
SEM	Scanning Electron Microscopy
CNF	Carbon Nano Fiber
CFRP	Carbon Fiber Reinforcement Polymer
CFRENCS	Carbon Fiber Reinforcement Epoxy Clay Nano composites
GO	Grapheme Oxide
MMC	Metal Matrix Composites
PMC	Polymer Matrix Composites
CMC	Ceramic Matrix Composites
PNC$_S$	Polymer Nano composites
PV	Photovoltaic
IEC	Ion-Exchange Capacity

Abbreviation

TiO_2	Nano titanium oxide
SiO_2	Nano silica oxide
ZrO_2	Nano zirconium oxide
σult.	Ultimate tensile strength
FTIR	Fourier Transform Infrared Spectroscopy

Chapter One

Introduction, Objectives, Scope and Significance of Study

1.1 Introduction

Composites are one of the most widely used materials because of their adaptability to different situations and the relative ease of combination with other materials to serve specific purposes and exhibit desirable properties. They provide ample scope and receptiveness to design changes, materials and processes. The strength-weight ratios of composites higher than other materials. Their stiffness and cost effectiveness offered, apart from easy availability of raw materials, make them the obvious choice for many applications. In composites, materials are combined in such a way as to enable us to make better use of their virtues while minimizing to some extent the effects of their deficiencies. This process of optimization can release a designer from the constraints associated with the selection and manufacture of conventional materials [1].

A composite material structure is made up of a combination of two or more constituents that combined level macroscopic and not soluble in each other.

A constituent called phase shows and one where it has been enshrined called matrix. Shows phase materials may be in the form of fibers, particles or flakes. The matrix phase materials were continuous in General. Composite materials, often shortened to composites or called the composition of materials, engineering or naturally occurring materials examples of composite system includes steel reinforced concrete and reinforced with fiber graphite epoxy, etc. Examples include wood, where the matrix reinforced with fiber lignin and cellulose bones where bone-salt plates made of calcium and phosphate ions strengthen collagen soft. Phase devoted to provide strength and stiffness. In most cases, the strengthening of things is harder, stronger, and stiffer from the matrix. The fiber reinforcement is normally or a particle. Particulate composites have dimensions that are about the same in all directions. They may be spherical, platelets, or any other fixed or not fixed geometry. Particle composites tend to be weaker and less intense than continuous fiber composites, but they are usually much less expensive. Particle reinforced composites typically contain reinforcement declined because processing difficulties and brittleness.

The fibers have a greater length compared to the diameter. The ratio of length to diameter is known as the aspect ratio and very different. Continuous fiber has a long aspect ratio, while continuous fibers have the aspect ratio of a short period. Continuous-
fiber composites usually have preferred orientation, while continuous fibers generally have a random orientation. examples of continuous assistance including unidirectional, woven cloth, and helical winding, while examples of continuous assistance are chopped fiber mat and random. Continuous phase was the matrix, i.e. the polymer, metal, or ceramic. Matrix (continuous Phase) to carry out several important functions, including maintaining fiber in the correct orientation and Spacing and protect them from abrasion and the environment. The type and quantity of reinforcement in determining the properties of the end [2].

Discovery of novel materials, processes and phenomena at the Nano scale, as well as the development of experimental techniques and theoretical research to provide new opportunities for the development of innovative nanostructured materials. Nano-composites term used in this report was taken to mean the material based on the polymer containing particles (equated or grown), or fibers with at least one dimension in the range 1-200 Nanometer. Particles or fibers can be inorganic (metals or ceramics, including external) or organic (e.g. polymers). This definition does not include metal-matrix Nano-composites, and so is the ceramic-matrix Nano-composites [3].

Definition of Nano-composite materials have been expanded significantly to cover a wide range of systems such as three-dimensional dimension, two-dimensional, and amorphous materials, made of components that are clearly different and mixed at Nano-meter scale. Nano-composite materials which explode in the 80 's with the development of chemical processes organic soft not only represents a creative alternative to design new materials and Academic Research, but also the characteristics they improved or are unfamiliar with allowing innovative industry application development [4].

Nanostructured materials are understood to be intermediate between classical and molecular- scale entities micro-sized. The introduction of Nanoparticles into polymer matrix ensures a significant increase with the level of the burden of the very property. Additive traditional micro-particle filler concentration requires a lot higher to achieve the same result. There are three basic reasons to see changes in the properties of the materials when they are reduced to the level of dimension Nano-meter [5].

1. Quantum confinement, where the energy levels of the atom, electron, or nucleus change as the size of the confined region changes; the well- known particle in a box situation. Since the quantized energy levels (En) vary inversely with the size of the box (L), small changes in L when that size is small amount to very large changes in the energy levels. Small changes in L when L is large do not result in large shifts in the energy levels. Therefore any property which depends on the value of the energy level, or the spacing between energy levels, will likely change when you have a material structure which will confine those particles, like electrons and atoms [6].

2. High interface area, where the number of atoms at an interface becomes very large. For a polycrystalline material, when the diameter of the crystals (e. g., grains) is on the order of microns, the fraction of atoms at the interface is only on the order of a half percent. As the dimension of the grain is reduced, the fraction of atoms at the interface increases quickly. Consequently, at large grain sizes, the properties of the material will be closely related to the properties of the atoms interior to the grains. Conversely, at small grain diameters, the material properties will be related to the properties of the interface atoms [7].

3. Closeness of the material lengths to the critical length scale of the property. Every property has a critical length scale associated with that property (e. g., the mean free path in electrical and thermal conductivity, diffusion length in atomic transport, wavelength in scattering behavior, penetration depth in absorption, and half-life in radioactive decay processes), and material behavior will typically change when a material length scale becomes comparable with that property length scale [8].

It is related to emphasize the differences and similarities between convectional composites (carbon-fiber and glass fiber reinforced polymer), Nano-composites, and conventional polymers containing fillers.

Dimensions of carbon fibers and conventional glass are in range of micro-meters, which is larger than nanotubes/fibers described below. While the relevant dimensions in terms of the fiber manufacturing process, what is more relevant is the dramatic improvement in mechanical properties and physical in carbon nanotubes and Nano-fibers related but much cheaper Many polymers today compounded with fillers to modify their properties. This is usually done to improve mechanical properties such as stiffness, or improve environmental stability against ultraviolet deterioration. In addition, various other additives can be used to modify the performance (color, transparency, magnetic properties, and others) is a polymer. Some additional material particles (aluminum compounds) are added to improve fire resistance. In most, if not all cases this supplement is from conventional particle sizes, usually in the range of 10 to 100 micrometer. Often quite large number of additives are required to obtain the desired property, resulting in an increase in density (the density of most of the additives have a significantly larger than the host polymer, and a reduction in the flexibility and fracture is a polymer [9].

There are side effects that disadvantage usually use conventional additives, especially the effects on the mechanical properties. While the elastic modulus can be increased, is a fracture and tensile strength/bend affected. One main advantage of the use of additives Nanoparticles is that mechanical properties are not affected, and that in fact tensile strength usually have been improved, often. Supplementary benefits in addition of Nanoparticles are that they can be combined with conventional carbon-reinforced glass fiber and conventional process Technology (resin transfer moulding, injection moldings, etc.) can be used. This is not possible with conventional (micrometer-size) filler [10].

1.2 Objectives of the Study

The important objectives of the present work are:-

1. Synthesize new hybrid epoxy nanocomposite material using TiO_2, SiO_2 and ZrO_2 Nano fillers.
2. Study the effect of TiO_2 ,SiO_2 and ZrO_2 nanoparticles additives on the mechanical properties of hybrid nanocomposite material.
3. Study the characterization of the tensile strength, hardness, impact strength and morphology of nanocomposite and hybrid nanocomposite material.
4. Investigate on the bonding type between reinforcement phase and epoxy based matrix.
5. Optimize fabrication process conditions by controlling of nanosized second phase dispersion in order to obtain best characterization and mechanical properties of nanocomposite and hybrid nanocomposite material.

1.3 Scope of the Study

In this work will study the morphological and mechanical characterization (tensile strength, hardness, Impact strength test, FTIR, and AFM) of nanocomposite (epoxy\$TiO_2$ and SiO_2) and hybrid nanocomposite material(epoxy\$SiO_2$-$ZrO_2$-$TiO_2$). by using the production of hybrid Nano composite material by mechanical stirring method. Note that those materials with industrial and engineering applications. The most important which is used in armor, vest coaster, vehicles, aerospace industry and biological application. It is also characterized by lightweight and high strength. This is engineering designs modern requirements.

1.4 Significance of the Study

Nanocomposites have gained much interest recently. Significant efforts are underway to control the nanostructures via innovative synthetic approaches by mechanical stirring method. The properties of Nano composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics and production new hybrid nanocomposite. By optimized fabrication process and controlled nanosized second phase dispersion, thermal stability and mechanical properties such as adhesion strength, flexural strength, toughness & hardness can be enhanced which can result into improved Nano dispersion some nanocomposite materials could be 1000 times tougher than the bulk component. In the present time hybrid nanocomposite materials is a fast growing area of scientific research.

Chapter Two
Theoretical and Basic Concepts

2.1 Introduction

There is a growing interest in the development of Nano composites consisting of organic polymers and titania (TiO_2) or amorphous silica (SiO_2) and nanoparticles (particles < 100 nm). This is based on positively perceived characteristics of these Nano composites. Such characteristics include mechanical performance, electric behavior, thermal properties, biodegradability, optical properties, bactericidal effects, magnetic characteristics and transport, permeation and separation properties [11]. Several authors have stressed the safety and environmental friendliness of Nano composites consisting of organic polymers and TiO_2 or amorphous SiO_2 nanoparticles. [12] called emulsion wall paint with amorphous SiO_2 nanoparticles: 'environmentally safe'. [13] stressed the 'non-toxic' nature of TiO_2 nanoparticles [14,15] characterized degradable polymer/TiO_2 nanoparticle Nano composite films as 'environment-friendly' and 'eco-friendly', respectively. [16] view titanium dioxide 'as an environmentally friendly additive' and nanocomposites of siloxane copolymers and nano-TiO_2 as 'environmentally safe'. [17] state that TiO_2 nanoparticles are 'non-toxic' and those nanoTiO_2/ethylene-vinyl alcohol copolymer composites are 'environmentally friendly'.During the lifecycle, nanoparticles may be released. Such release may be associated with the production, distribution and application of nanoparticles that are to be included in Nano composites. After Nano composite synthesis, amorphous SiO_2 and TiO_2 nanoparticles do not necessarily remain fixed in Nano composites. It has been pointed out that if TiO_2 nanoparticles are used in Nano composites with organic polymers, there can be a substantial increase in degradability under solar or UV irradiation [18], as compared with neat polymers Indeed.

[14,15,17] designed polymer/TiO_2 Nano composites for rapid UV degradability. Thermal degradation may also be enhanced by the incorporation of nanoparticles. Degradation might further the release of nanoparticles. When stability is important to Nano composite design, nanoparticles may still be released. [19] found a substantial release of TiO_2 from synthetic polymers coated with TiO_2 nanoparticles.

[20] provide evidence that TiO_2 nanoparticles used in polymeric wall paint are detached from new and aged facade paints by natural weathering. Tribological studies on SiO_2/acrylate Nano composites show that friction leads to the gradual loss of SiO_2 nanoparticles. In the case that SiO_2 nanoparticles are applied in tires, one may expect them to be released by wear. It has been shown that many of the particles released by the interaction between tires and road pavement are <100 nm. Furthermore, nanoparticles may be released when Nano composites are subjected to wear, such as sanding in the case of coatings and abrasive use in the case of dental fillings. Thus, it would seem proper to consider the impact of TiO_2 nanoparticles and amorphous silica after release.

2.2 History of Composite Materials

The biggest advantage of modern composite materials is that they are light as well as strong. By choosing an appropriate combination of matrix and reinforcement material, a new material can be made that exactly meets the requirements of a particular application. Composites also provide design flexibility because many of them can be molded into complex shapes. The downside is often the cost. Although the resulting product is more efficient, the raw materials are often expensive. The earliest man-made composite materials were straw and mud combined to form bricks for building construction. Ancient brick- making was documented by Egyptian tomb paintings. Wattle and daub is one of the oldest man-made composite materials, at over 6000 years old [21, 22]. Concrete is also a composite material, and is used more than any other man-made material in the world. As of 2006, about 7.5 billion cubic meters of concrete are made each year, more than one cubic meter for every person on Earth [23].

2.2.1 Natural Composites

Natural composites exist in both animals and plants. Wood is a composite, it is made from long cellulose fibers (a polymer) held together by a much weaker substance called lignin. Cellulose is also found in cotton, but without the lignin to bind it together it is much weaker. The two weak substances “lignin and cellulose” together form a much stronger one. The bone in your body is also a composite. It is made from a hard but brittle material called hydroxyapatite (which is mainly calcium phosphate) and a soft and flexible material called collagen (which is a protein). Collagen is also found in hair and finger nails. On its own it would not be much use in the skeleton but it can combine with hydroxyapatite to give bone the properties that are needed to support the body [24].

2.2.2 Early Composites

People have been making composites for many thousands of years. One early example is mud bricks. Mud can be dried out into a brick shape to give a building material. It is strong if you try to squash it (it has good compressive strength) but it breaks quite easily if you try to bend it (it has poor tensile strength). Straw seems very strong if you try to stretch it, but you can crumple it up easily. By mixing mud and straw together it is possible to make bricks that are resistant to both squeezing and tearing and make excellent building blocks. Another ancient composite is concrete. Concrete is a mix of aggregate (small stones or gravel), cement and sand. It has good compressive strength (it resists squashing). In more recent times it has been found that adding metal rods or wires to the concrete can increase its tensile (bending) strength. Concrete containing such rods or wires is called reinforced concrete [25].

2.3 Making Composites

Most composites are made of just two materials. One is the matrix or binder. It surrounds and binds together fibers or fragments of the other material, which is called the reinforcement [26].

2.4 Modern Examples

The first modern composite material was fiberglass. It is still widely used today for boat hulls, sports equipment, building panels and many car bodies. The matrix is a plastic and the reinforcement is glass that has been made into fine threads and often woven into a sort of cloth. On its own the glass is very strong but brittle and it will break if bent sharply. The plastic matrix holds the glass fibers together and also protects them from damage by sharing out the forces acting on them. Some advanced composites are now made using carbon fibers instead of glass. These materials are lighter and stronger than fiberglass but more expensive to produce. They are used in aircraft structures and expensive sports equipment such as golf clubs. Carbon nanotubes have also been used successfully to make new composites.

These are even lighter and stronger than composites made with ordinary carbon fibers but they are still extremely expensive.

They do, however, offer possibilities for making lighter cars and aircraft (which will use less fuel than the heavier vehicles we have now). The new Airbus A380, the world’s largest passenger airliner, makes use of modern composites in its design. More than 20 % of the A380 is made of composite materials, mainly plastic reinforced with carbon fibers. The design is the first large-scale use of glass-fiber-reinforced aluminum, a new composite that is 25 % stronger than conventional airframe aluminum but 20 % lighter [27].

2.5 Nanocomposites Basic Ingredients

There has been a great deal of interest in polymer nanocomposites over the last few years. There are different types of commercially available nanoparticles that can be incorporated into the polymer matrix to form polymer nanocomposites. The correct selection of particle is essential to ensure effective penetration of the polymer or its precursor into the interlayer spacing of the reinforcement and result in the desired exfoliated or intercalated product. Polymer Nano composites consist of a polymeric material (e.g., thermoplastics, thermosets, or elastomers) with reinforcement of nanoparticles. Polymer could be incorporated either as the polymeric species itself or via the monomer, which is polymerized in situ to give the corresponding polymer-clay nanocomposite. Most commonly used nanoparticles include[28]:

- Montmorillonite organoclays (MMT)
- Carbon Nano fibers (CNFs)
- Polyhedral oligomeric silsesquioxane (POSS)
- Carbon nanotubes
- Nano silica (N-silica)
- Nano aluminum oxide (Al_2O_3)
- Nano titanium oxide (TiO_2)
- Nano clay

Thermosets and thermoplastics used as matrices for making nanocomposites include [28]:

- Nylons
- Polyolefin, e.g. polypropylene
- Polystyrene
- Ethylene-vinyl acetate (EVA) copolymer
- Epoxy resins
- Polyurethanes
- Polyimides
- Poly ethylene terephthalate (PET)

2.6 Components of Composite Materials

2.6.1 Matrix: The matrix is the binder material that supports, separates, and protects the fibers. The matrix binds the fibers together, holding them aligned in the important stressed directions. Loads applied to the composite are then transferred into the fibers, the principal load-bearing component, through the matrix, enabling the composite to withstand compression, flexural and shear forces as well as tensile loads. The ability of composites reinforced with short fibers to support loads of any kind is dependent on the presence of the matrix as the load-transfer medium, and the efficiency of this load transfer is directly related to the quality of the fiber/matrix bond. Although matrices by themselves generally have low mechanical properties compared to those of fibers, the matrix influences many mechanical properties of the composite. These properties include transverse modulus and strength, shear modulus and strength, compressive strength, inter laminar shear strength, thermal expansion coefficient, thermal resistance, and fatigue strength. A ductile matrix will provide a means of slowing down or stopping cracks that might have originated at broken fibers: conversely, a brittle matrix may depend upon the fibers to act as matrix crack stoppers. Through the quality of its “grip” on the fibers (the interfacial bond strength), the matrix can also be an important means of increasing the toughness of the composite. By comparison with the common reinforcing filaments most matrix materials are weak and flexible and their strengths and moduli are often neglected in calculating composite properties. But metals are structural materials in their own right and in MMCs their inherent shear stiffness and compressional rigidity are important in determining the behavior of the composite in shear and compression. The potential for reinforcing any given material will depend to some extent on its ability to carry out some or all of these matrix functions, but there are often other considerations [29].

2.6.1.1 Organic Matrix Composites: Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. It follows, therefore, that high temperature resins are extensively used in aeronautical applications. Two main kinds of polymers are thermosets and thermoplastics. Thermosets have qualities such as a well-bonded three-dimensional molecular structure after curing. They decompose instead of melting on hardening. Merely changing the basic composition of the resin is enough to alter the conditions suitably for curing and determine its other characteristics. They can be retained in a partially cured condition too over prolonged periods of time, rendering Thermosets very flexible. Thus, they are most suited as matrix bases for advanced conditions fiber reinforced composites. Thermosets find wide ranging applications in the chopped fiber composites form particularly when a premixed or molding compound with fibers of specific quality and aspect ratio happens to be starting material as in epoxy, polymer and phenolic polyamide resins [30].

2.6.1.2 Polymer Matrix Composites (PMC): Recently, many advances have been made in the design, manufacture and application of composite materials which can be very strong and stiff, yet very light in weight, that is strength to weight ratio and stiffness to weight ratio are several times greater than steel and aluminum. These composites also exhibit fatigue and toughness properties better than common engineering materials. The main drawbacks of PMCs include low operating temperatures, high coefficient of thermal, moisture expansion, and low elastic properties in certain directions. Applications of PMCs range from tennis racquets to the space shuttle. Polymer matrix composites are being increasingly used in industry because of their unique combination of mechanical, electrical, and thermal properties. Typically they have high specific strength and modulus, excellent fracture toughness and fatigue properties, and good corrosion, thermal and electrical resistance properties. This combination of properties, particularly their high strength stiffness to weight ratio, make them very attractive materials for transport applications where there is commercial advantage in minimizing vehicle weight. One such application is in the transport and handling of bulk solids. Two main kinds of polymers are thermosets and thermoplastics[31].

Aramid-based composites are thermosets made up of long fibers of synthetic carbon embedded in an aromatic polyamide matrix. The most common use for these composites is in Kevlar as show in figure[31], the trade name for an aramid fiber product used in body armor and protective gear. Aramid-based composites are also used in aerospace equipment because rather than melting, their carbon fibers grow shorter and fatter when exposed to intense heat. They're also extremely lightweight and flexible.

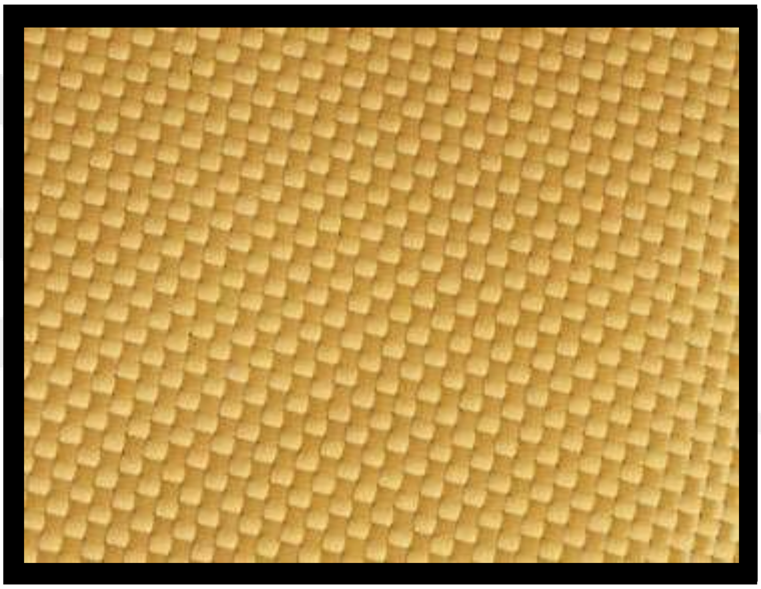


Fig. (2-1) Kevlar: aramid fiber product[31].

2.6.1.3 Metal Matrix Composites (MMC): Metal matrix composites, at present though generating a wide interest in research fraternity, are not as widely in use as their plastic counterparts. High strength, fracture toughness and stiffness are offered by metal matrices than those offered by their polymer counterparts. They can withstand elevated temperature in corrosive environment than polymer composites. Most metals and alloys could be used as matrices and they require reinforcement materials which need to be stable over a range of temperature and non-reactive too. However the guiding aspect for the choice depends essentially on the matrix material. Light metals form the matrix for temperature application and the reinforcements in addition to the aforementioned reasons are characterized by high moduli. Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase [32].

2.6.1.4 Ceramic Matrix Composites (CMC): Ceramics can be described as solid materials which exhibit very strong ionic bonding in general and in few cases covalent bonding. High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favorite for applications requiring a structural material that doesn‟t give way at temperatures above 1500ºC. Naturally, ceramic matrices are the obvious choice for high temperature applications. Ceramic Matrix Composites are composed of a ceramic matrix and imbedded fibers of other ceramic material (dispersed phase) [33].

2.6.2 Reinforcement: The strength, stiffness, and density of the composite material are very dependent on the reinforcing material. The ultimate tensile strength of a composite is a result of the synergy between the reinforcement and the matrix. The matrix forces load sharing among all the fibers, strengthening the material. The main types of reinforcements are continuous fibers, discontinuous (short fibers), whiskers, and particulates [34].

Continuous fibers are long strands of fibers having a small cross sectional area. The fibers are placed in bundles containing in between 1,000 to 12,000 fibers each depending on the parameters of the load the composite must carry. The bundles are then placed in the matrix in geometrical patterns. If aligned in a single direction, the resulting composite will have anisotropic properties. Anisotropic materials have different properties in different directions. When a load is applied in the direction of the fibers, the fibers become the principle load carrying constituent of the composite. Anisotropic composites are extremely strong in the fiber direction but are generally weak in a direction perpendicular to the fiber. This is analogous to bone, a natural composite. Sometimes one directional properties are not what is called for in the design. A composite may need to bend when it is twisted, or be able to withstand loads in two directions. Laminates, allow for such flexibility in design. Laminates are made by combining one directional composite which have fibers oriented at different angles. The properties of the laminate as a whole depend on the orientation and thickness of each layer. A second type of reinforcement is discontinuous (short) fibers, which are placed randomly into a matrix. The advantage of discontinuous fibers lies in the fact that the resulting composite tends to be more isotropic than continuous fibers and they are generally easier for industry to fabricate particularly for complex irregularly-shaped component geometries [35].

2.7 Nanocomposites: A nanocomposite is defined such that the size of the matrix or reinforcement falls within the nanoscale. The physical properties and performance of the nanocomposite will greatly differ from those of the component materials according to the type of matrix, nanocomposites can be classified into ceramic matrix nanocomposites, metal matrix nanocomposites, and polymer matrix nanocomposites [36].

These days' polymercomposites are undergoing extensive research because for many fields of the modern industry appreciable improvement of physiomechanical properties of polymeric materials are desirable. Nowadays, the most perspective decision of this problem is a modification polymer with nanostructure modifiers – creation of polymeric nanocomposites. Polymer nanocomposites (PNCs) are polymers (thermoplastics, thermo sets, elastomers) that have been reinforced with small quantities (less than 5% by weight) of nanosized particles. Molecular interaction between polymer and Nano fillers do not possess. Uniform dispersion of nanoparticles in polymer matrix produces ultra- large interfacial area per volume between the nanoparticle and the host polymer. This immense internal interfacial area and the nanoscopic dimension between nanoparticles fundamentally differentiate PNCs from traditional composites and filled plastics. Introduction to nanoparticles to polymer matrix ensure significant property improvements with very low loading levels. Traditional microparticles additives require much higher filler concentration to achieve similar results nanocomposites are found in nature, for example in the structure of the abalone shell and bone [37].

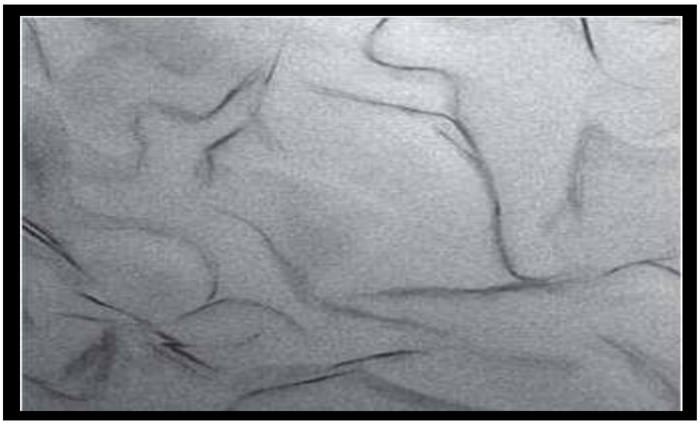


Fig (2-2) micrographs of a clay/epoxy Nano composite[37].

2.8 Non-Polymer Based Nanocomposites

Non- polymer based nanocomposite materials can be classified as follows:

2.8.1 Metal/Metal Nanocomposite: Bimetallic nanoparticles either in the form of alloy or core-shell structures or being investigated in some depth because of their improved catalytic properties and changes in the electronic/optical properties related to individual, separate metals. It is postulated their interesting Physico-Chemical properties, result from the combination of two kinds of metals and their fine structures [38].

2.8.2 Metal/Ceramic Nanocomposites: In these types of composites, the electric, magnetic, chemical, optical and mechanical properties of both phases are combined. Size reduction of the components to the Nano scale causes improvement of the above mentioned properties and leads to new application. The polymer precursors techniques offers an attractive rough to such composites proving a chemically inert and hard ceramic matrix[39].

2.8.3 Ceramic/Ceramic Nanocomposites: ceramic nanocomposites could solve the problem of fracture failures in artificial joint implants; these would extend patient’s mobility and eliminate the high cost of surgery. The use of zirconia-toughened alumina nanocomposite to form ceramic/ceramic implants with potential life spends of more than 30 years[40].

2.9 Polymer Based Nanocomposites

Polymer nanocomposites are composites with a polymer matrix and filler with at least one dimension less than 100 nm. The fillers can be (clay), high aspect ratio, nanotubes and lower aspect ratio or nanoparticles as show in figure (2-3) [41].

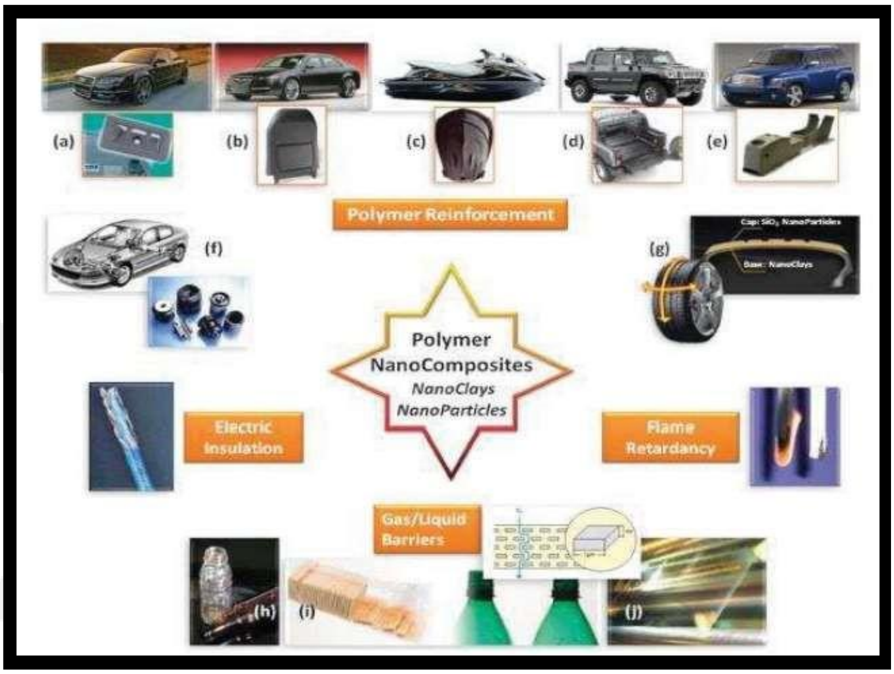


Fig. (2-3) Some commercial products based on polymer nanocomposites[41].

2.9.1 Polymer/ceramic Nanocomposite: Nano composites consist of single ceramic layers (1nm thick) homogeneously dispersed in a continuous matrix. the host ceramic layer tend to orient themselves parallel to each other due to dipole-dipole interaction. Natural Bone is a Nano composite-bone consisting of approximately 30% matrix (collagen) material and 70% Nano sized minerals (hydroxyapatite)[42].

2.9.2 Inorganic/ Organic polymer Nanocomposites: Metal polymer Nano composites attract attention because of unique properties of metal clusters which are dispersed in polymer matrix. the typical size of such metal cluster is approximately 1-10 nm. The properties of clusters and nanoparticles (band gap, spectral properties, the transport of electrons)are very different from those of bulk materials and from individual atom or molecules. The size and grains depends on mobility of the metal atoms on the polymer surface. For example, in the case of polymethylmethacrylite (PMMA) polymer the cluster size depends on the amount of the cross linking of the polymer, which obviously changes the mobility of the metal atoms[43].

2.9.3 Inorganic/Organic hybrid Nanocomposite: Hybrid inorganic/organic materials are not simply physical mixtures; they can be broadly defined as Nano composites with organic and inorganic components intimately mixed. Indeed, hybrids are either homogenous system derived from monomers and miscible organic/inorganic components, or heterogeneous systems (Nano composites) where at least one of the components has the scale of nanometer [44].

2.9.4 Polymer/ Layered silicate Nanocomposites: Polymer/Layered silicate (PLS) Nano composites materials are attracting considerable interest in polymer science research. In recent years the PLS Nano composites have attracted great interest both in industry and academia, because they often exhibits remarkable improvements in materials when compare with virgin polymer and conventional macro and macro composites. Hactorite and montmorillonite are among the most commonly used smectite-type- layered silicates for the preparation of the Nano composites [45].

2.9.5 Polymer/polymer Nanocomposites: Polymers are more than ever under pressure to be chip and offered property profiles. The gap between block co-polymer self-assembly and offer nanostructured plastic endowed with still unexplored combinations of properties is getting narrower. Mixtures of different polymers often phase separate,even when their monomer mixed homogenously[46].

2.9.6 Biocomposites: Metals and metal alloys are used in orthopedics, dentistry and other load bearing applications. Ceramics are used with emphasis on either their chemically inert nature or high bioactivity; all polymers are used for soft tissue replacements and used for many other non-structural application. Naturally occurring composites are within us all. Collagen is highly abundant and varies with more than 14 types discovered. All variations are formed from trope-collagen molecules, which are inelastic [47].

2.10 Application of Hybrid Materials

Commercial applications of technology preceded the formal recognition of this technology. Likewise, successful commercial inorganic–organic hybrids have been part of manufacturing technology since the 1950s [48].

2.10.1 Possible synergy between inorganic and organic components

For a long time the properties of inorganic materials (metals, ceramics, glasses, etc.) and organic compounds (polymers, etc.) shaped as bulks, fibers or coatings have been investigated with regard to their applications, promoting the evolution of civilizations. During the last fifty years with the help of new analysis techniques and spectroscopic methods the structure properties relationships of these materials became clearer and their general properties, tendencies and performances are well known. Some of these general properties are summarized in Table (2-1) [48]

Table(2-1) Comparison of properties of conventional organic and inorganic components [48]

Properties	Organics (polymers)	Inorganics (SiO2, TMO)
Nature of bonds	covalent [C–C] (+ weaker van der Waals or H bonding)	ionic or iono-covalent [M–O]
Tg(glass transition)	low (2100 C to 200 C)	high(200C)
Thermal stability	low (,350 Except polyimides,450C)	high (&100 C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity plasticity rubbery (depending on Tg)	Hardness Strength Fragility
Hydrophobicity,	hydrophilic	Hydrophilic
permeability	permeable to gases insulating to conductive	low permeability to gases insulating to semiconductors (SiO2, TMO)
Electronic properties	redox properties	redox properties (TMO)
Processability	high: .molding, casting .machining .thin films from solution .control of the viscosity	magnetic properties low for powders (needs to be mixed with polymers or dispersed in solutions) high for sol–gel coatings (similar to polymers)

2.10.2 Organic Molecules (dyes and ‘‘active species’’) in Amorphous Matrices:

Organic molecules play an important role in the development of optical systems: luminescent solar concentrators, dye lasers, sensors, photochromic, NLO and photovoltaic devices. However, the thermal instability of these compounds has precluded their incorporation into inorganic oxide matric, many organic dyes such as Rhoda mines, pyridines, spyrooxazines, chromes, diarylethenes, coumarone, NLO dyes, etc. have been incorporated into silica or aluminosilicate based matrices, giving transparent films or monoliths with good mechanical integrity and excellent optical quality, as illustrated in the figure (2- 4) [48].

Fig.(2- 4) Hybrid organic–inorganic materials containing organic chromospheres [48].

2.10.3 Biomaterials and bio-inspired hybrid constructions.

Natural materials offer remarkable hydrodynamic, aerodynamic, wetting and adhesive properties. Evident interesting applications concern surface coatings with anti-fouling,hydrophobic, protective or adhesive characteristics and also cosmetic products as show in the figure (2-5) [48].

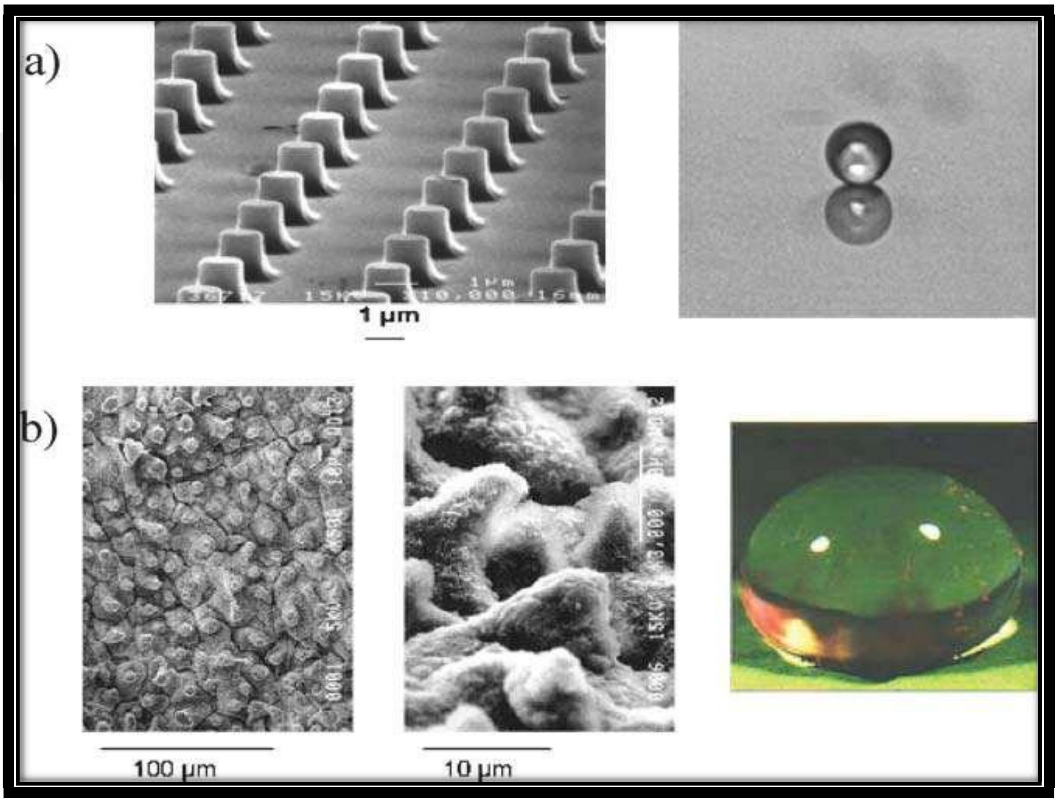


Fig. (2-5) (a) Artificial super hydrophobic coatings (b) inspired by lily leaves [48].

2.10.4 Rubbery hybrid

Rubbery hybrid can be specifically shaped, giving objects such as those illustrated in the figure (2-6) [48].

Fig. (2-6) Rubbery hybrids with different shapes [48].

2.10.5 Hybrid materials for protective and decorative coatings

One of the earlier examples of commercial hybrids with protective functions can be found in the painting industry. In fact, zinc-based sol–gel inorganic paints were and are still employed as corrosion-resistant primers and high-temperature coatings for steel**.** Hybrid ORMOCER1 coatings are even developed to strengthen parts of paper, to enhance specific properties of Polymers used in industry (polyethylene, cellulose, etc.)**.** Some interesting examples of protective ORMOCER1 coatings are provided by T_O_P GmbH, who produce Lacquers developed by the Fraunhofer ISC. In fact, lacquer synthesis facility enables a large scale production of coating materials like ABRASIL1, CLEANOSIL1 and DEKOSIL1. All these lacquers are colorless and highly transparent, which make them highly suitable for the ophthalmic market. Fig(. 2-7a) shows a plate half coated with ABRASIL1 and how the scratch traces from steel wool are observed on the uncoated half. This high scratch resistance is achieved with layer thicknesses of only a few micrometers. Figure (2-7b) shows an injection molded plastic part coated with ABRASIL1 [48].

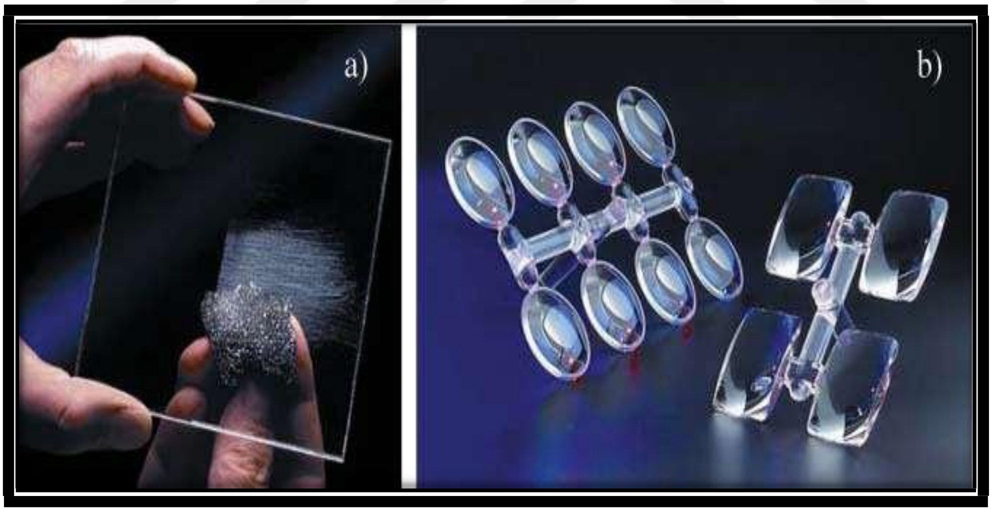


Fig. (2-7) Two examples of protective ORMOCER1 coatings: (a) plate half coated with ABRASIL1; (b) injection molded (plastic) part coated with ABRASIL1 and UV cured [48].

The examples are illustrated in figure 2-8(a,b) and represents a dishwasher-safe ORMOCER1 color coating on glass (DEKOSIL1). The main advantages in terms of the processing of these coatings are the easy reproducibility of the colours and the finishing by conventional wet painting procedures (low curing temperatures 200 C).

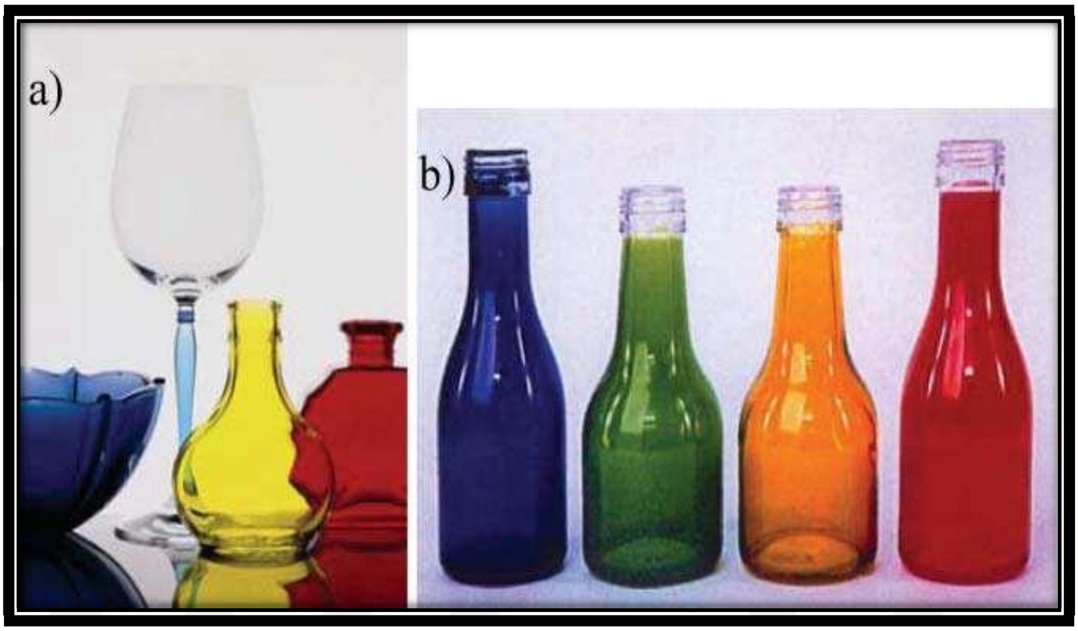


Fig. (2-8) Two examples of hybrid coatings with decorative interest: (a)glass ware demonstrating the high quality optical appearance of crystal glass and other types of glasses coated with dye colored hybrid coatings (courtesy of Fraunhofer ISC);115 (b) easy to recycle colored glass bottles coated by hybrid organic–inorganic materials [48].

2.10.6 Hybrid materials as barrier systems

The interest in hybrid materials as barrier systems has been increased in the last decades as a result of the requirements to develop much more sophisticated materials in fields such as solar cells, optics, electronics, food packaging, etc. New barrier coating materials based on ORMOCER1 have been developed by Fraunhofer ISC which together with a vapor deposited SiOx layer guarantee sufficient protection to ensure a long durability of encapsulated solar cells (see Fig. 2-9(a,b)). This new inorganic–organic hybrid coating represents a whole encapsulation system since apart from the physical encapsulation it acts as an adhesive/sealing layer barrier against water vapor and gases, as well as an outside layer for weather ability. All these functions are combined in one composite (‘‘one component encapsulate’’) and in this way the overall cost reduction for encapsulation reaches about 50 percent.

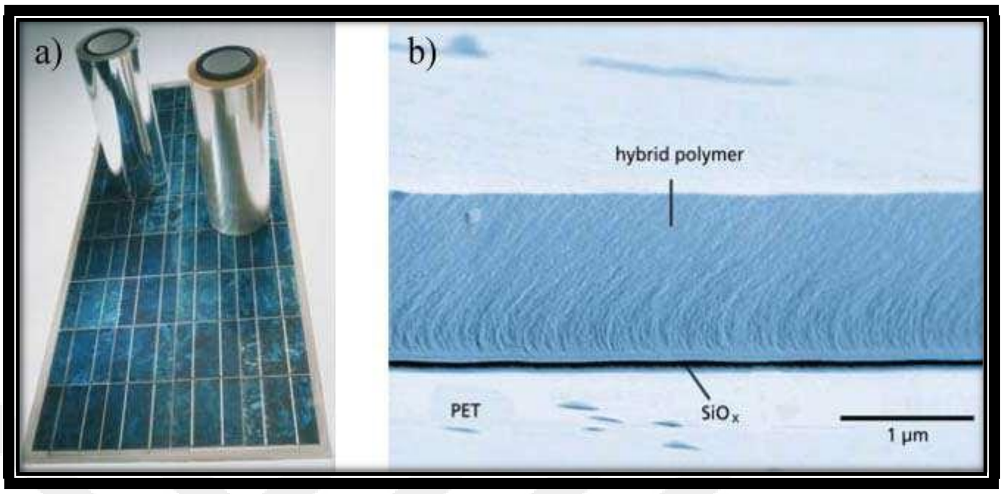


Fig. (2-9) Hybrid coatings as barrier systems. (a) Aspect of the hybrid coated solar modules with very high barrier properties. (b) Scanning transmission micrograph of a thin hybrid polymer coating on SiOx deposited on a flexible PET film[48].

2.10.7 Hybrid materials for dental applications

Inorganic–organic hybrid materials can be used as filling composites in dental applications. As schematized in Figure (2-10)(a), these composites feature tooth-like properties (appropriate hardness, elasticity and thermal expansion behavior) and are easy to use by the dentist as they easily penetrate into the cavity and harden quickly under the effect of blue light [48].

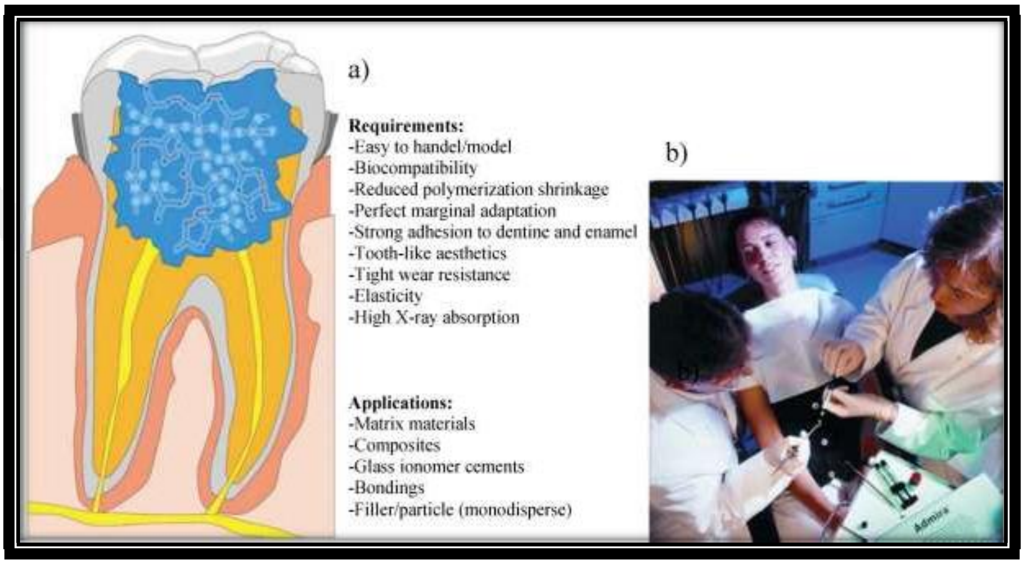


Fig. (2-10), (a) Requirements and possibilities of dental applications of ORMOCER1s. (b)Application of an ORMOCER1 as dental filling material [48].

2.10.8 Hybrid materials for microelectronics

Organically modified resins retain important roles in electrical component coatings such as resistors and molding compounds, as well as spin-on dielectrics in microelectronic interlayer and multilayer dielectric and planarization applications. The advantage of tuning the hybrid’s flexibility and adhesion properties allows their use on flexible substrates, even as optical waveguides. Figure (2 -11) shows ORMOCER1 waveguides in which the hybrid coating is deposited on a flexible foil [48].

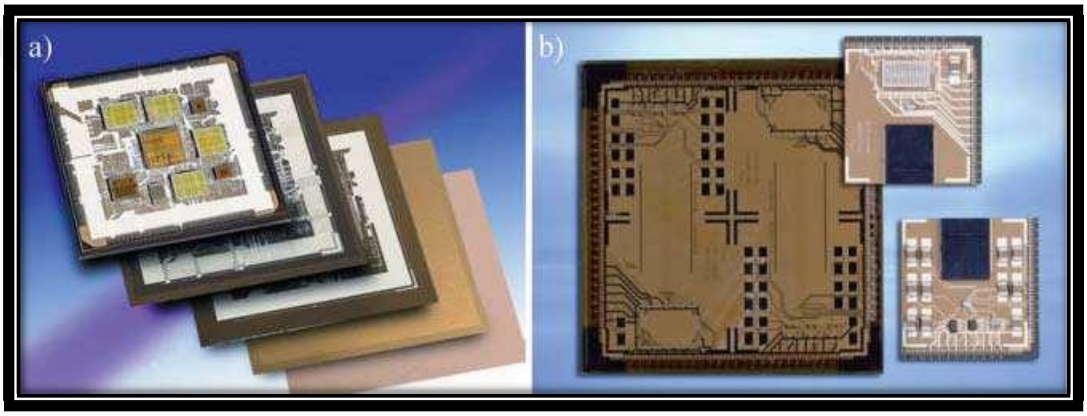


Fig.(2-11) (a) Smallest-sized Pentium1 MCM-L/D manufactured in ORMOCER1 multi-layer technology (ERICSSON/ACREO). (b)Electro-optical (o/e) MCM manufactured in ORMOCER1multilayertechnology (ERICSSON/ACREO/Motorola) [48].

2.10.9 Hybrid materials for micro-optics

Wafer-scale UV-embossing can be applied to substrates other than glass, for example Si and semiconductor III–V based wafers with prefabricated devices. In these cases, it is often advantageous to use the same hybrid materials in a combined lithographic and embossing mode to produce free-standing micro-optical elements, for example the lens let on VCSEL elements for fiber coupling (CSEM in collaboration with Avalon Photonics Ltd., CH-Zurich). Fig. 16 shows SEM images of processed micro optical components on VCSEL wafers: (a) diffractive lenses, and (b) an array of refractive lenses. All the Pyramid Optics’ collimator arrays shown in figure (2-12) are constructed with a silicon V-groove fiber array mounted with a micro lens array. The micro lens arrays are replicated in a ORMOCER1 thin film on a BK7 glass substrate [48].

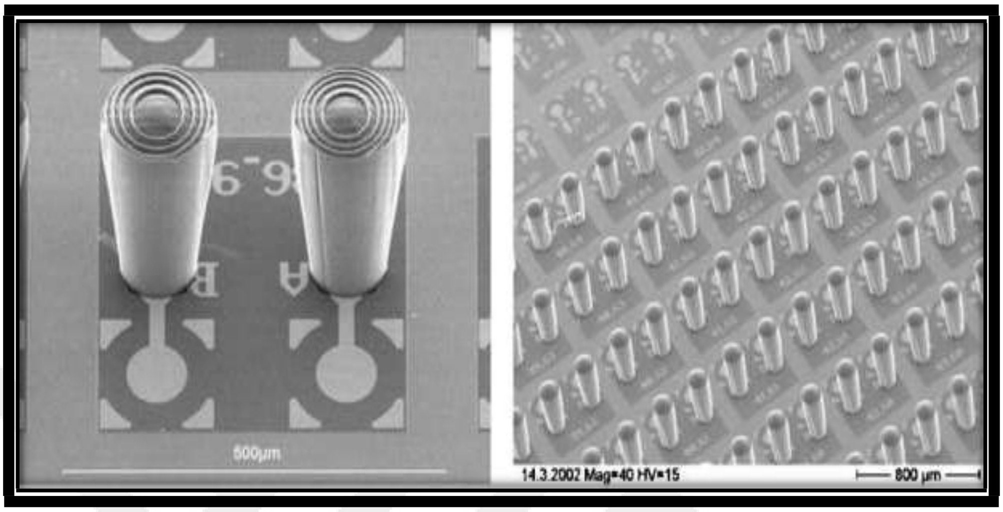


Fig.(2-12) Shows the Scanning electron micrographs of a lens array on VCSEL (courtesy of CSEM/Avalon**)** [48]

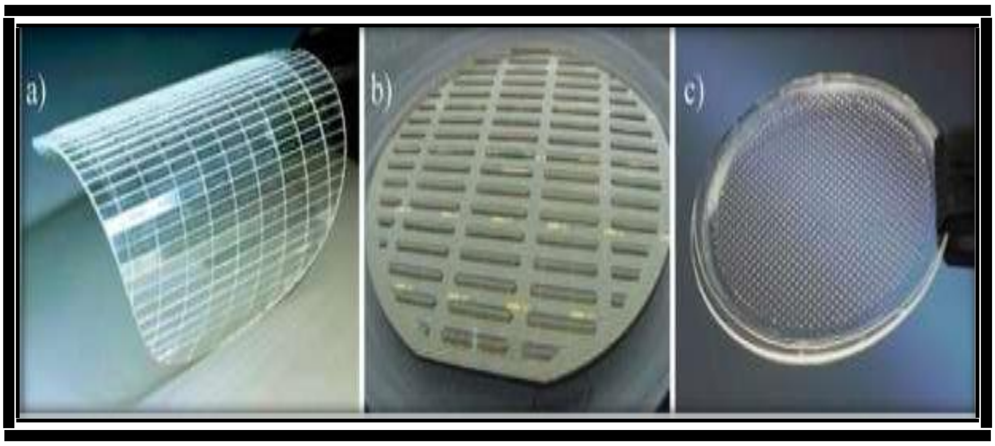


Fig. (2-13) (a) Sawed lens wafer: ORMOCER1 based micro-lenses on glass. (b) ORMOCER1 based collimation micro-lens arrays on InP VCSELs and (c) Large micro lenses on glass substrate (BK7) (courtesy of Fraunhofer IOF) [48].

2.10.10 Hybrid materials for batteries

Hybrid materials for batteries application as shown in figure (2-14).

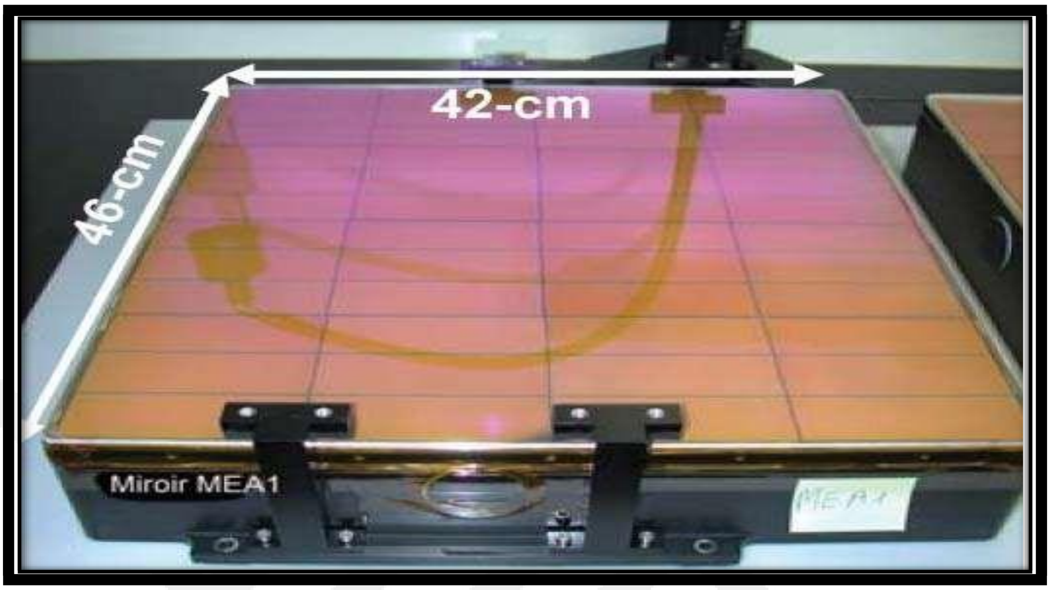


Fig.(2-14) Deformable laser-cavity mirror coated with Nano hybrid multilayer optical stack [48].

Recent developments at the Fraunhofer ISC aim at systems which can be applied without adding liquid plasticizers. Such electrolytes will have enhanced dimensional stability. So, very thin electrode foils without further encapsulation measures can be used. Such electrolytes have reached conductivities of about 5 6 1025 S cm21 at room temperature until now. These values are below those for systems containing liquid plasticizers but they are sufficient for only 20 mm thick layers which are achieved in the battery concept. This conductivity in addition to an electrochemical stability of 4.2 V shows the very high potential of this new electrolyte for thin film lithium–polymer batteries, see figure (2-15).

Among electrochemical devices, electro chromic displays using transition metal oxides (WO3, TiO2, MnO2, IrO2) as active electrodes can be built by using photonic conductor gels as electrolytes [48].

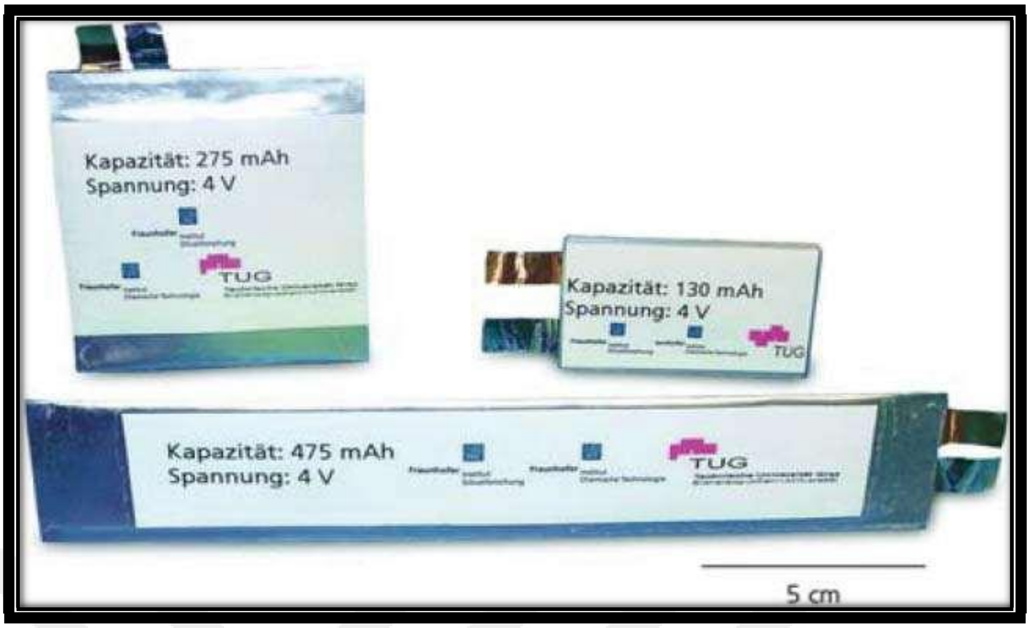


Fig. (2-15) Samples of flexible thin film batteries [48].

2.10.11 Hybrids for photovoltaic cell application

Up to now, the main photovoltaic (PV) devices are based on solid-state junctions, usually made of silicon and are profiting from the development of the semiconductor industry.

In this situation, a challenging new generation of solar cell is emerging, based on the use of interpenetrating network of Nano crystalline oxide and conducting electrolyte. A new promising work reports the development of mesostructured materials using the evaporation- induced self-assembly of surfactant templates in the reaction medium.203,204 Porous ordered structures of mesostructured semiconductor oxides compared to former random particle networks are supposed to simultaneously optimize the P–N surface area, the pore filling with the hole conductor polymer, charge carrier transportation and percolation. The use of an inorganic mesophase structure in the PV cell opens a large field of investigation in relation with the numerous accessible organized structure of the porosity (like the 3-D cubic Im3m phase) which can be optimized for enhanced energy conversion efficiency and therefore solar cell performance205, figure (2-16) [48].

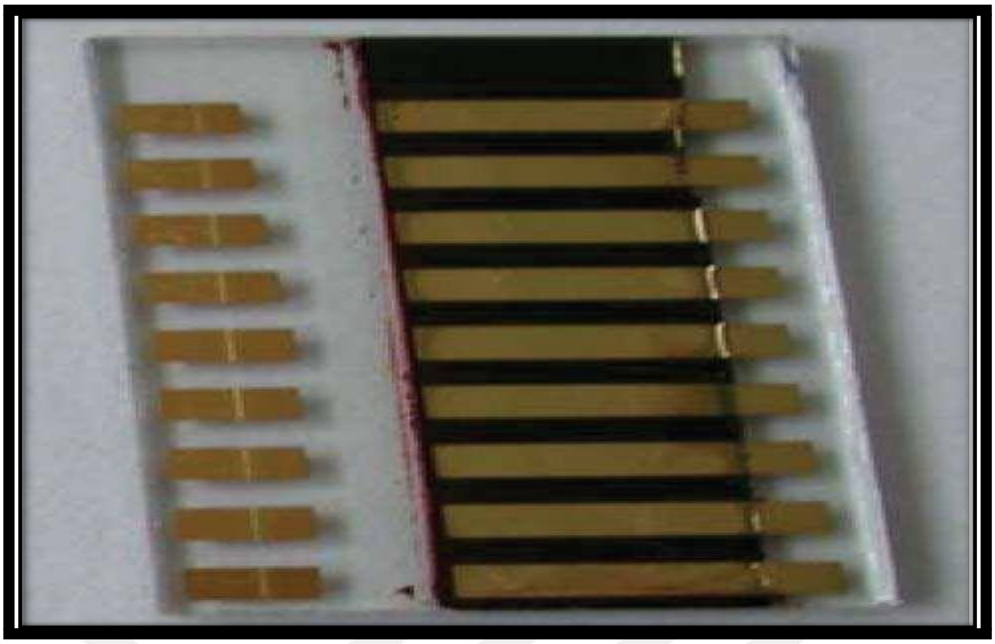


Fig. (2-16) First all solid-state monohybrid dye-sensitized prototype solar cell containing mesostructured titanium oxide as the semiconductor. An energy conversion efficiency of 1.3% has been measured (courtesy of CEA) [48].

2.10.12 Hybrids for proton-exchange membrane fuel cell (PEMFC)applications

The nanocomposite membrane is made of a polymeric matrix in which an inorganic phase is incorporated. The sodded phase is hydrophilic and therefore helps to retain moisture inside the membrane when d at high temperature. Conductivity is maintained and can be also enhanced when using an inorganic phase grafted with conductive groups (acidic or sulfonic functional groups). The inorganic phase is mostly oxide particles (SiO_2, Al_2O_3, TiO_2, ZrO_2) which can be mixed with Pt. Nano-crystals to help self-moisturizing of the membrane,219 or based on clays 220 or zeolites 221 The last two examples are interesting materials since both of them exhibit porosity (flexible or rigid respectively), enabling the storage of water above 100 uC. More often used clays are smectite-based: montmorillonite (natural) or laponite (synthetic). Such clays added to asulfonated-PEEK polymer increase moisturizing, mechanical, thermal and chemical stability and proton conductivity of the composite membrane high enough to compete with Nafion1 115 performance 222 besides the water retention, the Nano composite load should also prevent loss of total conductive group amount due to the incorporation of clay (decrease of ion-exchange capacity or IEC). This can be avoided with the functionalization of the mineral phase before mixing with the polymer. For example, the grafting of sulfonic groups to laponite-type clays via Para-styrene sulfonic acid reaction enables the IEC of the composite membrane to be increased.223 The contribution of a modified mineral phase homogeneously dispersed in the polymeric matrix is today demonstrated, see figure (2-17) [48].

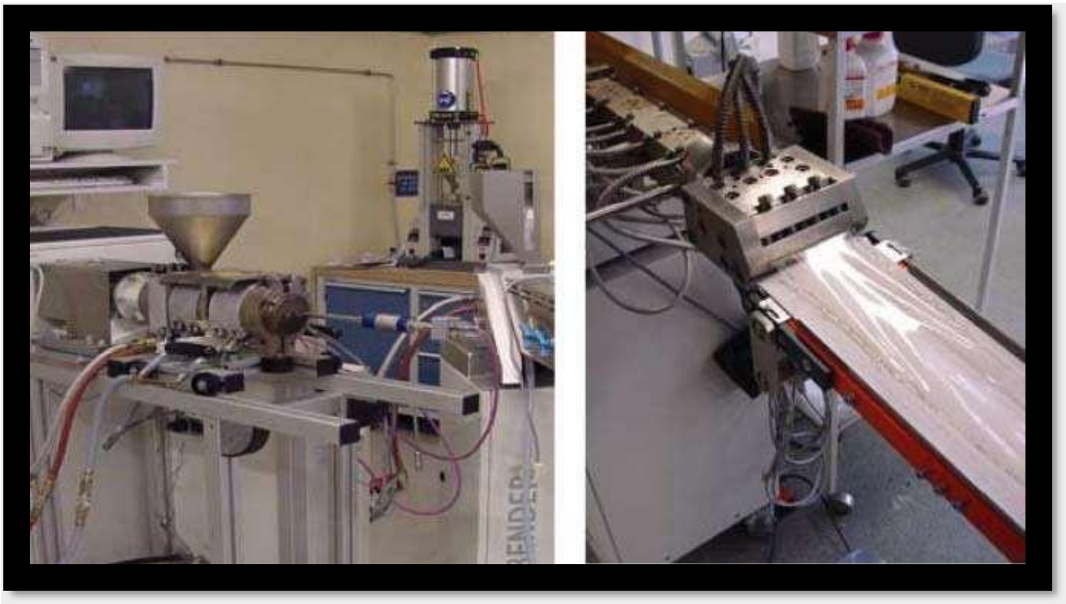


Fig.(2-17) Extruded nanocomposite PEMFC membranes are prepared using clays as inorganic moisturizing phase (courtesy of CEA) [48].

2.10.13 Other applications of hybrids

Another application of sol–gel derived hybrid materials not mentioned until now is as adhesives. In this field, the best examples of inorganic–organic hybrids are the organically derived siloxane resins. They are made of SiO_2 units cross-linked with trimethylsiloxy or hydroxyl groups, and exhibit molecular weights of 2000 to 10000. Their larger application concerns the pressure-sensitive adhesives (PSAs).231,232 Furthermore, these resins are also used in cosmetics, water-repellents and additives for paper release coatings [48].

2.11 Some indications about the Nano composites world market

Nanocomposites represent an important part of the activities in great companies such as Bayer, GE or Honeywell, as well as in more specialized enterprises. In Table 5 the wide range of resins used at the present time for polymer–clay nanocomposites is summarized. A new generation of synthetic nanomaterial’s as nanotubes or ceramic Nano fibers are also emerging, but these smart materials are at least five to ten years away from commercial realization. the total commercial value of thermoplastics is 3.5 times more important, fig.(2- 18)).Therefore, the estimation for 2008 is that thermoplastics should represent 77% of the production in volume and 85% in commercial value. As remarkable data: General Motors Corporation consumes around 245 tons of these Nano composites per year, most of them based on olefins; and BRG Townsend Inc. (package industry) estimated in 2002 that its nanocomposites consumption intended for 2007 should be 2200 tons per year and 45000 tons in 2011 [48].

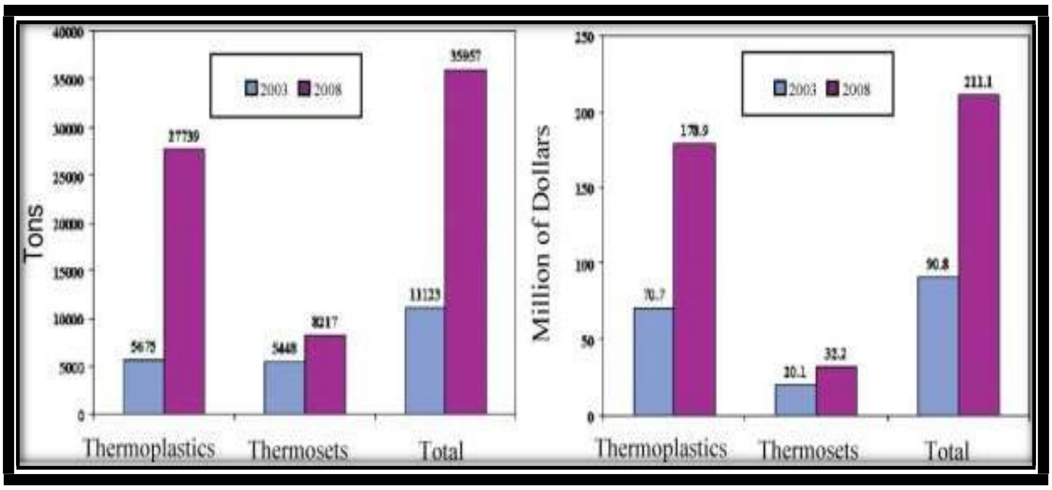


Fig. (2-18) World production of polymer nanocomposites [48].

Table(2- 2) List of some nanocomposites suppliers [48]

Supplier	Matrix resin	Nano-filler	Target market
Bayer AG	Nylon 6	Clay	Barrier films
Clarian	Polypropylene	Clay	Packaging
Creanova	Nylon 12	Nano-tubes	Electrically conductive
GE Plastics	PPO/Nylon	Nano-tubes	Painted automobile parts
Honeywell	Nylon 6	Clay	Films and bottles
Hyperion	PETG, PBT,PPS, PC, PP	Nano-tubes	Electrically conductive
Kabelwerkupenof Belgium	EVA	Clay	Wires and cables
Noncore	Nylon6,PP,Nylon MDX6	Clay	Beer bottles, molding
Polymeric Supply	Unsaturated polyester	Clay	Marine, transportation
RTP	Nylon 6, PP	Clay	Electrically conductive
Showa Denko	Nylon 6, Acetyl	Clay, mica	Flame retardance
Ube	Nylon 6, 12, 66	Clay	Auto fuel systems
Yantai Haili Ind.& Commerce of Chin	UHMWPE	Clay	Earthquake-resistance pipes

Looking to the 21st century, Nanoscience will be one of the fields that will contribute to a high level of scientific and technological developments. Hybrid organic–(bio)–inorganic materials will play a major role in the development of advanced functional materials. Research in functional hybrid organic–inorganic materials is being mostly supported by the growing interest of chemists, physicists, biologists and materials scientists to fully exploit this opportunity for creating smart materials benefiting from the best of the three realms: inorganic, organic and biological [48].

2.12 Literature Review

Lu et al. [49] studied the mechanical and wear properties of composites. Addition of Nano filler TiO_2 and SiO_2 significantly improve the impact and tensile strength which was almost 2-3 times as much as that of pure epoxy resins. The wear and friction performance of composites had been improved with addition of TiO_2 and SiO_2 Nanoparticles.

Yang et al. [50] studied that the SiO_2 nanoparticles were used to modify epoxy emulsion sizing of carbon fibers to improve the reinforced epoxy composites. For investigation of mechanical interfacial strength between fiber and matrix, fragmentation(The breaking of an entity into smaller parts) test and three point short beam sheet tests were conducted on unmodified sizing and nano-SiO_2 modified sizing. Dynamic contact analysis X-Ray photoelectron spectrometry and atomic force microscopy also performed on them. The results indicated that modified sizing with nano-SiO_2 1.0 wt% has maximum Interfacial shear strength and Interlinear shear strength values. Scanning Electron Microscopy (SEM) images show the fracture section of composites with modified sizing is more compact and fiber deboning is more difficult than that with unmodified sizing. From AFM analysis it was seen that modified sizing changed the surface roughness values on a microscopy scale. As a result nano-SiO_2 modified epoxy emulsion sizing for carbon fibers further improved the chemical and physical properties of the fiber surface, resulting in the increase of the mechanical interfacial properties of the composites.

Chowdhary et al. [51] used a Nanomaterials to modify the matrix of carbon fiber/SC-15 epoxy(SC-15 epoxy is used in many industrial applications and it is well known that the mechanical and viscoelastic properties of epoxy can be significantly enhanced when reinforced with nanofillers) composite to determine the effect of particle reinforcement on the response of these material to flexural and thermo mechanical loading. Nano clay with different percentage was dispersed in SC-15 epoxy with sonication route and after that hand layup process was used to manufacture plain weave carbon/epoxy Nano composite from Nano phased epoxy material.

Control samples for comparison purpose of woven carbon fiber/epoxy were fabricated. Using dynamic mechanical analysis and three-point bend flexure test effect of post curing was investigated on 8- and 3-layered samples. From the results it was shown that flexural strength and modulus for Nano clay reinforced composites as compared to the control samples was significantly improved and also enhancement in mechanical properties especially in storage modulus but in glass transition temperature no significant change was seen.

Zhou et al. [52] Conducted thermal and mechanical tests on carbon Nanofiber (CNF) filled epoxy and carbon fabric/epoxy composite. The optimal CNF content was 2.0 wt. %, which produced the highest improvement in tensile strength as compared to the neat epoxy resin. The composite fabricated with 2.0 wt. % CNF filled epoxy produced 22.3% improvement in flexural strength and 11% improvement in tensile strength. The addition of CNF in the epoxy matrix also improved the fatigue performance of the composite.

P. kumar and A. Thiagarajan et al. [53,54] studied the carbon fiber reinforced epoxy/clay nanocomposites (CFRECS) were manufactured through hot melt layup plus autoclave process. The CFRENCs have uniform fiber volume fraction very few dry spots and very few resin rich areas. The high pressure mixing method was used to disperse nanoclay into TGDDM .From the results of this method it proves to be good for disperse of nanoclay into TGDDM epoxy system. Mode I interlaminar fracture toughness of unidirectional carbon fiber composite was also increased by 53% and 85% with 2 and 4 nanoclay. A small amount of nanoclay also contributes to increase of flexural strength. But adding more clay does not improve the flexural properties more.

Chen et al. [55] studied the thermal and mechanical properties of nanocomposites with SiO_2 as a Nanofiller. With increasing SiO_2 loading, decrease in cure temperature and glass transition temperature occurred. At 10 wt %. of SiO_2 increase of 25% in tensile modulus and 30% in fracture toughness was obtained. Further addition of SiO_2 increase in modulus occurred but it decreased the strength and fracture toughness.

Kishore et al. [56] studied the failure mode and failure loads for multi-pin joints in unidirectional glass fiber epoxy composite laminates by taking different sizes of sample. With variation in pitch-to-diameter, side width-to-diameter and edge-to-diameter ratios. With using finite element analysis the theoretical results were validated with the experimental results.

Ogasawara et al. [57] studied the effect of fullerene dispersion on the mechanical properties such as tensile, flexural, compression, open hole compression, compression after impact, bending, short beam shear and intermolecular fracture toughness of laminates. Increase in tensile and compression strength had seen up to 2-12% improvement in intermolecular fracture toughness also seen. Fullerene dispersion was improving the CFRP strength.

Khan et al. [58] studied the effect of nanoclay inclusion on cyclic fatigue behavior and residual properties of carbon fiber reinforced composites after fatigue. To establish S-N curve tension-tension cycle fatigue test were conducted at various load levels. The residual strength and modulus were measured at different stage of fatigue cycles. From the results of these tests, it was shown that fatigue life significantly extended with the incorporation of Nanoclay to CFRP composite and the maximum improvement is about 74% with 3 wt% clay content. The clay-CFRP hybrid composites showed better performance in terms of residual tensile strength and modulus then the neat composite after a given fatigue cycle.

Osman Asi [59] studied the bearing strength behavior of pinned joints of glass fiber reinforced composite which was filled with different percentage of Al_2O_3 (7.7, 10, 15)wt%. Single-hole pin loaded specimens of each percentage composite was tested in tension. From the result it was shown that with increase in percentage of Al_2O_3 bearing strength of composite increased and further increase in percentage of Al_2O_3 bearing strength decreased. The highest bearing strengths were obtained for composite specimens with 10 wt% Al_2O_3 particle content. It compared with the bearing strength of the unfilled glass fiber reinforced epoxy composite, with the addition of 10 wt % Al_2O_3 particle in the matrix, bearing strength increased by 20%.

Jumahat et al. [60] implemented fiber kinking and fiber micro-buckling models to predict the compressive strength of the unidirectional (UD) HTS40/977-2 toughened composite laminate. SEM micrograph revealed that the failure of the UD HTS40/977-2 composite laminate was initiated by fiber micro-buckling and subsequent plastic kinking of the materials. Therefore, a combined modes model was developed to predict the compressive strength of the system. The combined modes model yielded a successful compressive strength prediction in which the predicted compressive strength was in a good agreement to the measured value. Considering all the parameters that had been investigated, the in- plane shear properties and the initial fiber misalignment angle between the fibers and the loading axis were identified as the most critical parameters that affect the compressive strength of the UD toughened composite laminates.

Khan et al. [61] studied the mechanical properties of clay-epoxy Nanocomposites and clay-carbon fiber reinforced polymer (CFRP) hybrid composites. For investigating the impact fracture toughness and quasi-static fracture toughness chirpy impact test and compact tension test was conducted on both the materials. The result showed that the properties were increased in both the material with addition of clay up to 3 wt% but decrease after further addition of clay. The impact and quasi-static fracture toughness values of clay-epoxy Nano composite was less than the clay-CFRP hybrid composite because of carbon fiber which showed additional toughening.

Zeng et al. [62] studied the epoxy matrix with rubber and silica nanoparticles either single or jointly and applied Double-cantilever-beam test to investigate the interlinear fracture toughness. From the result it was shown that the toughness was improved by the presence of these nanoparticles. nanorubber was more effective than Nano silica. Jointly addition of rubber and silica particles improve toughness but not more than single rubber if added or single silica.

Shadlou et al. [63] studied the carbon nano reinforcements of three different shapes for the mixed mode fracture behavior of epoxy-based nanocomposites. On the basis of experimental results, while the cylindrical carbon nanofibers (CNF) and platelets grapheme oxide (GO) particles were more successful in ameliorating the fracture resistance under mode I and mixed mode loading, the spherical (ND) particles developed better fracture resistance in pure mode II.

Zhou et al. [64] studied the effect of clay weight fraction on thermal and mechanical properties of the epoxy matrix. The dynamic mechanical analysis, thermo-gravimetric analysis and flexural test were perform in unfilled 1wt%, 2 wt%, 3wt% and 4 wt% clay filled SC-15 epoxy. From the result of analysis it was shown that 2 wt. % loading of MMT clays in SC-15 epoxy resin had the highest improvement in the strength as compared to neat and other Nano phased systems. The composite fabricated with 2.0 wt% clay filled epoxy produced 22.3 % improvement in flexural strength and 11 % improvement in tensile strength. The addition of clay in the epoxy matrix also improved the fatigue performance of the composite.

In the present research work will be study the effect of Nano filler added with percent (2, 4, 6, 8)wt% to epoxy matrix on the mechanical properties (tensile strength hardness, , impact strength) of hybrid nanocomposite material.

Chapter Three

Experiment Work

3.1 . Introduction

This chapter deals with the materials and equipments used in the preparation process of the hybrid nanocomposite materials, in this research the resulted cast materials have been cut according to the standard dimensions for different tests, the microstructure has been observed under atomic force microscope while the evaluation of tensile properties has been obtained by set up tensile test on testing machine. Also, the hardness of samples was measured by hardness of shore D type testing machine. Figure (3-1) shows the technological route of experimental processes used in this research.

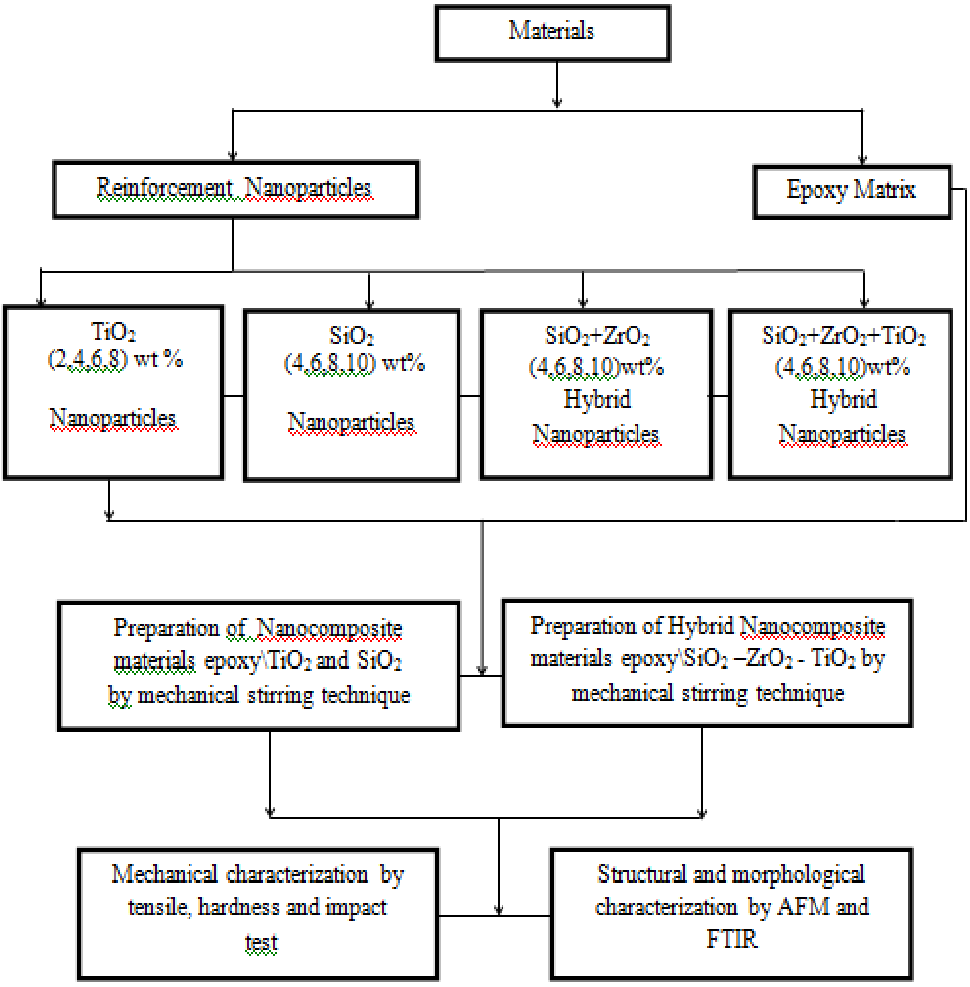


Fig. (3-1) Flow chart of experimental work steps

3.2. Materials

3.2.1 Matrix

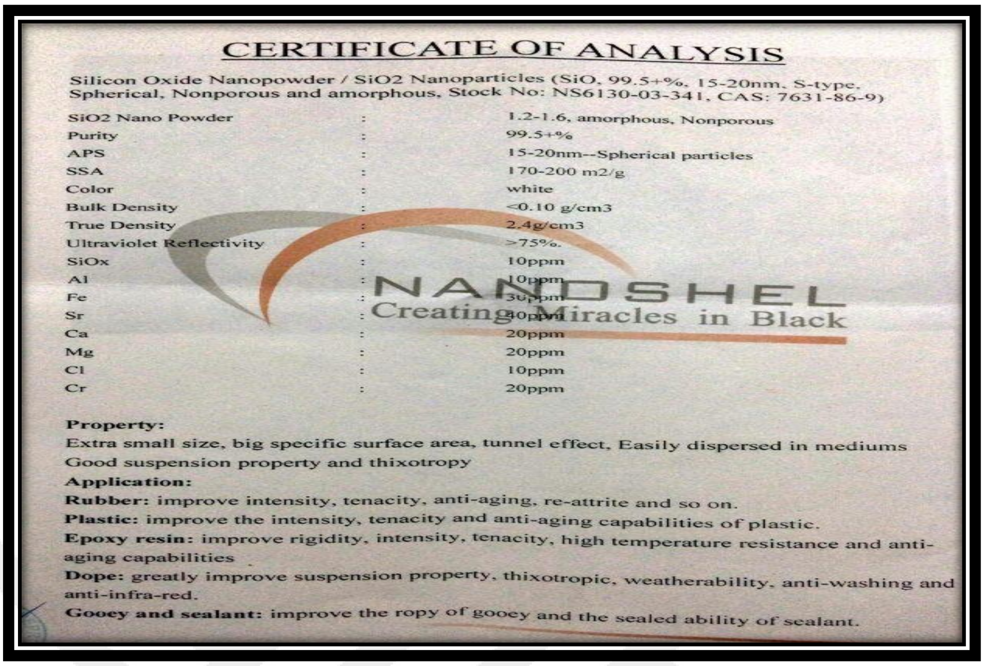
Diglycidyl ether of bisphenol-A (DGBA) (Epoxy Resin L-2, Hardener K-12, Accelerator K-13)

3.2.2 Reinforcement

3.2.2.1 TiO_2 surface area of 50+15 m^2/g and is 99% pure antase crystal, with average particle size of 30 nm. Properties of TiO_2 nanoparticles shown in the figure(3-2).

Fig.(3-2) specification of TiO_2 nanoparticles

3.2.2.2 SiO_2 Nanopowder of 99.5 % pure and 15 to 20 nm particle size. The properties of TiO_2 nanoparticles shown in the figure (3-3).



CERTIFICATE OF ANALYSIS

Silicon Oxide Nanopowder / SiO2 Nanoparticles (SiO, 99.5+%, 15-20nm, S-type, Spherical, Nonporous and amorphous, Stock No: NS6130-03-341, CAS: 7631-86-9)

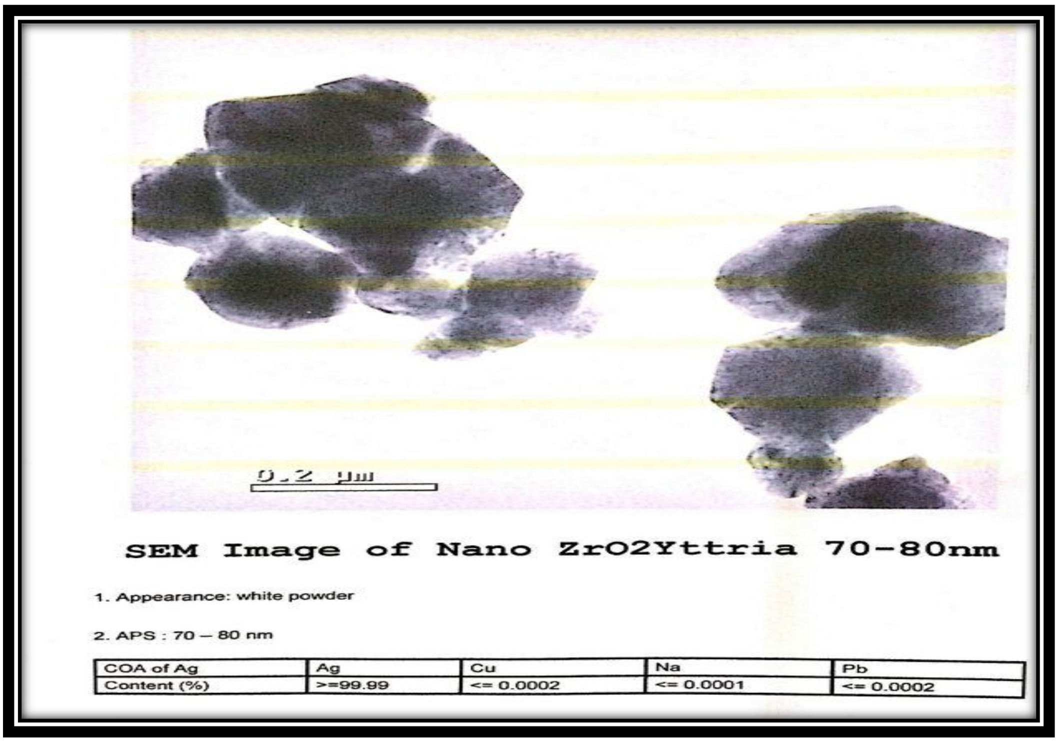
SiO2 Nano Powder : 1.2-1.6, amorphous, Nonporous
Purity : 99.5+%
APS : 15-20nm--Spherical particles
SSA : 170-200 m2/g
Color : white
Bulk Density : <0.10 g/cm3
True Density : 2.4g/cm3
Ultraviolet Reflectivity : >75%.
SiOx : 10ppm
Al : 10ppm
Fe : 30ppm
Sr : 40ppm
Ca : 20ppm
Mg : 20ppm
Cl : 10ppm
Cr : 20ppm

Property:
Extra small size, big specific surface area, tunnel effect, Easily dispersed in mediums
Good suspension property and thixotropy

Application:
Rubber: improve intensity, tenacity, anti-aging, re-attrite and so on.
Plastic: improve the intensity, tenacity and anti-aging capabilities of plastic.
Epoxy resin: improve rigidity, intensity, tenacity, high temperature resistance and anti-aging capabilities
Dope: greatly improve suspension property, thixotropic, weatherability, anti-washing and anti-infra-red.
Gooey and sealant: improve the ropy of gooey and the sealed ability of sealant.

Fig.(3-3)specification of SiO_2 nanoparticles

3.2.2.3 ZrO_2 Nano powder of 99.9% pure and 70 to 80 nm particle size. The physical and chemical properties of ZrO_2 nanoparticles shown in the figure (3-4).



SEM Image of Nano ZrO2Yttria 70-80nm

1. Appearance: white powder

2. APS : 70 – 80 nm

COA of Ag	Ag	Cu	Na	Pb
Content (%)	>=99.99	<= 0.0002	<= 0.0001	<= 0.0002

Fig. (3-4) specification of ZrO_2 nanoparticles

3.3 Nanocomposite Material Preparation

3.3.1 By addition TiO_2 Nanoparticles

To get the proper dispersion of epoxy and Nano filler mechanical stirring was done at 2000 rpm for 2 hours. TiO_2 of 2 wt%, 4 wt%, 6 wt% and 8 wt% were added to the epoxy resin and stirred for 2 hours as show in figure (3-5) .To reduce the viscosity of epoxy solution preheating at $60^{o}C$ for 30 min.

Fig (3.5) Mechanical Stirrer

In sonication sound energy is used to agitate particle in a mixture. Sonication breaks the intermolecular interaction and is used for speed dissolution. Sonication is usually carried out using an ultra-sonication bath or an ultra-sonication probe. Ultra sonication bath used for 2 hours as show in figure (3-6).

Fig (3.6) Ultra sonication Bath

After ultra-sonication, the solution was mixed with the hardener in the ratio of 1:1 by weight, Thereafter 1 wt% accelerator was added as per the instructions of the epoxy system resin. After mixing, mechanical stirring up to 15 minutes was done, followed by ultra-sonication for 15 minutes which results in proper dispersion of nanoparticles.

After mixing, stirring and sonication large amount of bubbles appear in the solution. If these are not removed than they can produce defects in the specimen and may affect the results. For removing these bubbles degassing is done. For degassing beaker is placed in vacuum oven for 2 hours. After degassing a bubble free mixture was then poured in the Teflon sheet mould and left in air for 24 hours. Epoxy is a very sticky material which sticks even on metal sheets. So a Teflon sheet would was used to prepare the sample sheets. After placing in air for 24 hours it is kept in electric oven (capacity of 300^{o}C) at 120^{o}C up to 2 hours for post curing. The specimens were cut manually as show in figure (3-7).

Fig (3-7) Cutting with Hacksaw Blade

The testing of the epoxy nanocomposite specimen for its tensile strength. The tensile test was performed with a test speed of 5 mm/min and a preload of 0.1 MPa.

3.3.2 By addition SiO_2 Nanoparticle

In the same method as before to get the proper dispersion of epoxy and nanoparticle of SiO_2 at 4 wt%, 6 wt%,8 wt% and 10 w% were added to the epoxy resin and stirred for 15 sec. as show in figure (3-8) .

Fig. (3-8) Mechanical stirrer

After that , the solution was mixed with the hardener in the ratio of 2:1 by weight. Therefore 2 wt% accelerator was added as per the instructions of the epoxy system resin. After mixing, mechanical stirring up to 15 minutes was done, followed by ultra-sonication for 15 minutes which results in proper dispersion of nanoparticles as show in figure (3-9).

Fig. (3-9) Ultrasonic Homogenizer.

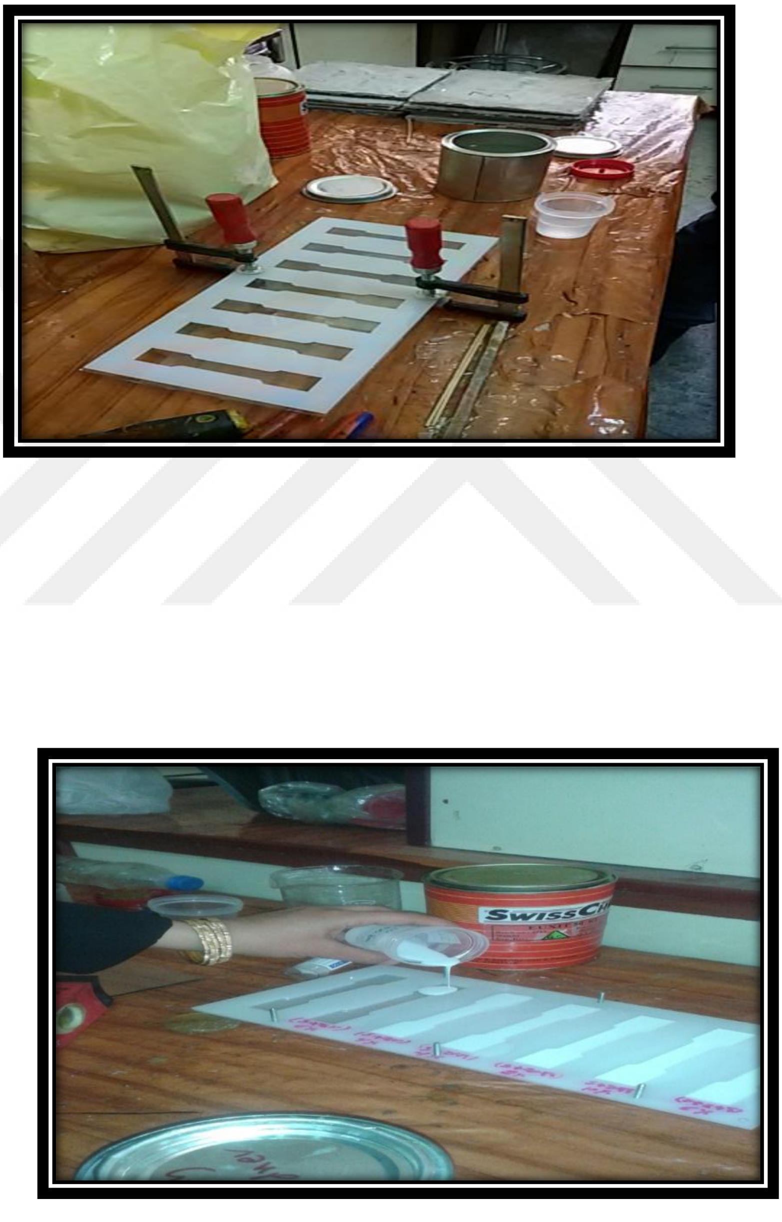
So a tensile mold was used to prepare the sample . after placing in air 17 hours. Its kept in electric oven (1 hour) at 50 C^0 as show in figure (3-10), model DHG, serial No.9053A.

Fig. (3-10) Electric Oven

3.4 Hybrid Nanocomposite Material Preparation

3.4.1 By addition SiO_2 , ZrO_2 and TiO_2 Nano particle

Hybrid nanocomposite material perpetrate by addition deferent percentage of ($SiO_{2+}ZrO_2$) and (SiO_2+ZrO_2+TiO_2) at 4 wt%, 6 wt%,8 wt% and 10 wt% to the epoxy resin and stirred for 15 sec. so the mixture molded in tensile mold as show in figure (3-11).



(A)

(B)

Fig. (3-11):(A) Molds and (B) casting process

After that placing the samples in electric oven at 50^0 C up to 1 hour for post curing.

3.5 Mechanical Tests

3.5.1 Tensile Test

Tensile testing will be performed to determine tensile properties. In tensile testing, a “dog-bone” shaped sample is placed in the grips of movable and stationary fixtures in a screw driven device, as shown in figure (3-12) below, which pulls the sample until it breaks and measures applied load versus elongation of the sample.

Fig (3-12) Tensile Test Equipment (WDW-50)

The testing process requires specific grips, load cell, and extensometer for each material and sample type. The load cell is a finely calibrated transducer that provides a precise measurement of the load applied. The extensometer is calibrated to measure the smallest elongations.

Output from the device is recorded in a text file including load and elongation data. Elongation is typically measured by the extensometer in volts and must be convserted to millimeters. Mechanical properties are determined from a stress vs. strain plot of the load and elongation data. Tensile testing is a destructive characterization technique.

The American Society for Testing and Materials (ASTM) provides the following relevant standard test method (ASTM D638) is one of the most common material strength specifications and covers the tensile properties of unreinforced and reinforced material. This test method uses standard “dogbone” shaped specimens under 14mm of thickness as shown in figure (3-13).A universal testing machine (tensile testing machine) is needed to perform this test. It calculates (Tensile properties).

- To perform ASTM D638, begin by cutting your material into a “dogbone” sample.
- Load the sample into a pair of tensile grips and attach your extensometer.
- The speed at which you separate your tensile grips depends on the shape of the specimen and can range from 0.05-20 inches per minute.
- End the test at sample break (rupture).

This device (Computer Controlled Electronic Universal Testing Machine) has serial No.(1202001) and manufacture company (LARYEE TECHNOLOGYCO,LTD), in laboratory in Material Engineering Department, University of Technology-Baghdad-Iraq.

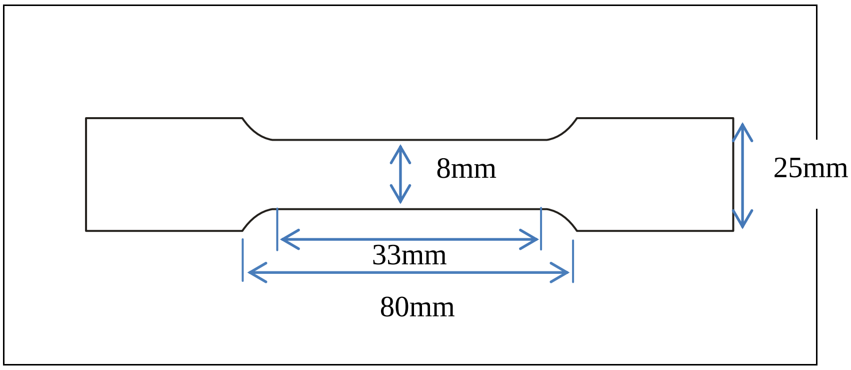


Fig (3-13) Specimen for Tensile Test as according ASTM D638 Standard

3.5.2 Hardness Test

Hardness testing is a method of determining a material’s hardness or resistance to penetration when test samples are very small or thin, or when small regions in a composite sample or plating are to be measured. , as shown in figure (3-14) below

Fig (3-14) Hardness Testing Equipment (Gewicht Shore D)
serial No.3279 and manufacture company Elcometer, in Material Engineering Department, University of Technology-Baghdad-Iraq.

3.5.3 Impact Test

The purpose of impact testing is to measure an object's ability to resist high-rate loading. It is usually thought of in terms of two objects striking each other at high relative speeds. A part, or material's ability to resist impact often is one of the determining factors in the service life of a part, or in the suitability of a designated material for a particular application. Impact resistance can be one of the most difficult properties to quantify. The ability to quantify this property is a great advantage in product liability and safety. The sample is placed under the hammer. The hammer then descends on it and the fracture energy indicated in the device is taken, as show in Figure (3-15).

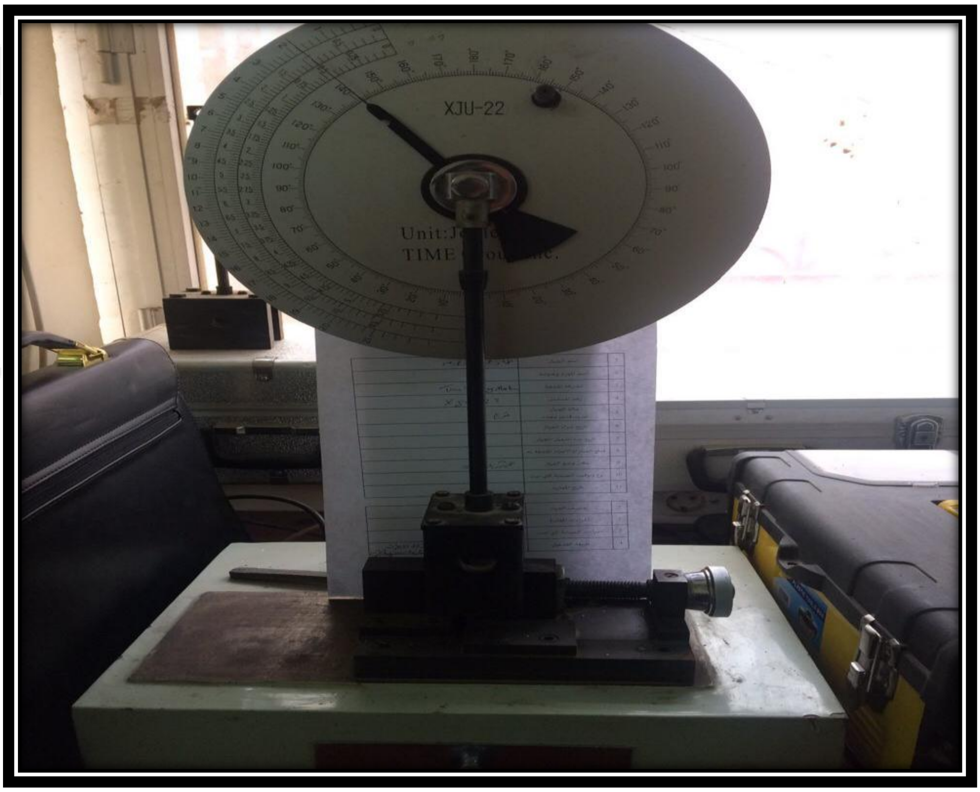


Fig. (3-15) Impact Testing Equipment (XJU-22)

The setup of tensile, hardness and impact test of all samples have been done in the polymer and strength laboratory of Material Engineering Department in University of Technology.Baghdad-Iraq. This device (Impact Test) has serial No.(XJU-22) and manufacture company (Time Testing Malin)

3.6 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) will be used to analyses the bonding between the polymer matrix and nanoparticles. FT-IR measures the absorption of infrared radiation by the sample material with respect to the wavelength of the radiation.

Fourier Transform-Infrared Spectroscopy (FTIR) device, figure (3-16) is an analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.

When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The(FTIR) spectrometer uses an interferometer to modulate the wavelength from a broadband infrared source. A detector measures the intensity of transmitted or reflected light as a function of its wavelength. The signal obtained from the detector is an interferogram, which must be analyses with a computer using Fourier transforms to obtain a single-beam infrared spectrum. The FTIR spectra are usually presented as plots of intensity versus wavenumber (in cm^{-1}). Wavenumber is the reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber.

Fig (3-16) Fourier Transform Infrared Spectroscopy (Perkin Elmer Spectrum 100)

3.7 Atomic Force Microscope (AFM)

Atomic force microscopy (AFM) is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.

Atomic force microscopy (AFM) is a type of scanning probe microscopy (SPM), (VEECO Multimode NanoscopeV) as shown in the figure(3-17) with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. The information is gathered by "feeling" or "touching" the surface with a mechanical probe. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable very precise scanning.

Atomic force microscopy is arguably the most versatile and powerful microscopy technology for studying samples at Nano scale. It is versatile because an atomic force microscope can not only image in three-dimensional topography, but it also provides various types of surface measurements to the needs of scientists and engineers. It is powerful because an AFM can generate images at atomic resolution with angstrom scale resolution height information, with minimum sample preparation.

Fig (3-17) Atomic Force Microscope (VEECO Multimode NanoscopeV)

Chapter Four

Result and discussion

4.1 Introduction

The results of the synthesized nanocomposite from(epoxy\$TiO_2$ and epoxy\$SiO_2$) with addition (2 , 4 , 6, & 8) wt% of TiO_2 and (4, 6, 8, &10) wt% of SiO_2 and synthesized hybrid nanocomposite (epoxy\$SiO_2$-$ZrO_2$ and epoxy\$SiO_2$-$ZrO_2$-$TiO_2$) have been discussed . The tensile properties, hardness, impact strength, FTIRS analysis and AFM examination have been reported for epoxy matrix before and after addition nanoparticles (reinforced) phase .

4.2 Tensile Strength Results of The Nanocomposite Materials

All tensile test curves of all specimens at deferent condition as shown in appendix(**A**)

4.2.1 Epoxy\TiO_2 nanocomposite materials

The different mechanical properties were tested on the prepared samples of Epoxy with variation of Nano TiO_2 and SiO_2 content. The results obtained by conducting tensile tests on prepared Nano composites using Universal Testing Machine.

An abrupt increase in tensile strength was seen from 2 wt% of TiO_2 to 4 wt% of TiO_2 and a gradual increase in tensile strength occurred from 4 wt% to extent of 8 wt% TiO_2 as shown in the table (4-1).The increase in the strength of the Epoxy matrix samples is due to the addition of TiO_2, when pure epoxy=8.97 MPa (Chinese origin).

Table (4-1) shows the result of tensile strength by addition TiO_2

Wt% TiO_2	**σult (MPa)**
2	6.77
4	20.22
6	32.33
8	33.46

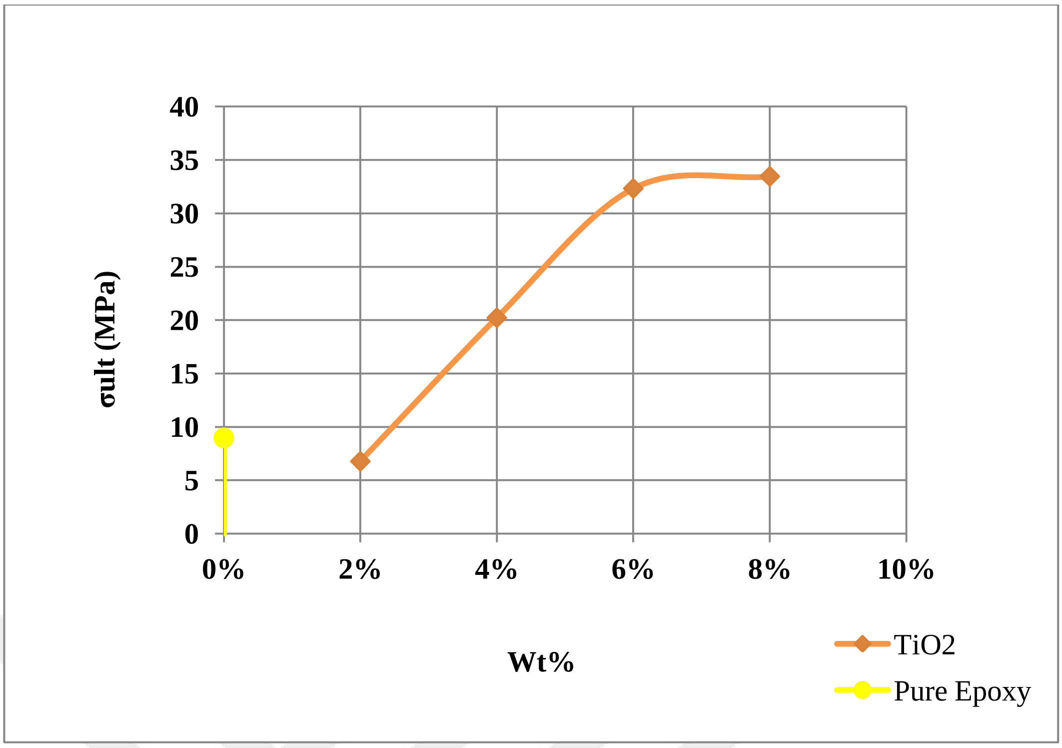


Fig. (4-1) Shows the relationship between tensile strength and weight percentages of TiO_2 nanoparticles additives.

4.2.2 Epoxy\\SiO_2 nanocomposite

Also, in table (4-2) show increase in tensile strength occurred from 4 wt% to 8 wt% of SiO2 after 8 wt% the tensile strength decrease to 10 wt% This shows the increase of nanoparticles may give adverse effect to the mechanical properties of the material. So the 8 wt% of SiO2 is optimize addition, when pure epoxy=4.510 MPa from American origin.

Table (4-2) shows the result of tensile strength by addition SiO_2

Wt %(SiO_2)	**$\sigma_{ult.}$MPa.**
4	4.75
6	6.65
8	10.8
10	2.6

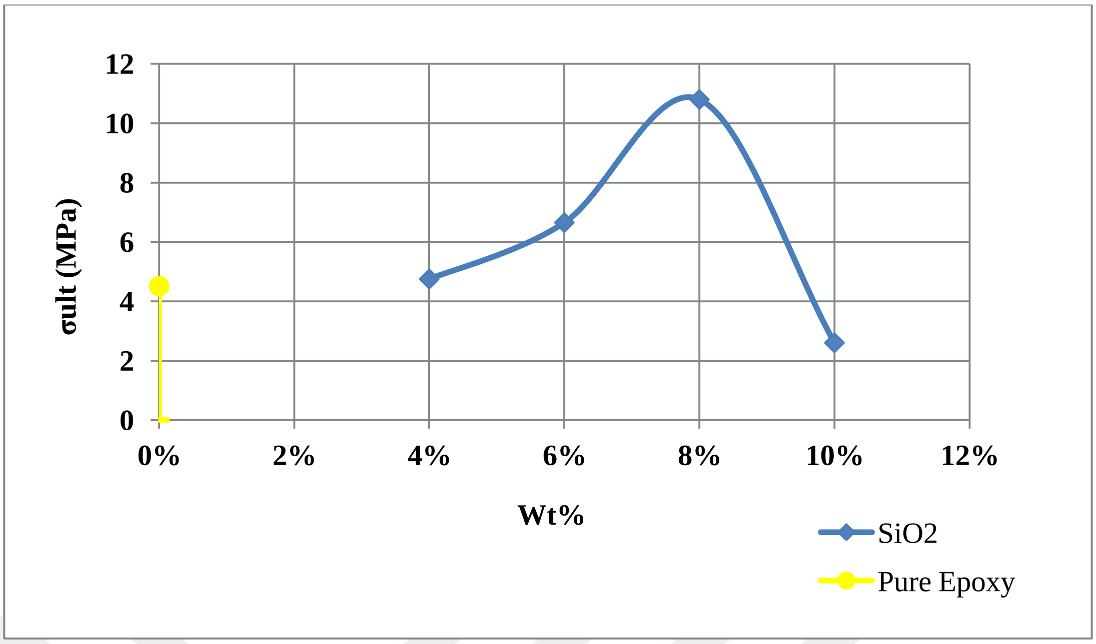


Fig. (4-2) Shows the relationship between tensile strength and weight percentages of SiO_2 nanoparticles additives.

Tables (4-1),(4-2) and figures (4-1), (4-2) show the effect of different percentage content of TiO_2 and SiO_2 nanoparticles reinforcement phase on the tensile strength. In this case the addition of TiO_2 and SiO_2 nanoparticles reinforcement to epoxy matrix increases the tensile strength of nanocomposite materials until reaching the maximum value at 8 wt % nanoparticles materials referred to strong interface between the phases that distributes and transfers the load from the matrix to the reinforcement resulted in tensile strength improvement .

4.3 Tensile Strength Results of Hybrid Nanocomposite Materials

The results obtained by re-conducting tensile tests on prepared hybrid anocomposites from additives (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) at (4, 6, 8, 10) Wt% to the epoxy resin.

4.3.1 Epoxy \(SiO_2+ZrO_2) hybrid nanocomposite materials

Table (4-3) Shows the tensile strength at different percentage of (SiO_2+ZrO_2) nanoparticle:

Wt %(SiO_2+ZrO_2)	**$\sigma_{ult.}$MPa.**
4	7.8
6	13.6
8	8.8
10	3.4

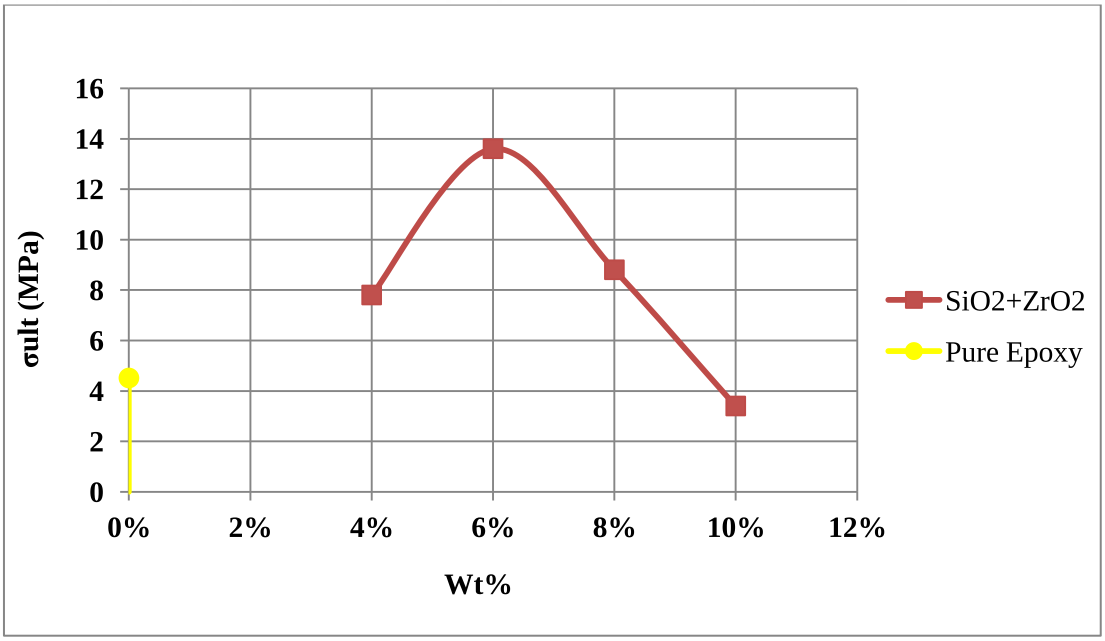


Fig. (4-3) Shows the effect of weight percentages of nanoparticles additives on tensile strength, (hybrid nanocomposite material).

4.3.2 Epoxy \($(SiO_2+ZrO_2+TiO_2)$ hybrid nanocomposite materials

Table (4-4) Shows the tensile strength at different percentage of (SiO_2+ZrO2+TiO_2) hybrid nanoparticle :

Wt % ($SiO_2+ZrO_2+TiO_2$)	**$\sigma_{ult.}$MPa.**
4	23.75
6	10.75
8	9.9
10	6.98

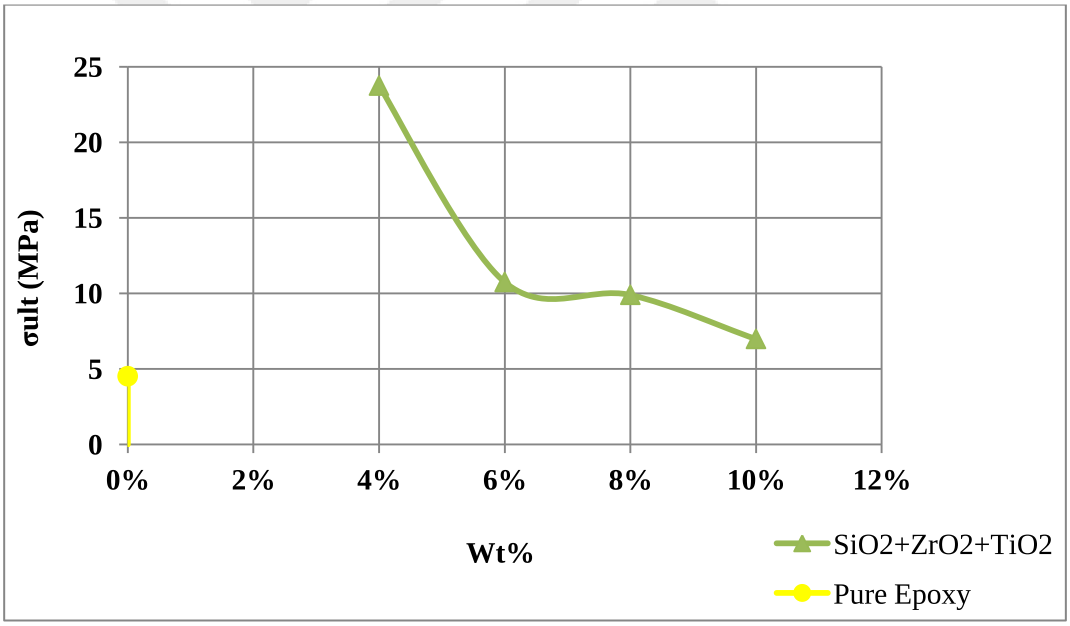


Fig. (4-4) Shows the effect of weight percentages of nanoparticles additives on tensile strength, (hybrid nanocomposite material).

Tables (4-3),(4-4) and figures (4-3), (4-4) show the effect of different percentage content of (SiO_2+ZrO_2) and ($SiO_2+ZrO_2+TiO_2$) nanoparticles reinforcement phase on the tensile strength.

In this case the addition of (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) nanoparticles reinforcement to epoxy matrix increases the tensile stress of hybrid nanocomposite materials until reaching the maximum value at 6wt % for (SiO_2+ZrO_2) and 4wt% for(SiO_2+ZrO_2+TiO_2) nanoparticles. Referred to strong interface between the phases that distributes and transfers the load from the matrix to the reinforcement resulted in tensile strength improvement. After maximum value the tensile strength decrease that may be an interaction between nanopartials may have occurred, with an increase in proportions, leading to adverse reactions.

Figure (4-5) show the best comparative condition at 4wt% (SiO_2+ZrO_2+TiO_2) that it given maximum tensile strength in less additives of nanoparticles.

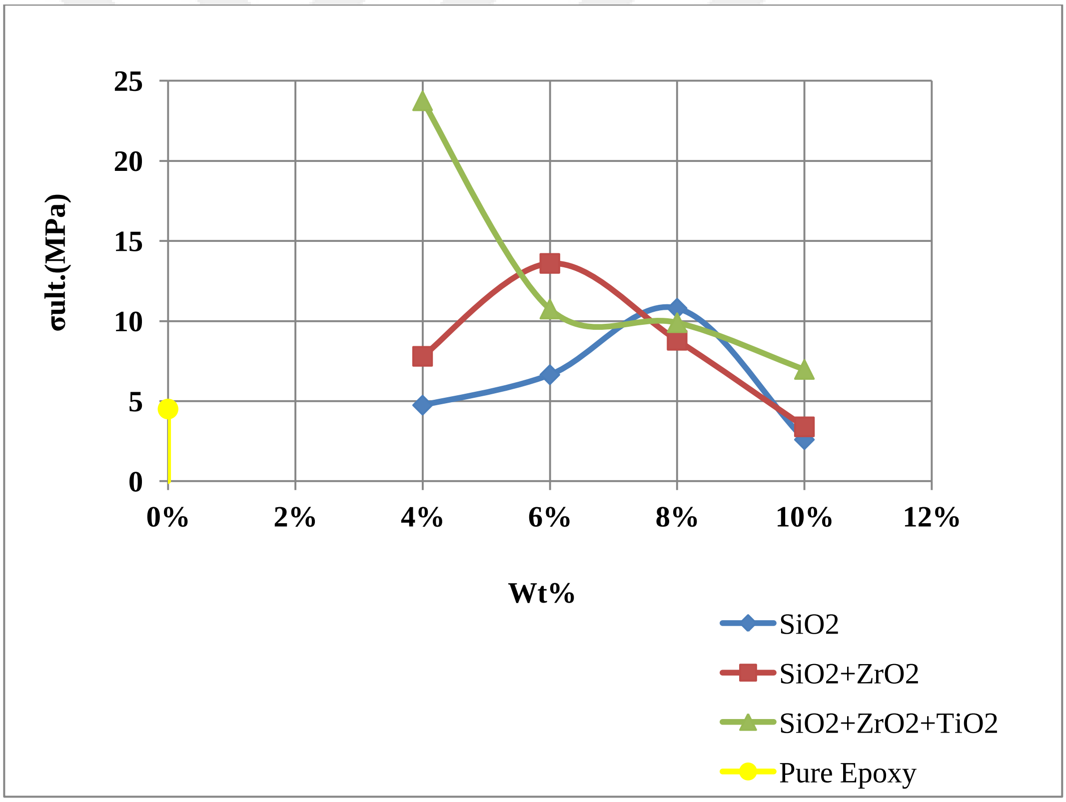


Fig. (4-5) the relationship between tensile strength and wt% of nanopartical

4.4 Hardness Results of Nanocomposite Materials

The hardness of specimen prepared at different wt% of TiO_2 and SiO_2 were evaluated.Tables (4-5), (4-6) below shows the experimental observations of the Nano composites with different TiO_2 and SiO_2 nanoparticle.An average hardness was calculated using average of three random indents in each specimen. There was a gradual increase in hardness from 2 wt% to 8 wt% of TiO_2, and from 4 wt% to 8 wt% of SiO_2.

4.4.1 Epoxy\TiO_2 nanoparticles

Table (4-5) Shows the hardness values at different percentage of TiO_2 nanoparticle Pure, Epoxy hardness=67.2 Kg.f\mm^2 (Chines origin).

Wt% TiO_2	**Hardness.kg.f/mm^2**
2	61.4
4	73.1
6	114.3
8	118.5

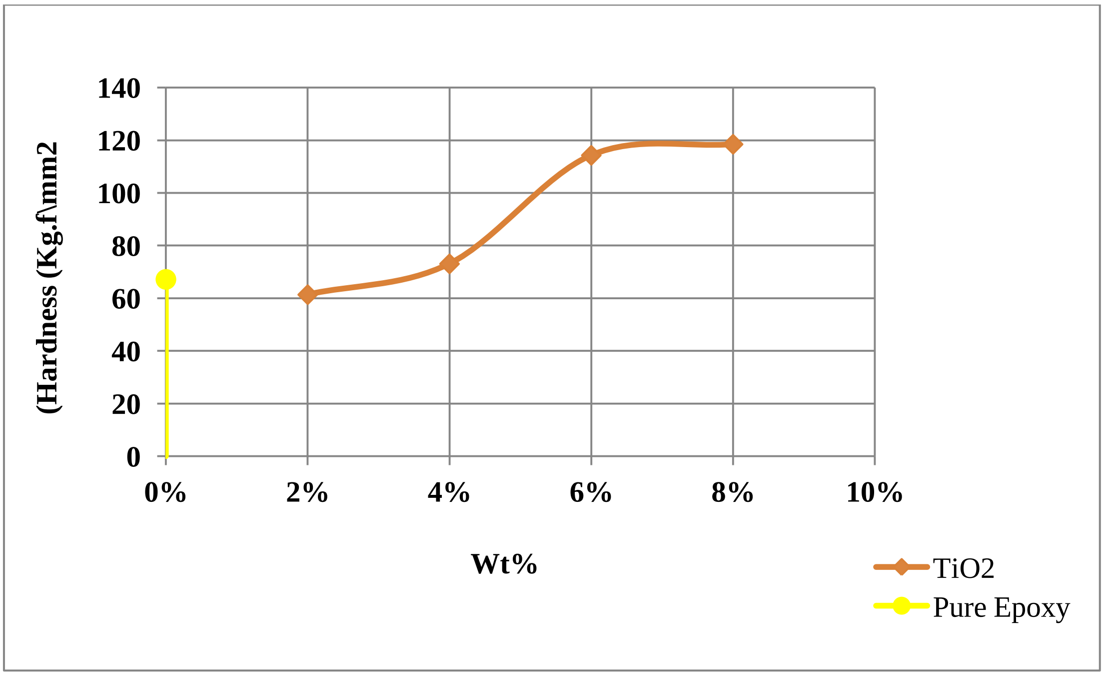


Fig. (4-6) Shows the effect of weight percentages of nanoparticles additives on the hardness.

4.4.2 Epoxy\SiO$_2$ nanoparticle

Table (4-6) Shows the hardness values at different percentage of SiO$_2$ nanoparticle, Epoxy Pure : 76.2 Kg.f\mm^2 (American origin).

Wt% SiO$_2$	Hardness.Kg.f/mm^2
4	78.1
6	79
8	80.2
10	79.2

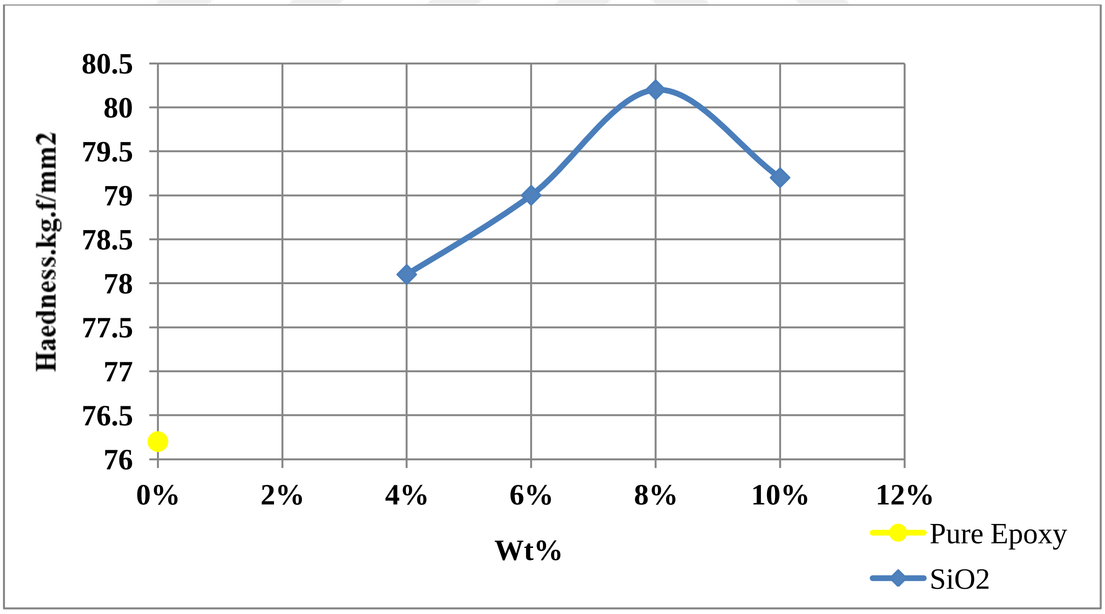


Fig.(4-7) Shows the effect of weight percentages of nanoparticles additives on hardness

The hardness of nanocomposite in general depends on the hardness value of matrix and the reinforcement according to the rule of matrix. Figures (4-6), (4-7) shows that the hardness of nanocomposite increase with the increase of weight percentage of (TiO_2), (SiO_2) nanoparticle, higher hardness value of nanocomposite materials might have contributed this increase. Also, this may be due to the increase in volume fraction of hard reinforcement phase, thus the resistance of dislocation movement increase. further, the strain energy increase at the sites of reinforcing particles dispersion in the epoxy matrix which lead to increase the hardness until it reaches to the maximum value at 8 wt % SiO_2 nanoreinforcement . Hardness is an important mechanical property used as indicator of plastic deformation resistance, often considered in design mechanical components.

4.5 Hardness Results of Hybrid Nanocomposite Materials

The hardness of specimen prepared at different weight percentage of (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) at (4, 6, 8, 10 wt%) and SiO_2 were evaluted. Tables (4-7), (4-8) below shows the experimental observations of the Hybrid Nano composites with different SiO_2, ZrO_2, TiO_2 contents. An average hardness was calculated using average of three random indents in each specimen.

4.5.1 Epoxy\ (SiO_2+ZrO_2) hybrid nanocomposite materials

Table (4-7) Shows the hardness values at different percentage of (SiO_2+ZrO_2) nanoparticle.

Wt%(SiO_2+ZrO_2)	**Hardness.Kg.f/mm^2**
4	79.3
6	82
8	80.4
10	79.6

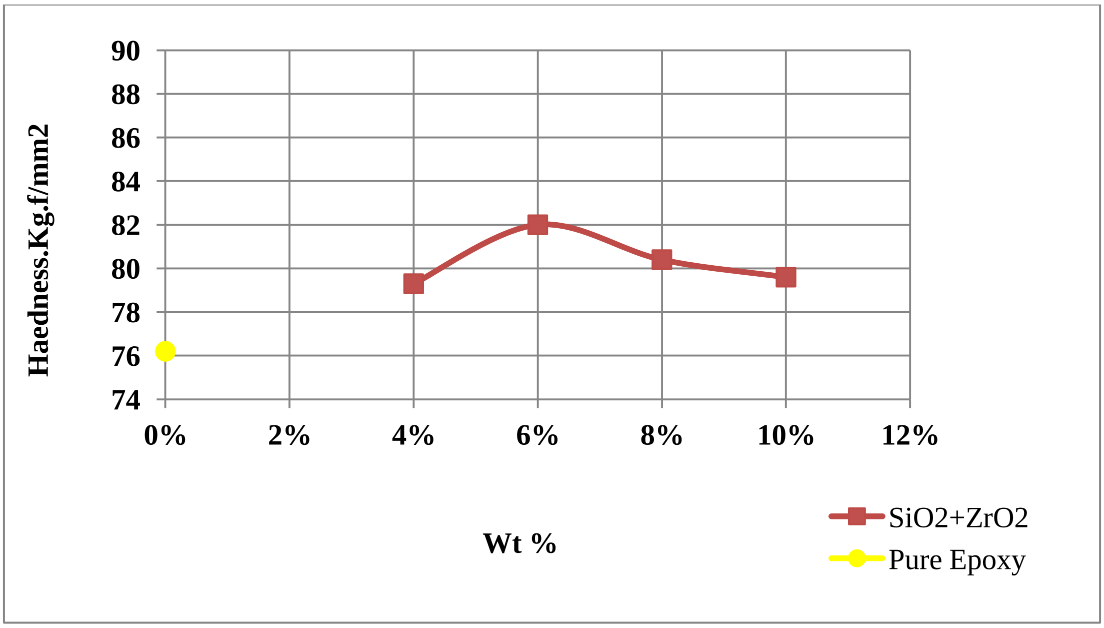


Fig. (4-8) Shows the effect of weight percentages of nanoparticles additives on the hardness, (hybrid nanocomposite material).

4.5.2 Epoxy\ (SiO_2+ZrO_2+TiO_2) hybrid nanocomposite materials

The effect of (SiO_2+ZrO_2+TiO_2) wt% on the hardnees may be shown on the table (4-8).

Table (4-8) the hardness values at different percentage of (SiO_2+ZrO_2+TiO_2) nanoparticle

Wt% SiO_2+ZrO_2+TiO_2	**Hardness.Kg.f/mm^2**
4	84.1
6	82
8	80.2
10	79.6

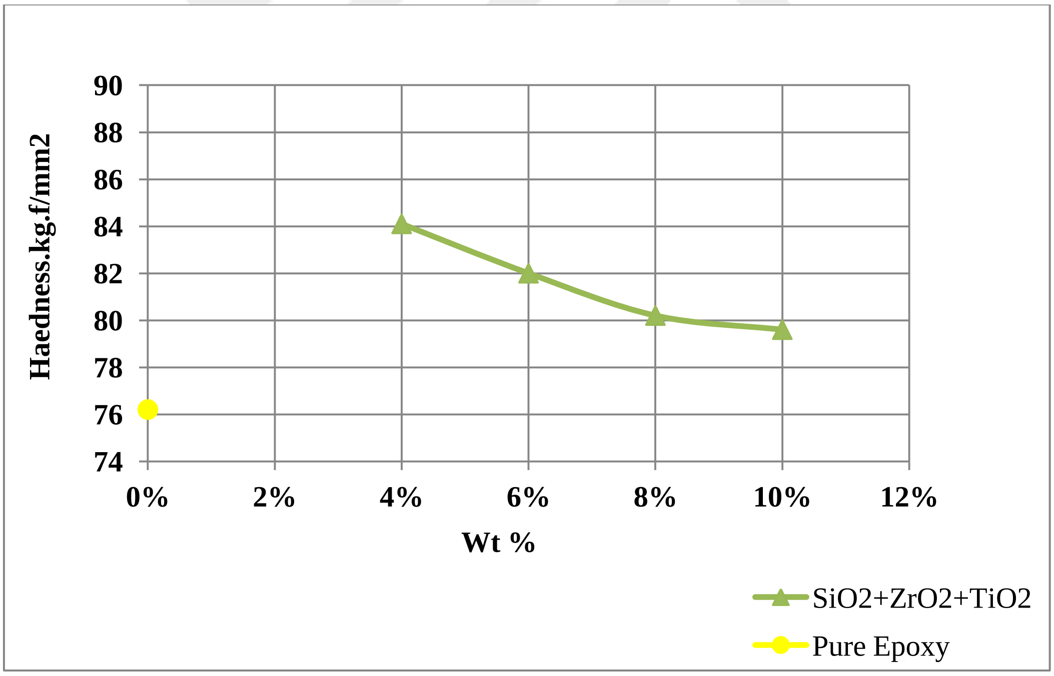


Fig. (4-9) Shows the effect of weight percentages of nanoparticles additives on the hardness, (hybrid nanocomposite material).

There was a gradual increase in hardness from 4 wt% to 6 wt% of (SiO_2+ZrO_2), and the maximum value of the hardness at 4 wt% of (SiO_2+ZrO_2+TiO_2) . The decrease is due to the possibility that increasing the ratios of nanoparticle leads to a conglomerate and distribution of heterogeneous and soften the mixture.

Figure (4-10) show the best comparative condition at 4wt% (SiO_2+ZrO_2+TiO_2) that it given maximum hardness in less additives of nanoparticles.

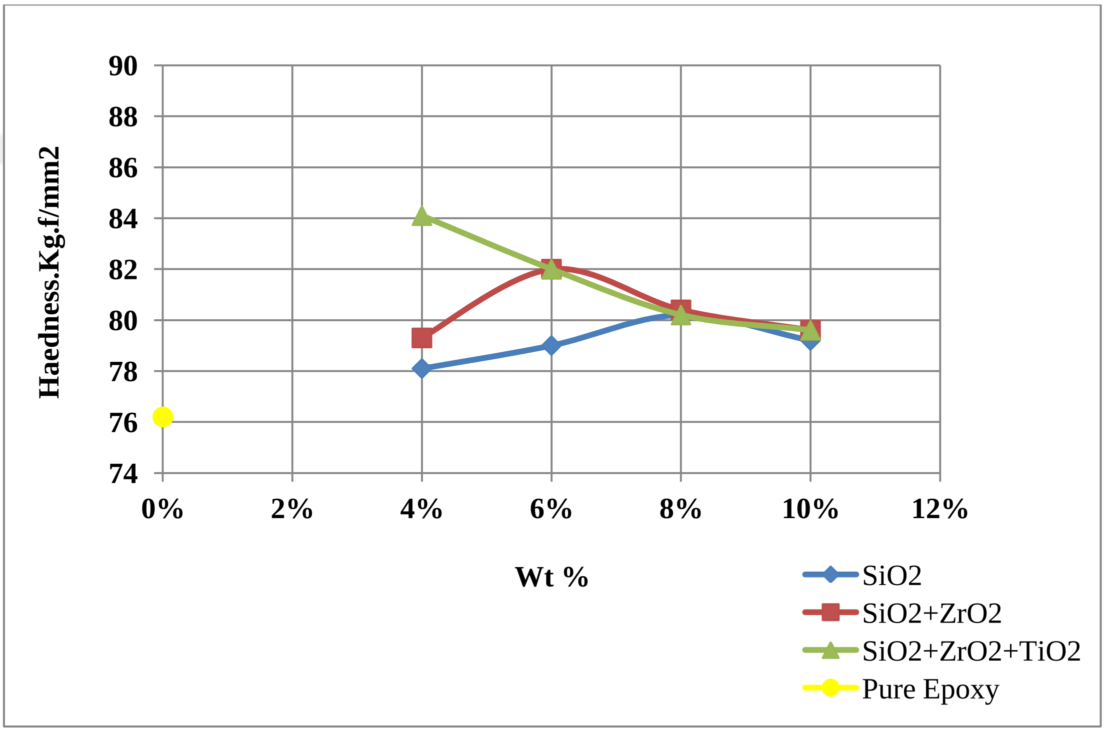


Fig. (4-10) the relationship between the hardness and wt% nanoparticles.

4.6 Impact Strength Results of Nanocomposite material

4.6.1 Epoxy\SiO$_2$ Nanocomposite Material

The impact strength of specimen prepared at different wt% of SiO$_2$ were evaluated. Table (4-9) and figure (4-11) below show the experimental observations of the nanocomposites with (4, 6, 8, 10) Wt % of SiO$_2$ nanoparticle, Impact strength of pure epoxy=0.15 J.

Table (4-9) Shows the impact strength at different percentage of SiO$_2$ nanoparticle

Wt% SiO$_2$	**Impact Strength(J)**
4	0.18
6	0.2
8	0.23
10	0.19

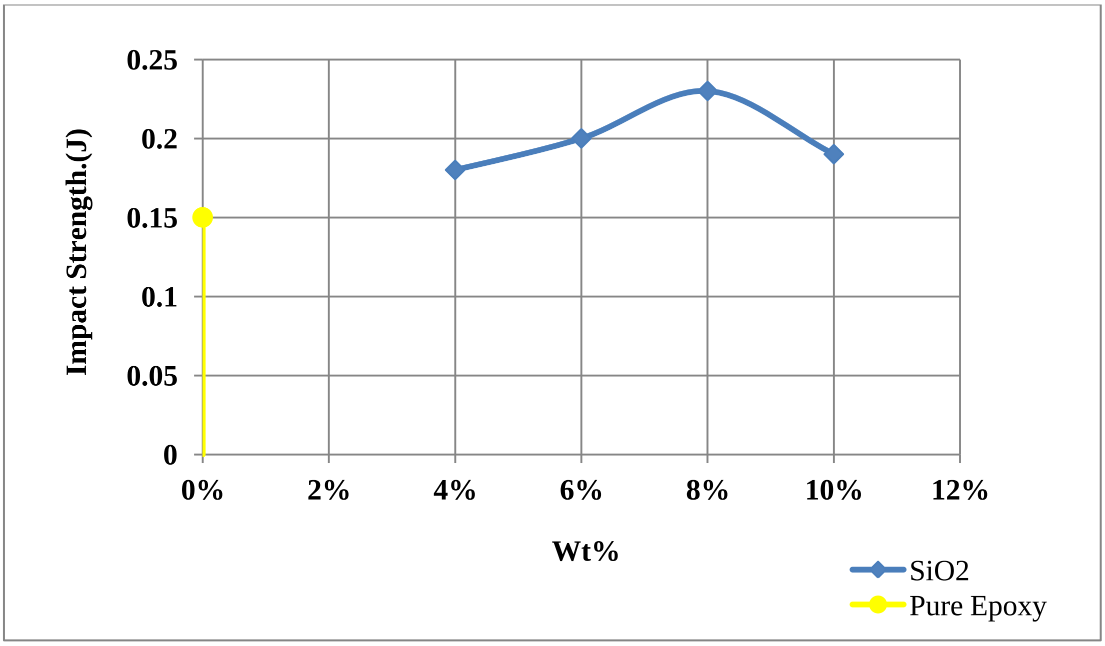


Fig. (4-11) Shows the effect of weight percentages of nanoparticles additives on impact strength.

Figure (4-11) shows the variation in impact strength as a function of the weight percentage of SiO_2 in the Epoxy. The addition of SiO_2 nanoparticle has a great effect on impact strength. At loading of 8 wt% an increase of (0.23 J), can be observed when compared with that of the original epoxy. However, at 10 wt % SiO_2, impact strength (0.19 J) decrease approximately to value given by the epoxy matrix (0.15 J). This variation can be explained in terms of nanocomposite Elongation.

It can be observed in figure (4-12) that the percentage at 10 wt% SiO_2 given maximum elongation , So due to decrease in the impact strength.

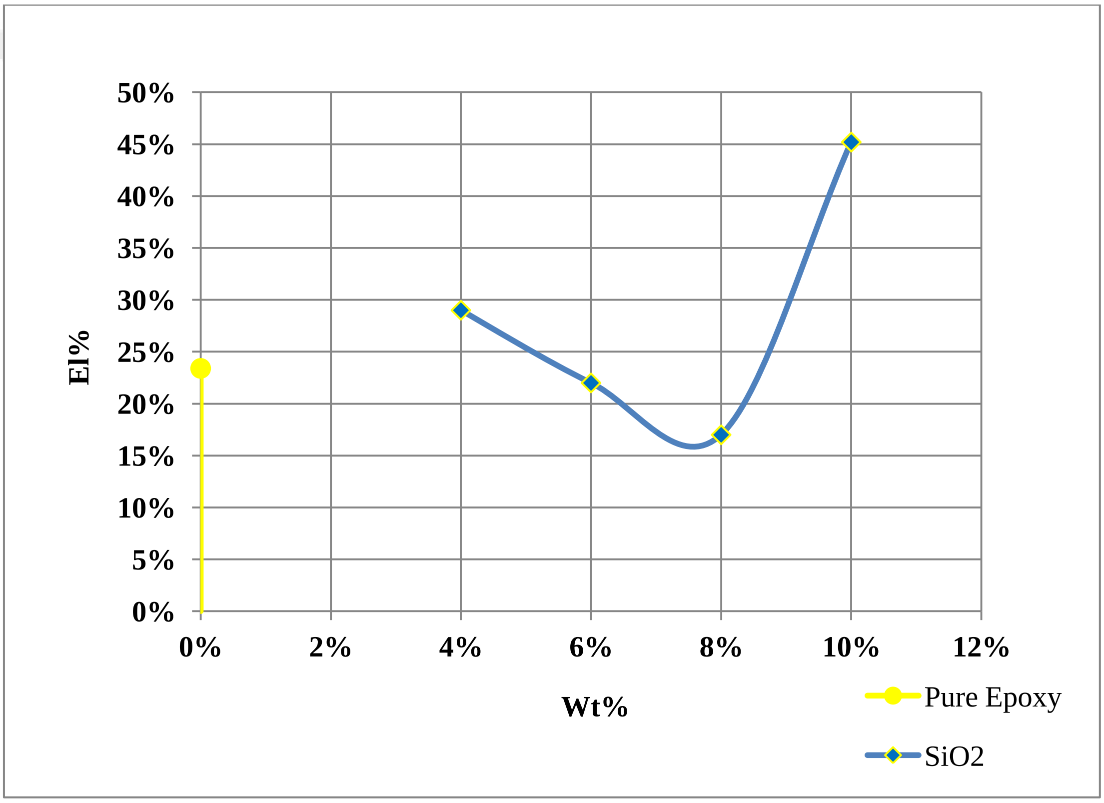


Fig. (4-12) Shows the effect of weight percentages of nanoparticles additives on Elongation percentage.

4.7 Impact Strength Results of Hybrid Nanocomposite Material

The impact strength of specimen prepared at different wt% of (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) were evaluated.

4.7.1 Epoxy\(SiO_2+ZrO_2) Hybrid Nanocomposite Material

below show the experimental observations of the nanocomposites with(4, 6, 8, 10) Wt % of (SiO_2+ZrO_2), impact strength Pure Epoxy=0.15 J

Table (4-10) Shows impact strength values at different percentage of (SiO_2+ZrO_2) nanoparticle:

Wt%(SiO_2+ZrO_2)	**Impact Strength(J)**
4	0.2
6	0.25
8	0.22
10	0.21

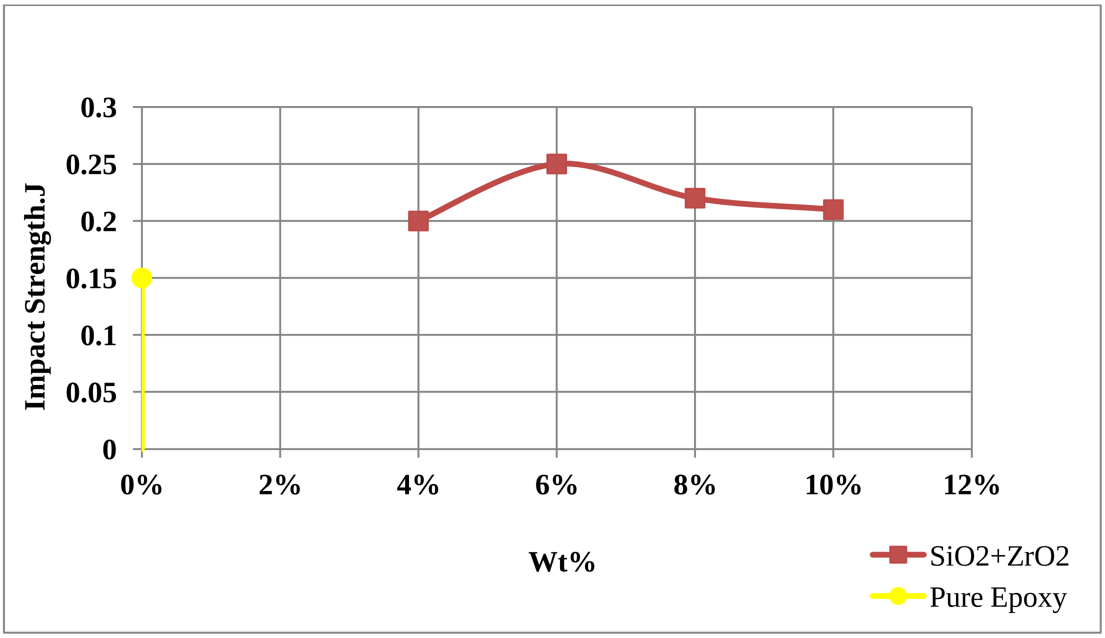


Fig. (4-13) Shows the effect of weight percentages of nanoparticles additives on impact strength, (hybrid nanocomposite material).

4.7.2 Epoxy\(SiO_2+ZrO_2+TiO_2) Hybrid Nanocomposite Material

Table (4-11) and figure (4-14) Shows the impact strength values at different percentage of (SiO_2+ZrO_2+TiO_2) nanoparticle:

Table (4-11) Shows impact strength values at different percentage of (SiO_2+ZrO_2+TiO_2) nanoparticle:

Wt%(SiO_2+ZrO_2+TiO_2)	**Impact Strength(J)**
4%	0.25
6%	0.23
8%	0.2
10%	0.18

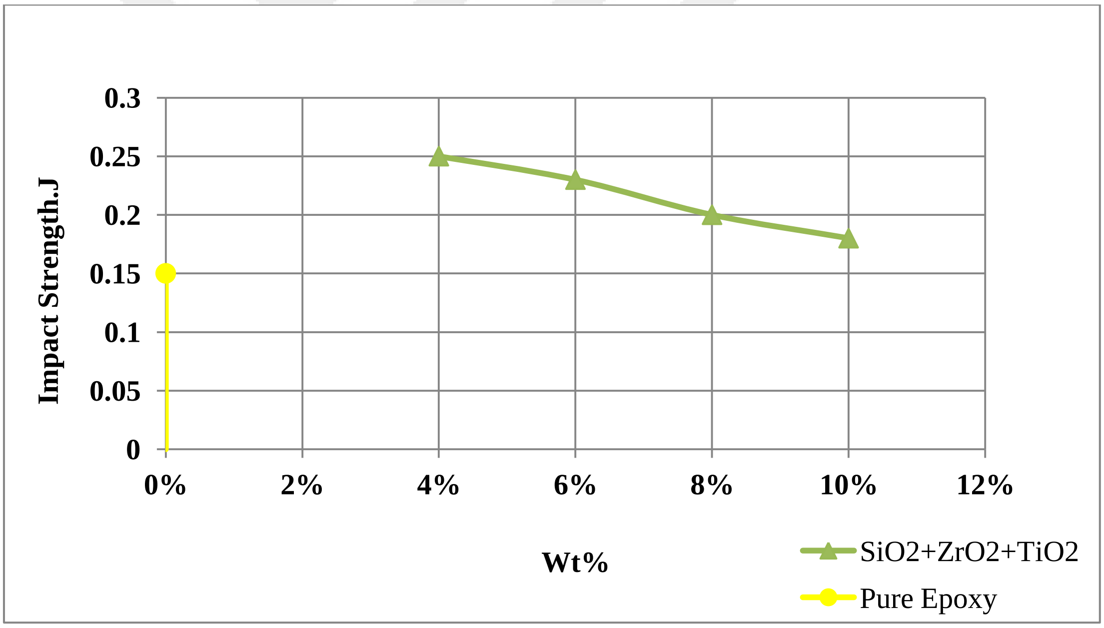


Fig. (4-14) Shows the effect of weight percentages of nanoparticles additives on impact strength, (hybrid nanocomposite material).

Figures (4-13),(4-14) shows the variation in impact strength as a function of the weight percentage of (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) in the Epoxy. The addition of nanoparticle has a great effect on impact strength. At loading of 6 wt% (SiO_2+ZrO_2) an increase of (0.25 J), can be observed when compared with that of the original epoxy.

However, at 8, 10 wt %,(SiO_2+ZrO_2) impact strength (0.22, 0.21 J) respectively, decrease approximately to value given by the epoxy matrix (0.15 J). This variation can be explained in terms of hybrid nanocomposite elongation.

It can be observed in figure (4-15) that the percentage at 8, 10 wt% (SiO_2+ZrO_2), given high elongation(24%,25.5%),Also at percentage 6, 8, 10 wt%SiO_2+ZrO_2+TiO_2 So due to decrease in the impact strength, while pure epoxy=23.4%.

Table (4-12) Shows the elongation percentage values at different percentage of (SiO_2+ZrO_2) and (SiO_2+ZrO_2+TiO_2) nanoparticle:

Wt%	**El%(SiO_2+ZrO_2)**	**El%(SiO_2+ZrO_2+TiO_2)**
4	7.40%	8.80%
6	13%	15%
8	24%	16%
10	25.50%	18.60%

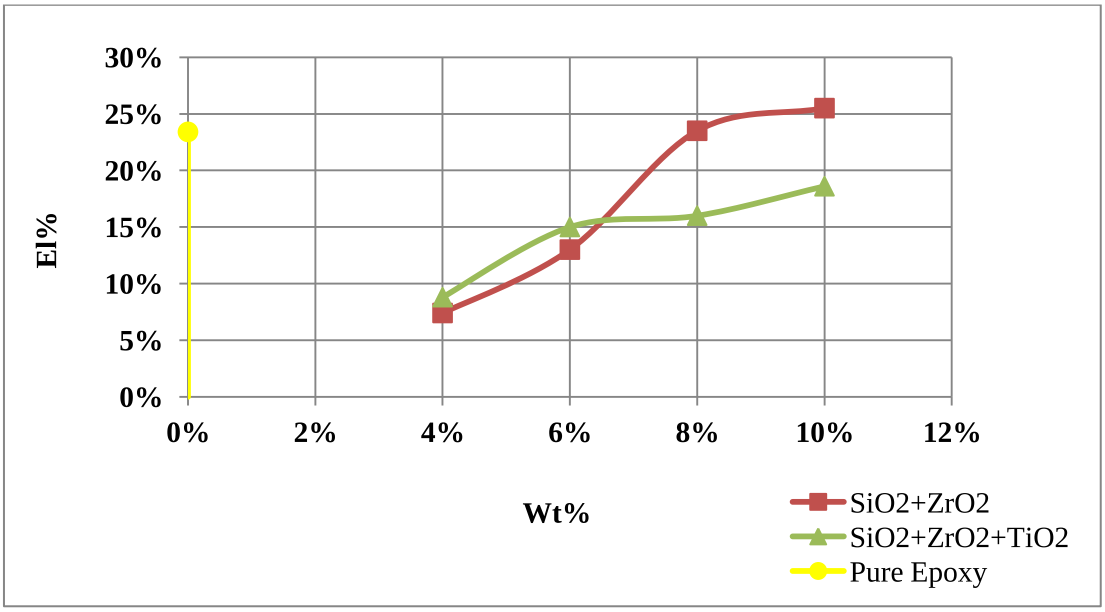


Fig. (4-15) Shows the effect of weight percentages of nanoparticles additives on elongation percentage, (hybrid nanocomposite material).

Figure (4-16) show the best comparative condition at 4wt% (SiO_2+ZrO_2+TiO_2) that it given maximum impact strength in less additives of nanoparticles.

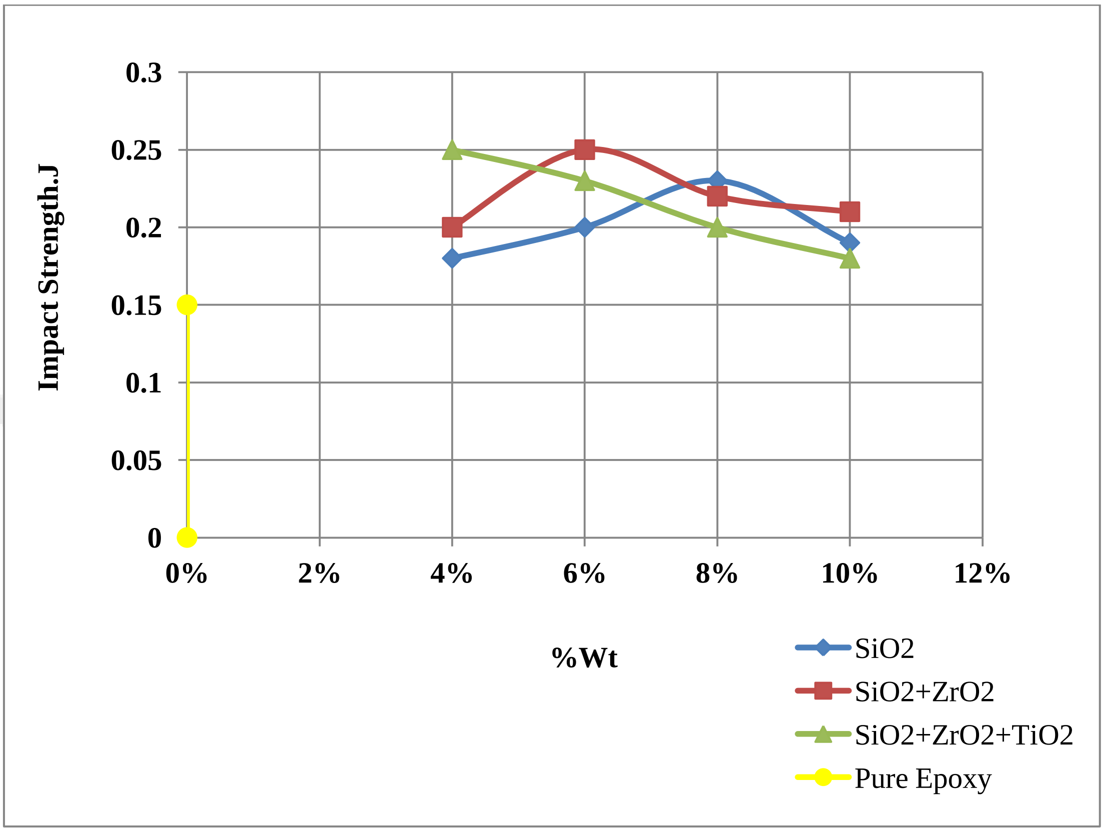


Fig. (4-16) the relationship between impact strength and wt% of nanopartical.

4.8 Fourier Transforms Infrared Spectroscopy (FTIR) Analysis Results

Figures (4-17) and (4-18) below are the FTIR spectra of Epoxy and Epoxy/SiO_2-TiO_2 hybrid nanocomposite material. The hydroxyl-stretching band of epoxy resin appears at 3507 cm^{-1} and oxirane absorption at 915 cm^{-1}.

There is the absorption peak at 3402 cm^{-1} (characteristic of –OH stretching, which is the unreactive Ti OH or Si OH groups in inorganic networks)and1108 cm^{-1} (Si O C). And there also was the broad absorption at lower wavenumber region. Especially 1100–920 cm^{-1} (characteristic of Si O Si and Si O Ti networks) at 900– 450 cm^{-1} due to Ti O Ti linkage in the titania matrix. The peak at 952 cm^{-1} is attributed to Si O Ti bonds.

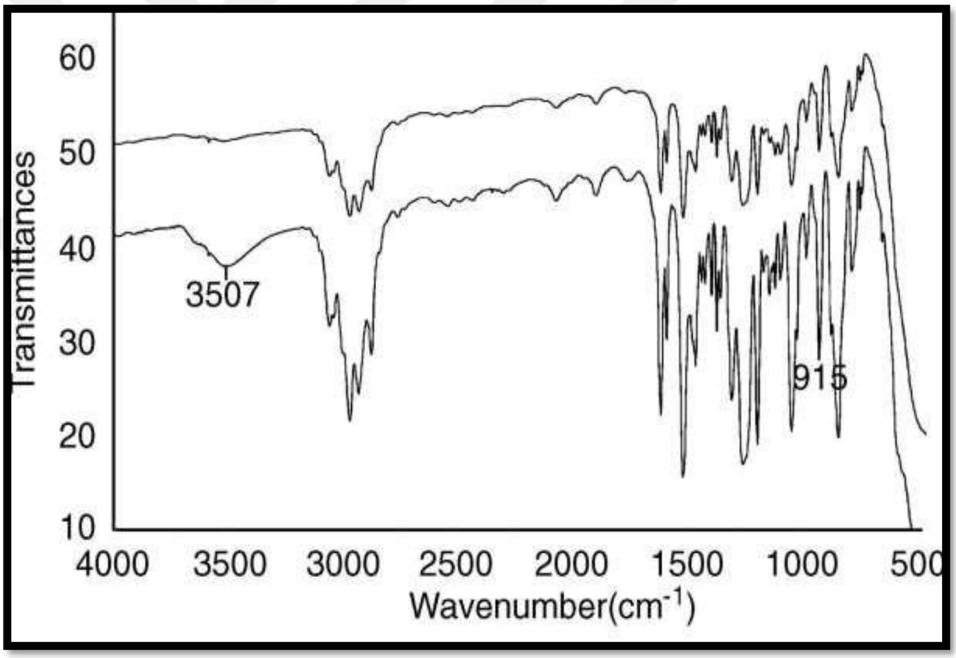


Fig. (4-17) Shows the FTIR Spectra of Pure Epoxy Matrix

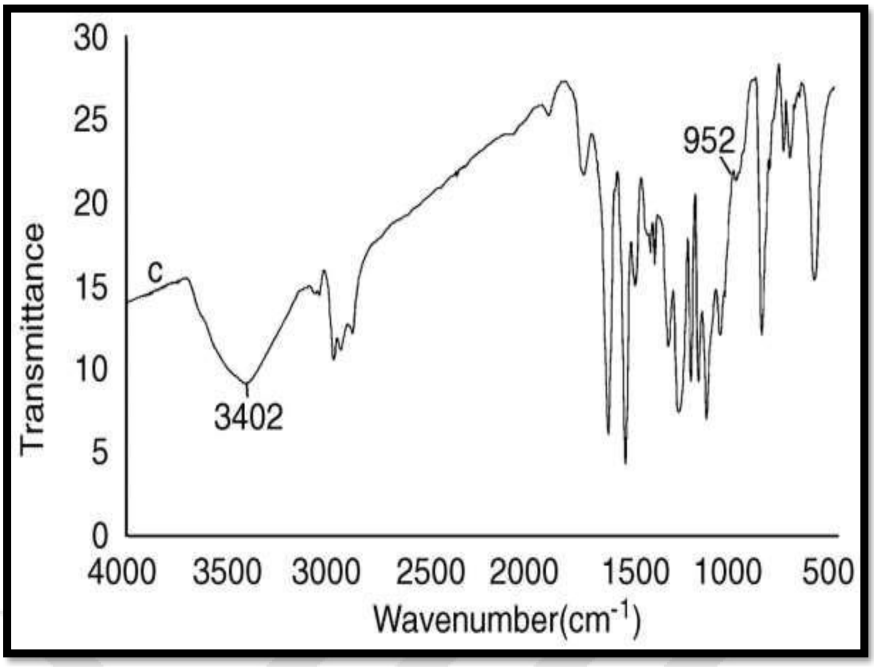


Fig. (4-18) Shows the FTIR Spectra of Epoxy/SiO_2-TiO_2 hybrid nanocomposite material.

SiO_2-TiO_2 nanoparticles can significantly improve mechanical properties of the composites, which contain an optimum amount of nanoparticles. The tensile strength are almost 2–3 times as much as that of the pure epoxy resin. The mechanism for this improvement is ascribed to increase the interfacial strength between nanoparticles and epoxy matrix through chemical bonding. When the material is subjected to tensile test, the epoxy/SiO_2-TiO_2 composites have generated micro phase separated for introducing of the SiO_2-TiO_2 particles, which may induce to crack propagation, and resulted in the performance of the epoxy/SiO_2-TiO_2 composites improved.

4.9 Atomic Force Microscope (AFM) Results

Atomic Force Microscope (AFM) surface image of hybrid Nano composite material, the surface topography structure of the hybrid film (SiO_2-TiO_2 content) is characterized by AFM. The film thickness is about 20 nm, the scan area is 3 µm × 3 µm. From the micrograph, it can be seen that the SiO_2-TiO_2 particle size is about 20–50 nm, this indicates that SiO_2-TiO_2 “composite” particles is homogeneously and well disperse in the hybrid material matrix as shown in the figure (4-19) and figure (4-20).

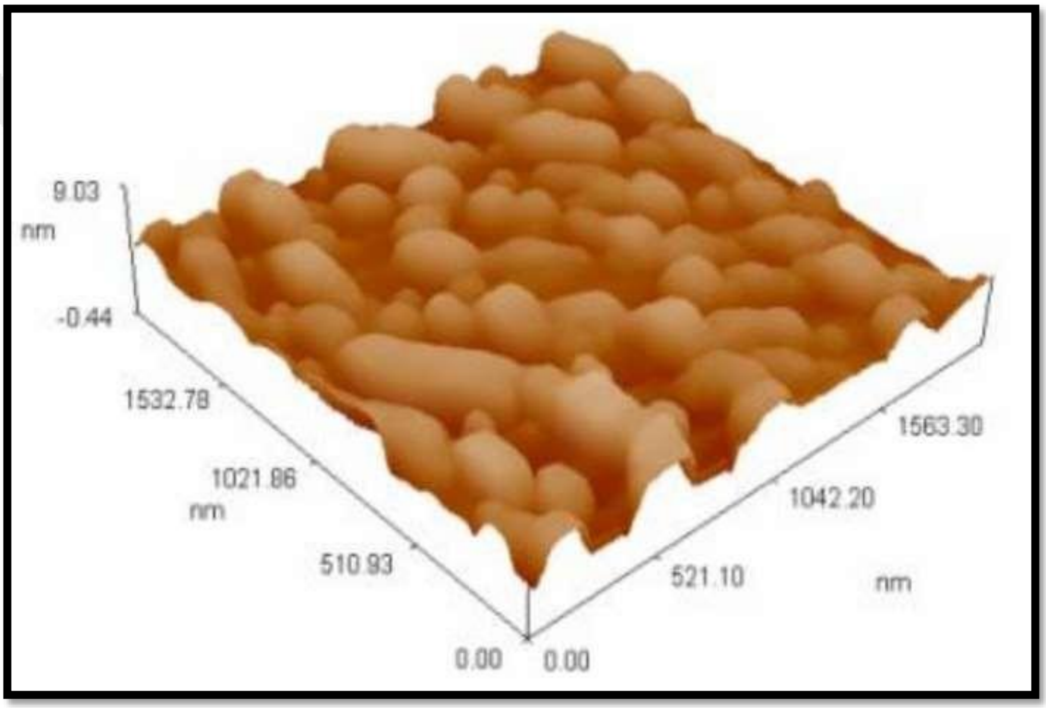


Fig. (4-19) AFM micrograph shows uniformity and a three-dimensional surface profile of TiO_2 nanospheres in the epoxy nanocomposite

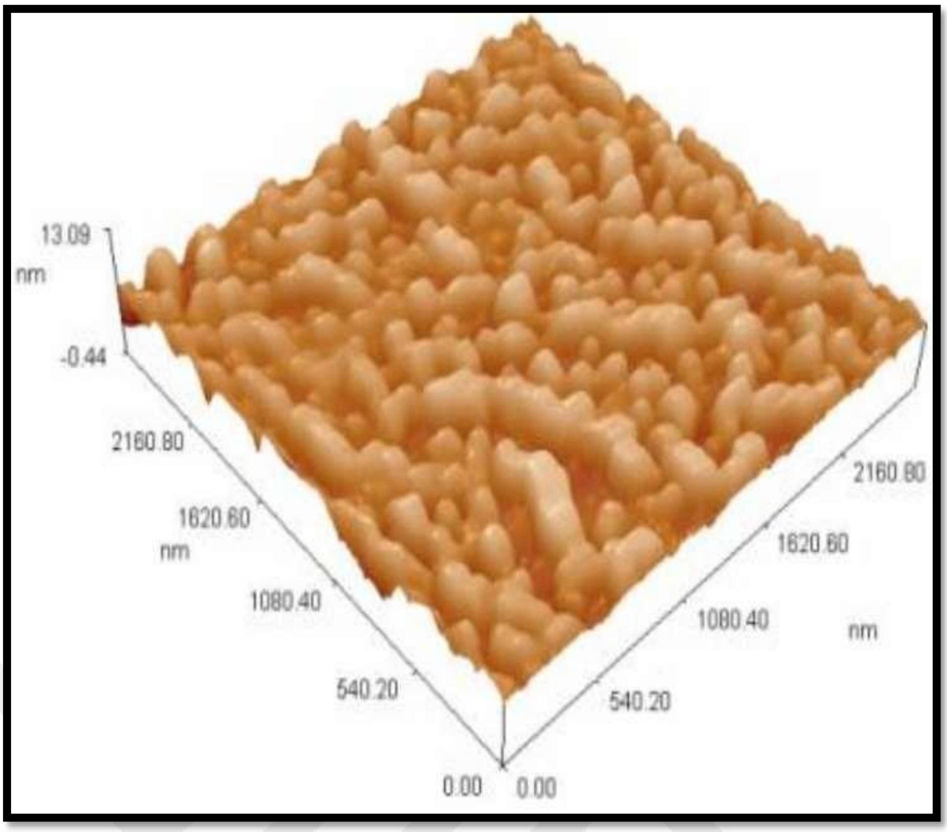


Fig. (4-20) AFM micrograph shows uniformity and a three-dimensional surface profile of SiO_2 nanospheres in the epoxy nanocomposite

Chapter Five

Conclusions and Suggestions For Future Work

5.1 Conclusions

The conclusions may be drawn from the present research work are as following:-

1- Present work successful with manufacturing and synthesize new nanocomposite and hybrid nanocomposite material by combination of different types of material; epoxy based matrix and nanoparticle (TiO_2,ZrO_2&SiO_2) as a reinforcement material.

2- Tensile strength of nanocomposite material increased gradually with increase (wt%) of TiO_2 nanoparticles from 2wt% to 8wt % TiO_2 , while the best tensile strength was at 8wt% TiO_2 .

3- Tensile strength of nanocomposite material increased gradually with increase (wt%) of SiO_2 nanoparticles from 4wt% to 8wt % SiO_2 ,while the best tensile strength was at 8wt% SiO_2 .

4- The hardness increases gradually with increasing(wt%) of TiO_2 nanoparticles from 2wt% TiO_2 to 8wt% TiO_2, so the maximum value of the harness was at 8wt % TiO_2.

5- The hardness increases gradually with increasing(wt%) of SiO_2 nanoparticles from 4wt% SiO_2 to 8wt% SiO_2, After that decrease at 10wt% of SiO_2 so the maximum value of the harness was at 8wt % SiO_2.

6- The addition of ZrO_2 nanoparticles to the nanocomposite material (Epoxy+SiO_2) in order to synthesize new hybrid Nano composite material resulted in increase in tensile strength from 4wt % to 6wt % (SiO_2+ZrO_2). Also, that the hardness and impact value increase from 4wt% to 6wt% (SiO_2+ZrO_2).So, the maximum value of all these tensile properties at 6wt% (SiO_2+ZrO_2) .

7- The addition of TiO_2 nanoparticles to the hybrid nanocomposite material (SiO_2+ZrO_2) in order to synthesize new hybrid nanocomposite material resulted the maximum in tensile strength at 4wt % (SiO_2+ZrO_2+TiO_2) . Also, that the hardness and impact maximum value at 4wt% (SiO_2+ZrO_2+TiO_2).

8- The best condition was at 8wt% of (TiO2) and (SiO2) nanocomposite material, At 6wt% of (SiO2+ZrO2) hybrid nanocomposite material and 4wt% (SiO_2+ZrO_2+TiO_2) hybrid nanocomposite material.

9- FTIR confirmed the formation of a charge transfer complex between the TiO_2 and SiO_2 nanoparticles 900→450 cm^{-1} and 952 cm^{-1} respectively.

10- Atomic Force Microscope images have been showed that the SiO_2 – TiO_2 particles size was about 20 – 50 nm , this indicates that TiO_2 – SiO_2 hybrid nanocomposite particles are homogenously and well disperse in the epoxy matrix.

5.2 Suggestion For Future Works

1- Synthesize advanced hybrid nanocomposite materials using different nanoparticles (TiN , SiC , WC , MgO)

2- Study the effect of nanoparticles (CeO, ZnO, Al_2O_3,WC, TiC, TiN, and SiC) on the microstructure and mechanical properties of hybrid nanocomposite materials.

3- Study the effect of nanoparticles size and weight percentage on the mechanical properties of hybrid nanocomposite.

4- Study the wear characteristics of polymer based hybrid nanocomposite materials.

5- Fatigue characteristics evaluation of polymer based nanocomposite materials.

6- Evaluation of fracture toughness of hybrid nanocomposite materials using Finite Element Method (FEM) and Design Of Experiment (DOE) technique.

References

[1] R. Hofmann, B. Ackert, C. Collins, R. Meirowitz, and T. Dylan, "Structural and other composite materials and methods for making same," ed: Google Patents, 2005.

[2] S. Peters, "Reuse and Disposal, Handbook of Composites," ed: Chapman & Hall, London, 1998.

[3] M. C. Roco, C. A. Mirkin, and M. C. Hersam, Nanotechnology research directions for societal needs in 2020: retrospective and outlook vol. 1: Springer Science & Business Media, 2011.

[4] J. V. Carstensen, P.-A. Lindgård, and R. K. Feidenhans'l, "Materials Research Department annual report 2001," 8755029892, 2002.

[5] K. Ariga, H. Kroto, and P. O'Brien, Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics: Royal Society of Chemistry, 2012.

[6] L. Kouwenhoven and C. Marcus, "Quantum dots," Physics World, vol. 11, p. 35, 1998.

[7] S. Tjong and H. Chen, "Nanocrystalline materials and coatings," Materials Science and Engineering: R: Reports, vol. 45, pp. 1-88, 2004.

[8] D. Redfield, "Transport properties of electrons in energy band tails," Advances in Physics, vol. 24, pp. 463-487, 1975.

[9] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, and A. K. Bhowmick, "A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites," Progress in polymer science, vol. 36, pp. 638-670, 2011.

[10] L. W. Hankla, "Mechanical properties of particulate-reinforced boron carbide composites," 2008.

[11] P. J. Borm and D. Berube, "A tale of opportunities, uncertainties, and risks," Nano Today, vol. 3, pp. 56-59, 2008.

[12] T. Mizutani, K. Arai, M. Miyamoto, and Y. Kimura, "Application of silica-containing nano- composite emulsion to wall paint: a new environmentally safe paint of high performance," Progress in Organic Coatings,Vol. 55, pp. 276-283, 2006.

[13] N. S. Allen, M. Edge, J. Verran, J. Stratton, J. Maltby, and C. Bygott, "Photocatalytic titania based surfaces: environmental benefits," Polymer Degradation and Stability, Vol. 93, pp. 1632-1646, 2008.

[14] L. Zan, L. Tian, Z. Liu, and Z. Peng, "A new polystyrene–TiO $_2$ Nano composite film and its photocatalytic degradation," Applied Catalysis A: General, vol. 264, pp. 237-242, 2004.

[15] N. Nakayama and T. Hayashi, "Preparation and characterization of poly (l-lactic acid)/TiO 2 nanoparticle Nano composite films with high transparency and efficient photo degradability," Polymer degradation and stability, Vol. 92, pp. 1255-1264, 2007.

[16] R. Mosurkal, L. A. Samuelson, K. D. Smith, P. R. Westmoreland, V. S. Parmar, F. Yan, et al., "Nano composites of TiO 2 and Siloxane Copolymers as Environmentally Safe Flame- Retardant Materials†," Journal of Macromolecular Science, Part A, Vol. 45, pp. 942-946, 2008.

[17] A. Kubacka, C. Serrano, M. Ferrer, H. Lünsdorf, P. Bielecki, M. L. Cerrada, et al., "High- performance dual-action polymer-TiO2 nanocomposite films via melting processing," Nano Letters,Vol. 7, pp. 2529-2534, 2007.

[18] X. D. Chen, Z. Wang, Z. F. Liao, Y. L. Mai, and M. Q. Zhang, "Roles of anatase and rutile TiO 2 nanoparticles in photooxidation of polyurethane," Polymer Testing,Vol. 26, pp. 202-208, 2007.

[19] L.-Y. Hsu and H.-M. Chein, "Evaluation of nanoparticle emission for TiO2 nanopowder coating materials," in Nanotechnology and occupational health, ed: Springer, 2006, pp. 157- 163.

[20] Kaegi R, Ulrich A, Sinnet B, Vonbank R, Wichser A, Zuieeg S, Simmler H, Burkhardt M, Boller M, Boller M. "Synthetic TiO$_2$ nanoparticle emission from exterior facades into the aquatic environment." Environ Pollut.156:233-239.2008

[21] G. D. Shaffer, "An archaeomagnetic study of a wattle and daub building collapse," Journal of Field Archaeology, Vol. 20, pp. 59-75, 1993.

[22] О. Л. Становський, О. Ю. Лєбедєва, А. Ш. О. М. Алі, О. М. Красножон, and П. С. Швець, "A computer-aided design technology for manufacturing rubber and metal products," Eastern- European Journal of Enterprise Technologies, Vol. 5, pp. 23-28, 2015.

[23] J. Lemay, "Ego Depletion and Boredom: Does Boredom Compromise Future Acts of Self- control?," 2013.

[24] S. Kalia, B. Kaith, and I. Kaur, Cellulose fibers: bio-and nano-polymer composites: green chemistry and technology: Springer Science & Business Media, 2011.

[25] H. Y. Atay, "Multi-functional materials for military aircrafts; radar absorbing and flame retardant composites," 2016.

[26] F. L. Matthews and R. D. Rawlings, Composite materials: engineering and science: Elsevier, 1999.

[27] D. Gay, Composite materials: design and applications: CRC press, 2014.

[28] L. Utracki, M. Sepehr, and E. Boccaleri, "Synthetic, layered Nano-particles for polymeric Nano composites (PNC's)," Polymers for advanced technologies, Vol. 18, pp. 1-37, 2007.

[29] E. J. Barbero, Introduction to composite materials design: CRC press, 2010.

[30] K. K. Chawla, Composite materials: science and engineering: Springer Science & Business Media, 2012.

[31] A. K. Senapati, A. Bhatta, S. Mohanty, P. Mishra, and B. Routra, "An extensive literature review on the usage of fly Ash as a reinforcing agent for different matrices," Int J InnovSci Mod Eng, Vol. 2, pp. 4-9, 2014.

[32] A. Mukhopadhyay, G. Raju, and B. Basu, "Ultra High Temperature Ceramics: Processing, Properties," MAX Phases and Ultra-High Temperature Ceramics for Extreme Environments, p. 49, 2013.

[33] P. K. Mallick, Fiber-reinforced composites: materials, manufacturing, and design: 2007.

[34] F. N. Cogswell, Thermoplastic aromatic polymer composites: a study of the structure, processing and properties of carbon fibre reinforced polyetheretherketone and related materials: Elsevier, 2013.

[35] A. K. Mohanty, M. Misra, and L. T. Drzal, Natural fibers, biopolymers, and biocomposites: 2005.

[36] J. Leng and A. k.-t. Lau, Multifunctional polymer Nano composites: CRC press, 2010.

[37] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, "Cellulose nanomaterials review: structure, properties and Nano composites," Chemical Society Reviews, Vol. 40, pp. 3941-3994, 2011.

[38] J. J. Watkins and T. J. McCarthy, "Polymer/metal Nano composite synthesis in supercritical CO2," Chemistry of Materials, Vol. 7, pp. 1991-1994, 1995.

[39] M. Sternitzke, "Structural ceramic Nano composites," Journal of the European Ceramic Society, Vol. 17, pp. 1061-1082, 1997.

[40] P. M. Ajayan, L. S. Schadler, and P. V. Braun, Nano composite science and technology: John Wiley & Sons, 2006.

[41] P.-C. Ma, N. A. Siddiqui, G. Marom, and J.-K. Kim, "Dispersion and functionalization of carbon nanotubes for polymer-based Nano composites: a review," Composites Part A: Applied Science and Manufacturing, Vol. 41, pp. 1345-1367, 2010.

[42] Y. Rao, S. Ogitani, P. Kohl, and C. Wong, "Novel polymer–ceramic Nano composite based on high dielectric constant epoxy formula for embedded capacitor application," Journal of Applied Polymer Science, Vol. 83, pp. 1084-1090, 2002.

[43] B. M. Novak, "Hybrid Nano composite materials—between inorganic glasses and organic polymers," Advanced Materials, Vol. 5, pp. 422-433, 1993.

[44] J. Gong, T. Zhou, D. Song, L. Zhang, and X. Hu, "Stripping voltammetric detection of mercury (II) based on a bimetallic Au− Pt inorganic− organic hybrid Nano composite modified glassy carbon electrode," Analytical chemistry, Vol. 82, pp. 567-573, 2009.

[45] E. P. Giannelis, "Polymer layered silicate Nano composites," Advanced materials, Vol. 8, pp. 29-35, 1996.

[46] A. B. Morgan and C. A. Wilkie, Flame retardant polymer Nano composites: John Wiley & Sons, 2007.

[47] A. Mohanty, M. Misra, and G. Hinrichsen, "Biofibres, biodegradable polymers and biocomposites: an overview," Macromolecular materials and Engineering, Vol. 276, pp. 1-24, 2000.

[48] Clement Sanchez, Beatriz Julian, Philippe Belleville, and Michael Popall,"Applications of hybrid
Organic-inorganic Nano composites, "Journal of materials chemistry, 15, 3559-3592, 2005

[49] S.-r. Lu, H.-l. Zhang, and X.-y. Wang, "Wear and mechanical properties of epoxy/SiO2-TiO2 composites," Journal of materials science, Vol. 40, pp. 2815-2821, 2005.

[50] Y. Yang, C. Lu, X. Su, and X. Wang, "Effects of emulsion sizing with nano-SiO_2 on interfacial properties of carbon fibers/epoxy composites," Journal of materials science, Vol. 42, pp. 6347-6352, 2007.

[51] F. Chowdhury, M. Hosur, and S. Jeelani, "Investigations on the thermal and flexural properties of plain weave carbon/epoxy-nanoclay composites by hand-layup technique," Journal of materials science, Vol. 42, pp. 2690-2700, 2007.

[52] Y. Zhou, F. Pervin, S. Jeelani, and P. Mallick, "Improvement in mechanical properties of carbon fabric–epoxy composite using carbon nanofibers," Journal of materials processing technology, Vol. 198, pp. 445-453, 2008.

[53] P. Kumar, "Investigation on the mechanical properties of TiO_2/SiO_2 epoxy hybrid Nano composites," THAPAR UNIVERSITY PATIALA, 2013.

[54] A. Thiagarajan, S. A. Prakash, A. Gilbert, and A. Govindaraj, "Mechanical Properties of Hybrid Glass Fibre/Epoxy Reinforced TiO2 Nano composites."

[55] C. Chen, R. S. Justice, D. W. Schaefer, and J. W. Baur, "Highly dispersed Nano silica–epoxy resins with enhanced mechanical properties," Polymer, Vol. 49, pp. 3805-3815, 2008.

[56] A. N. Kishore, S. Malhotra, and N. S. Prasad, "Failure analysis of multi-pin joints in glass fiber/epoxy composite laminates," Composite Structures, Vol. 91, pp. 266-277, 2009.

[57] T. Ogasawara, Y. Ishida, and T. Kasai, "Mechanical properties of carbon fiber/fullerene- dispersed epoxy composites," Composites Science and Technology, Vol. 69, pp. 2002-2007, 2009.

[58] S. U. Khan, A. Munir, R. Husain, and J.-K. Kim, "Fatigue damage behaviors of carbon fiber- reinforced epoxy composites containing Nano clay," Composites Science and Technology, Vol. 70, pp. 2077-2085, 2010.

[59] O. Asi, "An experimental study on the bearing strength behavior of Al 2 O 3 particle filled glass fiber reinforced epoxy composites pinned joints," Composite Structures, Vol. 92, pp. 354-363, 2010.

[60] A. Jumahat, C. Soutis, F. Jones, and A. Hodzic, "Fracture mechanisms and failure analysis of carbon fibre/toughened epoxy composites subjected to compressive loading," Composite structures, Vol. 92, pp. 295-305, 2010.

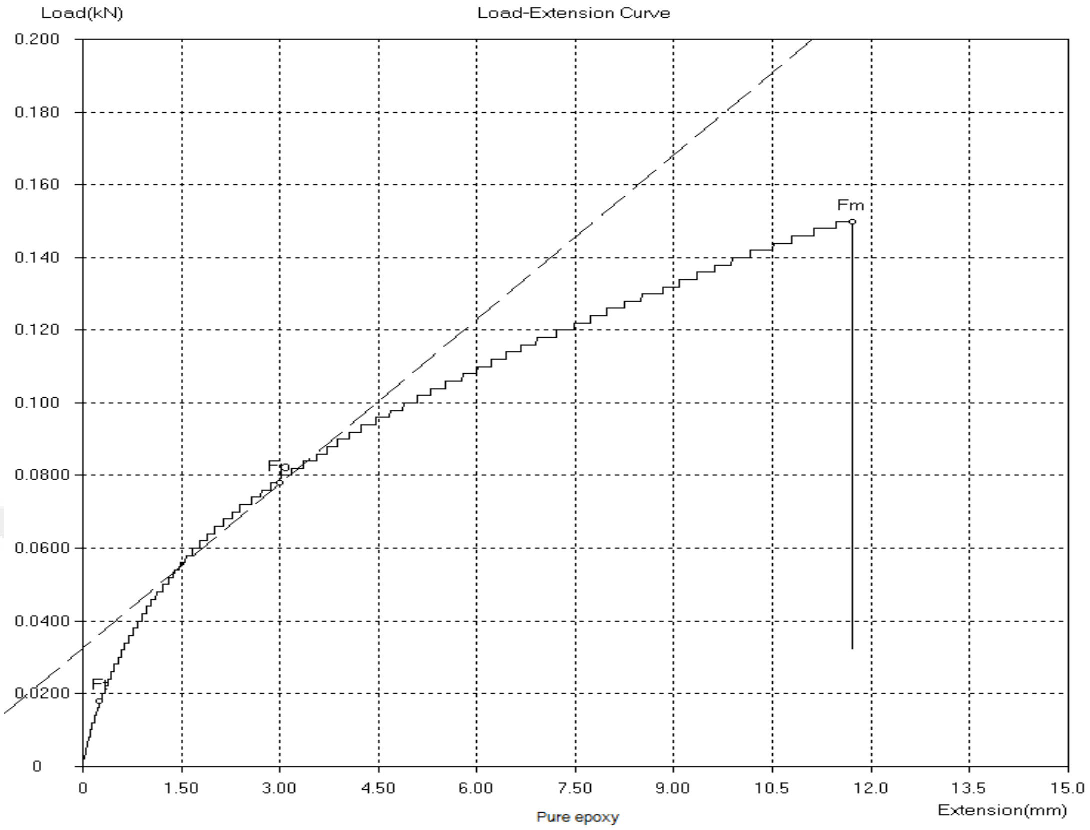
[61] S. U. Khan, K. Iqbal, A. Munir, and J.-K. Kim, "Quasi-static and impact fracture behaviors of CFRPs with Nano clay-filled epoxy matrix," Composites Part A: Applied Science and Manufacturing, Vol. 42, pp. 253-264, 2011.

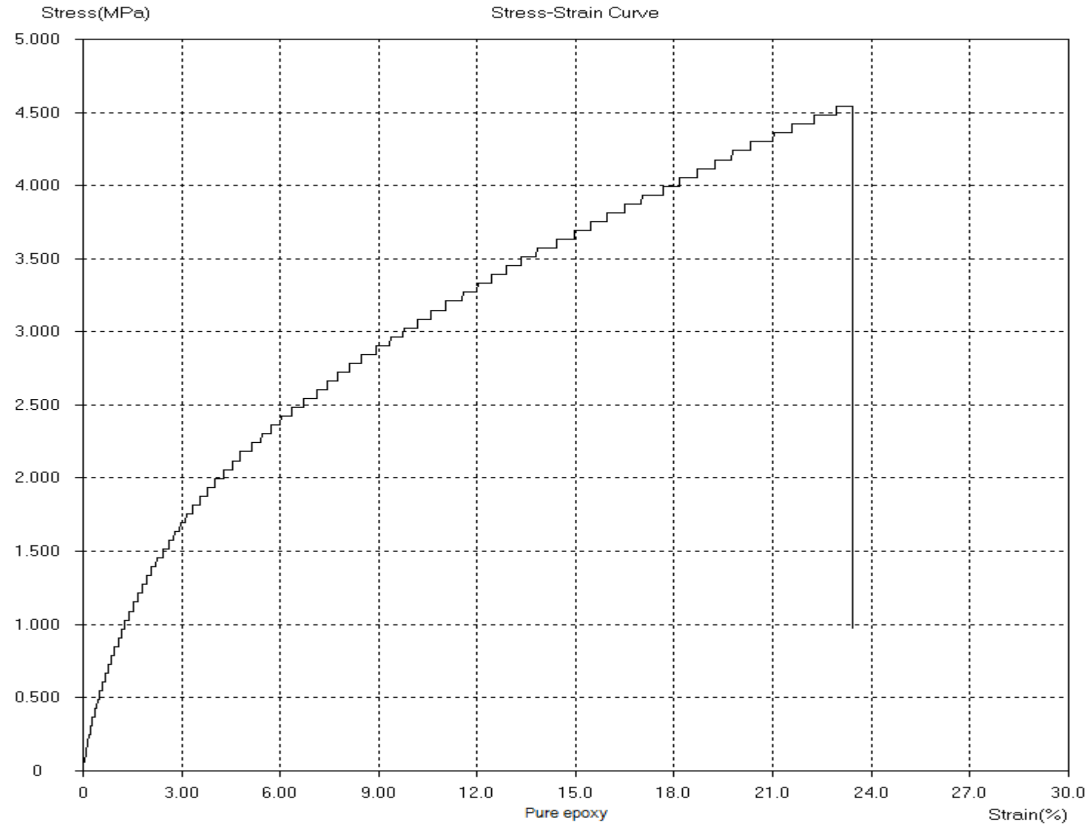
[62] Y. Zeng, H.-Y. Liu, Y.-W. Mai, and X.-S. Du, "Improving interlinear fracture toughness of carbon fiber/epoxy laminates by incorporation of Nano-particles," Composites Part B: Engineering, Vol. 43, pp. 90-94, 2012.

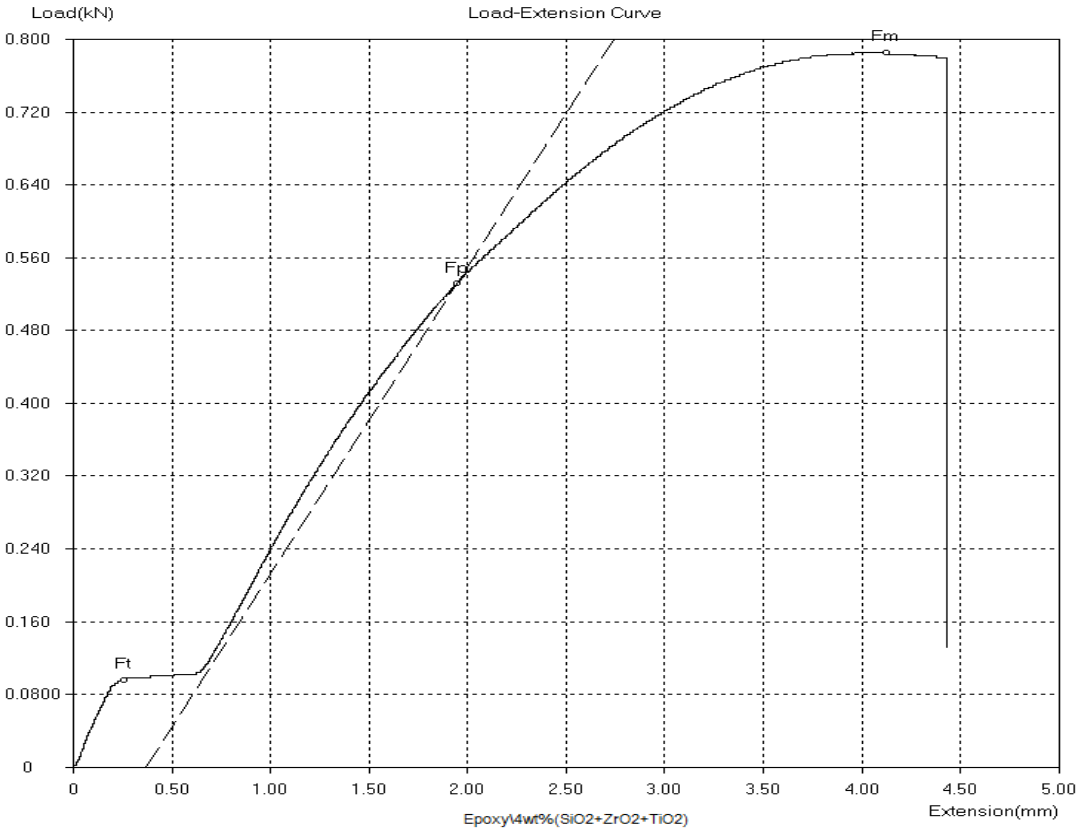
[63] S. Shadlou, E. Alishahi, and M. Ayatollahi, "Fracture behavior of epoxy Nano composites reinforced with different carbon Nano-reinforcements," Composite Structures, vol. 95, pp. 577-581, 2013.

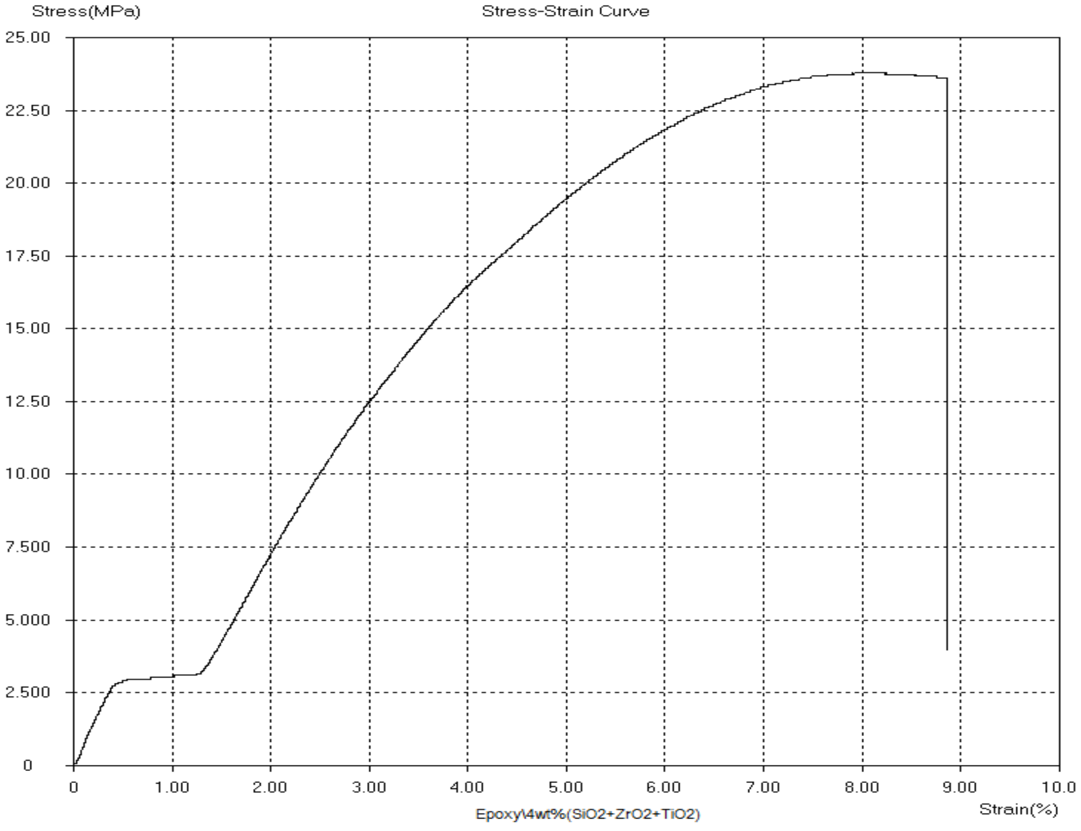
[64] Y. Zhou, M. Hosur, S. Jeelani, and P. Mallick, "Fabrication and characterization of carbon fiber reinforced clay/epoxy composite," Journal of Materials Science, Vol. 47, pp. 5002-5012, 2012.

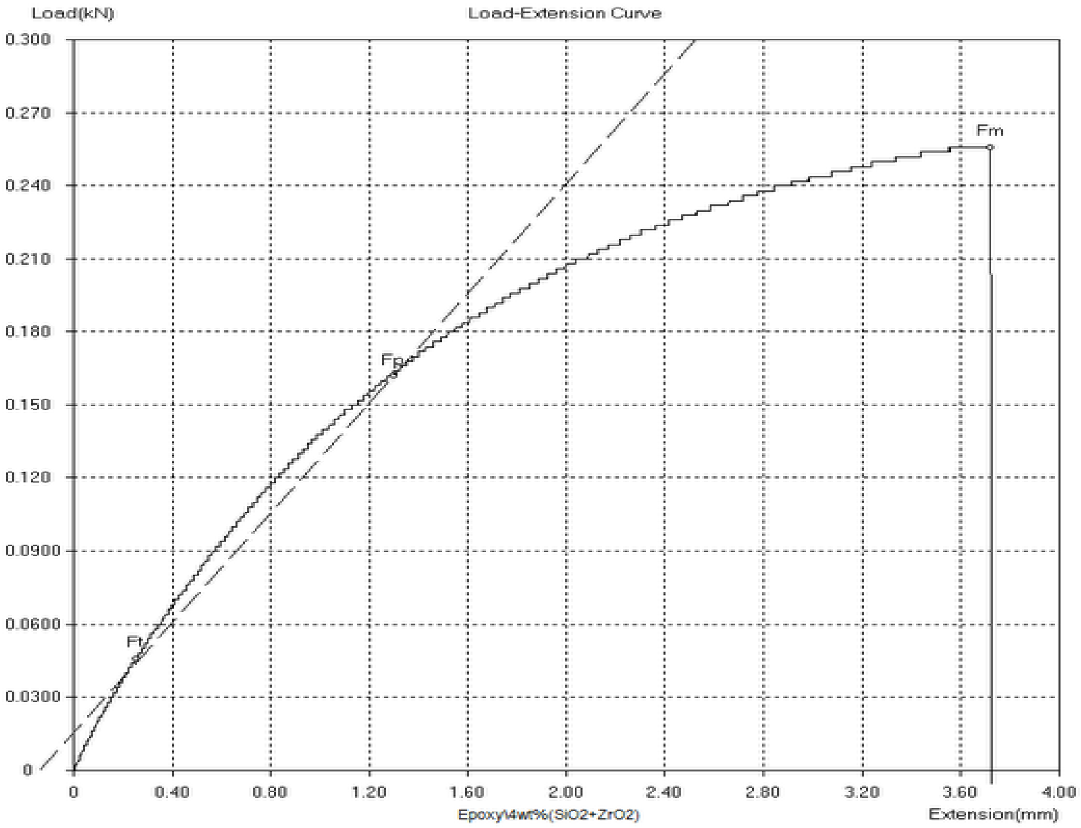
Appendix(A):Tensile test curve for (Pure epoxy, Epoxy-SiO_2, Epoxy-SiO_2+ZrO_2, Epoxy-SiO_2+ZrO_2+TiO_2)

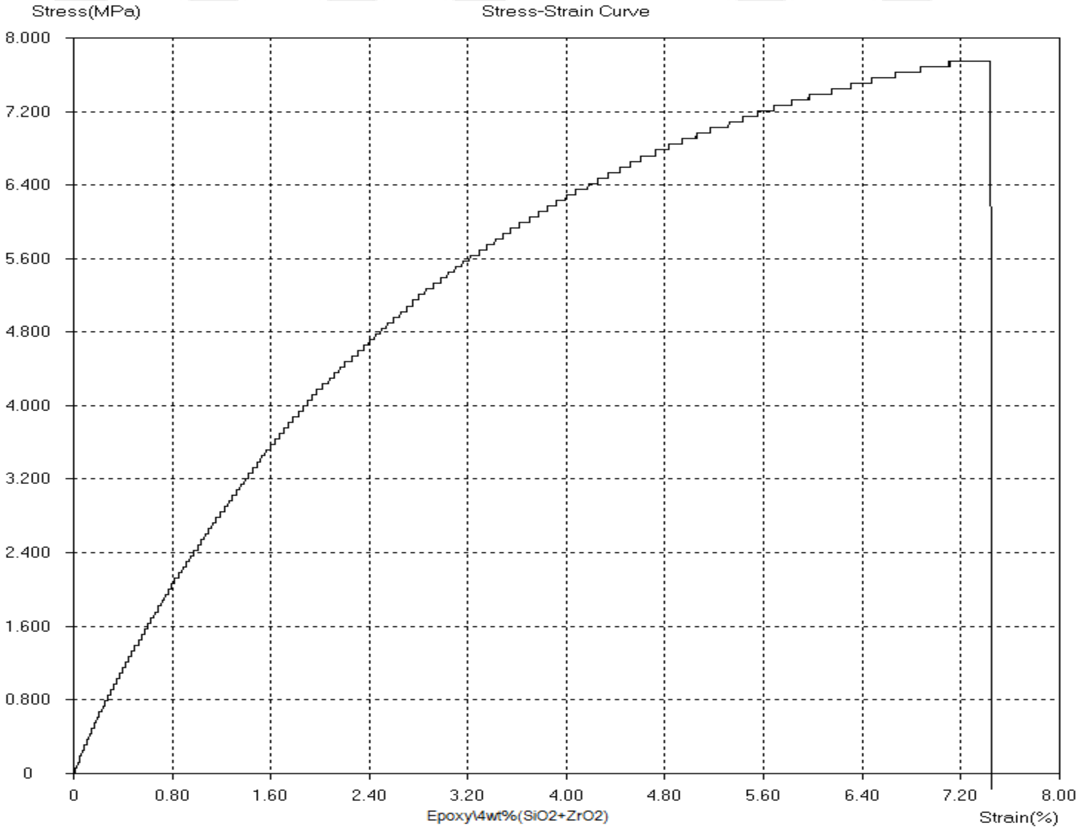


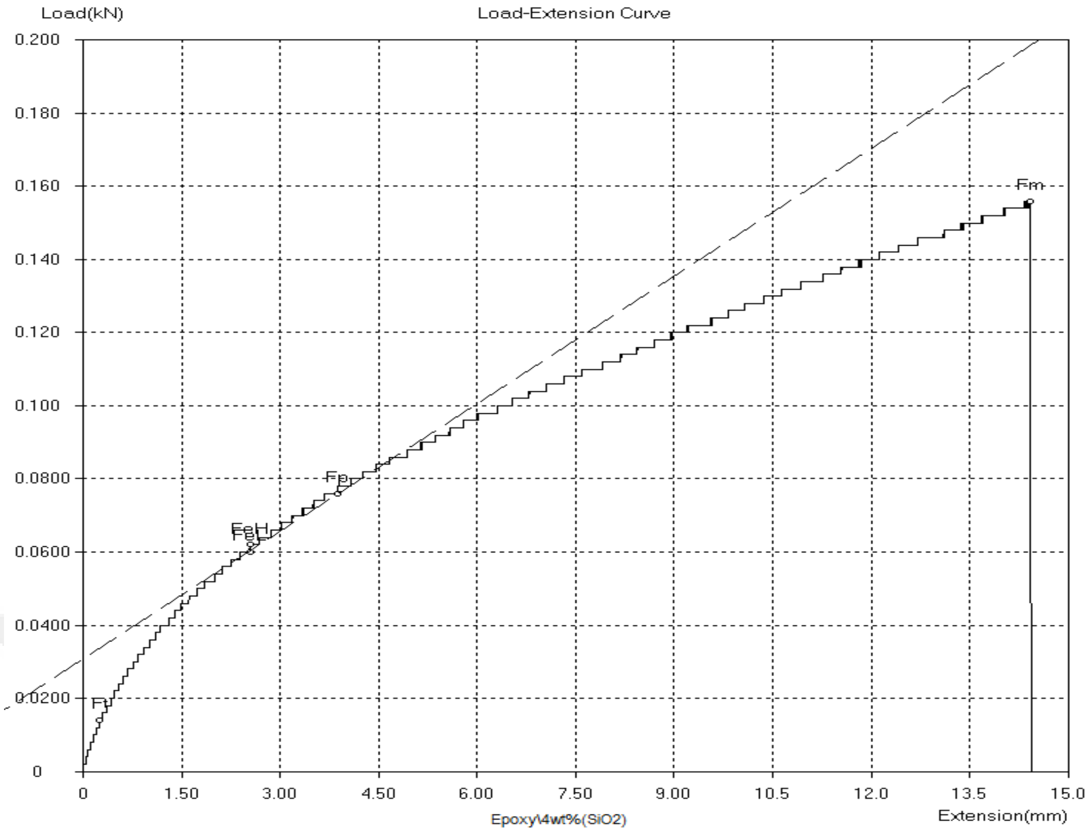


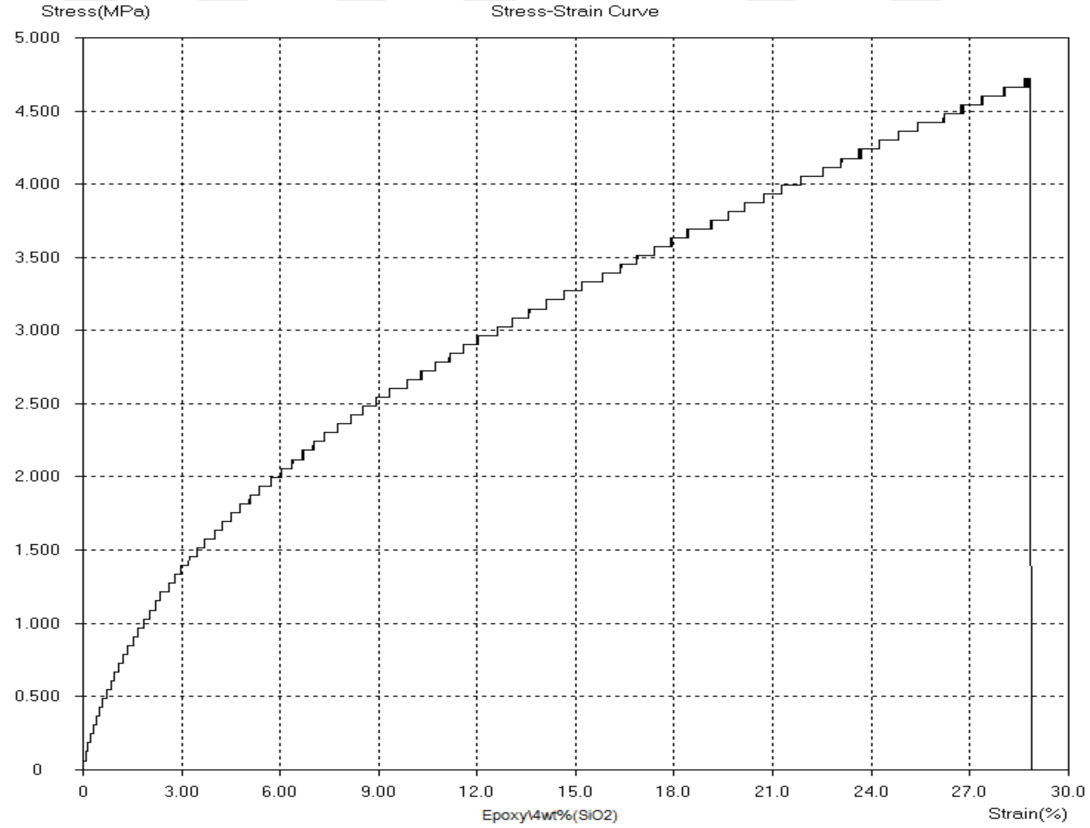

Load(kN)
Load-Extension Curve
0.800
0.720
0.640
0.560
0.480
0.400
0.320
0.240
0.160
0.0800
0
Fm
Fp
Ft
0
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
Extension(mm)
Epoxy\4wt%(SiO2+ZrO2+TiO2)

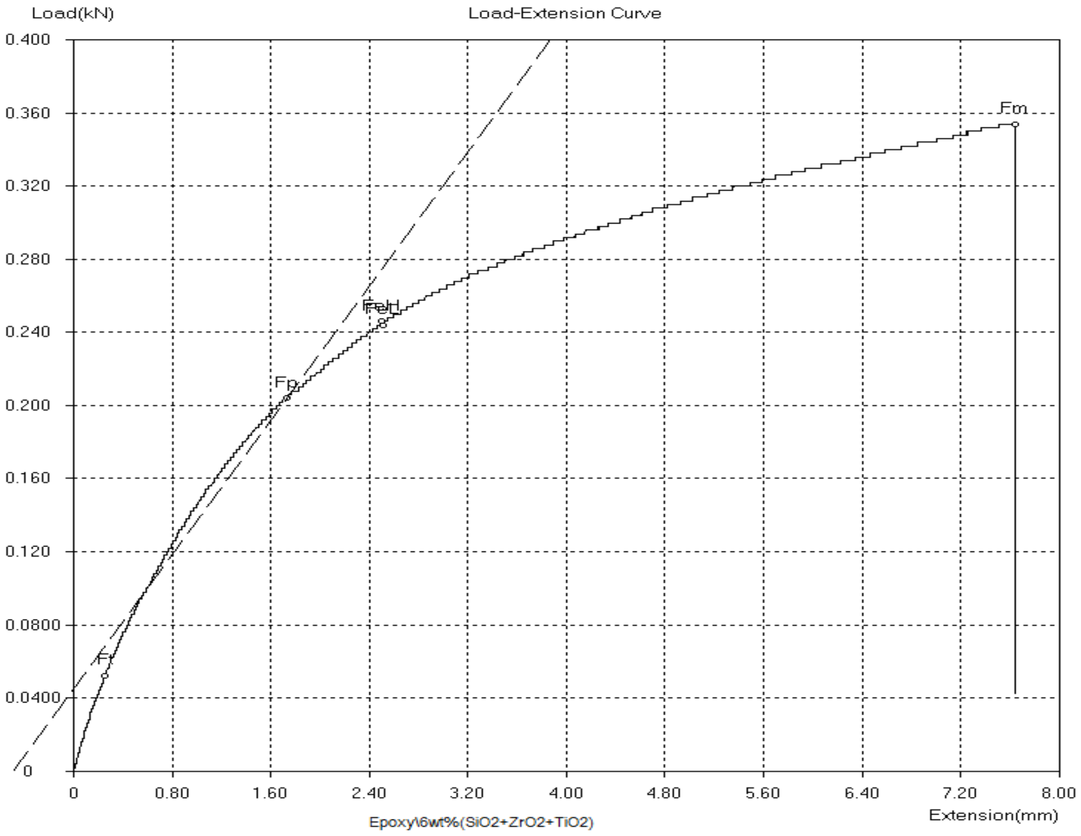

Stress(MPa)
Stress-Strain Curve
25.00
22.50
20.00
17.50
15.00
12.50
10.00
7.500
5.000
2.500
0
0
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.0
Strain(%)
Epoxy\4wt%(SiO2+ZrO2+TiO2)

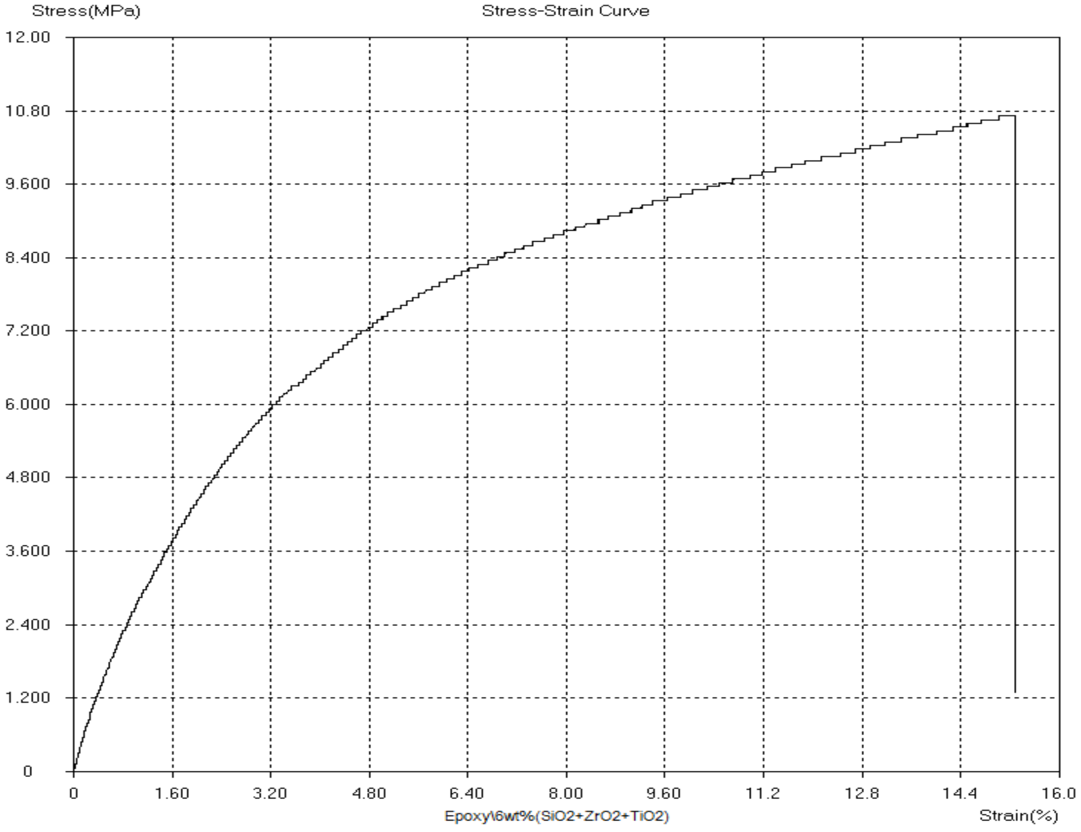

Load(kN)
Load-Extension Curve
0.300
0.270
0.240
0.210
0.180
0.150
0.120
0.0900
0.0600
0.0300
0
Fm
Fp
Ft
0
0.40
0.80
1.20
1.60
2.00
2.40
2.80
3.20
3.60
4.00
Epoxy\4wt%(SiO2+ZrO2)
Extension(mm)

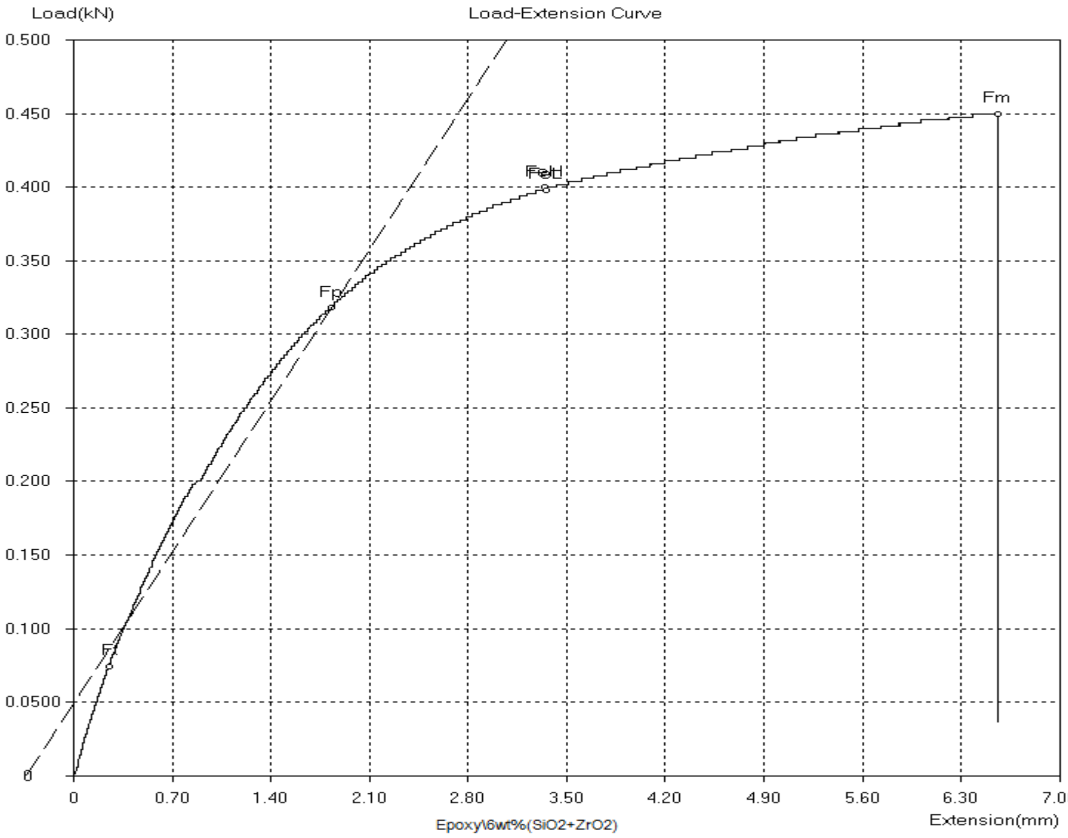

Stress(MPa)
Stress-Strain Curve
8.000
7.200
6.400
5.600
4.800
4.000
3.200
2.400
1.600
0.800
0
0
0.80
1.60
2.40
3.20
4.00
4.80
5.60
6.40
7.20
8.00
Epoxy\4wt%(SiO2+ZrO2)
Strain(%)

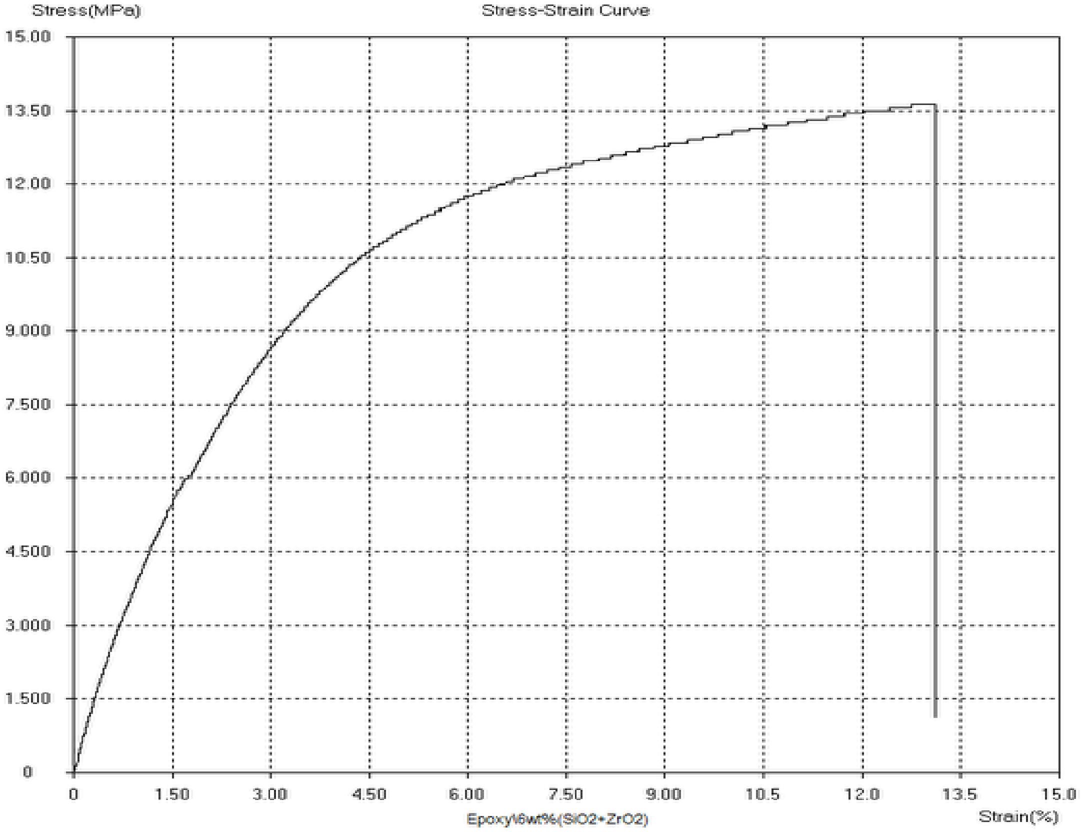

Load(kN)
Load-Extension Curve
0.200
0.180
0.160
0.140
0.120
0.100
0.0800
0.0600
0.0400
0.0200
0
Fm
Fp
FeH
FeL
Ft
0
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
Epoxy\4wt%(SiO2)
Extension(mm)

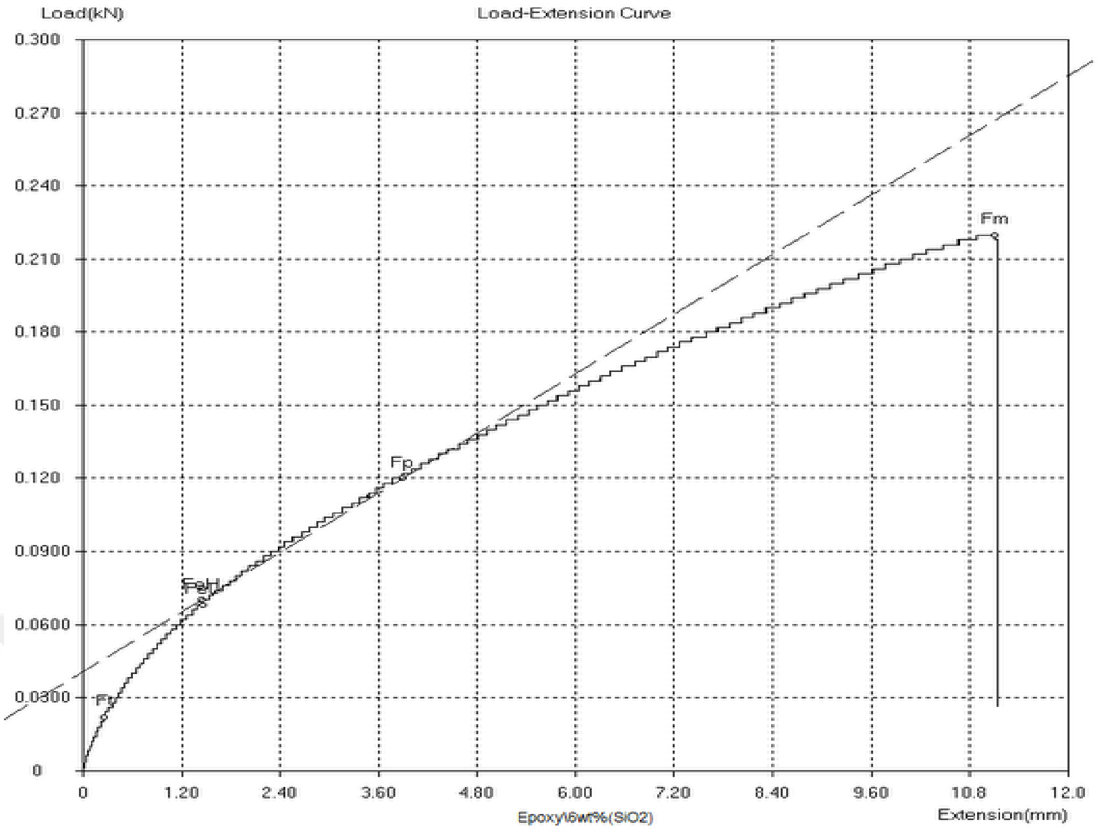

Stress(MPa)
Stress-Strain Curve
5.000
4.500
4.000
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0
0
3.00
6.00
9.00
12.0
15.0
18.0
21.0
24.0
27.0
30.0
Epoxy\4wt%(SiO2)
Strain(%)

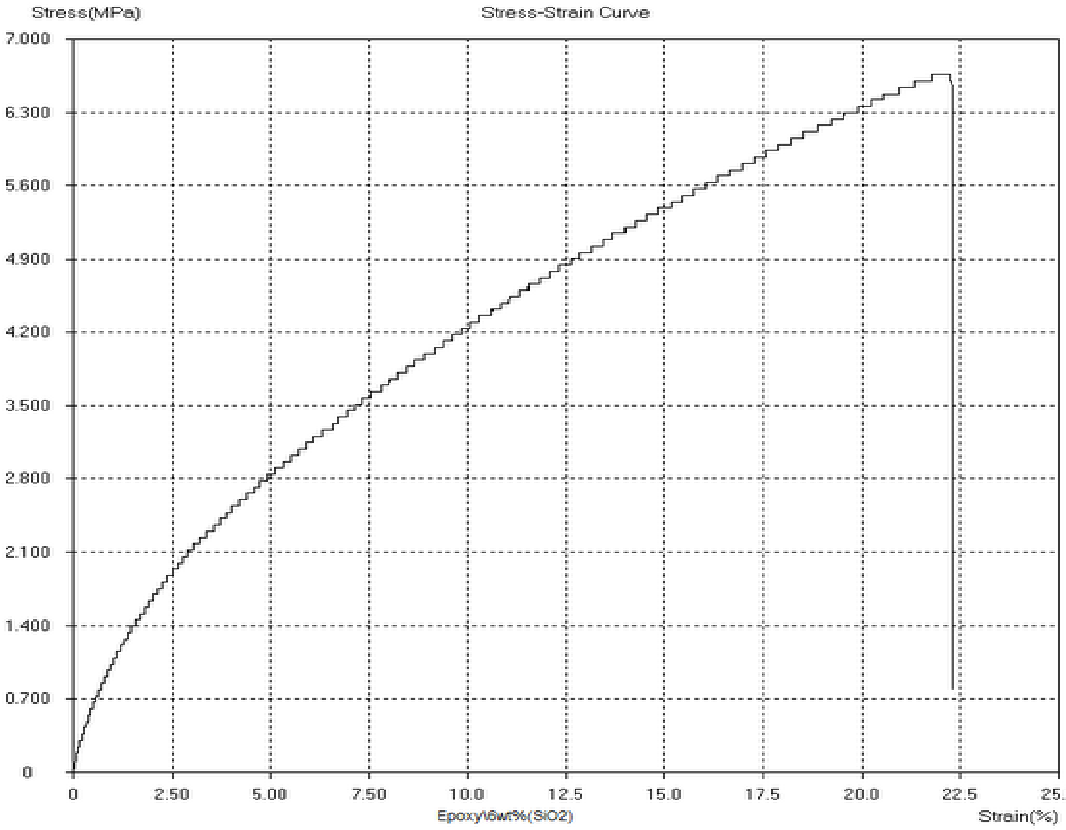

Load(kN)
Load-Extension Curve
0.400
0.360
0.320
0.280
0.240
0.200
0.160
0.120
0.0800
0.0400
0
Fm
FeH
FeL
Fp
Ft
0
0.80
1.60
2.40
3.20
4.00
4.80
5.60
6.40
7.20
8.00
Epoxy\6wt%(SiO2+ZrO2+TiO2)
Extension(mm)

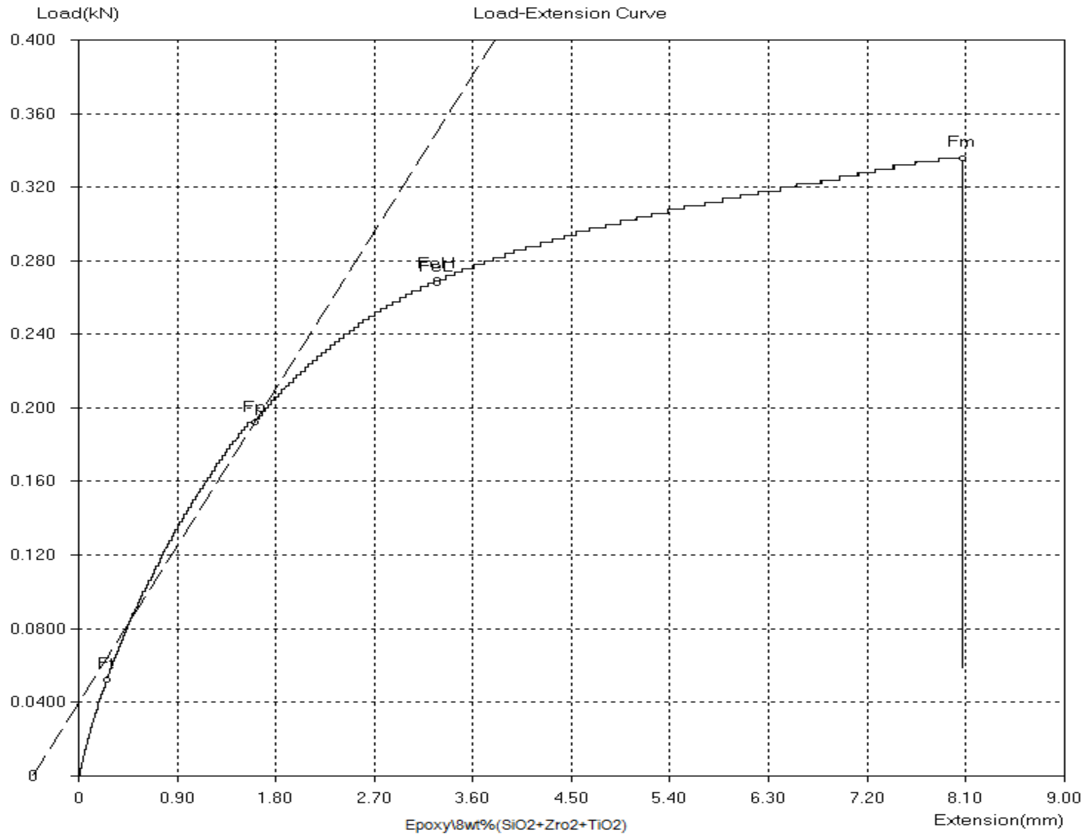

Stress(MPa)
Stress-Strain Curve
12.00
10.80
9.600
8.400
7.200
6.000
4.800
3.600
2.400
1.200
0
0
1.60
3.20
4.80
6.40
8.00
9.60
11.2
12.8
14.4
16.0
Epoxy\6wt%(SiO2+ZrO2+TiO2)
Strain(%)

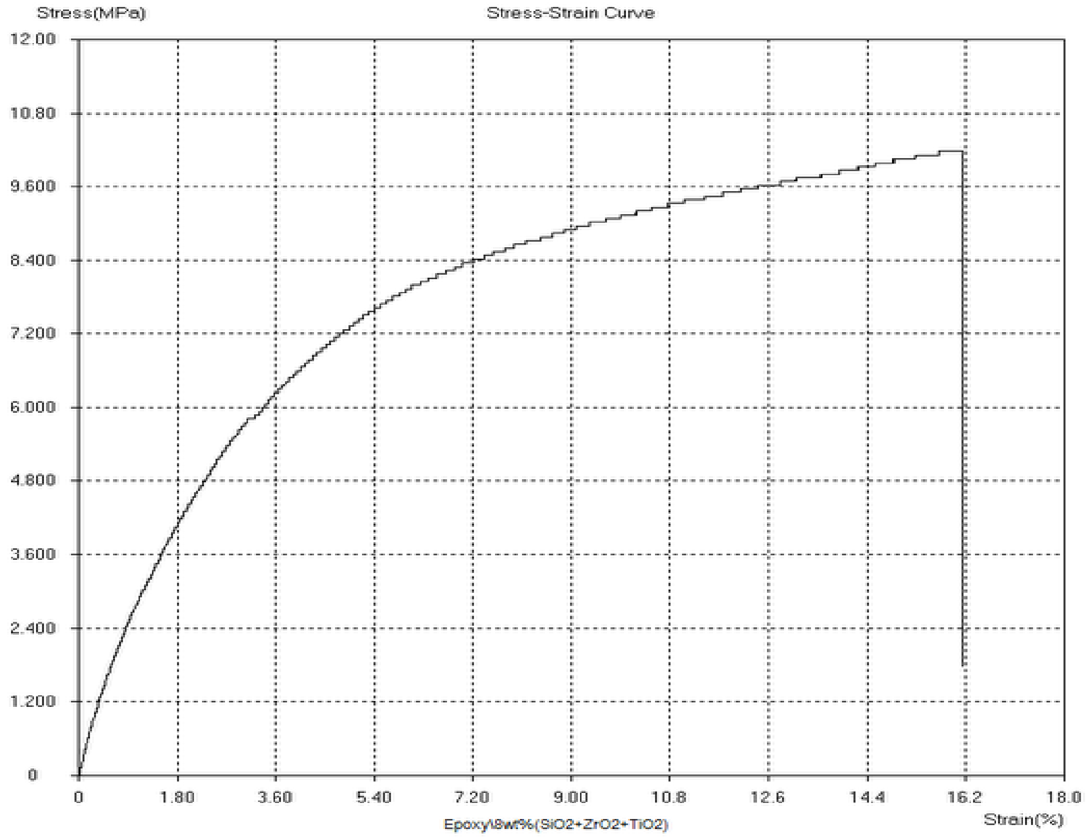

Load(kN)
Load-Extension Curve
0.500
0.450
0.400
0.350
0.300
0.250
0.200
0.150
0.100
0.0500
0
Fm
FeH
FeL
Fp
Ft
0
0.70
1.40
2.10
2.80
3.50
4.20
4.90
5.60
6.30
7.00
Extension(mm)
Epoxy\6wt%(SiO2+ZrO2)

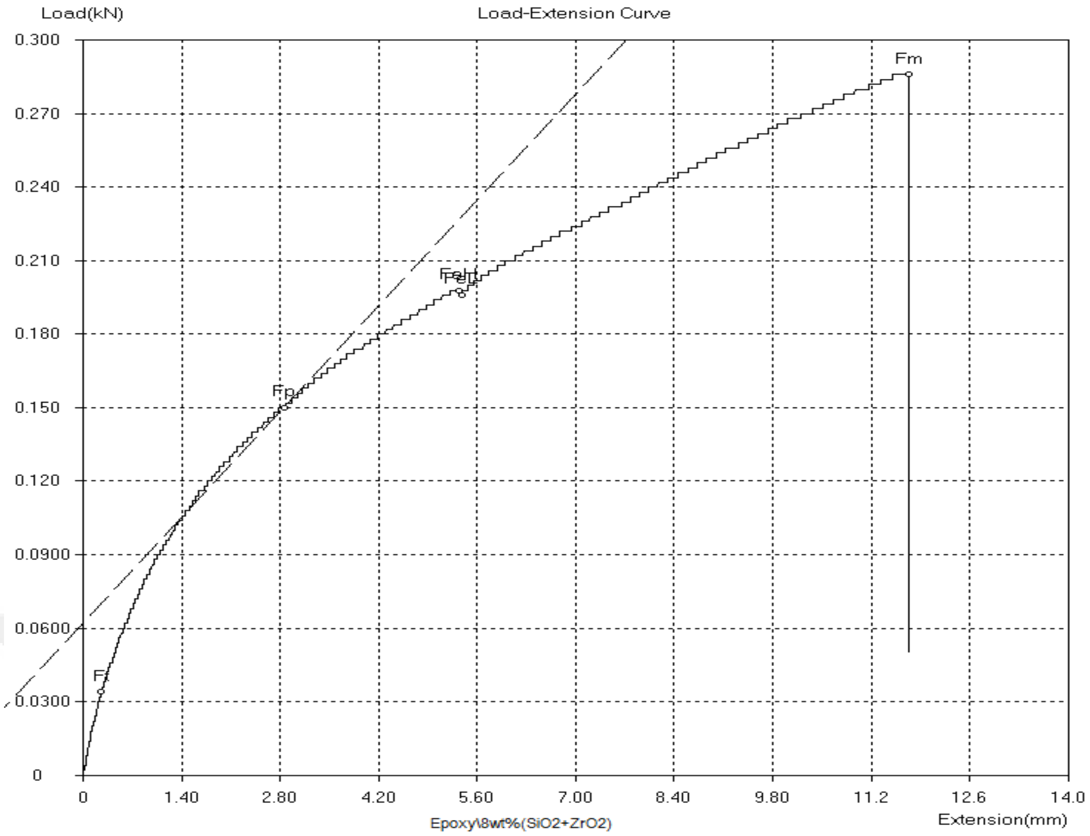

Stress(MPa)
Stress-Strain Curve
15.00
13.50
12.00
10.50
9.000
7.500
6.000
4.500
3.000
1.500
0
0
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
Strain(%)
Epoxy\6wt%(SiO2+ZrO2)

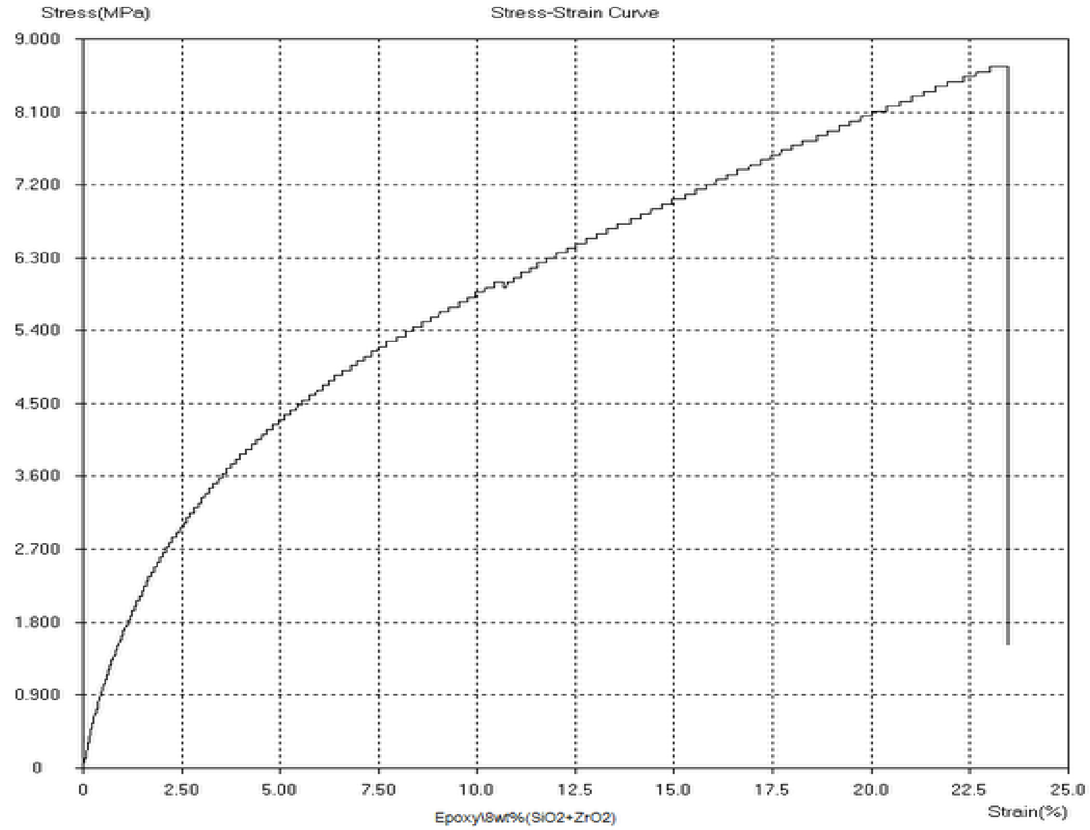

Load(kN)
Load-Extension Curve
0.300
0.270
0.240
0.210
0.180
0.150
0.120
0.0900
0.0600
0.0300
0
Fm
Fp
FeH
FeL
Fy
0
1.20
2.40
3.60
4.80
6.00
7.20
8.40
9.60
10.8
12.0
Epoxy\6wt%(SiO2)
Extension(mm)

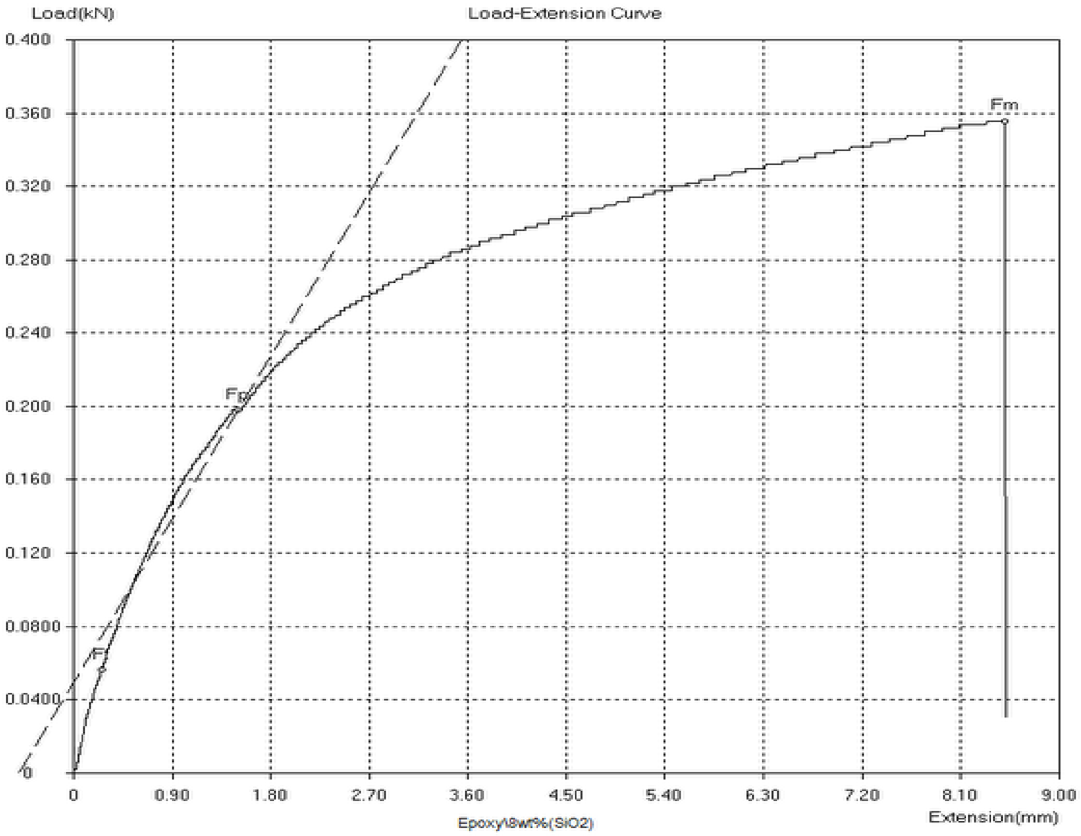

Stress(MPa)
Stress-Strain Curve
7.000
6.300
5.600
4.900
4.200
3.500
2.800
2.100
1.400
0.700
0
0
2.50
5.00
7.50
10.0
12.5
15.0
17.5
20.0
22.5
25.0
Epoxy\6wt%(SiO2)
Strain(%)

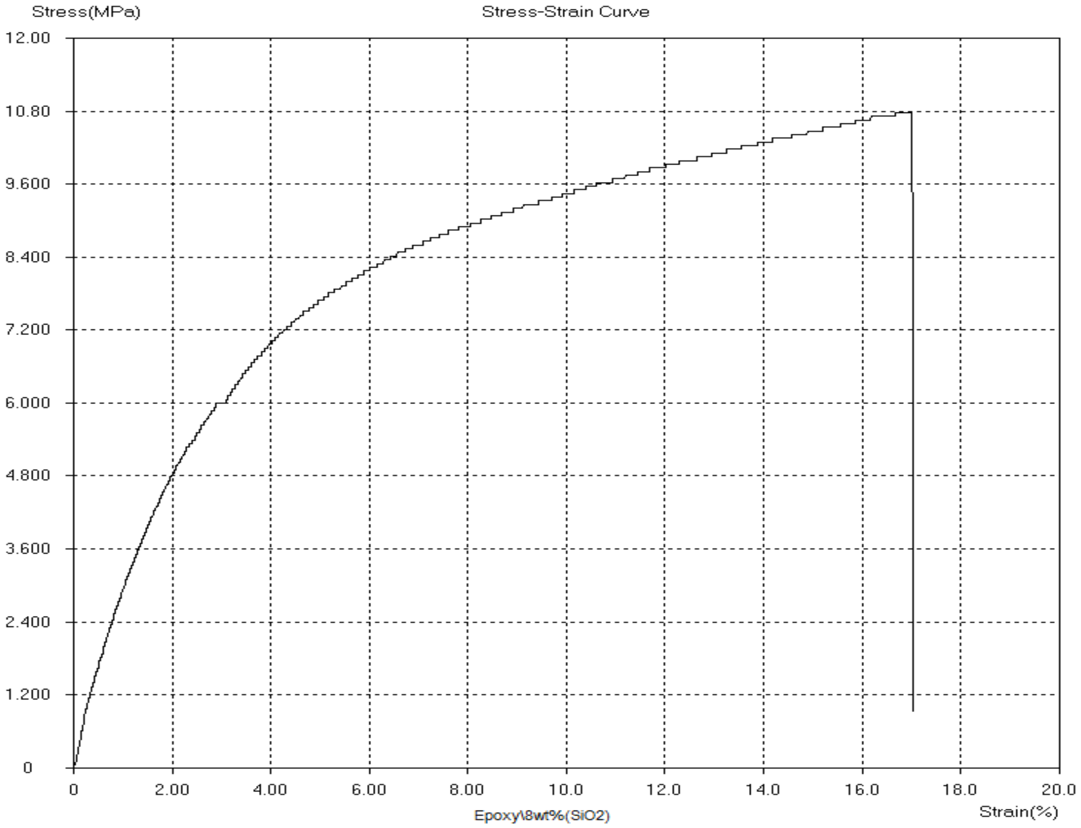

Load(kN)
Load-Extension Curve
0.400
0.360
0.320
0.280
0.240
0.200
0.160
0.120
0.0800
0.0400
0
Fm
FeH
FeL
Fp
Ft
0
0.90
1.80
2.70
3.60
4.50
5.40
6.30
7.20
8.10
9.00
Epoxy\8wt%(SiO2+Zro2+TiO2)
Extension(mm)

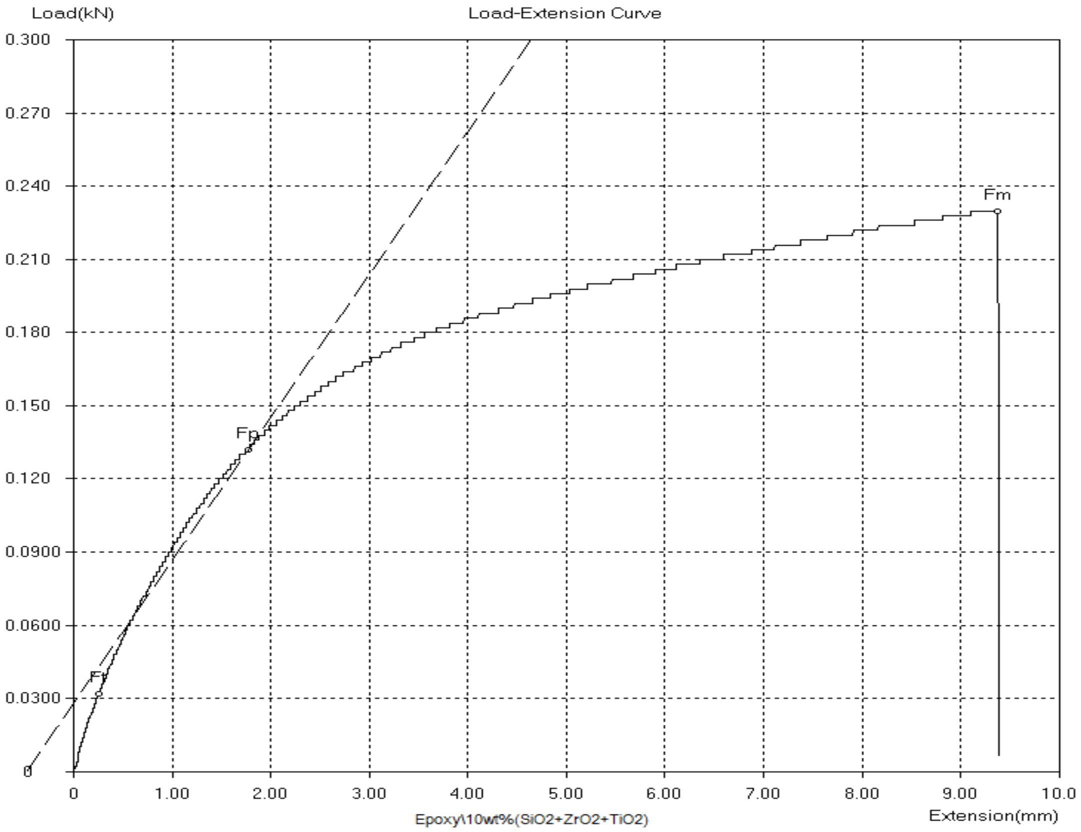

Stress(MPa)
Stress-Strain Curve
12.00
10.80
9.600
8.400
7.200
6.000
4.800
3.600
2.400
1.200
0
0
1.80
3.60
5.40
7.20
9.00
10.8
12.6
14.4
16.2
18.0
Epoxy\8wt%(SiO2+ZrO2+TiO2)
Strain(%)

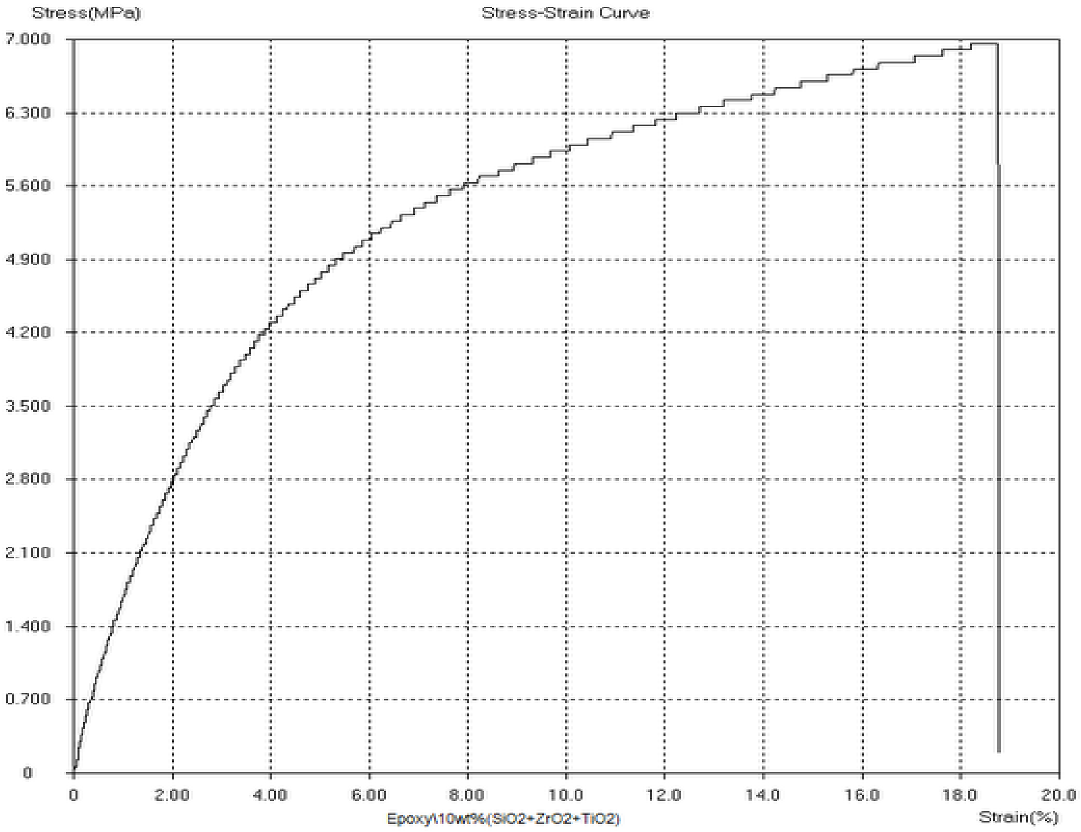

Load(kN)
Load-Extension Curve
0.300
0.270
0.240
0.210
0.180
0.150
0.120
0.0900
0.0600
0.0300
0
Fm
FeH
FeL
Fp
F
0
1.40
2.80
4.20
5.60
7.00
8.40
9.80
11.2
12.6
14.0
Extension(mm)
Epoxy\8wt%(SiO2+ZrO2)

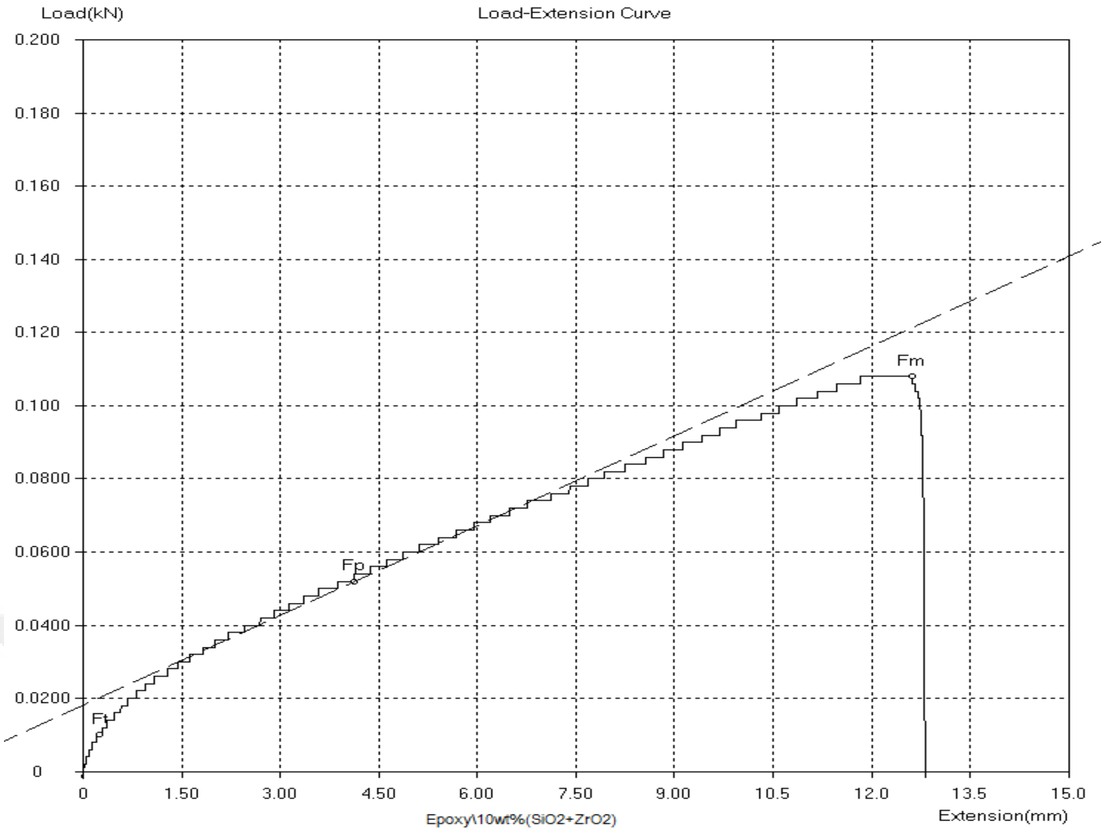

Stress(MPa)
Stress-Strain Curve
9.000
8.100
7.200
6.300
5.400
4.500
3.600
2.700
1.800
0.900
0
0
2.50
5.00
7.50
10.0
12.5
15.0
17.5
20.0
22.5
25.0
Strain(%)
Epoxy\8wt%(SiO2+ZrO2)

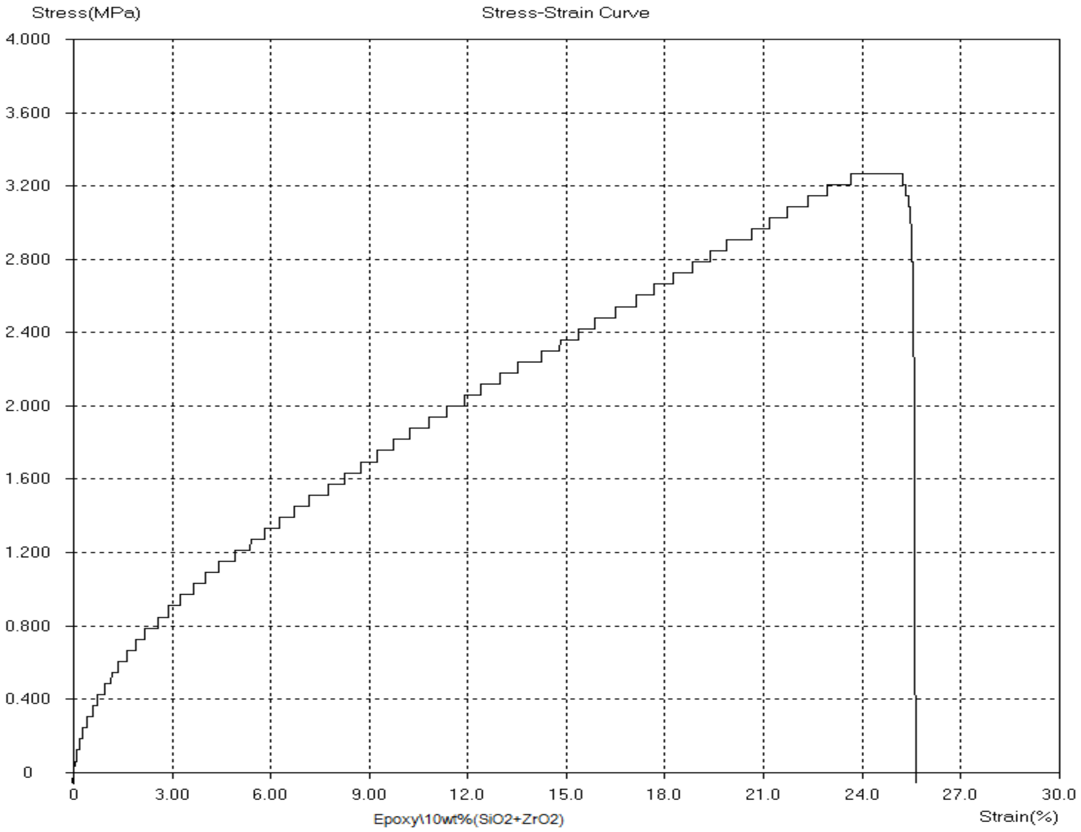

Load(kN)
Load-Extension Curve
0.400
0.360
0.320
0.280
0.240
0.200
0.160
0.120
0.0800
0.0400
0
Fm
Fp
Ft
0
0.90
1.80
2.70
3.60
4.50
5.40
6.30
7.20
8.10
9.00
Epoxy\8wt%(SiO2)
Extension(mm)

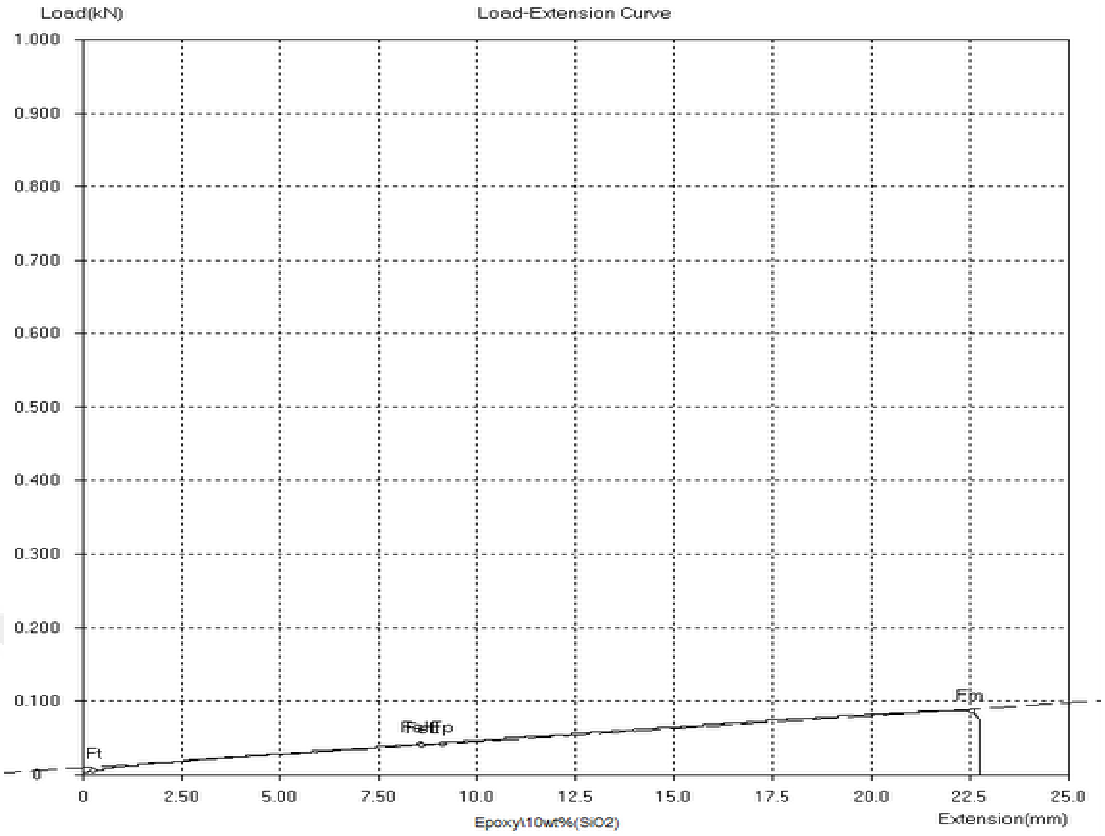

Stress(MPa)
Stress-Strain Curve
12.00
10.80
9.600
8.400
7.200
6.000
4.800
3.600
2.400
1.200
0
0
2.00
4.00
6.00
8.00
10.0
12.0
14.0
16.0
18.0
20.0
Epoxy\8wt%(SiO2)
Strain(%)

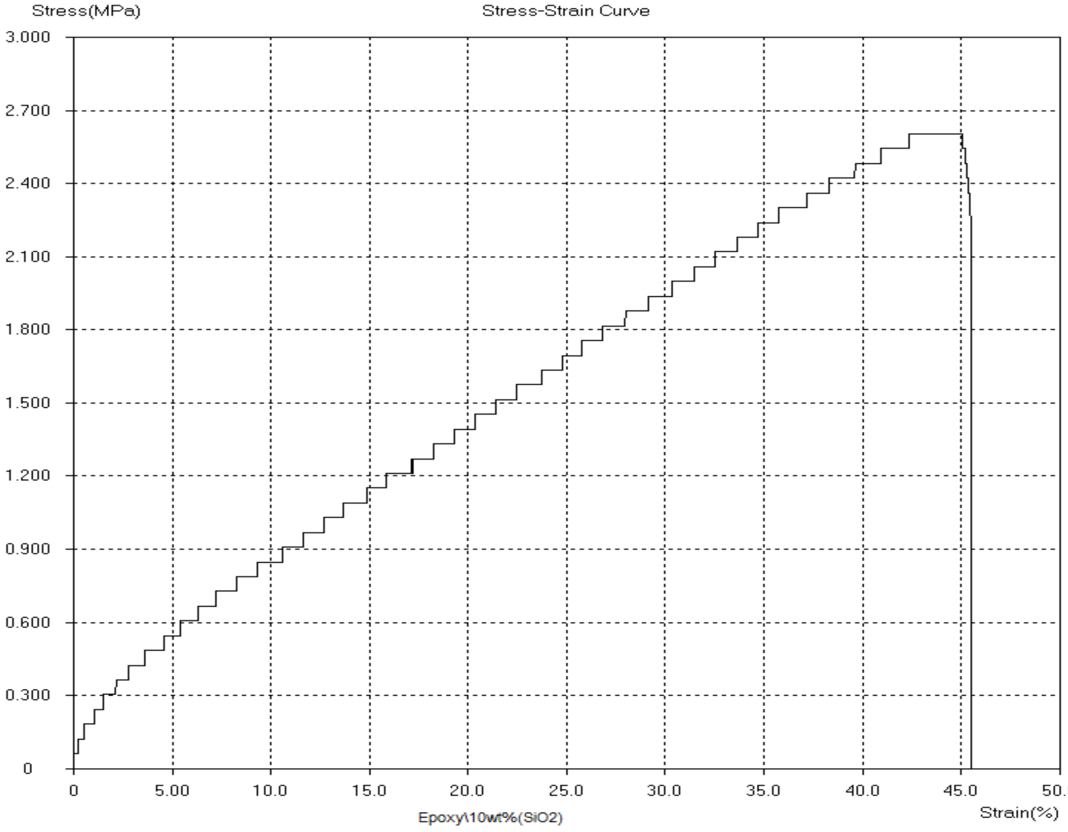

Load(kN)
Load-Extension Curve
0.300
0.270
0.240
0.210
0.180
0.150
0.120
0.0900
0.0600
0.0300
0
Fm
Fp
Ft
0
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.0
Epoxy\10wt%(SiO2+ZrO2+TiO2)
Extension(mm)


Stress(MPa)
Stress-Strain Curve
7.000
6.300
5.600
4.900
4.200
3.500
2.800
2.100
1.400
0.700
0
0
2.00
4.00
6.00
8.00
10.0
12.0
14.0
16.0
18.0
20.0
Epoxy\10wt%(SiO2+ZrO2+TiO2)
Strain(%)


Load(kN)
Load-Extension Curve
0.200
0.180
0.160
0.140
0.120
0.100
0.0800
0.0600
0.0400
0.0200
0
Fm
Fp
Ft
0
1.50
3.00
4.50
6.00
7.50
9.00
10.5
12.0
13.5
15.0
Epoxy\10wt%(SiO2+ZrO2)
Extension(mm)


Stress(MPa)
Stress-Strain Curve
4.000
3.600
3.200
2.800
2.400
2.000
1.600
1.200
0.800
0.400
0
0
3.00
6.00
9.00
12.0
15.0
18.0
21.0
24.0
27.0
30.0
Epoxy\10wt%(SiO2+ZrO2)
Strain(%)


Load(kN)
Load-Extension Curve
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0
Ft
FeH
FeL
Fp
Fm
0
2.50
5.00
7.50
10.0
12.5
15.0
17.5
20.0
22.5
25.0
Epoxy\10wt%(SiO2)
Extension(mm)


Stress(MPa)
Stress-Strain Curve
3.000
2.700
2.400
2.100
1.800
1.500
1.200
0.900
0.600
0.300
0
0
5.00
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
Epoxy\10wt%(SiO2)
Strain(%)