DESIGN AND DEVELOPMENT OF LOAD BEARING COMPOSITE SCAFFOLDS FOR BONE IMPLANTS

A

Thesis Report

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Submitted By

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CERTIFICATE

This is to certify that the work which is being presented in this thesis entitled "**Design and Development of Load Bearing Composite Scaffolds for Bone Implants**", in partial fulfillment of requirement for the award of the Doctor of Philosophy in Mechanical Engineering, submitted in the Mechanical Engineering Department, Thapar Institute of Engineering and Technology, Patiala, is an authentic record of the research work carried out by me under the guidance of Dr. Rajeev Mehta, Professor, Department of Chemical Engineering, TIET, Patiala and Dr. Rahul Chhibber, Assistant Professor, Department of Mechanical Engineering, Indian Institute of Technology, Jodhpur.

The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any other degree.

Dated: 17.08.2018

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This is to certify that the above statement made by the candidate concerned is correct to the best of my knowledge & belief.

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ABSTRACT

Biocomposites mimicking hard tissue in the process of bone repair and regeneration have been in development for several decades. Contributions of several researchers in selection of materials, development of preparation routes, conduct of post surgery response studies and clinical trials for continual developments are commendable. Among several disciplines involved in this process, engineers' role has been identified vital in materials and their processing.

Natural bone made up of Collagen and reinforcement ceramic phase, has dense structure at the middle of the bone and porous structure at the ends. Damaged or diseased bone needs regeneration with implant reinforcements for load sharing during healing process. Essential requirement of an implant is to share the load and to stimulate the bone growth by proper mechanics. Structural point of view, mechanical properties of an ideal implant shall match native bone properties.

Known the properties of Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ in bone applications for its bio active, bio conductive and bio inductive nature, it was chosen as bone material. Hydroxyapatite (HA) being ceramic, it suffers from low strength, low toughness and low tensile properties. In order to overcome the structural weaknesses of HA, Polyetheretherketone (PEEK-polymer) matrix was chosen to match the properties of Collagen.

The polymer part of composite, PEEK, by brand name VESTKEEP 2000FP, a non-medical grade polymer is a justified selection due to its inherent superior properties such as- semi-crystalline, high strength, temperature resistant, chemically inert, bio inert, bio conductive, radiolucent, clinically proven and approved by Food and Drug Administration (FDA)-U S A.

Hydroxyapatite, the reinforcing ceramic powder was extracted from chicken egg shells. Thoroughly washed egg shells were heated through predefined thermal cycles for the formation of CaO. Obtained CaO after thermal treatment has been chemically treated with tri-calcium phosphate (TCP) in wet condition at temperatures 1000^0C and above for the formation of HA. After ball milling and sieve separation, the obtained HA powder was characterized at International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad

For better bone native tissue interaction, HA was extracted from chicken eggshells. Fragile nature of HA had limited its content to a maximum of 40% in total biocomposite. Biocomposite with PEEK and egg shell extracted HA was synthesized and processed for i) dense composite through compression molding to mimic cortical bone and ii) porous structure through polymeric sponge method to mimic Cancellous bone.

Patient specific scaffold to repair damaged bone with precise geometry was successfully demonstrated in present work. CT/ MRI scan data in DICOM format was taken from KD Hospitals, Ambala (Haryana state), India. The obtained 2D images were converted in to 3D surface modeled at Central Tool Room (CTRL), Luthiana (Punjab) using 3D Doctor Software. 3D surface data was imported through IGES exchange protocol to PRO/E WF 3. Volume model of human pelvis was generated and exported in *stl* format to VANGUARD HS Selective Laser Sintering (SLS) machine. Scaled human pelvis was printed in Acrylonitrile-Butadiene-Styrene (ABS) material at CTRL, India.

Taguchi's orthogonal approach was used in design of experiments of dense specimens for effective and quicker experimentation. After several trials in arriving at the specimen formation, three influencing factors (or processing parameters) were identified viz., the constituent composition of PEEK and HA, the sintering temperature or maximum temperature and the rate of heating. Three fine levels of each processing parameters were arrived at after comprehending the properties of biocomposite components from literature and delimiting studies on dense specimens.

Two different sets of samples were prepared, the first one with PEEK/ HA (natural or eggshell extracted HA) and the second one with PEEK/ HA (synthetic or commercial, purchased from Clarion pharmaceuticals, New Delhi). Dense specimens mimicking cortical bone structure were produced in powder metallurgy route. Mechanical properties of dense specimens viz., flexure strength and Young's modulus of biocomposite were established through three point bend test as per ASTM D790 at Central Institute of Plastics Engineering& Technology, Hyderabad. The test results were revealing superior interaction of natural HA with PEEK.

Porous specimens to mimic Cancellous bone were prepared through Polymeric sponge method. A nylon mesh of 10 pores per inch was impregnated in Alumina slurry for preparation of

template. Alumina template was used for preparation PEEK/HA porous specimens with porosities 41%, 45% and 51%. First set of porous specimens as sintered were tested in unconstrained compression test to establish the mechanical properties. Second set of porous specimens exposed to artificial sea water for 25 days at 37^0C were tested in unconstrained compression to establish degradation of mechanical properties invitro. PEEK/HA composite was concluded to be hydrophobic as the degradation effect was minimal.

Thermal stability study was conducted on biocomposite to pave guide lines for processing of the material to ensure bone in-situ applications Higher contents of HA in PEEK was found to be delaying the degradation of the composite. Weight loss of composite was found to be negligible even at 500^0C. This test was establishing safe processing temperature of PEEK/HA could be as high as 350^0C.

Finally an effort was made to extrapolate the porous scaffold's mechanical behavior using DEFORM 3D software. Three sets of porosity (75%, 82% & 89%) in two different constituent percentages (PEEK/HA 70/30 and 80/20) were analyzed for load - deformation behaviour.

The total work entitled 'Design and development of load bearing composite scaffolds for bone implants' has been concluded as the dense and porous specimens were found prospective at load bearing sites with appropriate selection.

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Chapter 1 INTRODUCTION

1.1 Composite materials

A composite is a structural material that consists of two or more combined constituents that are combined at macroscopic level and are not soluble in each other. One of the constituents is called the reinforcing phase and the other one in which it is embedded is called the matrix. The matrix is the major phase of the composite material. The reinforcing phase material may be in the form of fibers, particles, or flakes. Examples of composite systems include concrete reinforced with steel, epoxy reinforced with graphite fibers and the soft Collagen reinforced with bone-salt plates made of calcium phosphate ions.

1.2 Necessity of composites

Synergistic approach in constituents' selection and formation of composite are the key factors in composite selection for a specified application. The application field may define required mechanical properties such as tensile strength, Young's modulus, toughness, properties at elevated temperatures, specific strength, specific Young's modulus, chemical/ electrical compatibility etc. The constituents of a composite are thus chosen based on various factors afore mentioned, manufacturing process adoptability and finally the required properties to be achieved.

1.3 Applications of composites

A space satellite which is exposed to unusual temperature variations between -160^0C to $+100^0$C needs retention of mechanical properties of structural elements and dimensional stability. Since no monolithic metal supports these requirements, it becomes ineviTable to go for composite material. Similarly, an aircraft needs easy propulsion by reducing its dead weight but without a compromise in its mechanical strength. All such modified properties otherwise not available in monolithic metals are obtained by formation of composites. Application of composites is found in several fields such as medical, engineering, structural etc.

Application of composites in biomedical field is growing by the advent of newer processing technologies. To name a few among the biomedical applications, Dentistry, Cardiovascular, Maxillofacial, bone/ joint prostheses, tissue engineering are prominent.

1.4 Classification of composite materials

a) Composite materials are classified in to three categories based on *matrix materials* viz., Metal Matrix Composites (MMC), Ceramic Matrix Composites (CMC) and Polymer Matrix Composites (PMC)[1]

Metal Matrix composites: These composites have metals as matrix such as Aluminium, Titanium, Magnesium etc,. Mechanical properties of such ductile, tough materials are enhanced by the addition of reinforcements like carbon fibers, silicon carbide, alumina etc. MMCs have high strength and high weight. On the other hand, mechanical properties of MMCs are vulnerable to temperature changes.

Ceramic Matrix Composites: Ceramic composites have their matrix as ceramic materials and reinforced by fibers such as carbon. These composites have high strength, low density and excellent heat resistance. Ceramics are brittle in nature.

Polymer Matrix Composites: Polymer matrix composites with polymers such as epoxy, polyester, urethane matrix are reinforced by fibers/ particulates. These polymers often suffer from low strength compared to MMC and CMC. Polyetheretherketone an advanced polymer has excellent strength unlike other polymer matrices. All polymers, compared to metals, are light in weight, easily processable, chemically inert and possess less frictional resistance.

b) Composites are classified into three more categories based on the *geometry of reinforcement* viz., fiber, particulate and flake or laminar [1]

Fiber reinforced polymer composites: Fiber reinforced composites are prepared by sintering, extrusion techniques. Polymers such as epoxy, phenolics, acrylic, urethane, and polyamide in matrix are reinforced by fibers like glass, carbon, Kevlar etc. Toughness of matrix, strength and rigidity of fibers are synergized to exhibit required properties.

Particle reinforced polymer: Polymer matrix of these composites are reinforced by ceramic, glass powder particulates. End effect of particle reinforcements on composite are seen in reduced ductility, improved modulus and strength. Special properties are acquired by the addition of piezoelectric/ magnetic/ super conductive particle reinforcements into these composites. Nano-sized particles (particles in the order of 100 nm sizes) attribute extraordinary properties to particle reinforced composites due to their surface area and well dispersant capabilities. Unlike fiber or flake composites, these composites are isotropic in nature.

Laminar reinforced polymer composites: These composites comprise layers of materials held together by polymer matrix. Typical flake/layer materials are glass, mica, aluminium, and silver. These composites exhibit excellent strength and high out-of-plane flexural modulus.

1.5 Bone implants

The term Biocomposites specially refers to those composites used in bioengineering where constituents do not dissolve in to each other although they act in concert and exhibit an interface between one another.

Most of the living tissues such as bone, dentin, Collagen, cartilage and skin are essentially composites. From structural point of view, majority of composites exhibit anisotropy excepting composites reinforced with particulates. The composites synthesized artificially are essentially a combination of two phases, i.e. a reinforcing phase such as fiber or particle and a continuous phase called matrix.

In present work, bone implants were chosen to mimic the natural bone properties. The challenges involved are,

i) To mimic the bone material, a composite made of Collagen- the polymer and Hydroxyapatite- the ceramic reinforcement
ii) To synthesize varied properties of bone, along the bone and across the bone
iii) To process high end polymers or polymer composites

High strength, bio-compatible, chemically inert and excellent temperature stability polymer Polyetheretherketone (PEEK) was chosen to substitute natural bone polymer Collagen. Reinforcement is chosen from bio-active bone ceramics, Hydroxyapatite (HA)- $Ca_{10}(PO4)_6(OH)_2$. In present work, preparation and structural property evaluation of a biocomposite formed by PEEK and eggshell extracted HA were presented.

Chapter 2 LITERATURE REVIEW

PART-I: INVESTIGATIONS ON BIOMATERIALS AND THEIR APPLICATIONS

2.1 Bioengineering and Biomaterial

Bioengineering is referred to the applications of concepts and methods of the physical sciences and mathematics in the Engineering approach towards solving problems in repair and reconstruction of lost, damaged or diseased tissues [2]. The materials which are used for this purpose are known as 'Bio materials'.

Biocompatibility is a descriptive term which indicates the ability of a material to perform with an appropriate host response, in a specific application [3]. Further this definition was extended to distinguish [4] between basic properties of biomaterials viz., Surface compatibility and Structural compatibility of an implant.

Surface compatibility means the chemical, biological and physical (including surface morphology) suitability of an implant surface to the host tissues.

Structural compatibility of an implant is the optimal adaptation to the mechanical behaviour of the host tissues. A *Biocompatible* material, meeting all surface compatibility requirements, should possess similar mechanical properties as that of the host tissue to enhance cell attachment, proliferation, migration and expression of native phenotypes [5]. Therefore, structural compatibility refers to the matching mechanical properties of implant material such as elastic modulus, tensile/compressive strength etc of the host tissue. Apart from strength and rigidity of the implant material, surface area to volume ratio, pore size, pore inter connectivity, and pore density are some of the critical factors in deciding the material, design and manufacturing methods. Hence success of the biomaterial in the body is qualified only when both the surface and structural compatibilities are met. Further, success also depends on several other factors such as surgical technique (degree of trauma imposed and sterilization methods etc), health condition of the patient and activities of patient [4]. Most medical devices are made from monolithic, homogeneous and isotropic materials such as metals, polymers, and ceramics.

Biomaterials

Biomaterials are the materials intended to functionally support the diseased tissue either by regeneration or by replacement [6]. Biomaterials were classified by researchers broadly into bioinert and bioactive, bio-stable and bio-degradable categories [7]. In the engineer's perspective, the biomaterials fall into one of the groups- viz., i) metals, ii) ceramics, iii) polymers, and iv) composites of former three. Fig 2.1 is a comprehensive presentation of repair site specific bio-material applications. Application point of view, following materials were found in biomedical applications [4].

Metals are known for high strength, ductility and resistance to wear. Most commonly used biocompatible materials are stainless steel, cobalt-chromium alloys, tantalum, titanium and titanium based alloys. The major disadvantages of metals in biomedical applications are their high stiffness compared to the host tissues as well as their tendency to create severs imaging artifacts in the most advanced diagnostic 3-D imaging procedures such as CT/ MRI due to their radio-opaqueness. Apart from structural property deviations, excepting titanium and titanium base alloys, most of the metals are sensitive to corrosion, thus releasing metal ions which may cause allergic tissue reactions [8].

A large number of **polymers** are widely used in various medical applications. Polymers application is increasing due to their availability in a wide variety of compositions, properties and forms (solids, fibers, fabrics, films and gels) and can be fabricated readily into complex shapes and structures. However for load bearing applications, they tend to be very flexible and too weak to meet the mechanical demands of certain applications e.g. implants in orthopedic surgery.

Ceramics are known for their good bio compatibility, corrosion resistance and high compression resistance. Drawbacks of ceramics include brittleness, low fracture strength, difficulty in fabrication, low mechanical reliability and lack of resilience.

These drawbacks in the traditional biomaterials have stimulated researchers and engineers to develop **composite materials** as an alternative choice in bioengineering applications. **Composites** are those materials that contain two or more distinct constituent phases, on a scale larger than the atomic. The term **Biocomposites** specially refers to those composites used in

bioengineering, where constituents do not dissolve in to each other although they act in concert and exhibit an interface between one another.

The primary motive in the development of Biocomposites is that by varying the type and distribution of the reinforcing phases in the composites, it is possible to obtain a wide range of mechanical and biological properties, and hence to optimize the structure and performance of the biomedical devices and their interaction with the surrounding tissues.

In general, tissues are grouped into two, *hard and soft tissues*. Bone and tooth are the only examples of hard tissues; whereas skin, blood vessels, cartilage and ligaments are a few examples of soft tissues. Hard tissues such as bones are generally stiffer (higher Young's modulus) and stronger (higher tensile/ compressive strength). Moreover they are essentially composite materials with anisotropic properties which depend on the roles and structural arrangements of various components (Collagen, elastin and Hydroxyapatite) of the tissues. For example, the longitudinal mechanical properties of cortical bone are higher than the transverse direction properties (refer Table.2.1). The anisotropy of the elastic properties of the biological tissues has to be essentially considered in design of implants using composite biomaterials.

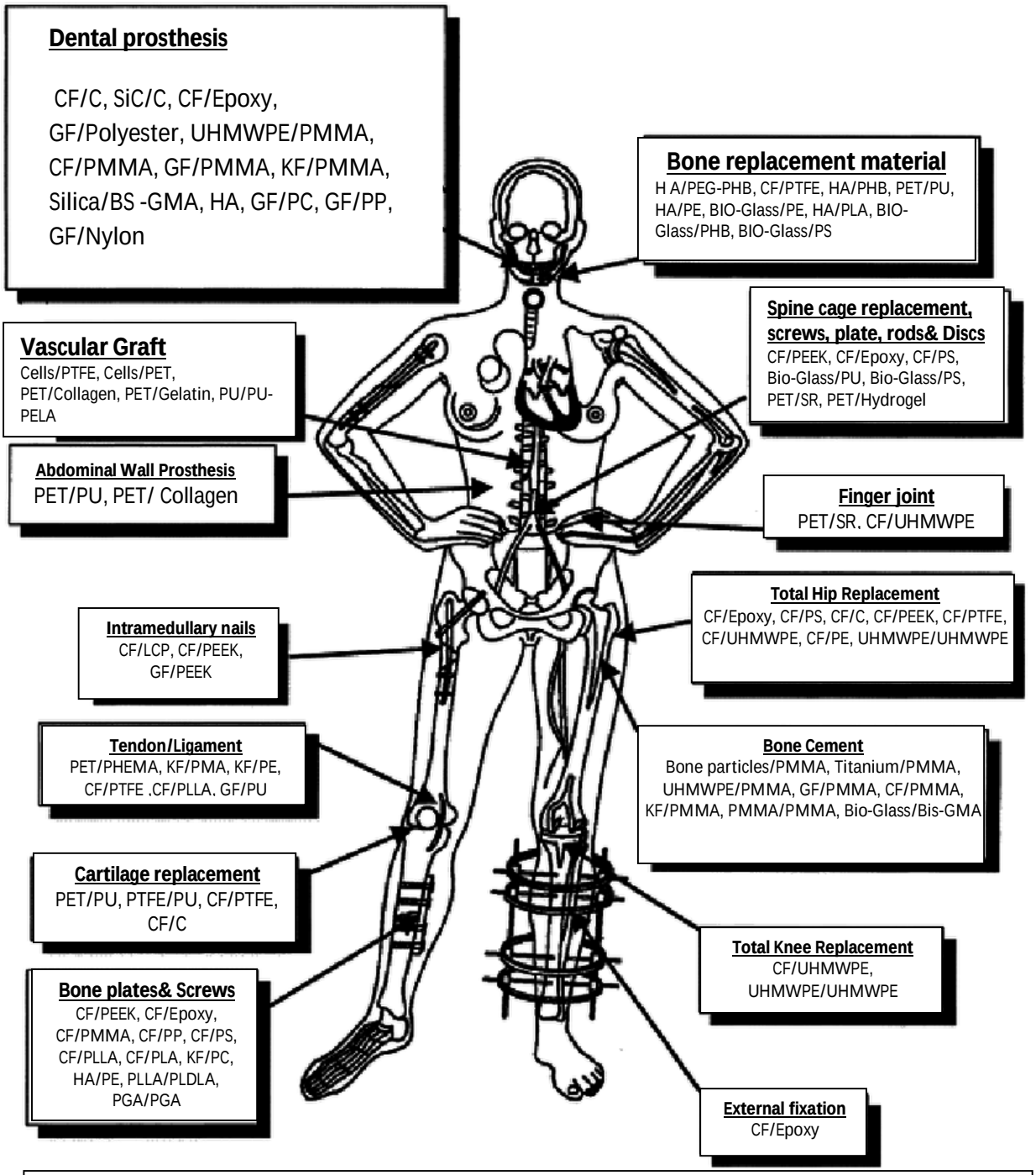


Fig. 2.1 Application of biomaterials at various repair sites

Biocompatible engineering materials

i) **Metals:** Gold, Tantalum, Stainless steel, Titanium, Titanium alloys, Co-Cr, Ni Ti;

ii) **Ceramics:** Alumina, Titania, Zirconia, Bio glass, Carbon, Hydroxyapatite(HA);

iii) **Polymers:** Polyethylene (PE), Polyurathene (PU), Polymethylmethacrylate (PMMA), Polytetrafluroethylene (PTFE), Polyacetal (PA), Polyethyleneterapthalate (PET), Silicon Rubber (SR), Polysulfone (PS), Polyetheretherketone (PEEK), Polyglycolic acid(PGA), Poly(lactic acid)(PLA), Ultra High Molecular Weight Polyethylene (UHMWPE) etc.

iv) **Composites:** Polymer/ceramic composites are in wide usage due to their inherent chemical, biological and mechanical advantages. Application oriented site specific composites such as HA/PA, HA/PEEK, Carbon Fibers (CF)/ PEEK, CF/ Epoxy, CF/UHMWPE, Silica/SR, Glass Fibers (GF) / PEEK, GF/UHMWPE have been presented [9] as in Fig. 2.1.

According to previous findings [10], polymer composite materials offer several other significant advantages over metals/ alloys and ceramics, they are:

1. Absence of corrosion and release of allergenic metal ions such as in Nickel or Chromium implants
2. High fracture toughness
3. High fatigue resistance
4. Adjustable radiolucent properties through contrast medium additives to the polymer
5. Polymer composites are highly compatible with diagnostic methods such as Computed Tomography (CT), and Magnetic Resonance Imaging (MRI.)
6. Ease in manufacturing desired shaped objects at high speeds.

Biocomposites are visualized in one of the following categories based on resorbability issues of human body. They are:

1. **Non resorbable biocomposites** - Total composite material will be biocompatible and bio- inert. Hence the implant/ medical device to be removed after healing.
2. **Partially resorbable biocomposites** - Either reinforcing material or matrix material is absorbed by the body and the rest will be bioinert and to be removed after healing.
3. **Fully resorbable biocomposites** - Both matrix and reinforcing materials are absorbable in the body, second surgery is not required to remove the implant or its traces.

Bio-resorbable polymers suffer from controlled degradation in concurrence with the healing process. The aggressive physiological conditions that prevail in human body complicate the study of biomaterials. The critical in-situ body conditions are [4, 6]:

1. pH values of body fluids varying between 1-9 depending on implant sites.
2. Severe mechanical stresses: Normal stresses in bones will be about 4 MPa in static conditions. The load on severely stressed hip joint typically varies between 3 to10 times the body weights depending on static to moving body conditions. It would go even high in impact loads on body.
3. The loads become cyclic and fatigue when the body/ limbs are in motion. Typically, in a year a hip joint is subjected to 1×10^6 cycles and heart muscles as high as 4×10^7 cycles.
4. Patient specific medication and radiation environments.

Natural bone: Bone is made up of a natural composite of Collagen (polymer), which provides a frame work, and bone material (ceramic), which provides strength. The two most important types of bone are cortical and Cancellous bone. Cortical bone is a dense structure with high mechanical strength and is also known as compact bone. Cancellous or Trabecular bone is an internal porous supporting structure present in the ends of long bones such as femur or within the confines of the cortical bone in short bones. Trabecular bone is a network of struts enclosing large voids (macro pores). Table 2.1 demonstrates anisotropy in bone mechanical properties and the large variation of mechanical properties between cortical and Cancellous bones [3]. Mechanical properties of metals and ceramics shown in Table 2.2 reveal they are too rigid compared to natural bone [3]. This deviation, causing stress shielding discussed in next article attracts the attention of researchers to incline to polymers shown in Table 3.3, with comparable properties to bone

Table.2.1 Mechanical properties of hard tissues

Hard tissue	Modulus, GPa	Tensile strength, MPa
Cortical bone, longitudinal direction	17.7	133
Cortical bone, transverse direction	12.8	52
Cancellous bone	0.4	7.4

Table.2.2. Mechanical properties of metallic and ceramic biomaterials

Material	Modulus, GPa	Tensile strength, MPa
Metal alloys		
Stainless steel	190	586
Co-Cr alloy	280	1085
Ti –alloy	116	965
Amalgam	30	58
Ceramics		
Alumina	380	300
Zirconia	220	820
Bioglass	35	42
Hydroxyapatite	**95**	**50**

Table.2.3. Mechanical properties of polymeric biomaterials

Material	Modulus, GPa	Tensile strength, MPa
PEEK- Polyetheretherketone	**3.3***	**110***
PE- Polyethylene	0.88	35
PU- Polyurethane	0.02	35
PTFE- Polytetrafluoroethylene	0.5	27.5
PA- Polyacetal	2.1	67
PMMA- Polymethylmethacrylate	2.55	59
PET- Polyethyleneterepthalate	2.85	61
SR-Silicone Rubber	0.008	7.6
PS- Polysulfone	2.65	75

*comparable to natural bone properties

2.2 Role of stress shielding in structural compatibility

Upon fracture, bone loses its load bearing capacity and becomes non functional. In order to serve the functional purpose of the bone, an immediate support is required. The support could be a plate or shaft implant. Based on the fracture site, the damage extent and bone loading are

assessed by surgeons and recommend either external bone fixators or the internal fixators. The main purpose of these supporting fixators is to share the load between the diseased bone and the implant. The bone implants are designed on the load calculations, i.e. the percentage of total load to be supported. Following mechanics of materials would explain the load sharing between bone and the implant.

$$P = P_B + P_I \quad (2.1)$$

Where, P = Total load on fully functional bone

P_B = Part of the total load P to be borne by the diseased bone

P_I = Part of the total load P to be borne by the bone implant

Further, the deformation compatibility between bone and implant of equal lengths is explained by

$$\frac{P_B}{A_B \times E_B} = \frac{P_I}{A_I \times E_I}, \text{ where A= Area and E= Young's modulus} \quad (2.2)$$

Upon rearranging the equation (2.2)

$$\frac{P_B}{A_B} = \frac{P_I}{A_I} \text{ x } \frac{E_B}{E_I} \quad (2.3)$$

From equation 2.3, it is clear that the load sharing of diseased bone depends on ratio of elastic moduli between bone and implant materials. The load bearing or the induced stress in the bone is inversely proportional to the elastic modulus of implant material, E_I. For higher values of E_I compared to E_B, the component of load on bone or the induced stress in the bone is smaller to that of implant. Or in other words major portion of the total load is borne by the implant.

Wolff's law explains the dependency of the internal structure and architecture of a bone in the healing stage to external stimuli. During bone healing, healthy and solid bone results in, when the bone part is sufficiently loaded or stressed compared to the implant. Conversely, the bone healing is impaired if the implant material is stiffer or loaded heavily than the fractured bone. Or in other words the stronger/ stiffer implants decelerate the bone repair. This phenomenon is known as 'stress shielding' or 'stress protection'. Stress shielding is thus proportional to degree of stiffness mismatch between bone and its implant. Structural compatibility is graded to be excellent if the degree of mismatch is zero or $E_B \approx E_I$. Analogy of plant stem with/ without support is given in following Fig. 2.2. A rigid support will lead to weaker stem of the plant and so is the case with bone implants to bone.

Fig. 2.2 Effect of stress shielding

With a closer look at the elastic moduli of bone and the metals presented in Table 2.2 and 2.3, metals have Young's modulus nearly 20 times greater than that of bone. This would lead to stress shielding and retarded healing of diseased bone. Whereas, from Table. 2.3, it is evident that, the elastic modulus of polymers is low and well comparable with the natural bone. This fact made the polymers and its composites to lead the race of bone implant materials. Polymer composites have a positive edge over all other implant materials in mimicking the anisotropic and tailored bone strength properties by appropriate reinforcements and processing techniques.

2.3 Investigations on non resorbable polymer composites

Investigations by several authors on non resorbable polymer composites such as CF/ PMMA [11], CF/PP [12], CF/PS [13,14,15,16], CF/ PE[17], CF/ Nylon, CF/ PBT[18], CF/ PEEK [19-25] have been illustrating the prospective features of polymer matrix in composite materials. Further, CF/ PEEK bone implants have been proven superior in following aspects:

- Excellent biocompatibility[26]
- Excellent resistance to hydrolysis and sterilization radiation[26]
- High strength and fatigue resistance[21,27]
- No reported carcinogenicity[28]

PEEK was identified as promising candidate for bone implants in 1990s. It was found to be indispensible polymer due to its mechanical strength. Researchers studied various reinforcements to tailor the Young's modulus in following lines:

- Short fiber composites[18]
- Continuous carbon fibers and knitted fibers[29,30]
- Braided fibers[23]

It was observed from afore mentioned studies that PEEK and high strength polymer composites surpassed Titanium implants.

2.4 Investigations on fully/partially resorbable polymer composites

The primary function of skeletal tissues is to support and to promote the damaged bone tissue in self healing [31, 32]. An internal or external fixation is required to reposition the native tissue by creating appropriate mechanical environment for functional healing. Such fixators are removed from the implant site upon achieving the required level of tissue growth. Removal of implants from the patient body requires a reoperation. Resorbable polymers' fixation in the body does not require a second surgical event as they are biodegradable. Required initial support in terms of mechanical properties such as Young's modulus and strength of the biocomposite and synchronized/ controlled rate of polymer degradation in tune with the healing process are expected from bio-resorbable implant composites. Several studies on in vivo resorption rates of PLA, PGA, PLLA and their composites were published [33-36].

However, due to inferior mechanical properties exhibited by resorbable composites, their usage was limited for very light load bearing sites [37].

Efforts were made to reinforce polymers such as PLA (resorbable) with CF (non resorbable) to enhance mechanical properties. Such studies under partially resorbable polymer composites were reported through publications [38-42].

Studies on partial resorbable composite, CF/ PLA reported superior invivo behavior in initial stages of implantation [42]. The too rapid in vivo PLA degradation of CF/PLA barred the composite for bone implantations.

The concerns left open for further research are:

i) Synchronized resorption of composite implants in tune with tissue healing rate [43]

ii) The effects of non resorbable fibers left in native tissue [44]

2.5 Role of mechanics in design of implants

Conventional plate bone implants share the load coming upon to the fractured bone but always the load axis being offset from the bone axis. These eccentric loads/ offset loads complicate bone stress system with additional bending and twisting loads. A new paradigm called to be 'Intra medullar implants' with GF/ PEEK gained popularity [45] and obviated above problems. Intra medullar implants pass through the bone coaxially and support the fractured bone. Though, intra medullar implants perform well in bearing axial and bending loads, they were found poor in shear resistance [46].

Spine cages and support implants made of CF/PEEK and CF/ PS were found excellent in spine fusion applications [22, 28]. The implants above mentioned were also rated well in flexure and fatigue by the same authors. Powder particulate composites have been reported for their damping characteristics [47]

Prior to PEEK regime, PTFE and UHMWPE in virgin form were considered to be prominent polymer materials [48-50] due to their superior in vivo behavior.

The loads estimated on hip, femur and knee sites amount as high as 3-10 times the body weight. Metallic implants, which were thought appropriate at the critical sites as above mentioned, were replaced by CF/PEEK implants. CF/PEEK gained the popularity due to its mechanical stability in both invitro and in vivo.

Augmented stiffness and improved cell attachment were promoted by porous scaffolds. Bioactive materials such as bio glass, glass ceramics, Hydroxyapatite and bio-polymers embedded in porous scaffolds were found accelerating cell growth and cell attachment [4].

2.6 Degradation studies

Biocomposite exposed to in vivo fluids or Simulated Body Fluids (SBF) invitro alters their physical, mechanical, tribological and chemical properties. Matrix-Reinforcement interfaces are largely prone to rapid degradation. Impaired interface between reinforcement and composite matrix deteriorate the implant life and hence implant cease to function well before expected. Several invitro studies were conducted on biocomposites such as GF/ epoxy, CF/PS in SBF for evaluating their invivo stability [16]. Polymer – reinforcement interfacial failures of CF/PC,

CF/PS, KF/PC and KF/PS composites in SBF invitro were concluded due to the presence of water and salt ions at interfacial sites [51]. The results were more discouraging when the tests were conducted in fatigue mode [52].

However, CF/ PEEK withstood SBF and reported excellent mechanical stability [53]. Unlike CF/PEEK investigations, HA/HDPE revealed poor mechanical strength and failed in SBF environment. Virgin UHMWPE was found good in SBF but failed as a composite due to polymer reinforcement detachment.

Several studies on cell attachment to prosthetic scaffolds were mentioning the phenomenon dependency on scaffold material, scaffold parameters- Pore size, pore shape, pore distribution and pore interconnectivity [4, 54-71].

At the end, it is worth mentioning to choose a polymer composite with biocompatibility, which would be stable in SBF and withstand loads arise under body dynamics.

PART- II. BIOCOMPATIBILITY OF POLYETHER ETHER KETONE

2.7 Introduction to aryl ketones and PEEK

Polyaryletherketone (PAEK) has been found increasingly in biomedical applications since 1980 with evidences of biocompatibility by FDA approval [72]. Two major polymers of PAEK family were investigated for biomedical applications viz., Polyetheretherketone (PEEK) and Polyether ketone ether ketone ketone (PEKEKK). Among the two, PEEK was researchers' interest due to its superior mechanical properties both at room temperature and at high temperatures, and retention of mechanical properties up to 300^0C [73]. Apart from mechanical properties, PAEK polymers exhibit better compatibility with reinforcing agents and application counterparts, and possess chemical inertness, thermal stability, and ease of manufacturability. Interestingly PEEK was found to be structurally compatible with natural bone by its strength and stiffness [74]. Virgin PEEK (without reinforcing components) with Young's modulus in the range of 3-4GPa and tensile/compressive strength 100 MPa was found to be easily tailored to the properties of cortical/Cancellous bone by proper reinforcement and suitable manufacturing process [75].

PEEK has emerged as potential polymer by 1990s due to positive clinical reports and proven in vivo stability [73]. Other polymers that were in use till 1990s were surpassed by PEEK as they were altered frequently or discontinued by the manufacturers.

PEEK was identified as an interesting polymer [73] and made it to be superior over metallic implants by virtue of its radiolucency, bio-inertness of wear debris and their resorption, cell proliferation and in situ cell attachment. At situations demanding for higher strength of implants (as in cortical bone) PEEK was either used as coating on metallic implants or in composite form with reinforcements such as Carbon fibers, Glass fibers, Hydroxyapatite [76, 77].

2.7.1 Crystalline structure

Like most of the polymers, PEEK is semi crystalline in structure with amorphous phase in coexistence with crystalline phase. The crystal structure of thermoplastic PEEK is orthorhombic. PEEK exhibits excellent and stable mechanical properties up to its glass transition temperature 143^0C and undergoes crystalline melting at 343^0C. Presence of amorphous phase and its percentage depends on the history of thermal processing and manufacturing process [73]. A PEEK rod extruded could be seen with amorphous structure at outer surface and crystalline at inner core due to cooling rates and surface phenomena in heat transfer. Surface cooling rates, mould design, composite fillers, and heat treatment processes further complicate the crystallinity of PEEK/ PEEK composites [78]. Crystallinity, processing, and mechanical properties being interlinked, processing methods are at demand for specific in-situ applications.

Thermal processing of PEEK play a vital role in resulting bulk density (1.265 g/cc to 1.4 g/cc), by influencing the percentage of amorphous phase as against the percentage of crystallinity [79]. Heat treatment after mechanical processing would be a tool to control crystallinity, density, and mechanical properties.

2.7.2 Chemical inertness

The macromolecule of PEEK shown in Fig 2.3 , with decolonized free electrons and with lowest potential energy, called to be in a *state of resonance stable structure*, is the key for PEEK chemical inertness [73]. It is highly unreactive to all solvents except to 98% concentrate Sulphuric acid. Virgin PEEK is a good water resistant (hydrophobic) material with a maximum solubility of 0.5% by weight and doesn't degrade for prolonged exposure even upto 260^0C[73-75]. However, PEEK in composite form has higher rates of water absorption due to the presence of reinforcing agents such as Hydroxyapatite, Carbon fibers/ Glass fibers etc. Water absorption in PEEK was found to affect crystallinity to a little extent [82].

Application of PEEK as biomaterial is justified through well established clinical studies on toxicity/ cytotoxicity [72,83,84], cell culture experiments [85,86,87], immunologenesis[88], genotoxicity [89].

Upon established physical,chemical, mechanical and clinical behaviour of PEEK, its composites were justified to be implants invivo. Human body temperature (37^0C) being well below glass transition temperature of PEEK(143^0C), thermal degradation point of view PEEK and its composites were found safe in invitro[90]. Due to inherent ketone locking in molecular arrangement, PEEK is stable under clinical radiation [91,92].

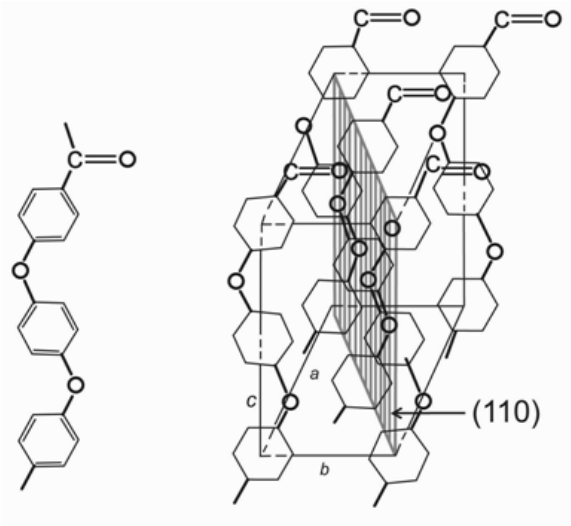


Fig. 2.3 Chemical formula and crystalline structure of PEEK

(reproduced from Exponent Inc.)

2.8 Mechanical behaviour of PEEK and PEEK composites

PEEK exhibits a linear relation between stress and strain up to 0.03 strain and defines a clear elastic modulus. The uniaxial tensile tests conducted on PEEK have established independency of Young's modulus from strain rates. The *change in slope* of stress- strain diagram, indicating yield criteria, was found to be dependent on strain rates, keeping all other parameters unaltered. Higher strain rates in simple tension have resulted in higher yield strength but reduced percentage of elongation [93].

Temperature effects on stress- strain behaviour of PEEK was predicTable and similar to any other material[93]. Rise in temperature didn't affect the elastic modulus but there was a noticeable drop in yield strength. The effect of temperature on mechanical properties was

noticeable only beyond 100^0C. Thermo mechanical behaviour of PEEK substantiates its functionality at human body temperature 37^0C.

PEEK was found to be superior in almost all biomedical applications such as trauma, spinal, and femoral implants [7]. Though PEEK is a good bearing material, its applications at hip and knee prostheses were limited [94,95]. Hip and knee prostheses need high load bearing capacities apart from excellent tribological properties. For load bearing applications, PEEK with carbon fiber reinforcement (CFR) is preferred. Presence of CFR was found complicating the prosthesis sites with carbon wear debris [96,97] in CoCr-PEEK CFR bearing surface combinations. Zirconia was found to be the favourable tribological candidate at hip and knee until the clinical trials detained its usage. Alumina was found and in use as best counterpart candidate for PEEK- CFR bearing sites. PEEK- CFR bearing surfaces were proven to be better performers at lower hip stress conditions as against UHMWPE [96]. Literature on orientation of reinforcements layers [98] in improving the mechanical properties of polymer composites is commendable.

PEEK was finally accepted to be the superior high performance thermoplastics both mechanically and biologically over its peer group[73]. The possible reasons could be summerized as below:

1. Inherent thermal, chemical, radiological and immunological inertness of PEEK
2. Excellent in situ cell attachment, proliferation and growth with reinforcements such as Hydroxyapatite, Tricalcium phospate, carbon fiber etc.
3. Processability of PEEK
4. Failure of other high performance thermoplastics in processing of polymer/composite at one or many stages
5. Established positive clinical trials of PEEK and its composites
6. Stable commercial supply of PEEK for medical applications

PART- III. SCAFFOLDS & MANUFACTURING METHODS

In Tissue Engineering (TE), **Scaffold** is a supporting structure made up of biocompatible materials and acts as a template for tissue growth in three dimensions at the site of implantation.

2.9 Scaffolds in Tissue Engineering

Osteoporosis is a common serious problem in orthopedics. Damaged bones or parts are treated in two ways. The first being total replacement using bioinert materials and the second is to transplant the required. The problem in the former is to go for several replacements to the original by surgery due to the life span of bioinert implants. This being painful, for large bone defects an alternative thought of was transplantations. The transplantations have lack of donors. Both of these techniques are tissue replacement techniques. A shift in the thinking necessitated scaffolds as alternative to these replacements. Scaffolds, in contrast to replacements, work on the principle of regeneration of damaged parts. One path to follow is the regeneration of bone using ceramic and glass scaffolds that mimic the structure of bone material, bond to bone and in some cases activate the genes within bone cells to stimulate new bone growth.

2.10 The need for biomimetics of bone

Bone is a natural composite of Collagen (polymer) frame work with a reinforcing bone material (ceramic). The two most important types of bone, cortical and Cancellous bone are shown in Fig 2.4. Cortical bone, also known as Compact bone is a dense structured bone with high mechanical strength. Cancellous or Trabecular bone with internal porous supporting structure is present at the ends of long bones such as femur or within the confines of the cortical bone in short bones. Trabecular bone is a network of struts enclosing large voids (macro pores). Osteoporosis is a disease in Cancellous bones where bone resorption occurs faster than a new bone is produced, causing the Trabeculae become thinner, reduced in bone density and strength. The disease eventually leads to fracture of bones especially in the hip, wrist, knee and spine. Till recent past, when osteoporotic fracture occurs in knee or hips, joint replacement is often required. Charnley total hip replacement, an orthopedic prosthesis made of bio inert materials can be quoted as an example to this situation. Reasons for failure of such replacements were reported due to mechanical aspects like mismatch in the Young's modulus of the bone and the metal stem. Many modifications and variations of the Charnley joint have been developed over the years, including coating the metal stem with a synthetic Hydroxyapatite layer that can bond to the bone mineral in the bone.

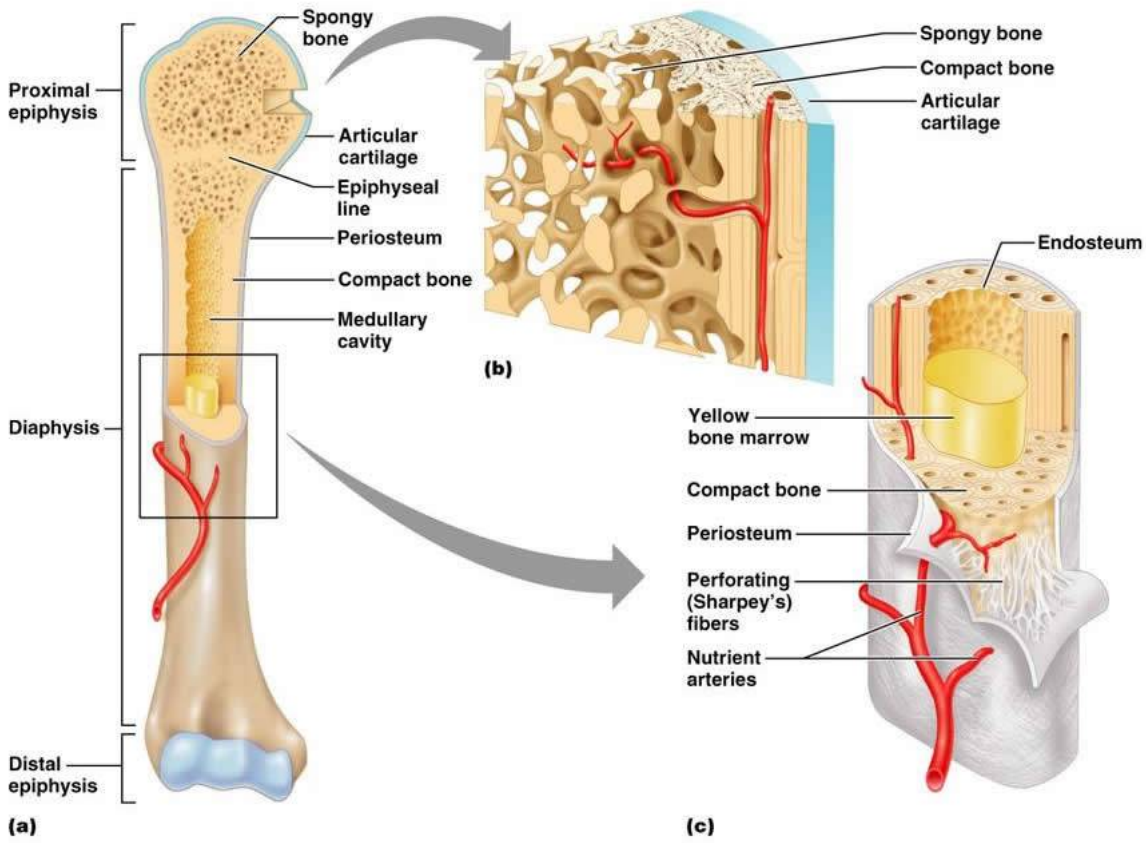


Fig. 2.4 Anatomy of bone a) Anatomy of long bone b) Section of Cancellous bone c) Section of Cortical bone

2.11 Strategies in bone damage repair

Present day orthopedic implants look for three of the most critical characteristics of living tissues:

1. The ability to self repair,
2. The ability to maintain a blood supply and
3. The ability to modify their structure and properties in response to environmental factors such as mechanical load.

All implants have a limited life span. As human life expectancy is continually increasing, it is proposed that a shift in emphasis is required from *replacement of tissue to regeneration of tissue* to satisfy the growing need for very long lasting orthopedic repair.

One way to restore damaged or diseased tissue to its original state and function would be successful tissue engineering in the laboratory. In a typical tissue engineering application, cells would be harvested from the patient and seeded on to a synthetic scaffold that acts as guide and stimulus for tissue growth in three dimensions creating a tissue engineering construct or living biocomposite. The biocomposite would then be implanted back in to the patient [99, 100]. Over time, the synthetic scaffold should resorb in to the body as non-toxic degradation products at the same rate that of the cells produce their extra cellular matrix [101].

To regenerate a Trabecular bone, a construct or scaffold is required to mimic the structure of Trabecular bone and to stimulate new bone growth when cultured with osteogenic cells (Osteoblasts) [102].

2.12 Ideal scaffold

An ideal scaffold would be one that mimics the extracellular matrix of the tissue that is to be replaced so that it can act as a template in three dimensions on to which cells attach, multiply, migrate and function. The criteria for an ideal scaffold for bone regeneration are:

1. It is made of a material that is biocompatible, i.e. not cytotoxic.
2. Acts as template for tissue growth in three dimensions.
3. Has an inter connected macro porous network containing pores with diameters in excess of 100μm for cell penetration, tissue in growth, vascularisation and nutrition delivery to the center of the regenerating tissues on implantation [101,103,104].
4. It is made from an osteoconductive material, i.e., bonds to the host tissue without the formation of scar tissue.
5. Exhibits a surface texture that promotes cell adhesion, adsorption of biological metabolites [105].
6. Influences the genes in the bone generating cells to enable efficient cell differentiation and proliferation.
7. Resorbs at the same rate as the tissue is repaired, with degradation products that are non toxic and can be easily excreted by the body, for example via the respiratory or urinary system.

8. Is made from a processing technique that can produce irregular shapes to match that of defect in the bone of the patient.
9. Exhibits mechanical properties sufficient to be able to regenerate tissue in particular application such as bone in load bearing sites.
10. Has the potential to be commercially producible to the required International Standard Organization (ISO) or Food and Drug Administration (FDA) standards.

2.13 Role of rapid prototyping

Although processes like gel-casting and direct foaming of solid gel mimic the structure of Trabecular bone, it was found poor control of these processes on pore interconnectivity. Rapid prototyping can rapidly produce highly complex 3D objects using Computer Aided Design (CAD) systems. Series of images of a defect in a patient are taken (by X-ray micro tomography, CT scan, etc) to develop 3D CAD computer model. Patient specific scaffold preparation was a major breakthrough with CAD and rapid prototyping. Scaffolds or patient specific 3D objects are produced layer by layer material addition rapid prototyping techniques such as- Fused Deposition Modelling (FDM), Selective Laser Sintering (SLS), 3D Printing, and Stereo Lithography [106]. Rapid prototyping is found to be useful in reproducible pore size and inter pore connectivity. However, the challenge is user specified material.

2.14 Conventional sintering versus microwave sintering

The potential use of Hydroxyapatite (HA) in bone replacement and reconstruction was emphasized in the synthesis of HA through microwave sintering route [107]. Hydroxyapatite synthesized from solution precipitation followed by spray drying technique was studied for HA load bearing capacity purpose. The findings were showing microwave sintering is time and energy efficient under prescribed conditions of heating and holding cycles over conventional sintering of HA. It also describes the densification and cracking of HA by microwave sintering. Authors found in one segment, 1100^0C for 3hours in conventional sintering was able to obtain a maximum HA density of 97%. Application of microwave sintering could accelerate the process of achieving 99% dense HA, at 1100^0C, within 0.5 hours. But minor cracks were observed due to microwave sintering.

Alumina and Zirconia, the other prominent bioceramics were synthesized through microwave sintering using modified kitchen micro wave oven [108]. The problem of non absorption of microwaves in sintering of Alumina and Zirconia has been resolved by Si C susceptor. SiC susceptor was used as heating element in thermal boosting of until the dielectric loss of ceramics. Effect of susceptor positions, full power and stepped power in microwave heating were explained as a function of time and prevailing temperatures. Rate of heating was concluded to be the key factor in microwave heating to obtain fine grain size thus leading to achievement of full density and improved strength.

Preparation of porous scaffolds through several routes were compared with rapid prototyping techniques and the strengths of rapid prototyping were attributed to ease of extraction of patient data (through CT scan, MRI etc), modeling the defects via Computer Aided Design (CAD) systems and producing complex 3D physical models for implantation [108].

Superiority of microwave processing over conventional processing of ceramics such as time and energy saving, rapid heating rates (>400^{0}C/min), considerably reduced processing time and temperature, fine microstructure, environmental friendly and improved mechanical properties was established through experimentation [109-114]. In this review, WC+ Co bodies were reported sintered within 10-30 minutes, one tenth of the time required in conventional sintering with better mechanical properties [115, 116]. It was found dramatic when reduced oxide precursors were used in synthesizing titanate and tantalate based electro ceramics. The microwave coupling in the presence of a defect structure (reduced) causes extremely rapid reaction kinetics and new reaction paths, producing materials at much lower temperatures than normally obtained by conventional heating method. It was also mentioned in this paper that the sintering of powdered metals and fabrication of transparent ceramics in a single step process as the significant development in microwave processing. Reasons for densification through microwave processing were explained by phenomenon, the concentration of electrical energy in the closed pores of the green ceramics.

2.15 Importance of composite ceramics

Biomaterials have been classified in to bioinert and bio-active materials. A major focus was put on ceramics. Biomaterials were defined as natural or synthetic materials suitable for introduction in to living tissue especially as a part of medical device [117]. Much of the bioinert materials discussions have been made on Alumina and Zirconia ceramics. These ceramics have good wear

resistance and negligible amount of ion release at the bearing contacts, promoting them to be used as femoral heads, total hip and knee replacements. These materials were reported to have a severe setback of possessing biological/ mechanical shielding between the implant and the bone. With these restrictions, bio inert ceramics are hardly used as bone fillers.

The bio-active ceramics were found to provide favourable surfaces for bone adhesion and bone in growth [118]. Regardless their load bearing capacity, calcium phosphate minerals mainly Hydroxyapatite (HA) and tri-calcium phosphate (TCP) were suggested as prominent bio-active ceramics due to their closeness to mineral part of bone. The major drawback of calcium phosphate and bio-active glass is their brittleness. Since high porosity is absolutely needed for osseointegration, the only way to achieve less brittle bone substitutes is to use intrinsically tougher materials, like ceramic – polymer composites. Water soluble polymers in bone cement have been suggested for better in situ bone cement settling.

2.16 Thermal stability and mechanical strength of HA

Synthesis of HA through three different routes viz., s-HA(stoichiometric HA prepared by wet solution precipitation method), d-HA(calcium deficient HA prepared by wet solution precipitation method) and m-HA (HA prepared through wet mechano-chemical method)[119] explains the impact of manufacturing route on their mechanical properties. It was observed that the wet m-HA results in high sintering density compared to s-HA and d-HA. But on the other side m-HA revealed very low porosity compared to the other two. In all the three HAs, it is found densification is nil or too low below 1000^0C sintering temperature. Densification is found to start occurring at lower temperatures in case of m-HA and d-HA as compared to s-HA. Experiments revealed that densification starts at early temperatures and depends on calcium deficiency (Ca/ P ratio less than1.67), i.e. m-HA and d-HA compared to s-HA (Ca/P=1.67). However the final sintering density depends on the particle size, the homogeneity and the agglomeration character of powder precursor. Due to the aforesaid reasons, it was found, the sintered m-HA density was maximum (93.5%) and followed by s-HA (89.4%), d-HA (76.8%) of theoretical density. These results were found to be partially disagreeing with the earlier findings [120, 121]. Finally, HA prepared by mechano-chemical route (m-HA) was found to be superior in densification, micro structural uniformity and mechanical loading properties (compressive

strength). Whereas, s-HA was found to be thermally stable up to 1200^0C. Compressive strength was found to be declining with an increase in porosity.

2.17 Solid free form fabrication of scaffolds (SFF)

SFF has been developed for the fabrication of scaffolds using powder constituents of the composite through Selective Laser Sintering (SLS) process [5]. SFF has been preferred to avoid organic solvents used in liquid based processing techniques as the traces of organic solvent residues were proven toxic invivo [122]. Properly mixed PEEK and HA powders were successfully sintered using Selective Laser Sintering. Experiments were conducted with three process parameters at a constant laser scan speed of 5080 mm/min viz., composition of constituents HA/PEEK, part bed temperature for preheating and laser power for powder melting. HA being brittle and delamination of reinforcement in polymer matrix as an additional challenge, weight composition of HA in PEEK/HA composite was limited to a maximum of 40%. Part bed temperatures (PBT) 110^0C and 140^0C were chosen on the basis of glass transition temperature of PEEK, T_G= 143^0C. Laser powers in watts were set in two steps i) at 10,12,14, 16 and ii) at 9,12,16,20,24,28 respectively at a PBT of 110^0C and 140^0C. PBT closer to T_G was found influencing for better bonding between composite particles. Laser powers less than 16w were found resulting in HA debonding. Authors suggested limiting HA in composite to 40% for better bonding between PEEK and HA. Results were found promising at 140^0C PBT and 21W laser power.

2.18 Polymeric sponge method for HA scaffolds

An indirect method to produce porous scaffolds was developed by authors [123] and demonstrated in HA. Preparation of porous nano Hydroxyapatite scaffold through polymeric sponge method was carried out in three stages viz., preparation of slurry, cellulosic sponge impregnation, drying and sintering with controlled parameters. Scaffold mechanical strength in compression was found to be better with higher apparent density of slurry resulted from prolonged stirring times. Higher rate of heating was reported in improved mechanical strength and Young's modulus and reduced amorphous structure. Maximum compressive strength of the bone was reported to be 10 MPa which mimics the Cancellous bone. Prolonged slurry stirring times and higher rate of heating were reported favourable for better mechanical properties.

2.19 PEEK fabrication using Mask-Image-Projection-based Stereo lithography (MIPS)

PEEK, the promising biomaterial yet challenging in processing, researchers [124] have attempted to explore the difficulties and solutions such as i) High melting point of PEEK (343^0C) and ii) High viscosity, iii) Chemically stable. An indirect rapid prototype assisted technique MIPS was developed to overcome the mentioned difficulties. Authors of this work have presented preliminary SLA technique to fabricate PEEK based photo curable liquid resin. Key discussions in this work suggest the ways to prepare PEEK composite slurry, Green parts fabrication through SLA and Sintering process for improved mechanical properties.

A photo curable resin S1500 obtained from Envision Tec Inc and PEEK 150PF obtained from Victrex Co were mixed properly to prepare viscous slurry. The viscosity of the slurry was reduced to required levels by addition of isopropanol in limited quantities. Slurry prepared was found flowable with PEEK less than 27.5 %. Percentage of PEEK higher than 27.5 was seen resulting in non flowable slurry.

Heat treatment/ Sintering of green parts at different temperatures were tested for mechanical properties. Sintering temperatures ranging between 275^0C-290^0C with a rate of heating 10^0C/ min were found resulting in better mechanical properties. Typical values of Young's modulus and hardness on Rockwell scale were ranging between 808 MPa-776 MPa and 59 HRF-61 HRF.

2.20 Biodegradable polymer composites

Biodegradable polymers being resorbable do not require a second surgery. Attracting the attention of several authors [125], the role of biodegradable polymers and bioactive ceramics in scaffold preparation were comprehended. Extensive discussions have been presented on materials, processing methods, mechanical integrity of scaffolds and drug delivery concepts. Degradation kinetics of resorbable polymers such as PLA, PLLA, PGA, PDLLA, Polypropylenfumerate (PPF), Polyhydroxyalkanotes etc., were discussed in this presentation. Authors broadly commented on in vivo degradation of such materials and the same was ascribed to crystallinity of polymers. Crystalline materials were mentioned of their superior degradation stability compared to amorphous structure.

Mechanics of bioactivity in ceramic phases was explained with supporting publications [102,126]. Hydroxycarbonateapetite (HCA) formation on the surface of bioceramic implants invitro/ in vivo was found to be the key factor in bone attachment / osteoconductivity. Bioactive

glasses, glass ceramics, Hydroxyapatite and calcium phosphate minerals were conferred of bioactivity by formation of HCA at the implant/ native bone interface. HA and calcium phosphates were identified with excellent bone attachment. Further, silicon substitution in to HA has been identified as bone in growth promoter [127].

2.21 Processing PEEK/nHA biocomposite

A composite of PEEK and synthetic nano HA(nHA) was experimented through conventional sintering methods [128]. nHA with a particle size of 100nm prepared through chemical precipitation route was used in PEEK/nHA composite. PEEK/nHA blend was prepared by magnetic stirring with ethanol as dispersant followed by vacuum filtering and sintering at 350^0C in vacuum. TG and DSC studies revealed thermal stability of PEEK/nHA composite and substantiated a gradual increase in decomposition temperature and maximum weight loss with the increase in fractional amount of HA in the composite. Also observed was a slight drop in decomposition temperature of the composite when the HA fraction was raised above 30%. The compressive strengths of dense composite specimens were reported nearly 235 MPa as against the requirement in cortical bone, 133 MPa. Increase in HA was reported affecting the compressive strength.

2.22 Polyetherketoneketone biocomposite with HA whiskers reinforcement

A study on non degradable, porous biocomposite scaffold with Polyetherketoneketone (PEKK) polymer matrix reinforced by Hydroxyapatite whiskers [129] has been exhibiting the supremacy of Polyaryletherketones (PAEK family). Hydroxyapatite whiskers measuring 21.6 (+16.9/-9.5)µm long and 2.8(+0.8/ -0.6) µm wide produced in laboratory were used as reinforcement in PEKK matrix.

The prepared specimens were tested in unconfined, uni-axial compression mode with a cross head speed of 1mm/ min. The following findings have been noted.

i) Increased porosity resulted in decreased Young's modulus and yield strength with a power law between density and mechanical properties.
ii) Young's modulus was found increasing with an increase in HA between 0- 20% by volume. HA beyond 20% was found decreasing the Young's modulus. Highest Young's

modulus, 149 MPa was reported at 20% HA whisker reinforcement with 75% porosity and 375^0C sintering temperature.

iii) Increase in HA was found to decrease the yield strength and associated strain. 2.2 MPa was observed as the maximum yield strength at 20% HA whisker reinforcement with 75% porosity and 375^0C sintering temperature.

iv) Increased mould temperature resulted in increased Young's modulus, yield strength and strain.

Chapter 3 PROBLEM FORMULATION- METHODOLOGY

3.1 Motivation behind the proposal of present work

Over last seven decades and odd years, biomedical researchers are continuously working for the improved life expectancy of human. The area being open to several fields such as chemists, pharmacists, engineers, doctors etc, role of every individual disciplines is contributing for improvement. Every little effort towards the improvement of implant's life would definitely be felt a greater contribution at the global level of this field.

Mandate role of an engineer is evident in selection of materials, processing of materials, design of implants, process planning, computer applications and processes integration, thermal treatments, manufacturing with accuracy and precision, finally testing for implant's life and modifications thereof.

Importance of non degradable polymers such as PEEK was described by several authors. Though degradable polymers were the option of biomedical reserchers, PEEK application was not surpassed due to its interesting properties viz., mechanical strength and modulus, thermal stability in the process of manufacturing and in situ functionality, ease in processability, adsorption capabilties with reinforcements, chemical inertness, non toxic, non carciogenic, superior tribological nature, bio-conductive, high strength to weight ratio etc.

On the other side, PEEK being bioinert and less rigid compared to natural bone, Hydroxyapatite is found to be irresistable option to meet bio medical and bio mechanical requirements. Apart from PEEK/HA being a superior bio bearing coating, coating on metal shafts and screws, it can out perform all metallic supports with proper design and processing.

Proven bioconductive and inductive properties of HA were attractive. Further, natural extraction of HA from egg shells has been reported with added advantages of bone native cell affinity [130,131].

Improvement in mechanical properties with conventional methods, improved cell affinity through natural HA, indigenous economical processing without much compromise in quality were few prompting parameters in selection of present work.

3.2 Problem formulation and methodology

Demand for geometrically precise implants with appropriate biomaterials has become evident from literature review. Invivo response studies and clinical trials have been demanding continuous improvements in materials and their processing techniques. Load bearing sites were of particular importance to engineers, where structural compatibilities through material mechanics were necessitating. Hence role of an engineer working concurrently with biomedical researchers was prominently noticed in

1. Selection/ synthesis of materials
2. Utilizing the computer models for design or/ and analysis
3. Development of manufacturing/ processing methods
4. Testing and validation of bio implants invitro and assistance in in-vivo

Selection and synthesis of materials: Application of Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, commonly referred to as HA was clearly understood from the literature in the fields of orthopaedic and dental prostheses due to its excellent biocompatibility and bioactivity properties. Hydroxyapatite is chemically similar to the mineral component of bones and hard tissues in mammals. Cost of commercially available synthetic HA being high and natural HA extracted from egg shells, fish bone etc being cited proactive in bone regeneration, a major concern was shown for HA processing in this work.

Despite superior biological interaction of HA with native bone tissue, it was discouraged as structural material due to its ceramic nature. Poor toughness and tensile properties of HA were barriers in engineering perspective. Hence, concept of biocomposite has been thought of improving mechanical properties of HA afore said without a compromise in its biological activity.

Polyetheretherketone (PEEK) was chosen to be matrix constituent of biocomposite to establish superior mechanical and biological properties with HA as reinforcement. Application of this composite has been aiming at bone implants, support plates, spinal fusion, and surgical accessories such as screws etc.

Application of PEEK/ HA biocomposite was necessitating manufacturing methods to suit for dense or compact bone (cortical bone) and Cancellous (spongy or porous) bone. Two methods were brought forth to meet the bone requirements:

1. Compression moulding followed by thermal treatment and
2. Indirect method of porous scaffold preparation

Computer assistance in converting patient physiological data in to implant geometry, acquiring highest geometrical accuracy and repeatability in processing implants was found vital.

Invitro degradation studies on this composite throw a light on applicability as structural material. Simulated Body Fluid invitro testing was the tool applied to establish the facts. Mechanical property assessment through material testing and thermal stability studies were planned to comprehend structural compatibility.

Computer assistance in assessment of porous scaffold deformation behavior has been added to study several porous structures beyond the fabricated porosities.

Chapter 4 EXPERIMENTATION

4.1 SYNTHESIS AND CHARECTERIZATION OF HYDROXYAPATITE

Hydroxyapatite has several identified biological roles such as reinforcement, tissue adhesion, bone growth etc. Chemical, thermal and mechanical stability requirements of HA in severe human body conditions demand for careful synthesis and characterization. Following sections explain the attainment of requisite properties.

4.1 .1 Extraction of HA from Egg shells

Identifying the biological interaction with bone tissue, an attempt was made to develop HA powder from eggshells, a natural apatite rich substance through hydro thermal treatment. Eggshell, a cheaper and abundantly available source of HA is discarded as waste material during egg processing in baking of breads making industry. Commercially available HA is very costly and price would be tens of thousands to lakhs in INR per kilogram, depending on the quality of HA.

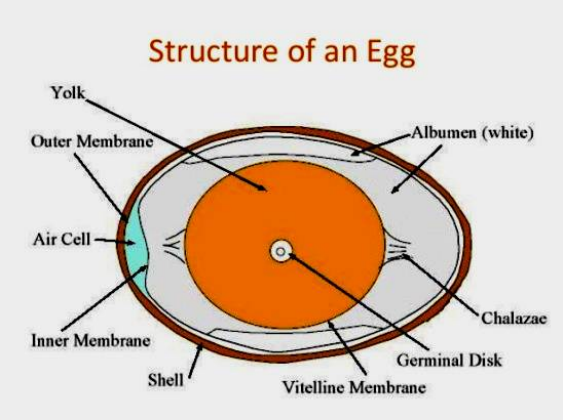


Fig. 4.1 Structure of an egg

The steps involved in preparation of Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$ ceramic powder p from the extracts of egg shells through thermal treatment followed by chemical processing with TCP as explained in [132] are:

1. Collection of egg shells and mechanical cleaning

2. Soaking in boiling water for 30 minutes to remove organic material
3. Drying for about 2 h
4. Simultaneous chemical and thermal treatment of dried egg shells in muffle furnace

Egg shell, the outer most part of an egg shown in Fig. 4.1 is a protective structure with sufficient porosity for passage of air. The shells discarded were collected from local bakery at Hyderabad and washed in running water to remove sticky matters. Washed shells were crushed manually and soaked in boiling water for about 30 minutes to remove organic matters left after washing. Dried egg shells were heated in muffle furnace equipped with PID control shown in Fig 4.2 at a controlled rate of heating, up to a temperature 300 °C and for 2 h in furnace. Organic material was burnt during this first cycle of thermal treatment. This cycle of heating was followed by a second heating to reach 600 °C temperature maintained for 2 h and third heating to reach 900°C temperature maintained for 2 h. The appearance of eggshells at the end of each cycle of heating is shown in Fig 4.3. By the end of the third cycle, the calcium carbonate transforms into calcium oxide through the evolution of carbon dioxide according to the following equation:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$

Fig. 4.2 Muffle furnace with programmable temperature controller

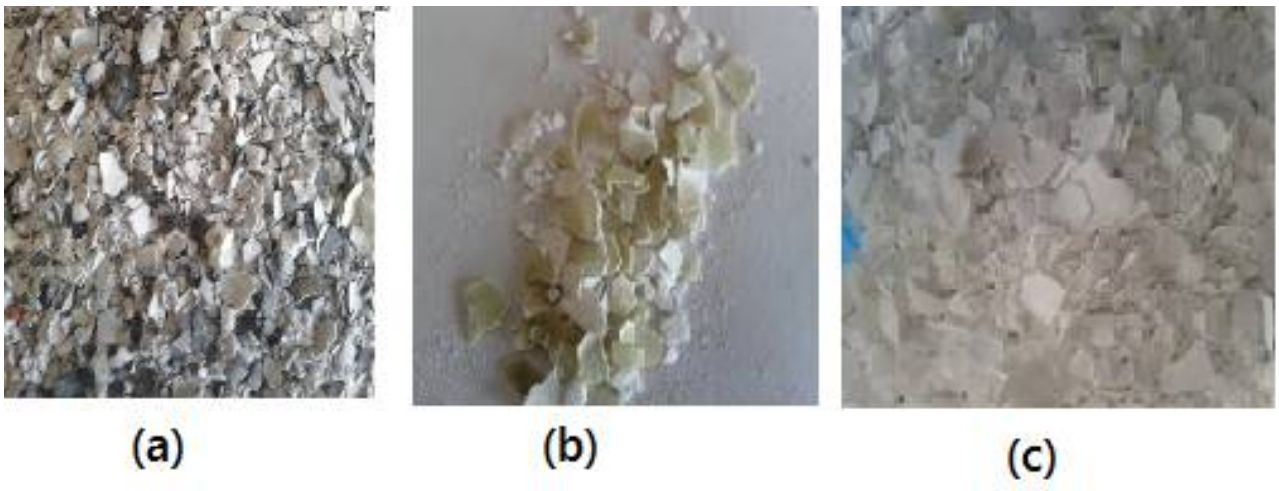


Fig.4.3 Appearance of eggshells during thermal treatment at (a) 300^0C (b) 600^0C (c) 900^0C

Formation of CaO was confirmed through XRD report obtained from IICT Hyderabad as shown in the Fig 4.4. The CaO was transformed into HA by reaction with tricalcium phosphate (TCP, $Ca_3(PO_4)_2$) in wet condition. The reactants with a ratio of 5.54g of CaO to 1g of $Ca(PO_4)_3$ for a Ca/ P ratio 1.67 of HA was followed as suggested by R Roy et al.1974 through their findings. The reaction was carried out at 1000°C for 3 h in a moist atmosphere. In the first place, when the calcium oxide was mixed with water, a reaction between CaO and H_2O took place to give Ca $(OH)_2$. Therefore, this phase was present as initial reactant, as well as during the subsequent reaction. Then Hydroxyapatite (HA) was obtained according to the following equation:

$$3Ca_3(PO_4)_2 + Ca(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

The resulting HA was ball milled for 4 hours and sieved through 120 grit size mesh to obtain uniform spherical particulates. SEM images shown in Fig 4.5 were confirming a near spherical shape of the HA particles.

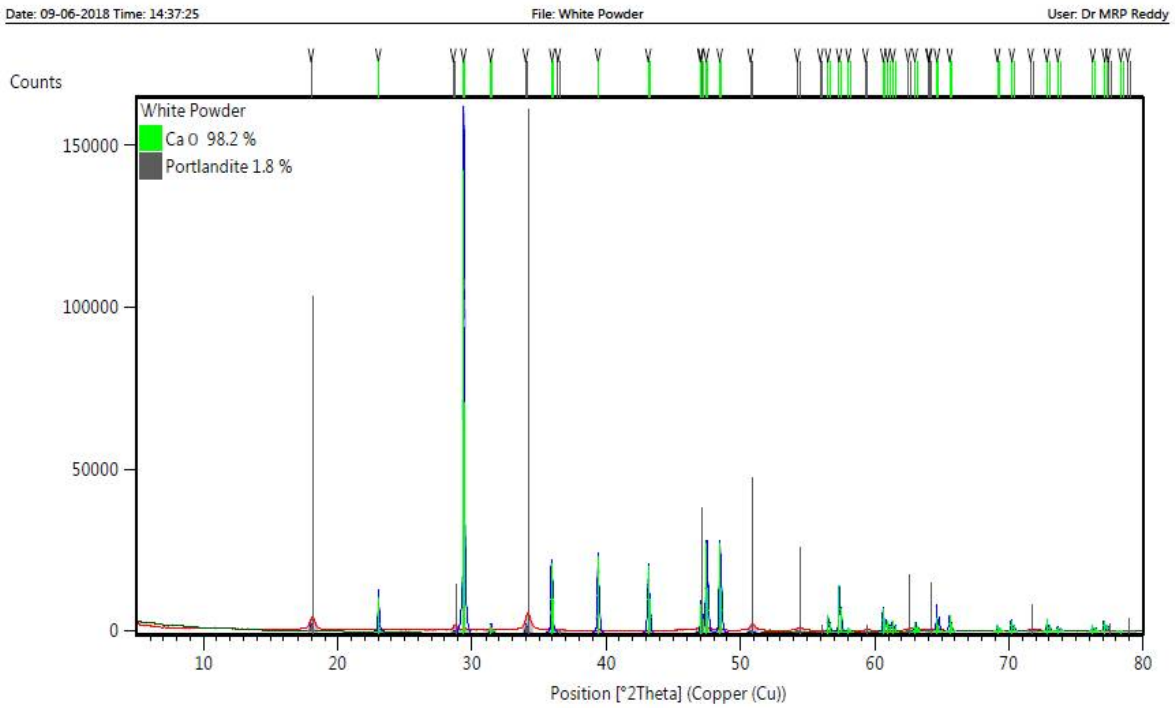


Fig. 4.4 XRD image of calcined egg shell

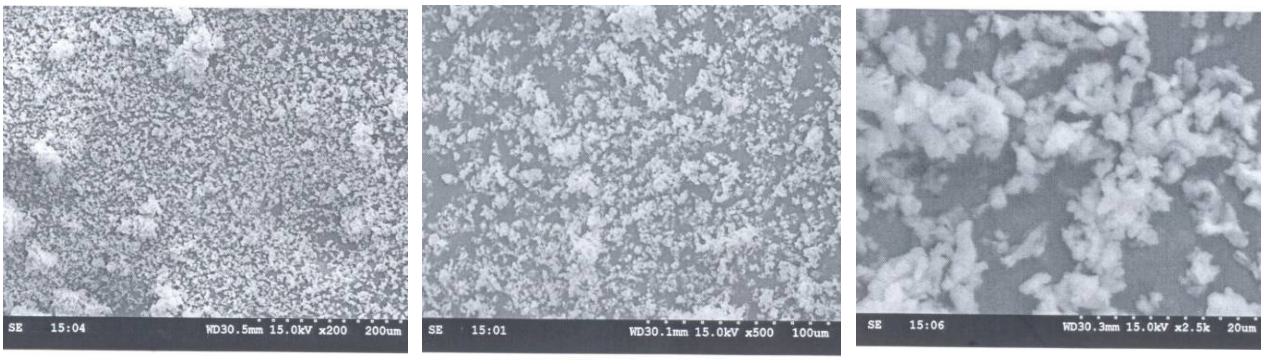


Fig. 4.5 SEM of HA

4.1.2 Thermal stability of HA

Thermal stability of the Hydroxyapatite is clear from the DTA shown in following Fig 4.6. Crystalline effects after 500^0C are clear from DTA revealing endothermic set. The change in mass was found negligible even up to 1000^0C from the results of TGA shown in Fig 4.7. Further it is concluded that HA is thermally and structurally stable for applications up to 1000^0C.

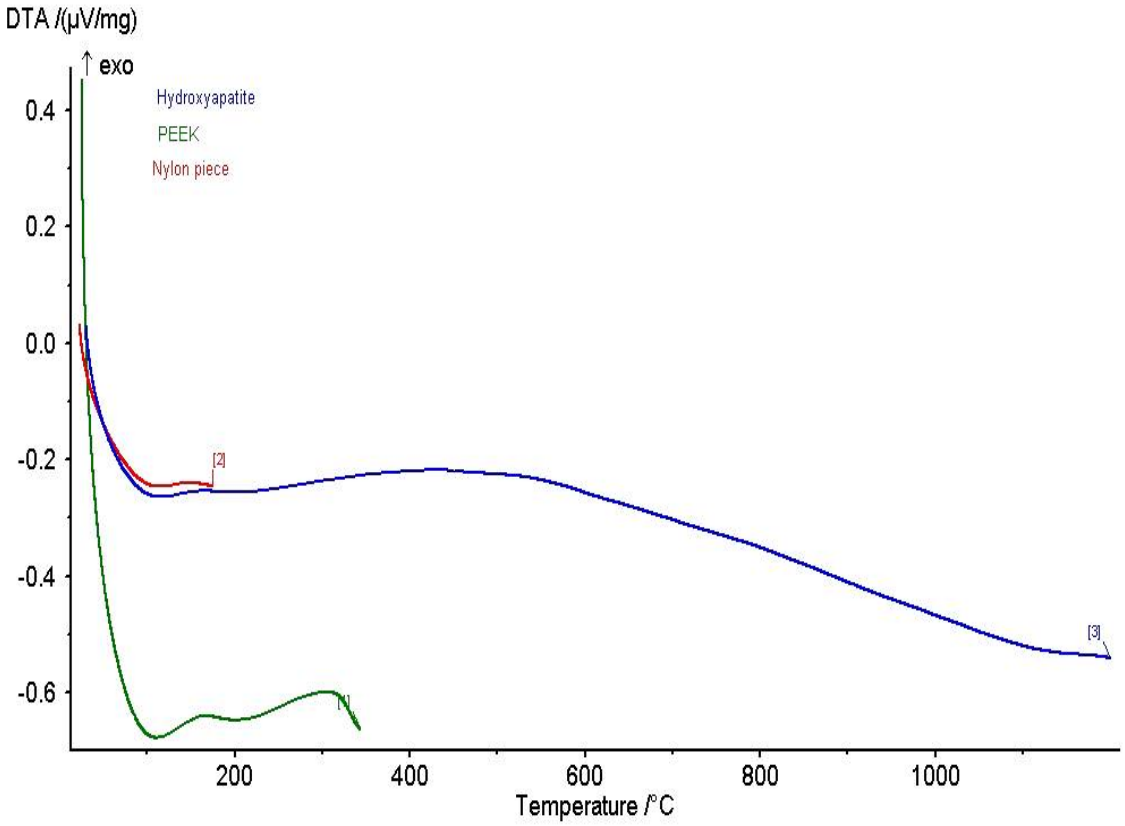


Fig. 4.6 Differential Thermal Analysis of HA (curve 3)

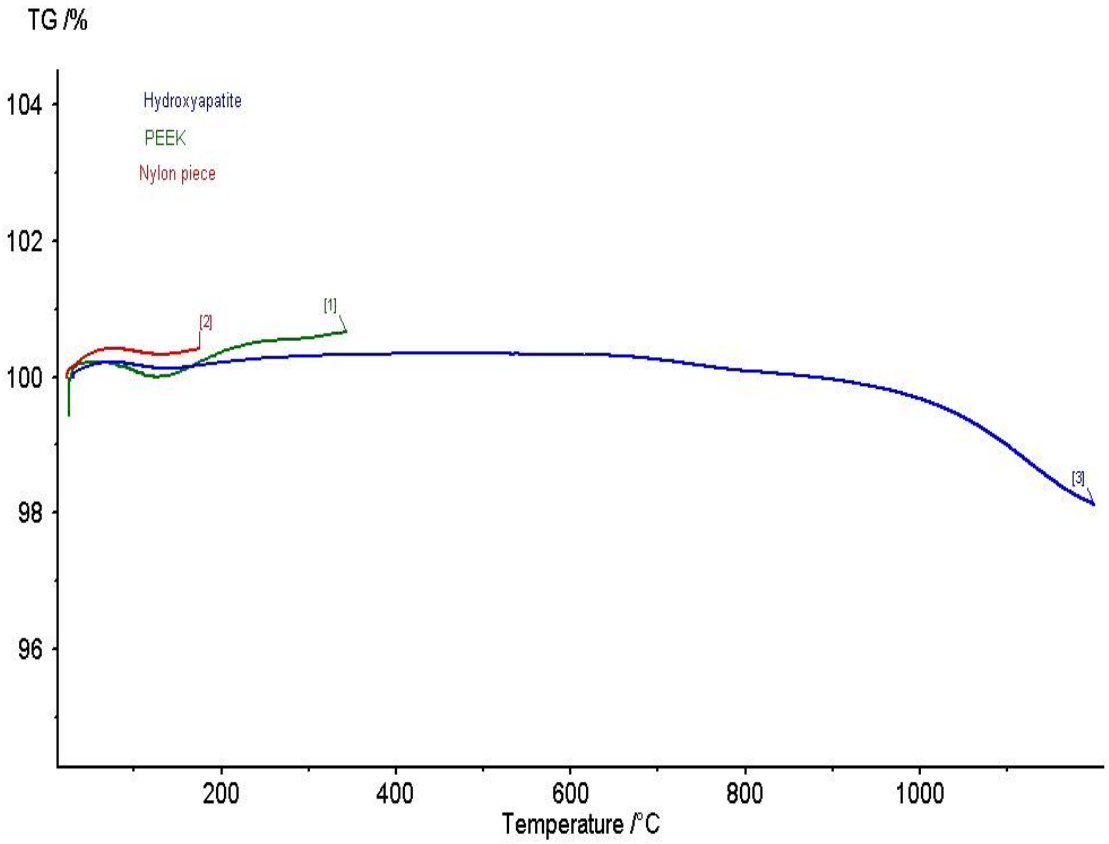


Fig. 4.7 Thermo Gravimetric Analysis of HA (curve 3)

4.1.3 Density of HA

The density of powder particulate is expressed in two ways, viz.

1) Apparent density and
2) Compensate or green density

Apparent density is defined as the weight per unit volume of a powder, in contrast to the weight per unit volume of the individual particles. The powder is firstly filled in a small container of known volume then the mass of the same powder used to fill the container is to be calculated. The ration of these two quantities gives us the apparent density of the powder.

The apparent density of sample of HA manufactured was found to be 0.5666gm/cc.

Green density or compensate density is the ratio of powder mass to the external volume of the powder in the form of pellets, and is a measure of how tightly packed the powder particles in the pellet are. The pellets are formed by using hydraulic press and a die. The powder of known quantity of mass was placed in the die and a force of 4 Tons was applied on the free powder in the die to get the required shape of cylindrical pellet. The volume of this cylindrical sample was calculated. The compensate density of HA processed was found to be 2.1 gm/cc.

4.1.4 Particle size determination

Particle size analysis was performed on MS3000, Malvern Instruments Ltd., UK at ARCI, Hyderabad. MS3000 is capable of measuring particle sizes between 10nm to 3500µm. Particle size is measured using laser diffraction. In a laser diffraction measurement a laser beam passes dispersed on to a particulate sample. The angular variation in intensity of the scattered light is measured. Scattered angular laser deviation depends on the curvature of particulate surface. The test report through screen shot is shown in Fig. 3.8. The test report reveals the average size of HA particle is 4384 nm.

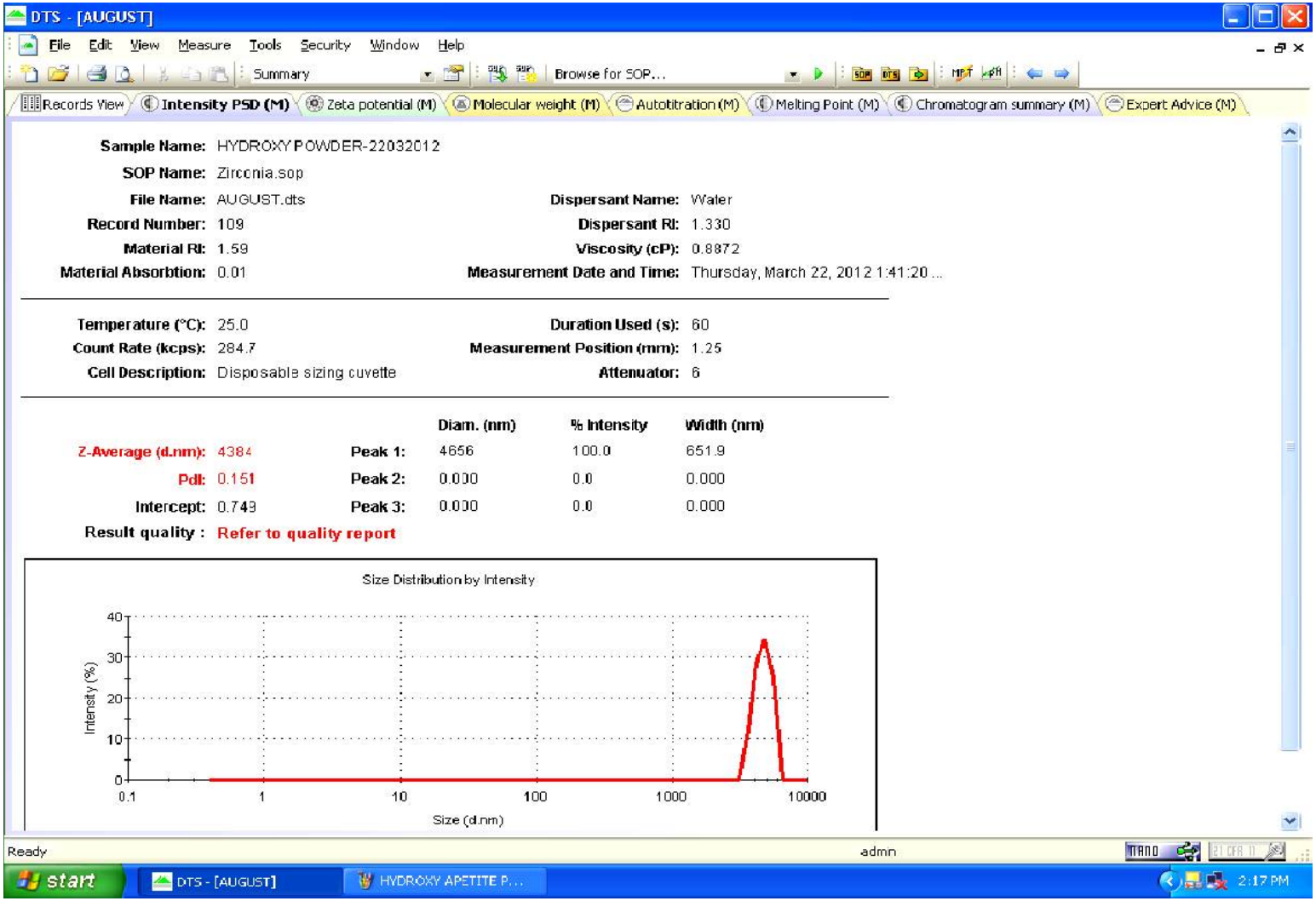


Fig. 4.8 Particle size analysis of HA

4.1.5 X-Ray diffraction of HA

Anchor Scan Parameters

Sample Identification:	EGG SHELL HYDROXY SPATITE
Measurement Date / Time:	20-06-2017 11:06:57
Operator:	User-1
Scan Axis:	Gonio
Start Position [°2Th.]:	11.0006
End Position [°2Th.]:	80.0046
Step Size [°2Th.]:	0.0130
Scan Step Time [s]:	97.9200
Scan Type:	Continuous
PSD Mode:	Scanning
PSD Length [°2Th.]:	3.35
Divergence Slit Type:	Automatic
Irradiated Length [mm]:	10.00
Specimen Length [mm]:	10.00
Anode Material:	Cu
K-Alpha1 [Å]:	1.54060
K-Alpha2 [Å]:	1.54443
Generator Settings:	40 mA, 45 kV
Diffractometer Type:	0000000011135814
Goniometer Radius [mm]:	240.00
Incident Beam Monochromator:	No
Spinning:	No

Graphics

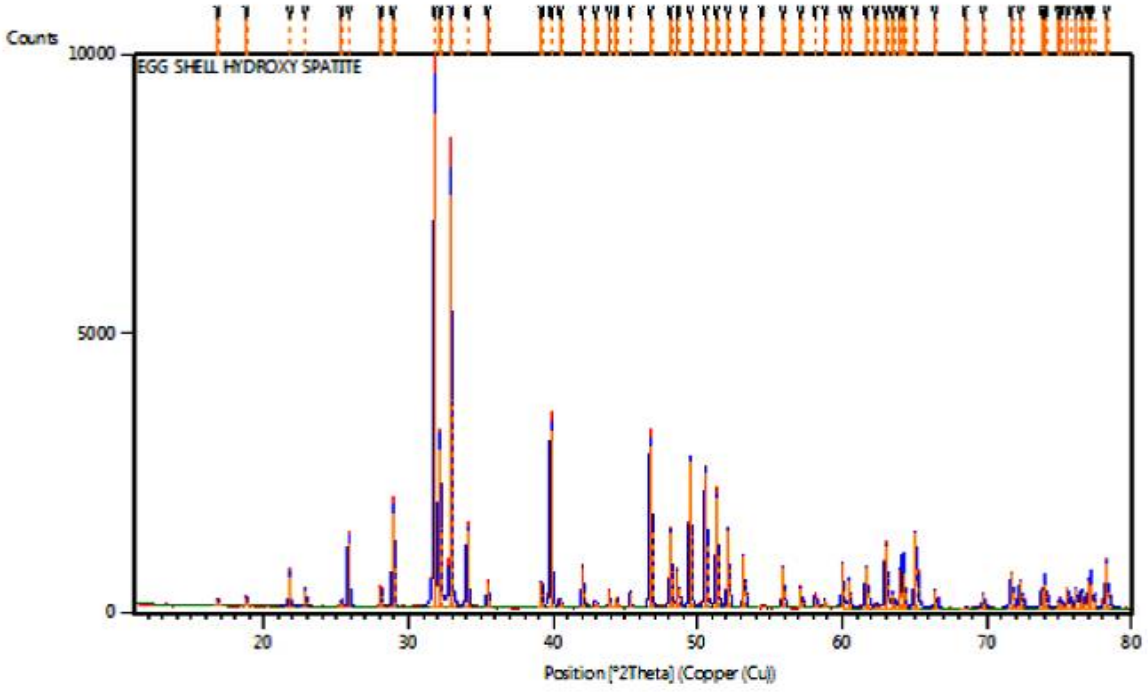


Fig. 4.9 Anchor scan parameters and XRD image of HA extracted from egg shells

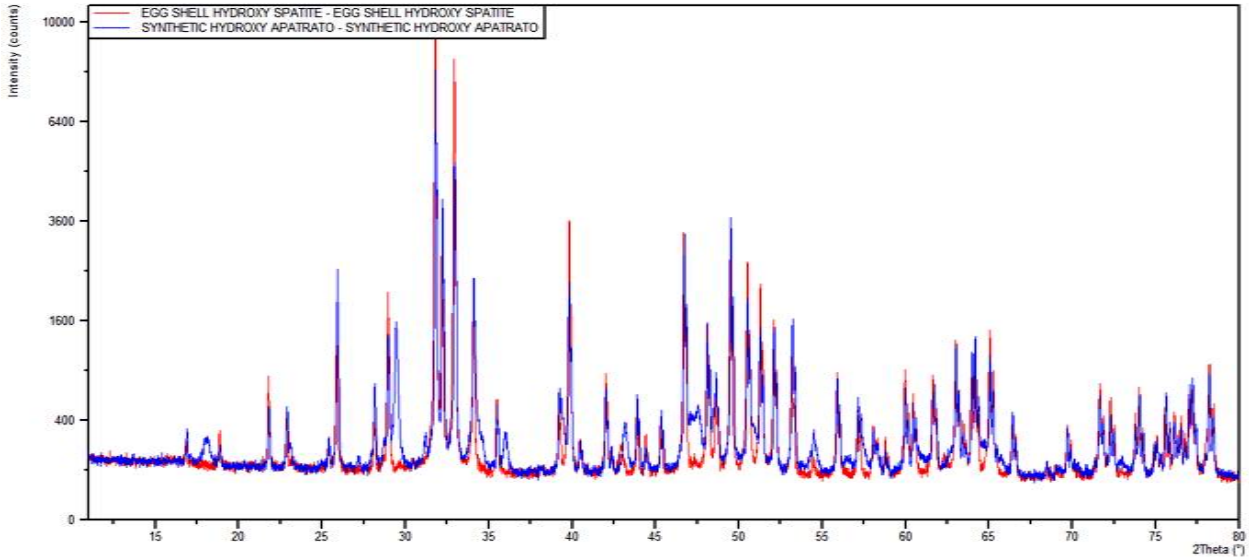


Fig. 4.10 Comparison of XRD images of Natural (egg shell extracted) and synthetic HA

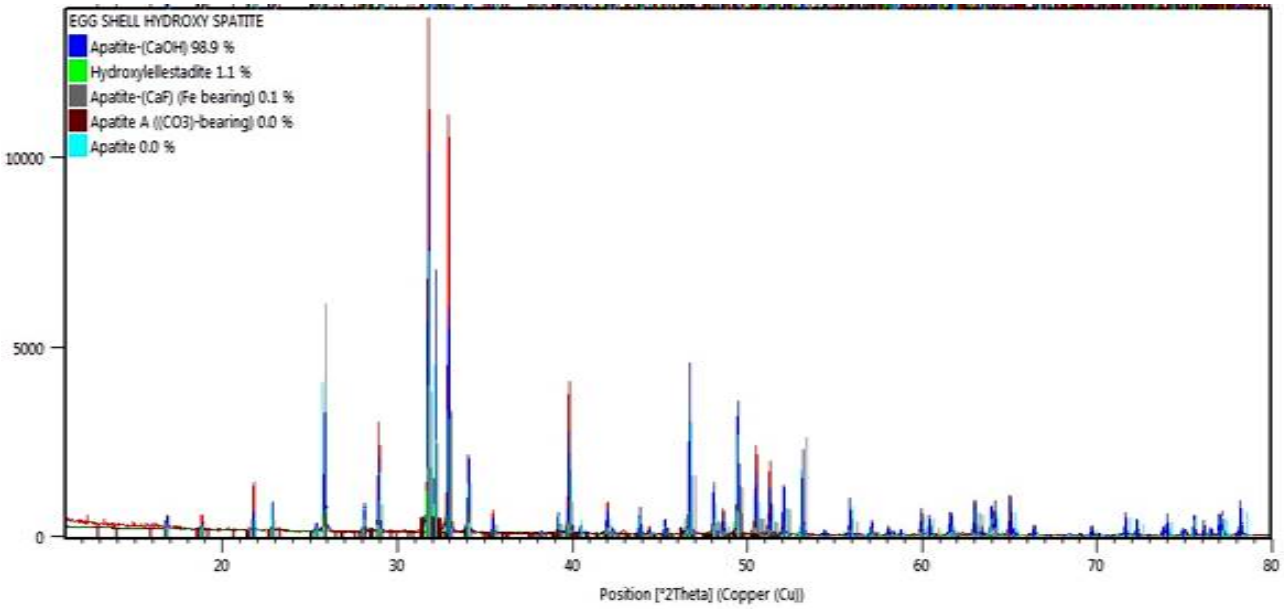


Fig. 4.11 XRD of HA extracted from eggshells

The formation of HA was confirmed by comparing the major peaks (2θ values) of XRD (Referring to Fig 4.9 thru 4.11) at 21.78, 25.86, 31.78, 31.86, 32.18, 32.29, 32.92, 33, 34.05, 39.82, 39.92, 46.7, 46.82, 48.09, 49.46 and 49.6 with past literature [133]. Hydroxylellestadite

formation from Fig. 4.11 is a positive indication, which is a bone growth promoter. Peaks beyond 70^0 were found comparatively low and negligible.

The XRD profile of egg shell extracted natural HA was compared with that of commercially available synthetic HA supplied by M/s Clarion pharmaceutical, New Delhi. The resulting XRD profile and peaks data was presented through Fig. 4.10 and 4.11. The peaks in Fig. 4.11 confirm the formation of HA.

4.2 Polyetheretherketone (PEEK)

Wide varieties of virgin and reinforced PEEK polymers are commercially available in the market for engineering and medical applications. Some of the PEEK manufacturers with brand names are listed in Table 4.1

Table 4.1 PEEK manufacturers and commercial brand names

S No	PEEK manufacturer	PEEK brand Name
1.	Ensinger	TECAPEEK
2.	Evonic	Vestakeep
3.	Lehmann & Voss	Luvocom
4.	Sabic	LNP
5.	Solvay	Ketaspire, Zeniva
6.	Victrex	Victrex

Initially two brands of PEEK viz., Victrex and Vestakeep were tried for procurement. Vestakeep (PEEK form Evonic Industries) was purchased from Miku traders, Vadodara, India due to retail selling convenience. Vestakeep -2000FP was the PEEK, medium viscous fine polymer chosen for present study. Properties of this particular variant are listed in Table 4.2 as certified by the Evonic industries. SEM images of the PEEK powder in Fig. 4.12 reveals the flaky shape of PEEK.

Table 4.2 Properties of PEEK

S No	Property	Property details
1.	Density	$1.30 g/cm^3$
2.	Tensile strength at yield	100 MPa
3.	Tensile strain at yield	5%
4.	Strain at break	30%
5.	Tensile modulus	3700 MPa
6.	Temperature of	155^0C

	deflection	
7.	Melting temperature	340^0C
8.	Melt volume flow rate (380^0C)	$7cm^3$/ min
9.	Average particle size	50µ
10.	Charpy notched impact strength (23^0C)	6 J/m^2

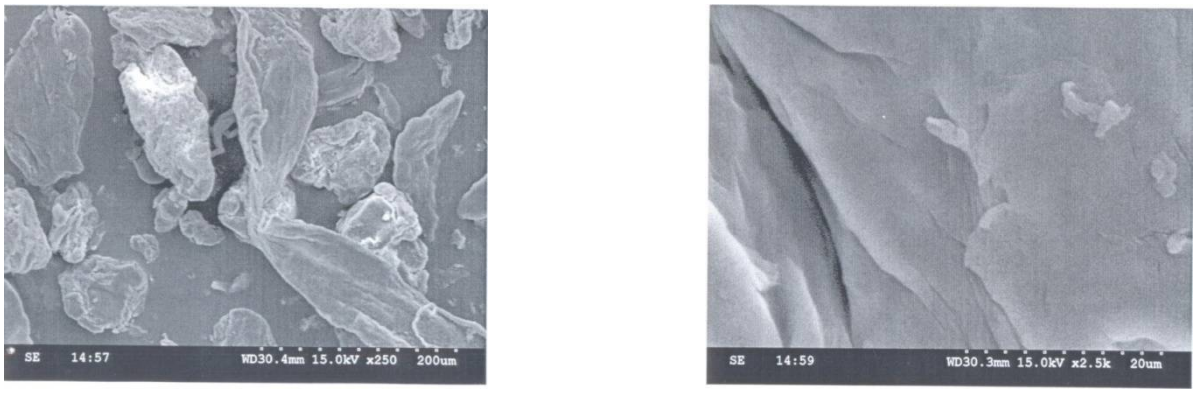


Fig. 4.12 SEM of PEEK at 250x and 2500x

4.3 PEEK/ HA biocomposite

A biocomposite of PEEK and HA has been planned to obtain better Young's modulus from HA reinforcement and better toughness/ tensile/ compressive strengths from PEEK. Bioactivity of HA and bio inertness of PEEK were prominent in choosing PEEK/ HA composite.

4.4 Conversion of CT/ MRI to CAD models

Computed Tomography (CT) is an extended X-ray technique, in which a patient data is collected from series of X-ray photographs. The person under medical diagnosis would lay down on CT bed/ Table. The Table passes through a machine tunnel, which is built in with X-ray emitters and signal receivers. The human body passing through X-ray spirals is exposed to X-rays and the image of that particular section of the body is received by the computer. All such sectional images received are stored in sliced 2 D images in computer. These files can be any one of the forms such as DICOM, TIFF, JPEG, BMP, PNG etc. The sliced images possess simultaneous image data of several tissues of human body of that particular section. The images of hard tissue such as bone appearing in white colour are differentiated from the soft tissues which are in grey colour. In contrast to soft and hard tissues, air appears in dark black colour.

Magnetic Resonance Imaging (MRI) produces similar slice data but with magnetic activation of hydrogen nucleus in water content of body in contrast to X-ray in CT images.

The output of CT/MRI scans will be in 2D sliced data in DICOM format. The 2D images on slices are stacked by software such as 3D doctor, MIMICS etc to form 3D objects in a way similar to papers (2D) stacked one over the other to form a book (3D). When it comes to above softwares, the sliced data is recognized by its boundaries. The boundaries of sequential slices are connected through special interpolation techniques by the softwares. This would generate surface data of the objects such as bones. Surface data is further converted in to volume data by the data on adjacent sides of the boundaries by colour contrast. The scheme is represented in following Fig.4.13

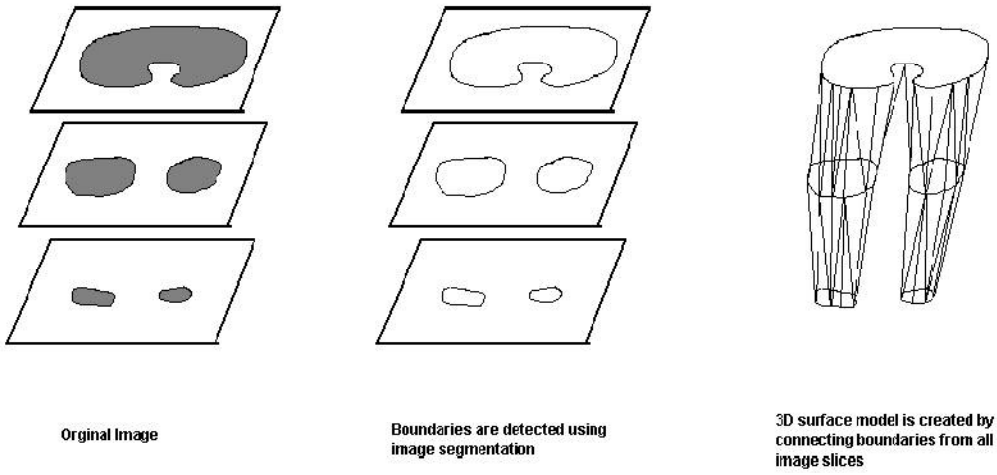


Fig. 4.13 MIMICS work flow in converting 2D images to 3D model

A case study was taken up from KD Hospitals, Ambala Cantt, Haryana state INDIA. The patient data was collected through DICOM files and processed in 3D doctor at Central Tool Room Ludhiana (CTRL), Punjab state, INDIA. The data images are shown in Fig 4.14 and Fig 4.15

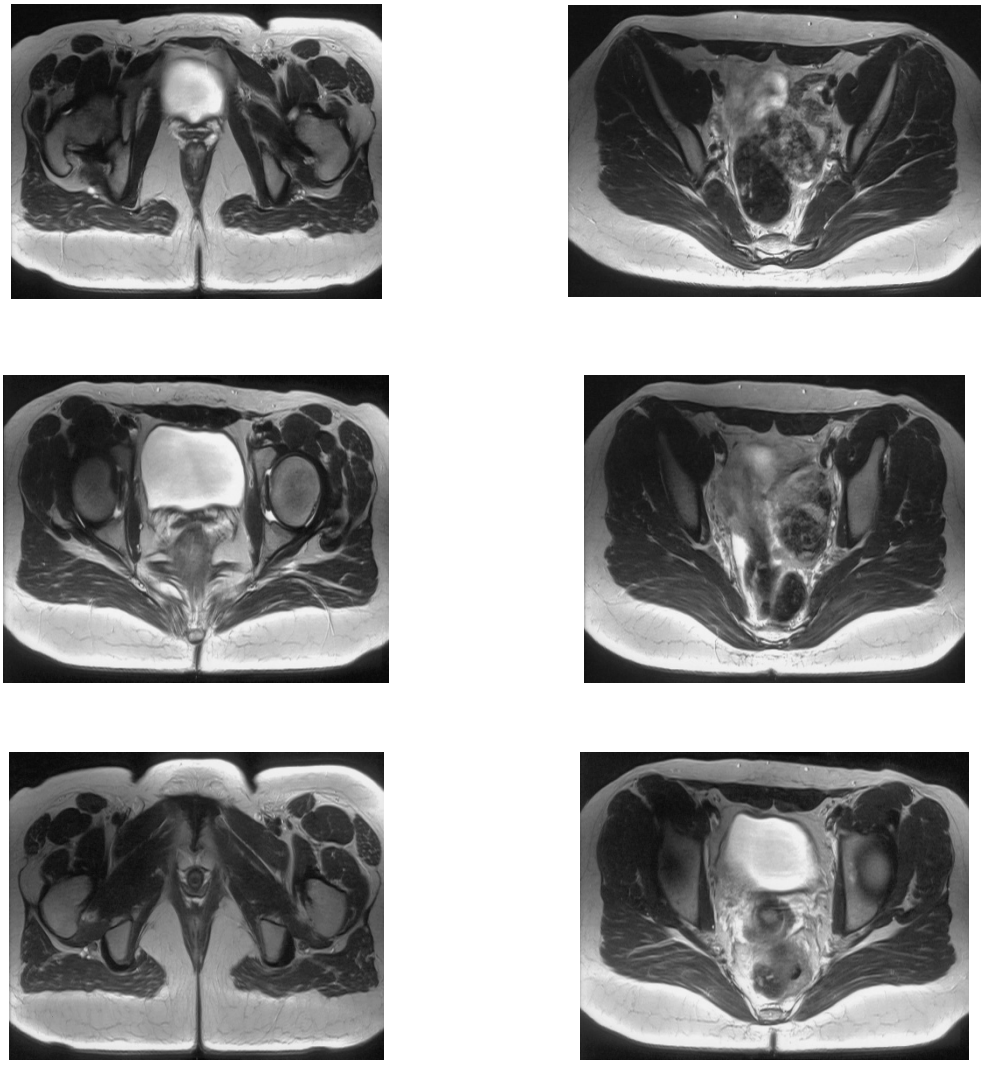


Fig. 4.14 CT scan 2D images of human pelvis

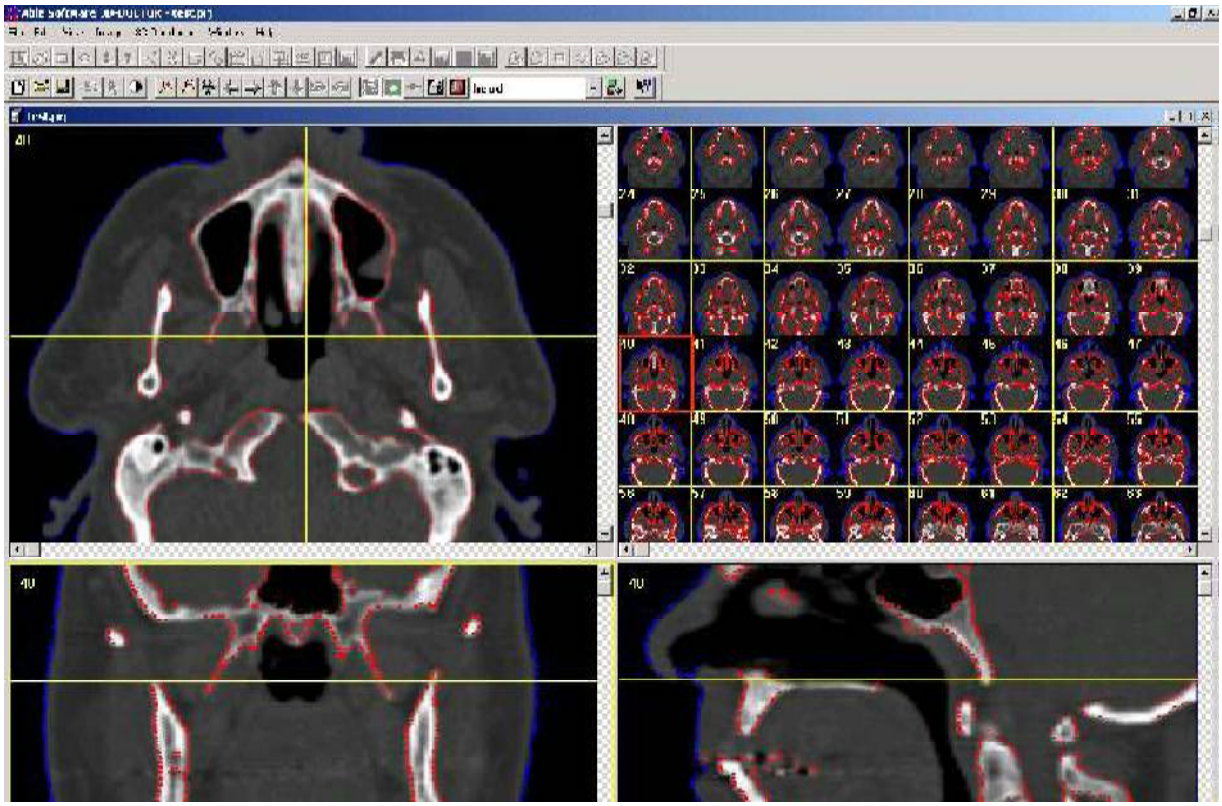


Fig. 4.15 Sliced data of human pelvis

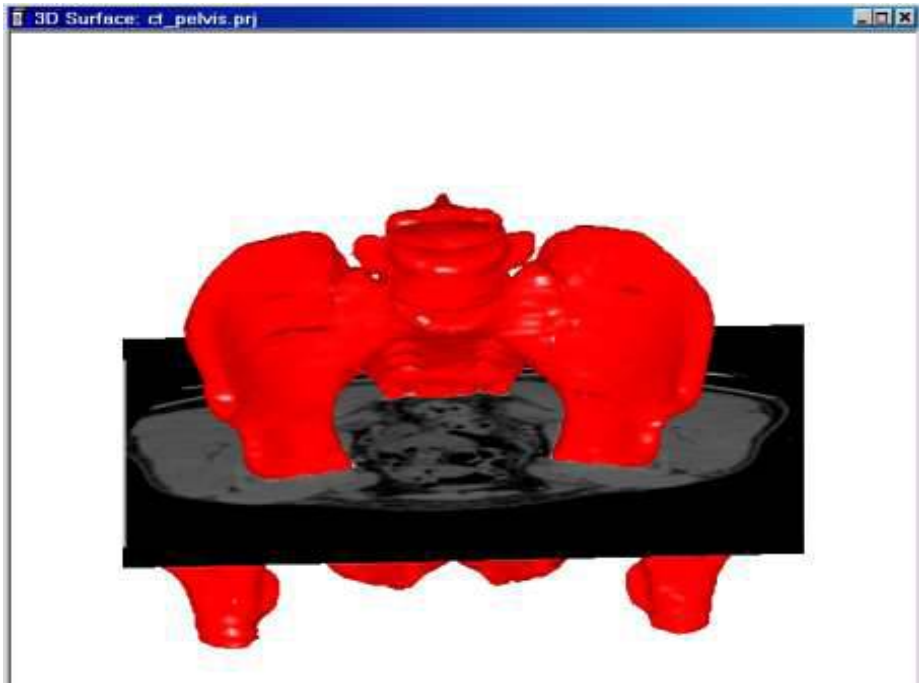


Fig. 4.16 3D Doctor surface model constructed from 2DCT scan images

The output model of 3D doctor super imposed on one of its 2D slices is shown in Fig 4.16. Later it was imported in to Pro/ Engineer 3.0 (At Ambala college Engineering and applied Research, Ambala, Haryana state, INDIA) via IGES data exchange file to create volume images. Different views of the generated image are shown in Fig 4.17

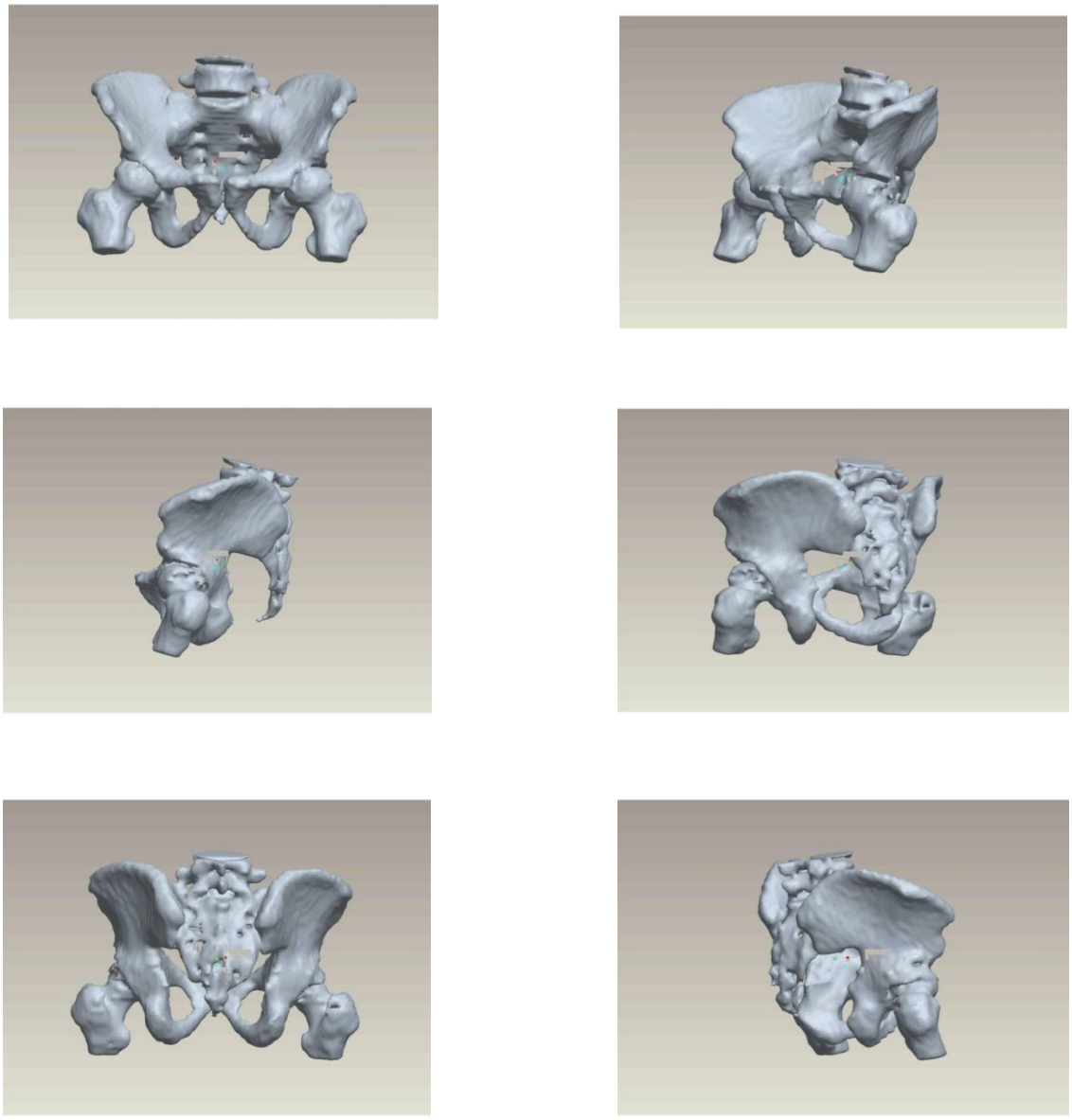


Fig.4.17 Volume models of pelvis from PRO/E 3.0 software

The left hip ball joint of pelvis shown in above Fig 4.17 was isolated from PRO/ E images and exported to VANGUARD HS Selective Laser Sintering Machine through *.stl* file for manufacturing in ABS material at CTRL. The sintered final product is shown in Fig 4.18 in different views

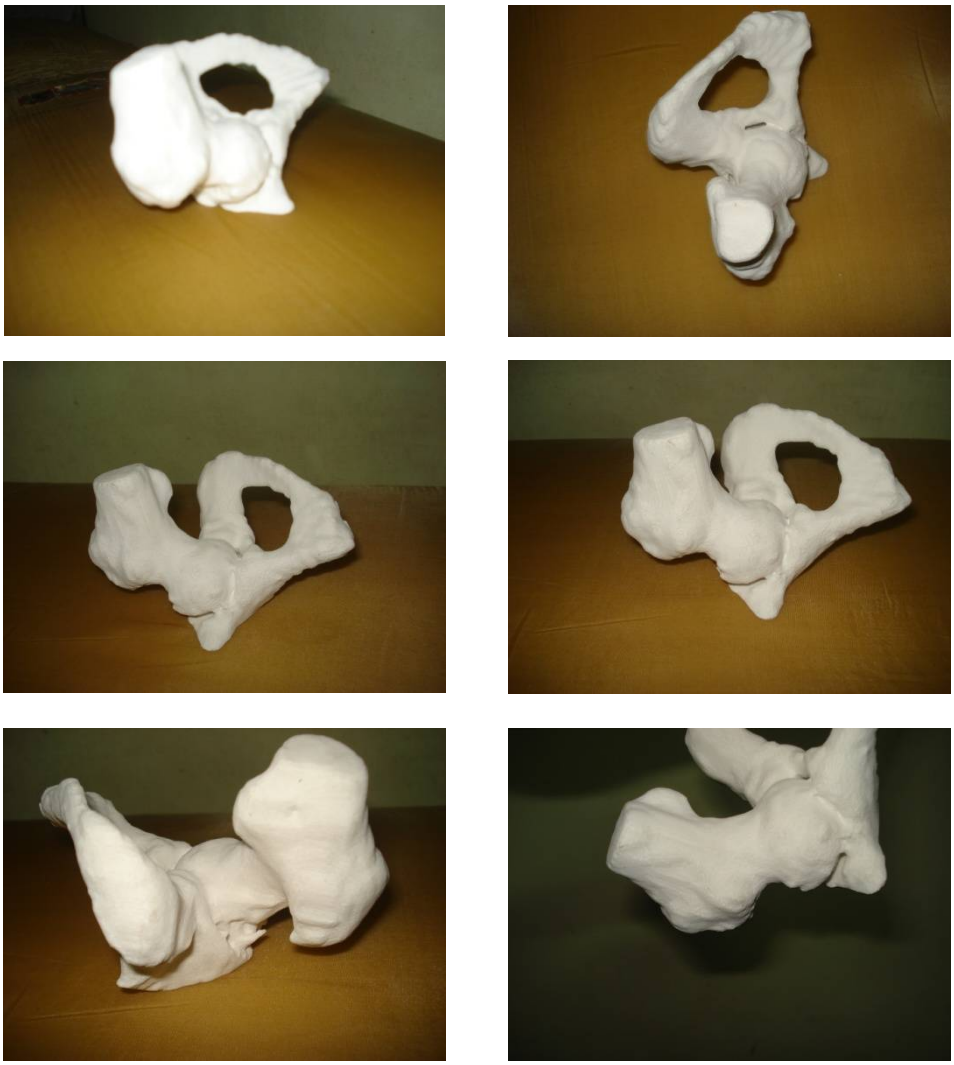


Fig. 4.18 Hip joint prepared through SLS

Finally, with the advent of sophisticated CT/ MRI scans, conversion softwares, CAD modelling softwares and Rapid Prototyping machines, it was possible to convert patient data in to 3D part. This could be surgeon's option to use the 3D model for design and fabricate prosthesis for repair at damaged site. The model was made out of ABS, on VANGUARD HS SLS, at CTR, Ludhiana.

4.5 Design of Experiments (DOE)

The concept involved in DOE is devising a methodology in the conduct of experimentation to acquire predictive knowledge in a multi variable process so as to optimize the experimental process through minimum number of trials.

Among the several design of experiments available, TAGUCHI ORTHOGONAL APPROACH was chosen in this work to minimize the number of experiments. Minimization of number of experiments is substantiated by the proven performance of this approach and associated difficulties such as raw material procurement, waiting times in sample preparation, testing processes etc.

The major influencing factors were identified from available literature, understanding general behavior of raw material and working process parameters. The process parameters identified in the composite formation are listed in Table 4.3 with reasoning for inclusion/ exclusion in experimentation.

Table 4.3 Process variables in design of experiments

S No	Influencing factor	Justification
1	Percentage of Components in Composite	PEEK and HA are the components of the composite having well defined roles of each of them. HA is bioactive, bio-inductive, and bio-conductive bone ceramic. PEEK, a bioinert polymer as major matrix with HA ceramic reinforcement is chosen for enhancement of mechanical properties of HA. Percentage of individual components is included as one of the influencing factors in this work
2	Maximum Processing temperature	HA being reinforcement, major focus was on melting temperature of PEEK. Melting temperature of PEEK as bench mark, this process parameter is identified as influencing parameter and hence included.
3	Rate of Heating (ROH)	Softening, melting and bonding of components of composite are influenced by rate of heating or the time availability in thermal cycle. Time of heating and Rate of heating are identified interdependent for a given maximum processing temperature. ROH is chosen as one of the influencing factors
4	Compacting pressure	Retention of specimen geometry while holding, transferring and heating are influenced by compacting pressure. However, upon identifying minimum pressure required to retain the shape of specimen, this parameter is maintained constant. Hence this factor is not included in studies.
5	Particle size	Size of PEEK is preferred in as supplied condition. HA extracted from eggshells is refined from mechanical processes

		to the lowest possible. Hence particle sizes of PEEK (50µ) and HA (4.5µ) were excluded from this study.

The major influencing factors chosen are:

1) **Percentage of components** of Biocomposite: Brittle and fragile nature of HA ceramic has been limiting the percentage of HA in total composite to a maximum of 50%. Literature and delimiting studies suggested HA percentage could be a maximum of 40%.
2) **Maximum Temperature** in processing of the composite was limited by the melting point temperature of PEEK polymer (T_m= 343^{0}C). Upon conducting delimiting studies, this parameter was upper bounded at 330^{0}C.
3) **Rate of Heating** was found influencing the bonding procedure between PEEK and HA particulates. Delimiting studies were taken in to consideration and ROH range levels are refined. The maximum ROH was limited to 1.5^{0}C/ min.

Response variables, or the output parameters to be optimized were identified by the problem definition and they are a) Young's modulus of the composite and b) Flexural strength of the composite.

Levels of factors were limited after refinement to three based on the range of each parameter.

Finally, Taguchi orthogonal array L9 is chosen with following two stage parameter/ level selection.

For delimiting studies, following factors and levels are finalized.

1. Percentage of HA varies between 10-40% with equal intervals, while the PEEK complements HA.
2. Maximum temperature is set to 350^{0}C, keeping HA presence in PEEK. The levels of temperatures are set as 300^{0}C, 330^{0}C, and 350^{0}C
3. Rate of heating is chosen as 1^{0}C/ min, 1.5^{0}C/ min, and 2^{0}C/ min

Taguchi L9 orthogonal array was chosen for sample preparation in first stage of experimentation. Combination of process parameters for all 9 specimens is shown in Table 4.4.

Table 4.4 Taguchi L9 orthogonal array for sample preparation

Experiment No.	Control Factors		
	Polymer (P)+ Ceramic(C)	Maximum Temperature, ^{0}C	Rate of Heating, ^{0}C/ min
1	50%P+50%C	300	2.0
2	50%P+50%C	330	1.5
3	50%P+50%C	350	1.0
4	70%P+30%C	330	2.0
5	70%P+30%C	350	1.5
6	70%P+30%C	300	1.0
7	90%P+10%C	350	2.0
8	90%P+10%C	300	1.5
9	90%P+10%C	330	1.0

Upon obtaining the results of delimiting studies, the levels of parameters were refined as below mentioned in Table 4.5

Table 4.5 Taguchi L9 orthogonal array for sample preparation with refined levels

Experiment No.	Control Factors		
	%Polymer (P)-%Ceramic(C)	Maximum Temperature, ^{0}C	Rate of Heating, ^{0}C/ min
1	60-40	310	1
2	60-40	320	1.25
3	60-40	330	1.5
4	70-30	310	1.25
5	70-30	320	1.5
6	70-30	330	1
7	80-20	310	1.5
8	80-20	320	1
9	80-20	330	1.25

Finally it was planned to study the influence of all parameters to suggest the processing of biocomposite for optimum performance/ response variables.

Studies on porous structures was planned to limit for optimal case found from dense specimens' results.

4.6 Preparation of dense specimens

Dense specimens for flexure test were prepared according to ASTM D790 as shown in Fig 4.19. Specimens were prepared in four stages viz., 1) Blending of powders 2) Compacting3) Sintering at controlled rate of heating and 4) Annealing

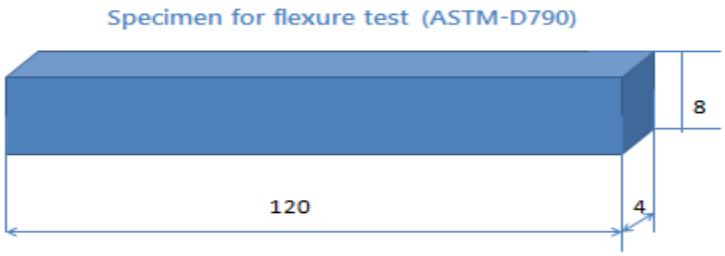
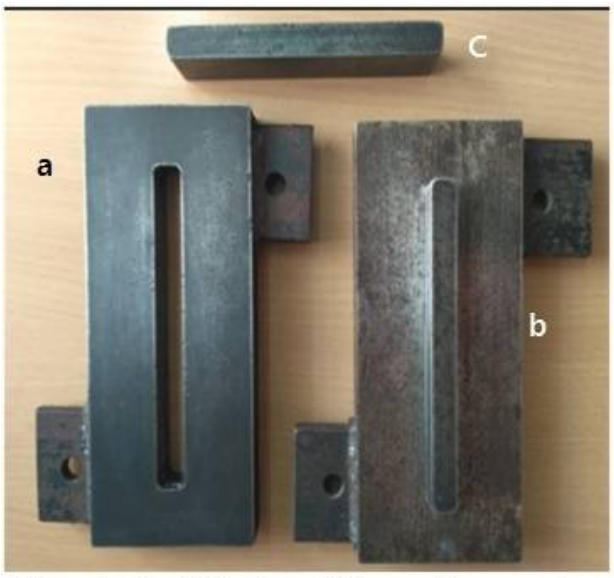


Fig. 4.19 Flexure test specimen (ASTM D790)

Powder Blending: Requisite amounts of PEEK and HA were taken by green weight proportions to suite for five samples in each combination. The powders were thoroughly mixed in ball mill for about four hours. Similar process was followed for different proportions and powders were kept ready slightly in excess to the required quantities.

Compacting: A three piece compacting die shown in Fig 4.20 was designed and fabricated in En24 at Balanagar, Hyderabad. The die was given an in built electrical heating with controller for preheating while compacting. Calculated amounts in exact weights of composite mixtures were filled in female die pre assembled with ejecting die. The weight of the composite powder was picked using 'Metro electronic pocket scale MH series 200gm (least count 0.01gm)' digital balance. The die was closed properly by punch compactor and loaded on to computer controlled digital compression/ compaction machine AIMIL make, EM 500 model, 2000kN capacity shown in Fig 4.21 with ensured alignment. After few trials, the compacting load was arrived at 120kN.The machine was pre programmed to exert a nominal compressive stress of 250 MPa on composite powder by reaching a maximum compressive load of 120kN. The die set was taken out and reverted and pressed manually to eject the green specimen. Fig 4.22 shows the green specimen which was capable of retaining its shape even after two days without any bulging in dimensions.



a) Female die b) Ejector c) Compacting punch

Fig. 4.20 Three piece compacting die

Fig. 4.21 Programmable compacting machine

Fig 4.22 Green specimen

Sintering: The green specimen ejected from compacting die was transferred to muffle furnace show in Fig 4.2. The detailed specifications of muffle furnace are furnished in Table 4.6

Table 4.6 Specifications of muffle furnace

Parameter	Specifications/ details
Model	BST/MF/1100
Temperature Controller	PID controller
Max. Temperature	1100°C
Working Temperature	1000°C
Temperature Accuracy	+/- 1°C
Heating Element	Kanthal A-1
Power Supply	220 Volts, 50Hz AC
Internal Chamber Construction	Ceramic Board & Grooved Refractory Chamber as per Temp. Requirement
Insulation	Ceramic wool insulation

PID controller of the muffle furnace has a programmable facility for several segments of a heating cycle. User has flexibility to program i) starting and ending temperatures of a particular segment of heating cycle in ^{0}C ii) either rate of heating in ^{0}C/ min or time (min) for heating and iii) maintaining the furnace temperature constant for specified amount of time. This programmable facility was used to control the maximum temperature in sintering and rate of heating.

i**v) Annealing:** The Specimens were left in furnace at constant temperature at the end of each thermal cycle for about 4.5 hr to avoid thermal shocks.

Fig. 4.23 Specimens prepared for delimiting studies

(%HA- %HA in PEEK / HA Composite; 50, 30, and 10; T-Maximum temperatures: 300^{0}C, 330^{0}C, and 350^{0}C; ROH-Rate of heating: 1^{0}C/ min, 1.5^{0}C/ min and 2^{0}C/ min)

The photograph of specimens fabricated with various process parameters for delimiting studies are presented in Fig 4.23. Details of specimens PEEK/ HA eggshell extracted composite and PEEK/ commercial HA (bought from Clarion Pharmaceuticals, New Delhi) are furnished with details in Table 4.7 and Table 4.8

Table 4.7 Process parameters and photographs of specimens prepared with natural HA

Sample No	Details of specimen process parameters			Specimens reinforced with eggshell extracted HA (Natural) after sintering/ annealing
	Composition (% PEEK, %HA)	Max temp, ^{0}C	Rate of heating, ^{0}C/min	
1	60,40	310	1	
2	60,40	320	1.25	
3	60,40	330	1.5	
4	70,30	310	1.25	
5	70,30	320	1.5	
6	70,30	330	1	
7	80,20	310	1.5	
8	80,20	320	1	
9	80,20	330	1.25	

Table 4.8 Process parameters and photographs of specimens prepared with synthetic HA

Sample No	Specimen process parameters details			Specimens reinforced with synthetic HA (Clarion pharma, New Delhi) after sintering/ annealing
	Composition (% PEEK, %HA)	Max temp, ^{0}C	Rate of heating, ^{0}C/min	
1	60,40	310	1	
2	60,40	320	1.25	
3	60,40	330	1.5	
4	70,30	310	1.25	
5	70,30	320	1.5	
6	70,30	330	1	
7	80,20	310	1.5	
8	80,20	320	1	
9	80,20	330	1.25	

A microwave furnace shown in Fig 4.24 a) and b) was proposed for better strength properties of sintered specimens through microwave heat treatment. This was not used as the microwave heating was not effective for PEEK/HA polymer composite. All samples were sintered and annealed with controlled heating rate in muffle furnace.

(a) (b)

Fig.4.24 Microwave oven furnace a) PLC unit b) Domestic microwave oven with PLC unit

4.7 Preparation of porous specimens

Preparation of porous specimens, to mimic the Cancellous bone was the second target of this work. Porosity, in percent of pore volume of the total specimen volume, pore size and through pore connectivity were the focused targets. All the three afore mentioned would be obtained from material addition or RPT methods such as SLS, SLA, FDM and powder 3D printing by injection of binder. However, these methods were found suitable for machine specified materials. Manipulating materials on commercial machines is not possible for several untold reasons. A novel but not new approach was chosen here to exploit the benefits of RPT in processing the user specified biomedical materials. Polymeric sponge method with commercial sponge/ SLS printed sponge was the approach chosen to establish the scaffold preparation. This process involves the following stages:

1. Printing of template in Nylon by SLS (or to use readily available nylon mesh)
2. Coating of template with alumina to remove Nylon at a later stage (Optional)
3. Preparation of PEEK/ HA composite slurry
4. Impregnation of template in composite slurry and drying
5. Sintering and annealing

Nylon template of 4.3” cube was printed using PROX SLS 500 machine through ‘Think 3D, Hyderabad’. The properties of Nylon as listed by the company are shown in Table 4.9. A template printed on SLS with nylon is shown in Fig 4.25 a). And a commercially available mesh

is shown in Fig. 4.25 b for comparison. Template cubes of 1” side are shown in Fig 4.26 for polymeric slurry impregnation.

Table 4.9 Nylon properties used in template printing

Overview	
Material	Nylon
Applications	Industrial
Material Properties	
Characteristics	high fatigue resistance, strong chemical resistance, high strength
Specific Gravity	1.00
Mechanical Properties(conditioned*)	
Tensile Strength	46 MPa
Izod Impact (Notched)	135 J/m
Flexural Strength	67 MPa
Hardness	
Elongation at Break	30%
Flexural Modulus	1276 MPa
Thermal Properties	
Deflection Temperature	97 °C
Vicat Softening Point	
Max operating temp	
3D Printing	
Technology	SLS/FDM
Possible Post Processing	
Molding Shrinkage	0.5-1.5%
Accuracy	
Min Wall Thickness	
Min Layer Resolution	
Melt Flow	

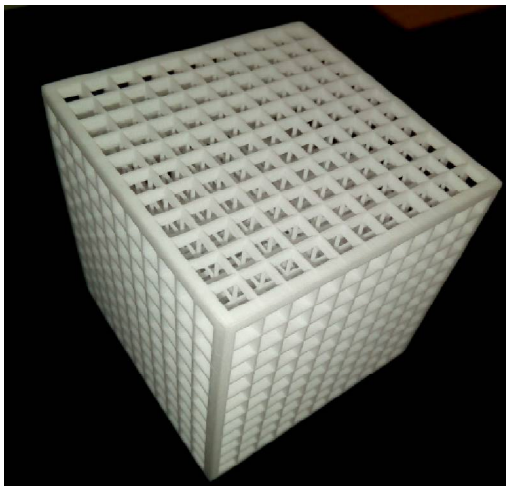


Fig. 4.25 Porous template a) Nylon cube template printed on PROX SLS500

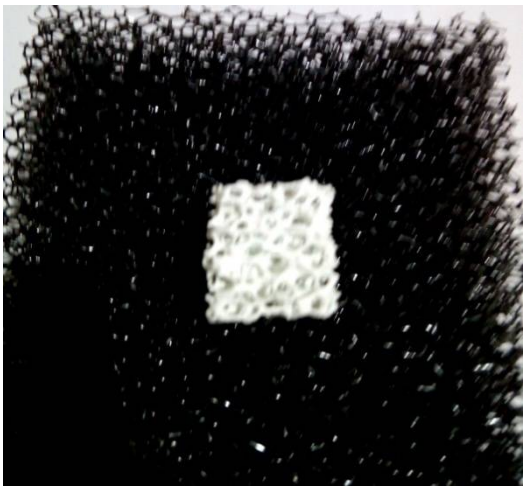


Fig. 4.25 b) Commercial Nylon mesh (black), porous specimen prepared from mesh(white)

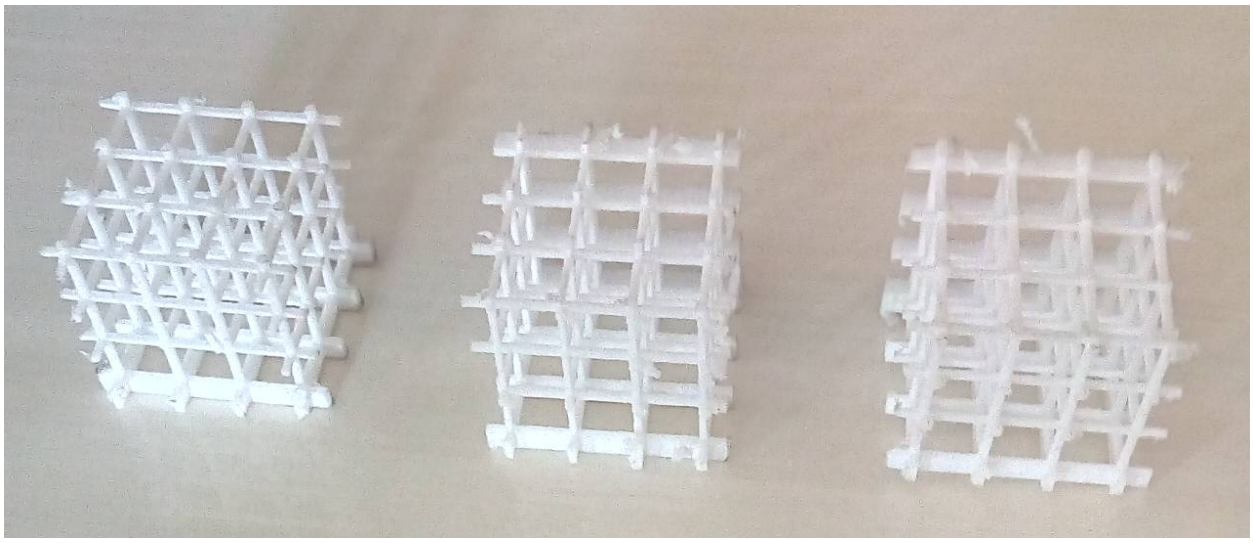


Fig. 4.26 Specimen templates for composite slurry impregnation

Composite slurry of PEEK/ HA was prepared for optimum composition based on dense specimen results. The selection was justified, as the same would be exhibiting better mechanical properties in porous structure among the specimens of same porosity parameters. Composite slurry preparation was carried out at ARCI, Hyderabad and Indian Institute of Chemical Technology (CSIR -I I C T), Hyderabad. The process of porous specimen preparation using

polymeric sponge method involves preparation of alumina template and preparation of PEEK/HA scaffold. In first stage alumina template was prepared to guide the customized biocomposite scaffold preparation in second stage.

Stage 1: Preparation of Alumina template

Alumina template preparation through *commercially available nylon mesh* of 10 pores per inch shown in Fig 4.25b was chosen (Same process with few modifications could work for template shown in Fig 4.26 and it was suggested for future study). Template was prepared by impregnating nylon mesh in alumina slurry followed by drying and sintering. The slurry preparation additives and proportions are shown in Table 4.10a followed by detailed procedure for alumina template preparation.

Table 4.10 (a) Preparation of Alumina Slurry

Additives→	**Solvent**	**Dispersant**	**Binder**	**Ceramic**
Commercial Name→	Distilled water	DARVAN CT	Poly(vinyl alcohol)	Alumina
Quantity in g →	420	2	10	1000

Procedure:

1. Add DARVAN CT in weighted proportion to distilled water gradually by mixing with magnetic stirrer
2. Heat the solution continually to 70^0C, add PVA in weighted proportion slowly under continued stirring
3. Stir for uniform dispersion and stop heating
4. Add alumina in calculated proportion and continue stirring for about 4h or till homogeneity is observed in slurry
5. Impregnate sponge in to the slurry. Take out the sponge, compress and immerse in to slurry. Repeat 3-4 times till the sponge is sufficiently filled with slurry
6. Take out the sponge and dry with hot air
7. Transfer the dried alumina impregnated sponge in to furnace. Heat the furnace at a rate of 10^0-15^0C/ min to reach final temperature about 600^0C so that all organic matter including sponge fired for removal.
8. Sinter the left out at 1200^0C for about 2 h.

Stage 2: Preparation of PEEK/ HA scaffold

Alumina template prepared in stage 1 was used to guide the PEEK/ HA scaffold with the template left covered by PEEK/ HA composite. Alumina template was chosen to support the PEEK/HA composite. The whole process involves PEEK/ HA slurry preparation, template impregnation, drying and sintering. Table 4.10(b) and the detailed procedure following it explain the process for preparation of PEEK/ HA scaffold.

Table 4.10 (b) Preparation of PEEK/HA slurry

Additives→	**Solvent**	**Dispersant**	**Binder**	**Composite**
Commercial Name→	Distilled water	DARVAN CT	Poly(vinyl alcohol)	PEEK/ HA-70/30
Quantity in g →	500	1.5	15	150

Procedure:

1. Add DARVAN CT in weighted proportion to distilled water gradually by mixing with magnetic stirrer
2. Heat the solution continually to 70^0C, add PVA in weighted proportion slowly under continued stirring
3. Stir for uniform dispersion and stop heating
4. Add PEEK/HA-70/30 in calculated proportion and continue stirring for about 4h or till homogeneity is observed in slurry
5. Impregnate Alumina template and ensure PEEK/HA slurry to flow inside.
6. Dry the porous scaffold and transfer it to furnace.
7. Raise the temperature to 145^0C with a heating rate of 15^0C/min and maintain the furnace for 10m
8. Raise the temperature up to 320^0C with a heating rate of 1.5^0C/min
9. Shut down the furnace for 30min and remove the specimen

Porosity of the scaffold was calculated on the basis of net pore volume left after two stages explained. The resulting sample specimens are shown in Fig 4.27 a, b and c. The core of sample left with alumina is justified for i) removal of nylon mesh from specimen and ii) alumina to induce apatite in bone formation [134].

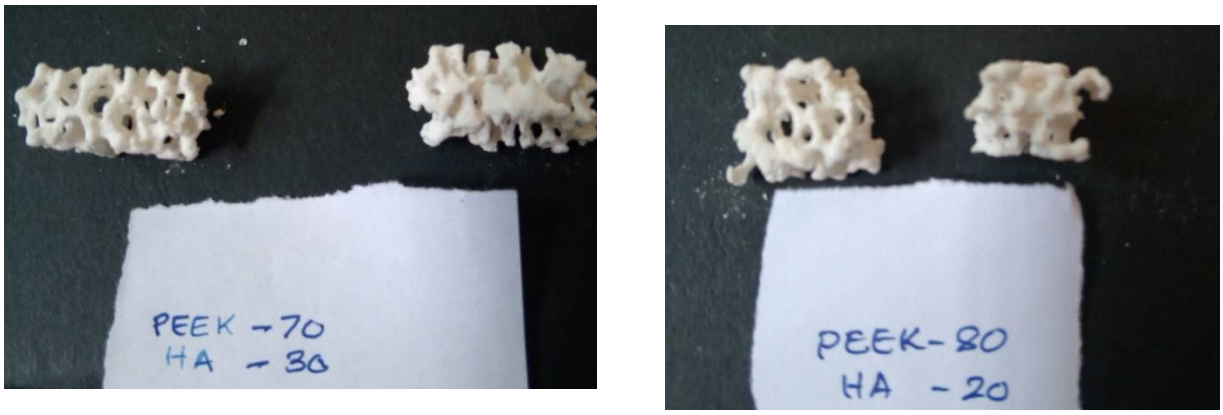


Fig. 4.27 Porous specimens PEEK/HA

a) 70/30 **b) 80/20**

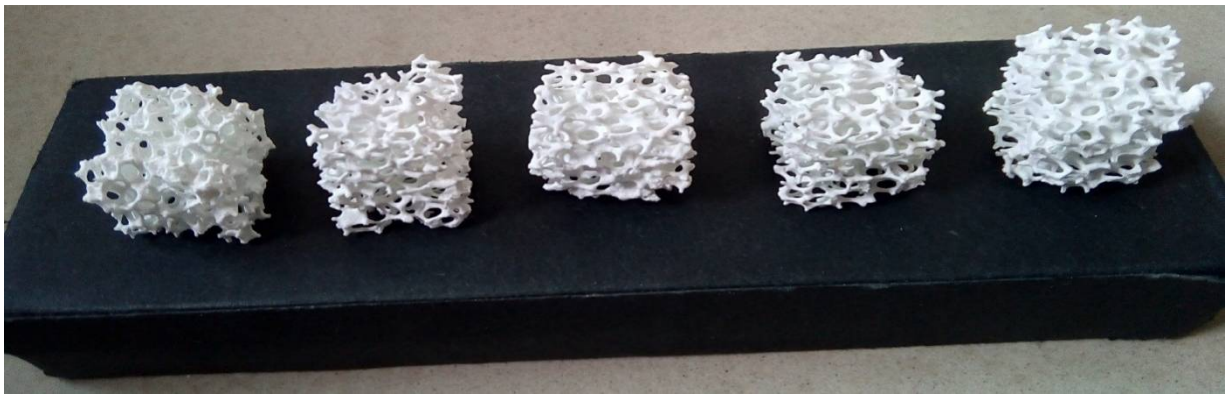


Fig. 4.27 c) Porous specimens of 1" cube

4.8 Testing of Specimens

Mechanical properties of biocomposite were evaluated in two different ways. Dense specimens were tested in 3 point bend test to evaluate Young's modulus and flexural strength. Porous specimens were tested in unconstrained simple compression test. The flexural test results were interpreted on outer layers with a close approximation of skin stress and skin strain. The approximated mechanical behavior of dense specimen layers was rendered to porous specimens using DEFORM 3D software to predict the load elongation behavior of porous specimens.

Dense specimens were pressed at a compacting pressure of 250 MPa. Since porous specimens were prepared without compaction, the strength of the composite depends mainly on thermal binding forces between PEEK/ HA and strut structure. Despite the known behavior of porous specimens against dense specimens, an attempt was made through DEFORM 3D software to assess the rigidity of the specimen by examining load- elongation curves.

Apart from mechanical behavioural tests mentioned above, thermal stability tests through Thermal gravimetric analysis (TGA), Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and degradation studies for prolonged exposure in Simulate Body Fluid (SBF) conditions were conducted.

4. 8.1. Three point bend test

Laboratory practices for evaluation of mechanical properties of brittle materials or materials behave like brittle materials due to their manufacturing techniques such as powder metallurgy [135A, 136]. The preferred testing depicted in Fig 4.28 was explained by these authors under 3 point transverse bend test. Failure of composite specimens prepared by powder compaction technique was explained by these authors due to skin strains. When the skin strains on a side opposite to mid span load exceeds a tolerable limit, the specimen cracks and fracture propagates. This was observed by a linear load vs. deflection behavior of bent beam specimen, indicating brittle failure.

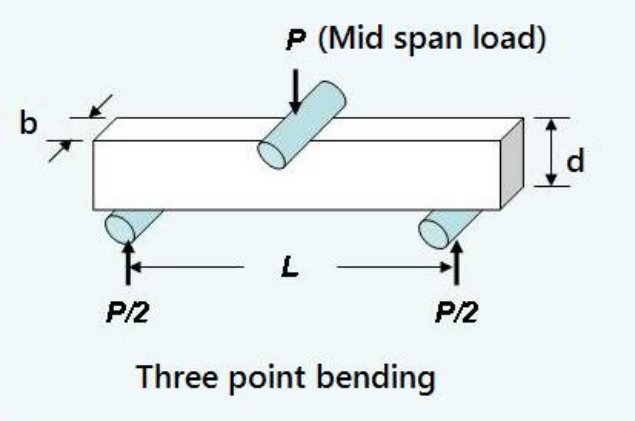


Fig 4.28 Three point bend test setup

Evaluation of Mechanical Properties

1) Stress produced at any instance of applied load P could be expressed as

$$\sigma = \frac{3\,P\,L}{2\,b\,d^2} \qquad (4.1)$$

Where (referring to Fig. 4.28),

σ = Stress produced or strength at any applied load, N/mm^2
P = Applied load at that instant, N
L = Beam span between bottom supports, mm

b = Breadth of the beam, mm
d = depth of the beam, mm and if,
D = deflection of the beam beneath the central load, mm

The corresponding strain produced, $\varepsilon = \frac{6\ d\ D}{L^2}$ (4.2)

Using equations 4.1 and 4.2, instantaneous stress and strain at any applied load P with measured deflection D are calculated. Yield strength, breaking strength and corresponding strains are calculated using the above equations.

2) The Young's modulus of the specimen material is found by the slope of P-D curve, more specifically in the linear portion of the curve or with a tangent to the curve.

Young's modulus, $E = \frac{m\ L^3}{4\ b\ d^3}$ (4.3)

Where E = Young's modulus in N/mm^2
m = Slope of the curve

4.8.2 Thermal stability analysis

Thermal studies on polymers, ceramics and composites help in processing of composites by knowing their melting temperature, percentage of weight loss and onset for polymer/ ceramic/ composite degradation respectively from DSC, TGA and DTA. The thermal stability of Biocomposites in field application would be justified by thermal studies afore mentioned.

4.8.3 Invitro degradation studies of biocomposite in SBF

Testing of specimens in the prolonged exposure to SBF was carried out to study degradation of mechanical properties invitro. Artificial sea water was used for degradation study.

a) Preparation of KOKUBO's Simulating Body Fluid

This solution shown in Fig 4.29 was prepared in chemistry laboratory, with the procedure laid down [137]. The reagents mentioned in Table 4.11 were mixed slowly with a continuous stirring for 2 liters quantity.

Table 4.11 Details of reagents for preparation KOKUBO SBF

S No	Reagent	Quantity/ lt
1	NaCl	7.996 g
2	$NaHCO_3$	0.350 g
3	KCl	0.224 g
4	$K_2HPO_4 \cdot 3H_2O$	0.228 g
5	$MgCl_2 \cdot 6H_2O$	0.305 g
6	1M-HCl	40 mL
7	$CaCl_2$	0.278 g
8	Na_2SO_4	0.071 g
9	$(CH_2OH)_3CNH_2$	6.057 g

Fig 4.29 KOKUBO (SBF) solution

The pH concentration KOKUBO was maintained at 7.4 by controlled addition of HCL.

b) Preparation of artificial sea water for degradation test

Artificial sea water is chosen as immersion media to mimic the degradation of porous specimens in the presence of SBF and for prolonged exposure. The solution is prepared in laboratory with the constituents and concentrations [138] shown in Table 4.12. The constituents mentioned in

Table 4.14 were mixed slowly with a continuous stirring for preparation of 2 liters quantity. The pH value was maintained at 8.2 by controlled addition of NaOH

Table 4.12 Chemical composition of artificial Sea water

Constituents	Concentration(g/lt)
NaCl	24.53
$MgCl_2$	5.20
Na2SO4	4.09
CaCl2	1.16
KCl	0.695
NaHCO3	0.201
KBr	0.101
H3BO3	0.027
SrCl2	0.025
NaF	0.003

Fig 4.30 Temperature controlled SBF test setup

4.8.4 Compression test for porous specimens

The specimens were taken out of the SBF and dried in still air for 24h. They were tested in unconstrained simple compression. The load bearing behavior of the specimens was tested

against the deformation. Young's modulus in compression was estimated using initial slope of stress – strain curve derived from the Load- Contraction curve.

4.8.5 Study on load bearing capabilities of PEEK/ HA composite using DEFORM software

Porous specimens shown in Fig 4.31, modeled through CATIA with porosities 75%, 82% and 89% were imported into DEFORM software and the geometry was discretized with number of elements 40918 (for 82% porous specimens). The load bearing capacity of the specimen was assessed with incremental deformation in one hundred steps. Testing of the specimen was stopped at a stage where the load- elongation curve encounters a hick up.

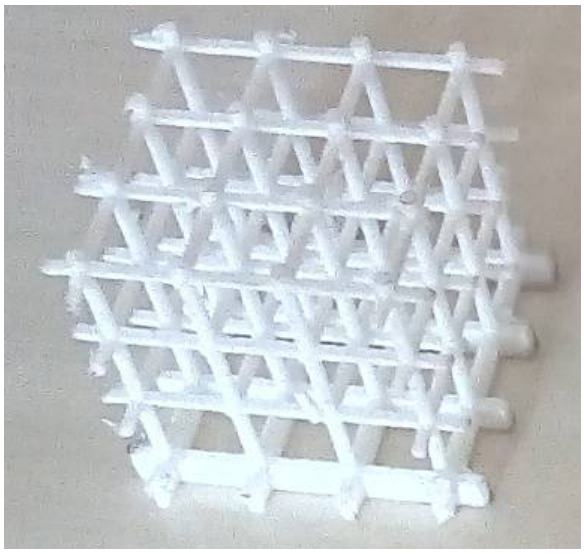


Fig. 4.31 Geometric model of porous specimen used in DEFORM

Chapter 5 RESULTS AND DISCUSSION

Results obtained from experimentation and DEFORM software along with discussion are presented in this chapter. The sequence is below mentioned:

1. Mechanical properties of dense specimens of PEEK/HA composite evaluated through three point bend test. HA extracted from eggshells was used here as ceramic reinforcement in PEEK matrix. The results obtained were used to delimit the refined study in stage 2.
2. Mechanical properties of dense specimens of PEEK/HA (natural-extracted from eggshells) composite evaluated by 3 point bend test but with refined range of influencing factors.
3. Mechanical properties of dense specimens of PEEK/HA (Synthetic) composite are evaluated for comparison with PEEK/HA (natural).
4. Statistical analysis of results using MINITAB software: Interaction plots and regression analysis of PEEK/HA(both Natural and synthetic) dense specimens
5. Thermal stability analysis of PEEK/HA(natural) bio composite through TGA, DTA and DSC tests
6. Results of invitro degradation of PEEK/HA(natural) porous specimens in simple compression for porous specimen material with optimal strength and modulus values obtained from PEEK/HA(natural) dense specimens
7. Results of PEEK/ HA(natural) porous specimens at best two optimal values obtained from PEEK/ HA(natural) dense specimens using DEFORM software

5.1 Delimiting study on PEEK/ HA (natural) composite

Influencing factors (or the process parameters) were chosen from the behavior of composite components PEEK and HA. Several initial tests were conducted before the actual study to affirm the specimen formation. Range of composition, sintering temperature and rate of heating were studied in this phase. Finally, the process parameters were established. Table 5.1.1 lists the results obtained from 3 point bend test for PEEK/HA (natural) composite.

Referring to Fig 5.1, Fig 5.2 and Table 5.1, the results were indicating higher Young's modulus at higher percentage of HA and higher flexural strength at higher percentage of

PEEK. With few exceptions, the flexural strength and Young's modulus were found gradually increasing with an increase in percentage of PEEK and HA respectively. Further it was also found that the lower sintering temperature, 300^0C was badly affecting the flexural strength due to insufficient melting/ bonding of PEEK to HA. Maximum flexural strength 114.85 MPa was observed in a specimen of PEEK/HA 90/10 at a sintering temperature of 330^0C with a ROH of 1^0C/min. Similarly maximum Young's modulus was also observed with slow heating 1^0C/min at a temperature 350^0C but with higher composition of HA i.e.50%. Hence a concern on sintering temperature nearer to melting temperature of PEEK was suggested by this study. Further lower rate of heating (ROH) was found to be promoting better bonding between PEEK/HA from Young's modulus and flexural strength observations. This inference was suggesting the ROH could be chosen as minimum as possible. It was found from earlier findings that HA content could be a maximum of 40% of the total composite to avoid fragile composite. Keeping these observations in view, the influencing parameters were adjusted to higher sintering temperatures, lower ROH and percentage of HA not more than 40% of the total composite. Green compacting pressure of 250 MPa was chosen as it was found optimum to retain the specimen shape and size. Compacting pressure was not chosen as the process parameter, as pressures beyond 250 MPa were not much influential on mechanical properties. Time of ball milling could be one of the parameters left for future scope.

Higher percentage of PEEK, higher sintering temperature and lower ROH were found to be favourable in improved strain from Fig 5.3. Improved strain through strategic management of process parameters would help in improved toughness of the composite.

Table 5.1 Mechanical properties of PEEK/HA composite- Delimiting study

Specimen	Composition, %PEEK , %HA	Sintering temperature, ^{0}C	Rate of Heating, ^{0}C/ min	Thickness, mm	Width, mm	Length, mm	Max. force, N	Max. deflection, mm	Flexural strength, MPa	Young's modulus, MPa	Max strain
1	50,50	300	2	4.21	12.62	60	39.58	1.44	15.92	3294	1.01
2	50,50	330	1.5	4.22	12.65	60	141.52	2.41	56.53	5010	1.69
3	50,50	350	1	3.97	12.67	60	142.69	2.539	64.15	5651	1.67
4	70,30	330	2	3.73	12.36	60	136.16	4.471	71.22	4794	2.78
5	70,30	350	1.5	4.29	12.53	60	214.91	3.659	83.87	4787	2.62
6	70,30	300	1	3.97	12.36	60	138.78	3.826	64.12	4670	2.53
7	90,10	350	2	3	16	60	158.672	9.525	99.16	4211	4.76
8	90,10	300	1.5	3.86	12.42	60	43.15	1.836	20.98	2819	1.18
9	90,10	330	1	2.83	17.37	60	177.531	12.37	114.85	4621	5.84

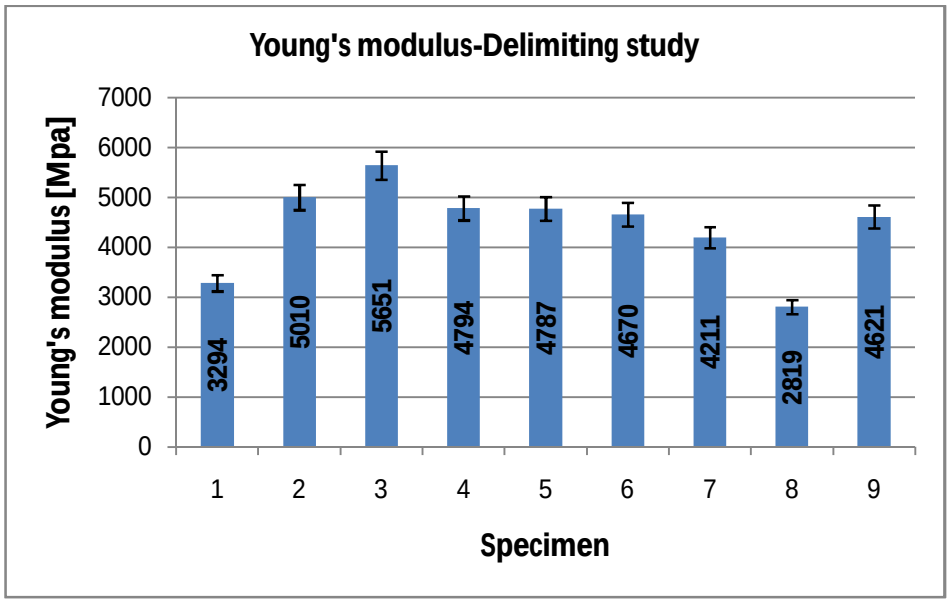


Fig. 5.1 Effect of process parameters on Young's modulus of PEEK/ HA composite

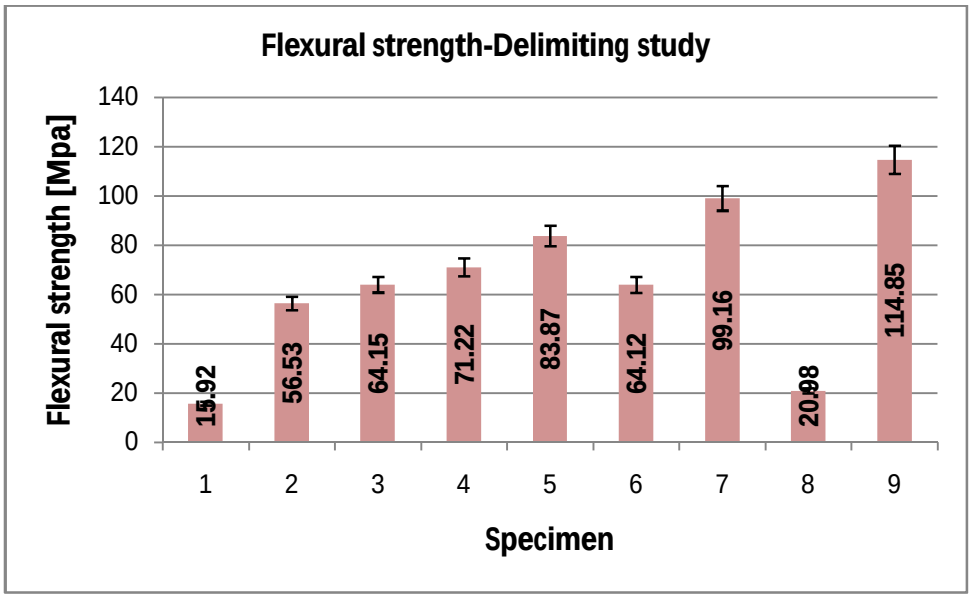


Fig. 5.2 Effect of process parameters on flexural strength of PEEK/ HA composite

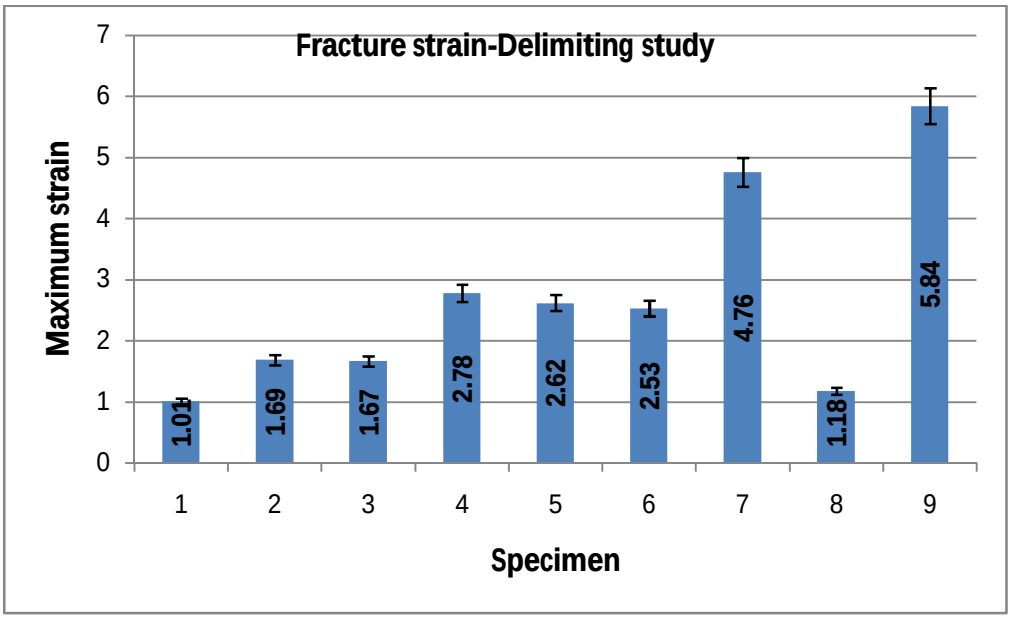


Fig. 5.3 Effect of process parameters on maximum strain of PEEK/ HA composite

Highest Young's modulus 5.65GPa was observed in PEEK/HA composite with HA composition 50%, sintered at 350^{0}C with a ROH of 1^{0}C/min. However, Differential scanning calorimetry of PEEK suggests the limiting temperature as 338.2^{0}C. Also seen practically was charred nature of appearance of specimens at 350^{0}C. Highest maximum flexural strength of 114.85 MPa was observed in PEEK/ HA specimen with 90/10 respective percentages in total composite at 330^{0}C

sintering temperature with a ROH 1^0C/ min. Since 10% HA was not felt bio inductive, refined studies were proposed at higher percentages of HA, i.e. more than 10%.

5.2 Mechanical properties of PEEK/HA (natural) dense composite

With the acquired knowledge from delimiting studies, the process parameters were modified to improve the bonding between components of the composite. Improved bonding could be proven resulting in better mechanical properties. Proposed influencing factors/levels are presented in Table 5.2a.

Table 5.2a) Modified process parameters/levels

Study	Composition, PEEK/HA			Sintering temp, ^{0}C			ROH, ^{0}C/min		
Delimiting	50/50	70/30	90/10	300	330	350	1.0	1.5	2.0
Refined	60/40	70/30	80/20	310	320	330	1.0	1.25	1.5

Refined process parameters as described in Table 5.2a were used to prepare dense composite specimens for evaluation of mechanical properties through three point bend test. The tests were conducted at Central Institute of Plastics Engineering and Technology, Hyderabad. Tests results and load-elongation curves are reproduced in Fig 5.4a and presented in Table 5.2b.

Table 5.2b) Mechanical properties of PEEK/HA natural composite- dense specimens with refined process parameters

Specimen	Composition, %PEEK , %HA	Sintering temperature, ^{0}C	Rate of Heating, ^{0}C/ min	Thickness, mm	Width, mm	Length, mm	Max. force, N	Max. deflection, mm	Flexural strength, MPa	Young's modulus, MPa	Max strain
1	60,40	310	1.0	3.98	12.53	64	64.92	1.72	31.40	4861	1.002
2	60,40	320	1.25	4.01	12.45	64	167.86	3.3	80.49	6625	1.938
3	60,40	330	1.5	4.16	12.37	64	146.27	3.16	65.59	4637	1.926
4	70,30	310	1.25	4.1	12.48	64	161.39	3.01	73.85	5377	1.809
5	70,30	320	1.5	3.71	12.78	64	191.42	3.75	104.47	7238	2.038
6	70,30	330	1.0	3.89	12.34	64	173.81	4.06	89.36	5593	2.315

7	80,20	310	1.5	3.19	13.43	64	162.53	6.54	114.17	6288	3.054
8	80,20	320	1.0	4.0	12.41	64	185.02	4.27	89.45	5240	2.504
9	80,20	330	1.25	3.27	16.0	64	170.67	6.84	95.77	4842	3.275

Fig. 5.4 to 5.7 present the results in graphical form. Interpretation of specimen details such as composition, maximum sintering temperature and ROH by specimen number are referred to Table 5.2b

Shape: Plate

	Thickness	Width	Lower Support
Units	mm	mm	mm
60-40-310	3.9800	12.5300	64.0000
60-40-320	4.0100	12.4500	64.0000
60-40-330	4.1600	12.3700	64.0000
70-30-310	4.1000	12.4800	64.0000
70-30-320	3.7100	12.7800	64.0000
70-30-330	3.8900	12.3400	64.0000
80-20-310	3.1900	13.4300	64.0000
80-20-320	4.0000	12.4100	64.0000
80-20-330	3.2700	16.0000	64.0000

Name	Max_Force	Max_Disp	Max_Stress	Max_Strain	Modulus
Parameter					20 Points(2-20)
Units	N	mm	MPa	%	MPa
60-40-310	64.9219	1.71900	31.4011	1.00219	4861.06
60-40-320	167.859	3.30000	80.4931	1.93843	6624.63
60-40-330	146.266	3.16100	65.5929	1.92623	4636.59
70-30-310	161.391	3.01200	73.8529	1.80896	5376.51
70-30-320	191.422	3.75000	104.468	2.03796	7238.05
70-30-330	173.813	4.06200	89.3589	2.31463	5593.44
80-20-310	162.531	6.53600	114.170	3.05418	6288.83
80-20-320	185.016	4.27400	89.4516	2.50430	5240.32
80-20-330	170.672	6.83600	95.7674	3.27447	4841.60

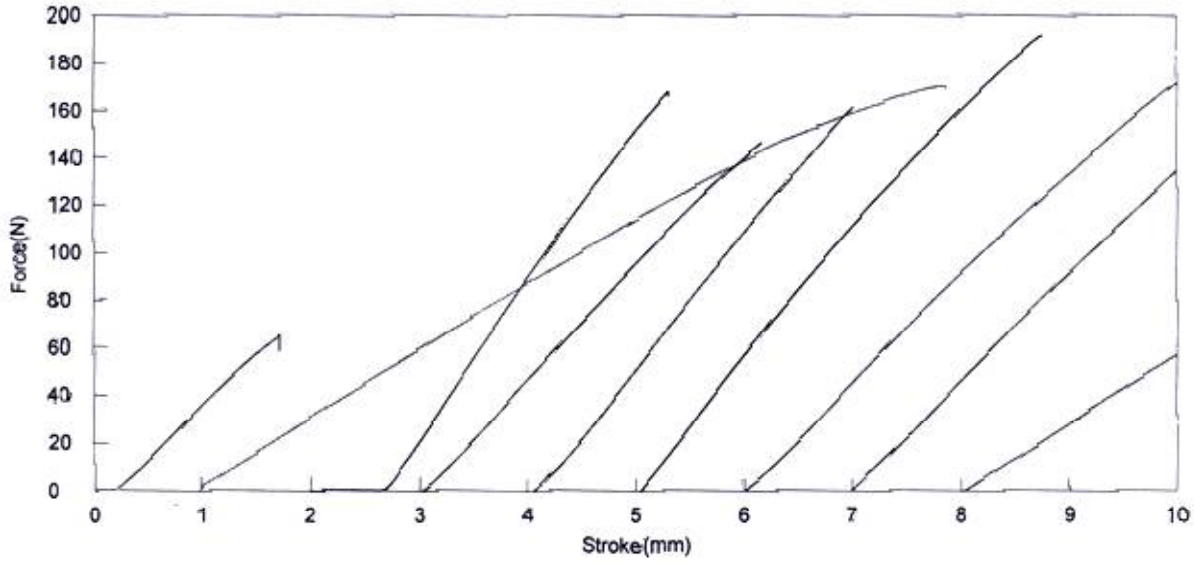


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Fig. 5.4a) Flexural test results and load plot for dense PEEK/ HA (natural) composite specimens

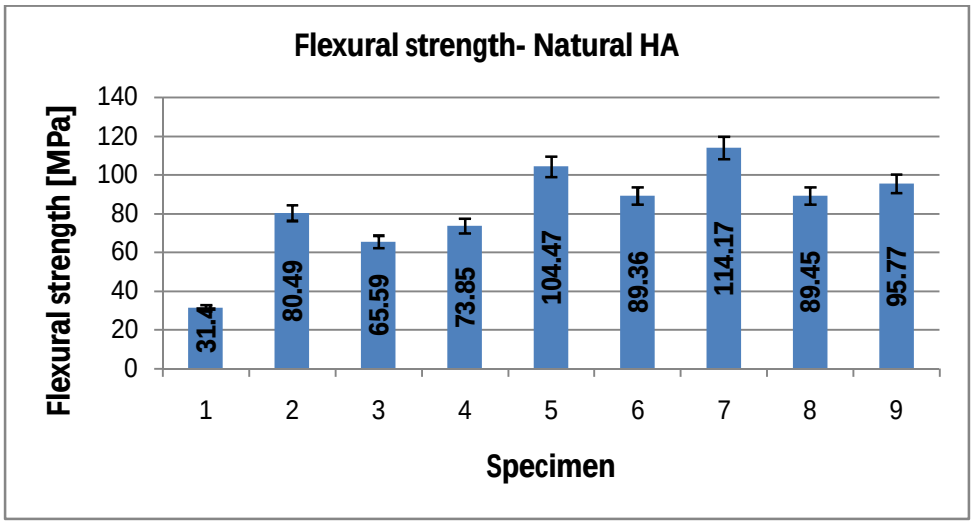


Fig. 5.4b) Effect of process parameters on Flexural strength of PEEK/ HA (natural) composite

Referring to Fig 5.4a and 5.4b, the maximum flexural strength 114.17 MPa was exhibited by specimen 7 having PEEK/HA composition ratio in total composite 80/20. Corresponding sintering temperature and ROH respectively 310^0C and 1.5^0C/min were found favourable to attain maximum strength. High sintering temperature along with prolonged heating or low sintering temperature i.e. less than 300^0 C and high/low ROH observed in delimiting study were affecting the composite formation and resulting in poor flexural strength. In higher middle compositions of PEEK, preferred ROH was identified as 1.5^0C/ min for better flexural strength. These aspects are covered in detail at interaction plots.

Load plots and strain values in Fig 5.4a) will be helpful in assessing the toughness of the composite. Detailed individual load plots (not presented here) with load versus elongation would deliver the data on the processability of the composite and evaluation of toughness.

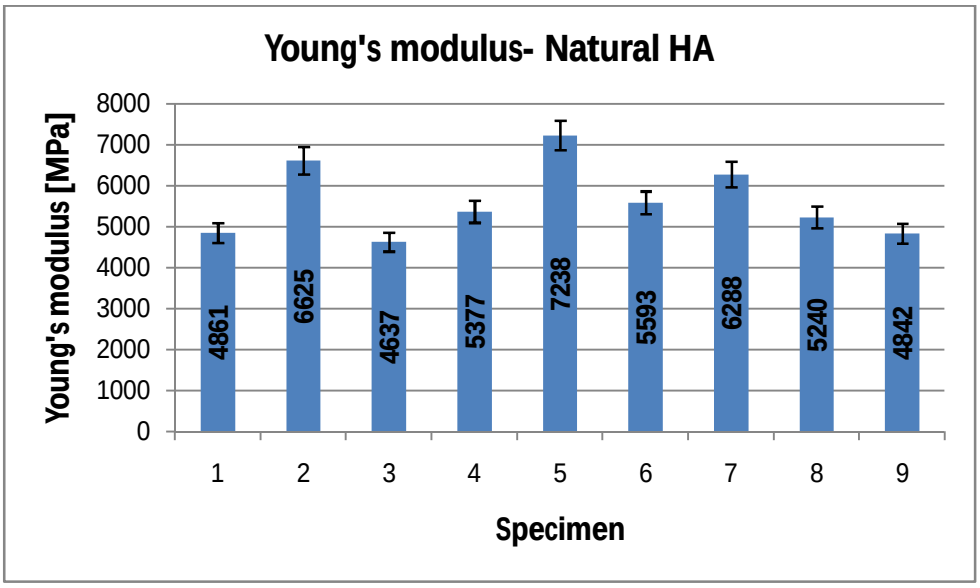


Fig. 5.5 Effect of process parameters on Young's modulus of PEEK/ HA(natural) composite

From Fig 5.5, the highest Young's modulus noticed was 7238 MPa. This is a noticeable achievement [139], a research on nano HA with PEEK. PEEK/ nano HA findings of these authors were reported to reach a maximum Young's modulus of 7850 MPa with high sophistication in their experiments. Interestingly, ROH 1.5^0C/ min and sintering temperatures more than 310^0C were found favourable for higher Young's modulus achievement, and also for higher flexural strength as discussed earlier. It was also noticed from the results that, higher values of Young's moduli were not restricted to higher composition percentages of HA unlike in delimiting studies. Rather a down shift in HA composition percentages but with refined ROH and sintering temperatures were understood resulting in enriched mechanical properties. SEM of broken specimen surfaces shown in Fig 5.38a& b would further help in deciding the adsorption of PEEK with its counterparts. This was a route identified for tailored properties of this biocomposite.

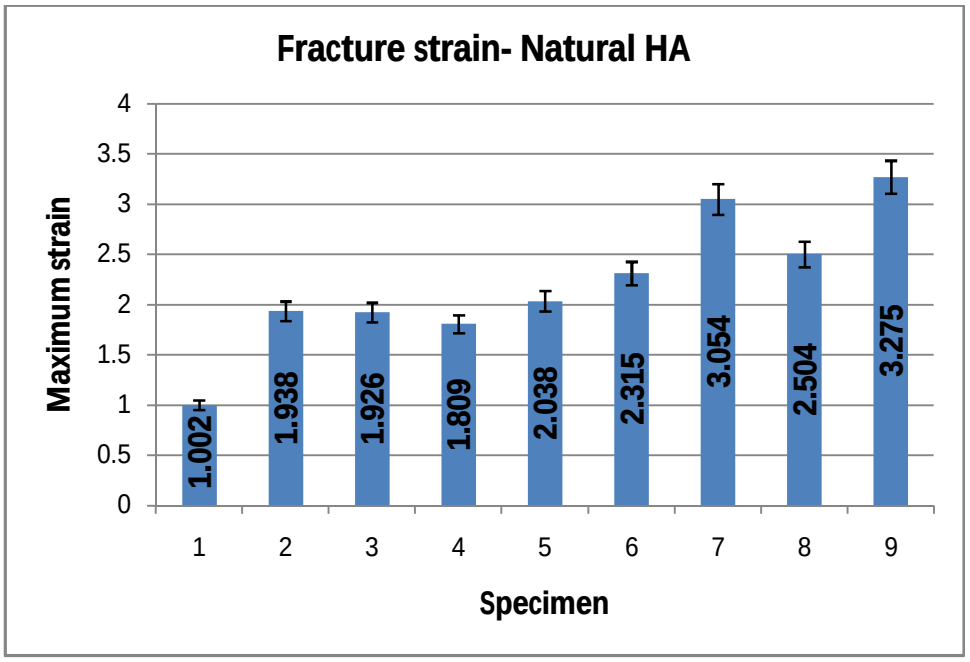


Fig 5.6 Effect of process parameters on Maximum strain of PEEK/ HA(natural) composite

From Fig 5.6, it was concluded that higher sintering temperature, low rate of heating and high percentages of PEEK in composite are favourable for high fracture strains or better yielding before fracture. Higher strain rates with higher Young's modulus, such as specimens 5 and 7 would be interpreted for higher fracture toughness. Increased sintering temperature with an increase in %HA was suggested for better tailored properties with better bioactivity.

5.3 Mechanical properties of PEEK/ HA (synthetic) dense composite

Mechanical properties of synthetic specimens evaluated through 3 point bend test at central Institute of Plastics Engineering and Technology, Hyderabad are reproduced in Fig 5.7a and presented in Table 5.3

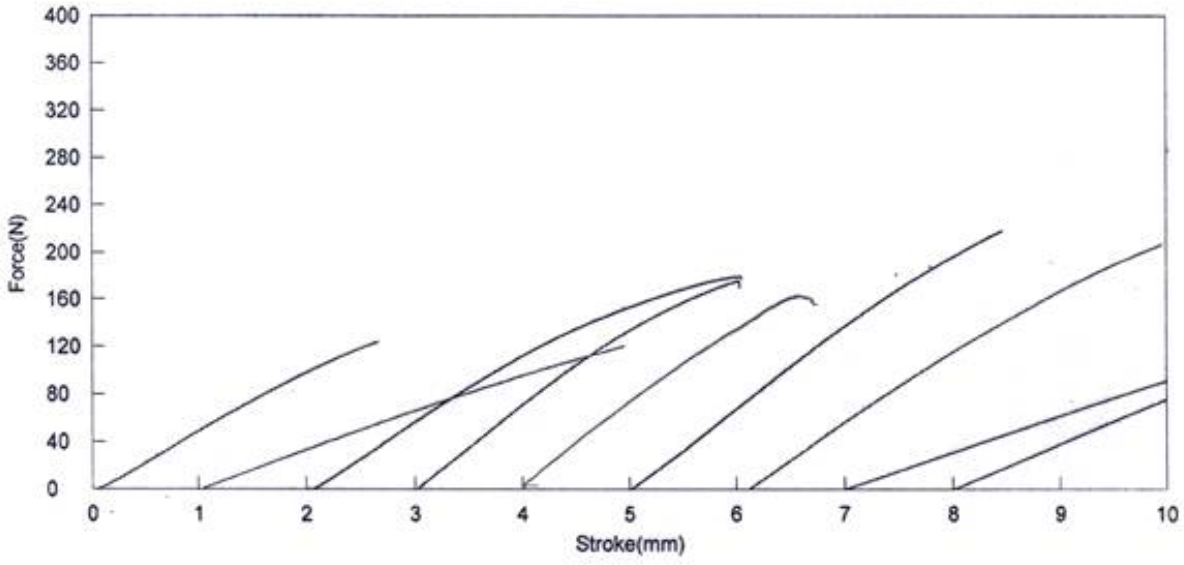
Table 5.3 Mechanical properties of PEEK/HA (synthetic) composite- dense specimens

Specimen	Composition, %PEEK , %HA	Sintering temperature, ^{0}C	Rate of Heating, ^{0}C/ min	Thickness, mm	Width, mm	Length, mm	Max. force, N	Max. deflection, mm	Flexural strength, MPa	Young's modulus, MPa	Max strain
1	60,40	310	1.0	4.0	12.36	64	124.297	2.659	60.34	5470	1.558
2	60,40	320	1.25	3.9	12.5	64	179.75	4.026	90.76	6371	2.3
3	60,40	330	1.5	4.0	12.6	64	175.5	3.013	83.57	6677	1.765
4	70,30	310	1.25	4.5	12.4	64	180.2	2.915	83.13	6721	1.726
5	70,30	320	1.5	4.4	12.3	64	218.984	3.454	88.28	5202	2.226
6	70,30	330	1.0	4.2	13.5	64	217.266	4.271	87.59	4987	2.628
7	80,20	310	1.5	3.5	16	64	185.328	8.488	90.77	4105	4.352
8	80,20	320	1.0	4.1	12.5	64	206.63	7.507	94.14	3911	4.509
9	80,20	330	1.25	3.5	15	64	177.25	8.433	92.60	5085	4.324

Shape: Plate

	Thickness	Width	Lower Support
Units	mm	mm	mm
60-40-310	4.0000	12.3600	64.0000
60-40-320	3.9000	12.5000	64.0000
60-40-330	4.0000	12.6000	64.0000
70-30-310	4.5000	12.4000	64.0000
70-30-320	4.4000	12.3000	64.0000
70-30-330	4.2000	13.5000	64.0000
80-20-310	3.5000	16.0000	64.0000
80-20-320	4.1000	12.5000	64.0000
80-20-330	3.5000	15.0000	64.0000

Name	Max_Force	Max_Disp	Max_Stress	Max_Strain	Modulus
Parameter					20 Points(2-20)
Units	N	mm	MPa	%	MPa
60-40-310	124.297	2.65900	60.3383	1.55801	5470.30
60-40-320	179.750	4.02600	90.76	2.30001	6370.46
60-40-330	175.500	3.01300	83.5714	1.76543	6676.91
70-30-310	67.3750	3.06600	83.1387	1.76636	6720.85
70-30-320	218.984	3.45400	88.2823	2.22621	5201.86
70-30-330	217.266	4.27100	87.5850	2.62767	4986.94
80-20-310	185.328	8.48800	90.7730	4.35176	4104.96
80-20-320	206.063	7.50700	94.1440	4.50860	3910.90
80-20-330	177.250	8.43300	92.6041	4.32356	5084.85



Comment
SAMPLE-CODE-6366

Fig. 5.7 a) Flexural test results and load plot for dense PEEK/ HA (synthetic) composite specimens

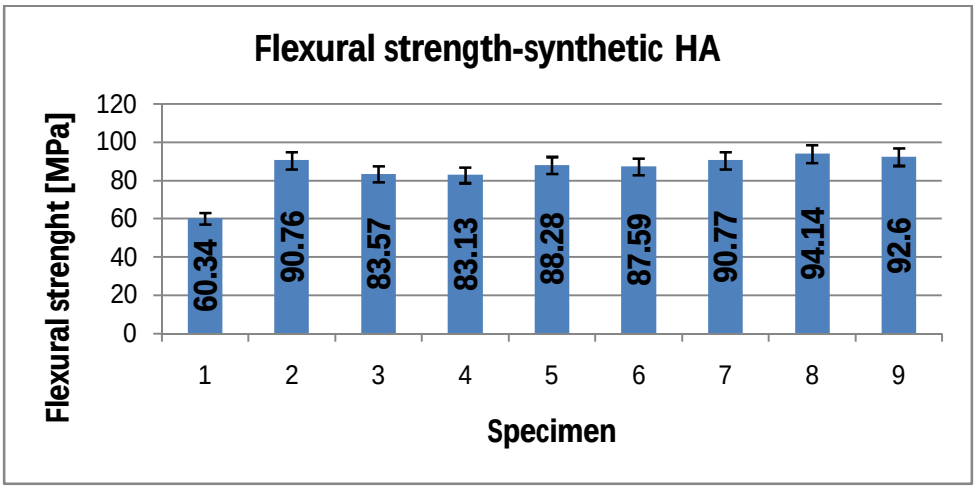


Fig. 5.7b) Effect of process parameters on Flexural strength of PEEK/ HA (synthetic) composite

Referring to Table 5.3 and Figs 5.7a) and b), the maximum flexural strength of the specimen could reach up to 94.14 MPa at PEEK/HA 80/20 in total composite. However this result indicates that the maximum flexural strength 114.17 (Fig. 5.4b and Table 5.2) obtained from natural (egg shell extracted) HA has superior interaction with polymer matrix as compared to synthetic HA reinforcements. One of the possible reasons could be the difference in HA particle size between natural HA (average diameter- 4.5µ) and synthetic HA (average diameter- 45 µ). Maximum flexural strength was reported in both natural and synthetic HA reinforcements at 80/20 component composition of PEEK/ HA in total composite and the values respectively were 114.17 MPa and 94.14 MPa.

Referring to Fig 5.8 and Table 5.3 and further comparing with Fig 5.5, it was found that the maximum Young's modulus in natural HA reinforcement is 7.7% higher than that of the synthetic HA reinforcement. In both the cases, maximum Young's modulus was observed at 70/30 composition of PEEK /HA components of total composite. Young's modulus was reaching as high as 7238 MPa in natural HA reinforced PEEK composite leaving its counterpart synthetic HA reinforced PEEK composite at 6721 MPa. Smaller HA particle size and higher sintering temperature in PEEK/ HA (natural) could be favourable for higher Young's modulus.

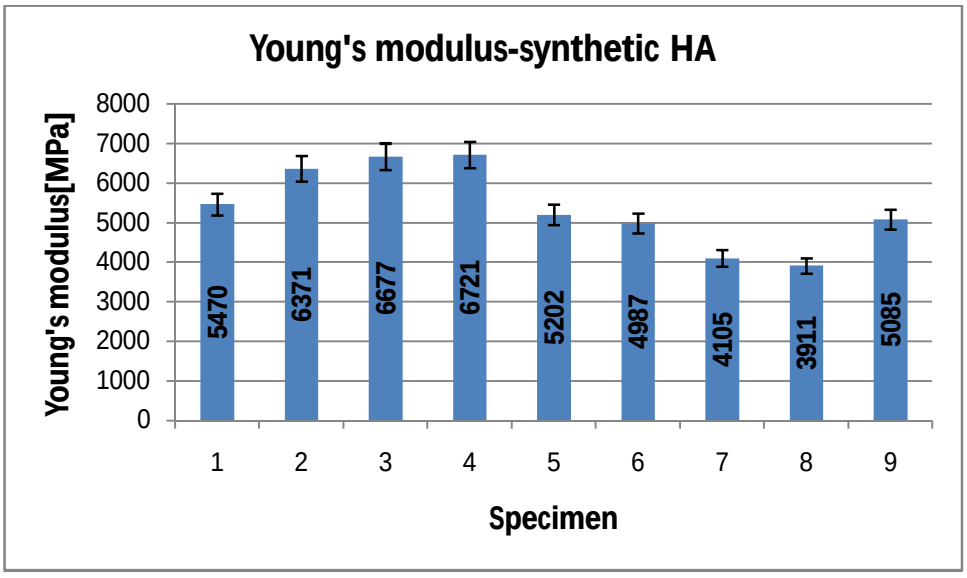


Fig. 5.8 Effect of process parameters on Young's modulus of PEEK/ HA (synthetic) composite

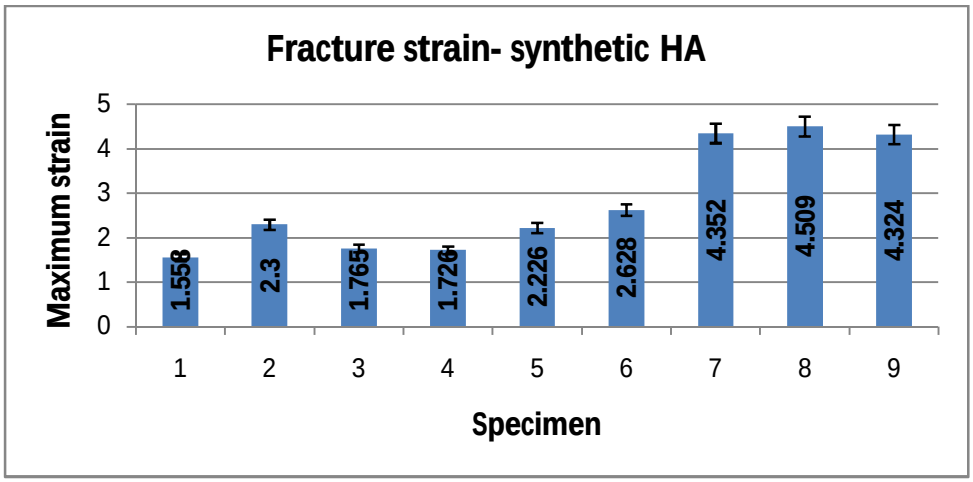
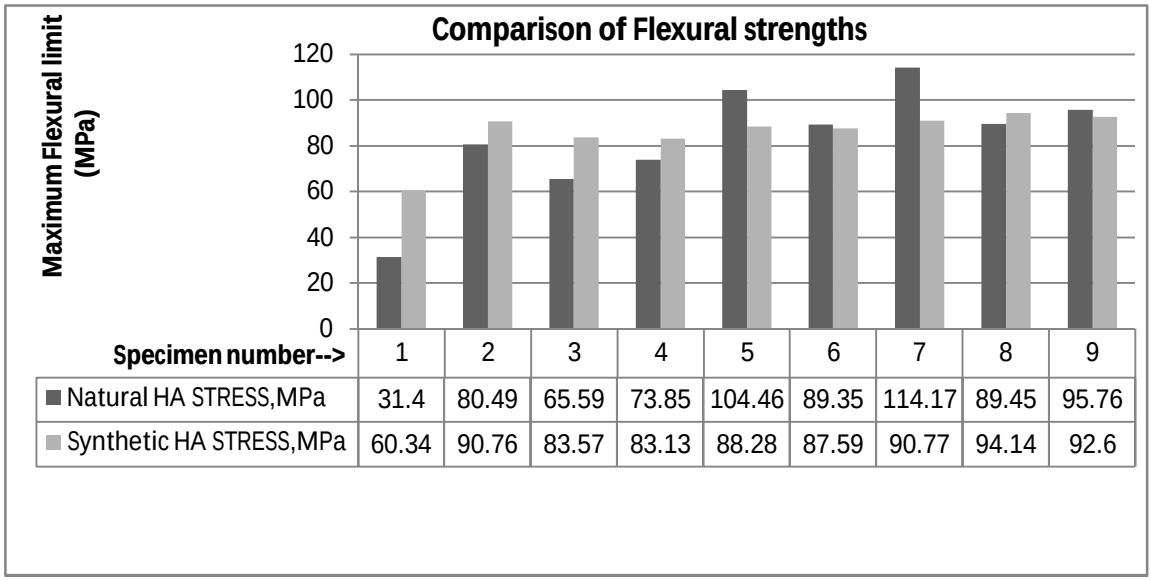


Fig. 5.9 Effect of process parameters on Max strain of PEEK/ HA (synthetic) composite

Maximum fracture strain of PEEK/ HA (synthetic) composite shown in Fig. 5.9 was found to be higher than that of PEEK/ HA (natural) composite. The observations from Fig. 5.9 are: Higher fracture strain in composite with higher percentage of PEEK; Regardless the other process parameters, for a given component ratio of PEEK/ HA, the fracture strain remains almost constant at higher percentages of PEEK in composite.

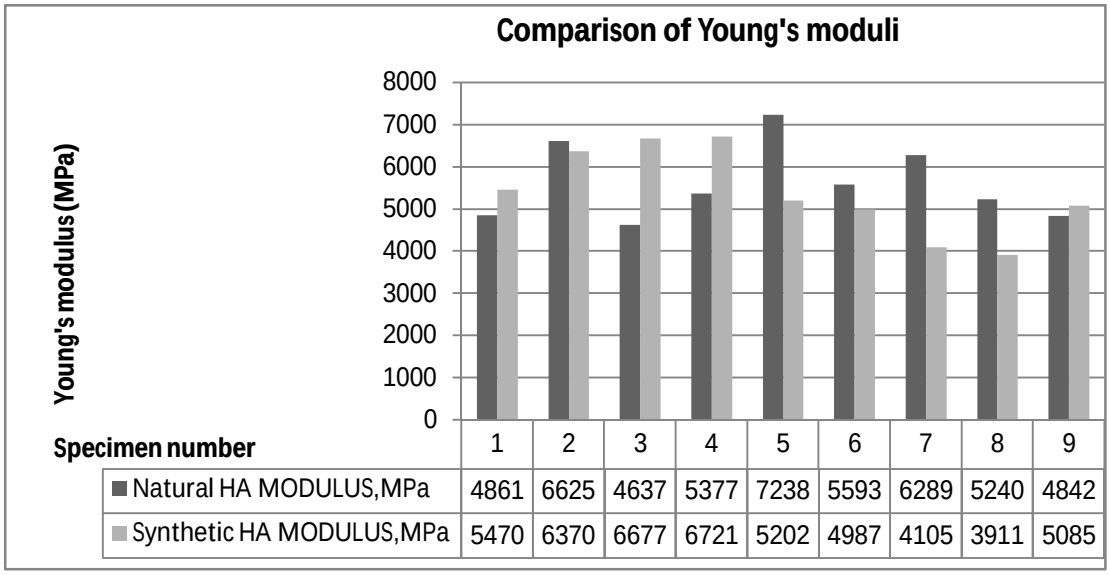
Fig.5.10, 5.11 and 5.12 were presented for comparison of mechanical properties of the composites with natural and synthetic HA reinforcements. From the comparisons of flexural

strength and Young's modulus between composites of natural and synthetic HA reinforcements, natural HA interacts in a better manner with matrix PEEK as compared to synthetic HA. Maximum flexural strength as presented in Fig. 5.10 for 80/20 composition in natural HA presence is 114 MPa as against 94 MPa in synthetic HA presence. From Fig. 5.11, the maximum Young's modulus in PEEK/natural HA is observed to be 7238 MPa and higher than 6677 MPa as in case of PEEK/synthetic HA.



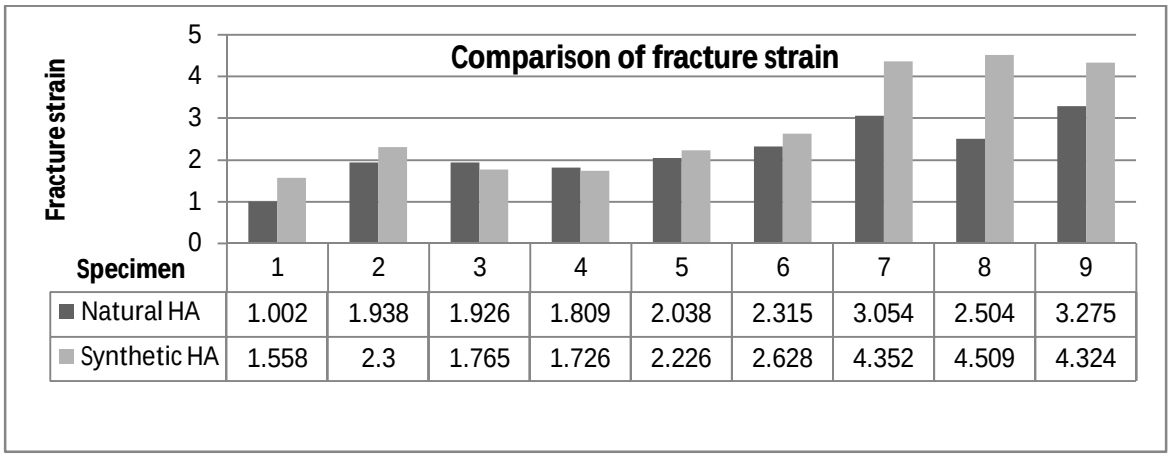
Specimen number-->	1	2	3	4	5	6	7	8	9
Natural HA STRESS,MPa	31.4	80.49	65.59	73.85	104.46	89.35	114.17	89.45	95.76
Synthetic HA STRESS,MPa	60.34	90.76	83.57	83.13	88.28	87.59	90.77	94.14	92.6

Fig. 5.10 Comparison of Flexural strength in composites with natural HA and synthetic HA



Specimen number	1	2	3	4	5	6	7	8	9
Natural HA MODULUS,MPa	4861	6625	4637	5377	7238	5593	6289	5240	4842
Synthetic HA MODULUS,MPa	5470	6370	6677	6721	5202	4987	4105	3911	5085

Fig. 5.11 Comparison of Young's moduli in composites with natural HA and synthetic HA



Specimen	1	2	3	4	5	6	7	8	9
Natural HA	1.002	1.938	1.926	1.809	2.038	2.315	3.054	2.504	3.275
Synthetic HA	1.558	2.3	1.765	1.726	2.226	2.628	4.352	4.509	4.324

Fig. 5.12 Comparison of fracture strain in composites with natural HA and synthetic HA

5.4 Main effects plot, interaction plot and regression analysis using MINITAB

Main effect plots explain the influence of each process parameter on response variable. The influence of each process parameter being independently studied, the main effect plots fail to explain the interactive effect on response variable.

Interaction plots give an explicit idea on combined effect of process parameters on response variable.

Regression analysis is helpful in interpolation studies and predicting the effect of process parameters on response variable even away from selected levels through regression equation.

5.4.1 Interpretation of main effects plot and interaction plot

Main effect plots presented through Figs 5.13 -5.16 explain the influence of individual process parameters on flexural strength and Young's modulus of the composite. Fig. 5.13 explains for better flexural strength, the preferred process parameters are: composition 80/20; Rate of heating 1.5^0C/min; and maximum temperature 320^0 C. From Fig 5.14, preferred process parameters for better Young's modulus are: composition PEEK/HA 70/30; Rate of heating 1.5^0C/min; and maximum temperature 320^0 C.

Interpretation of main effect plots are consolidated in Table 5.4

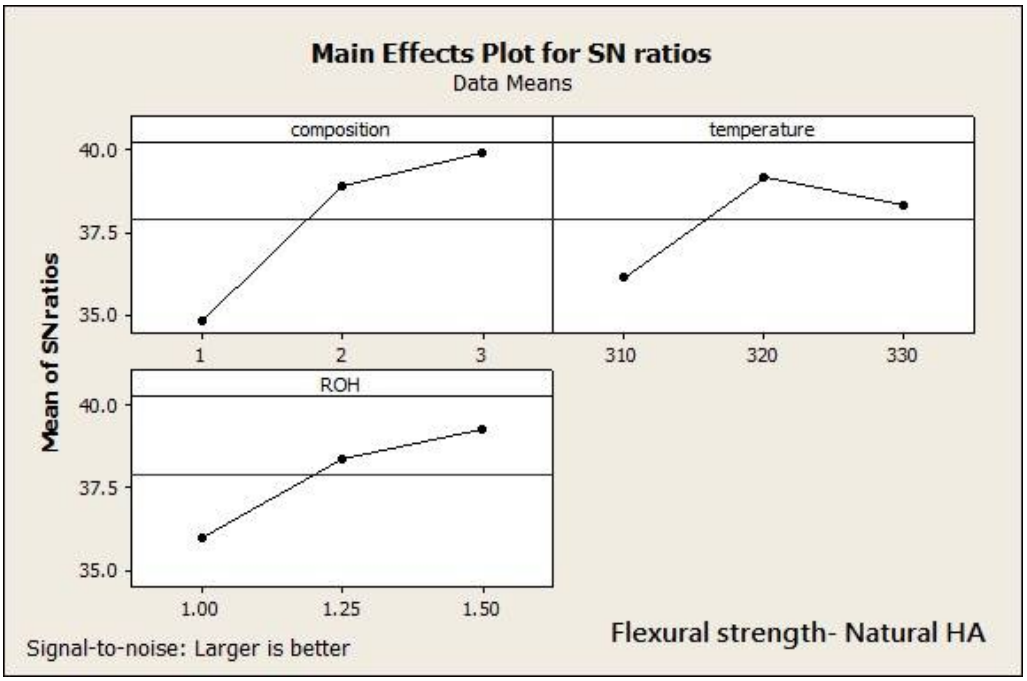


Fig. 5.13Main effects plot- influence of process parameters on flexural strength of composite with natural HA

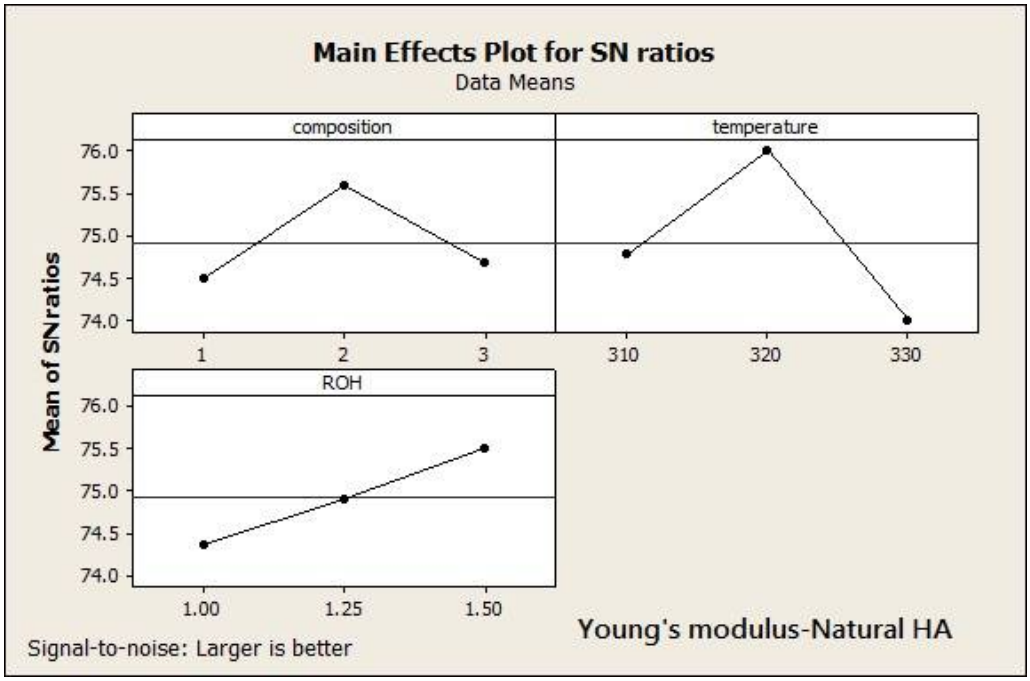


Fig. 5.14 Main effects plot- influence of process parameters on Young's modulus of composite with natural HA

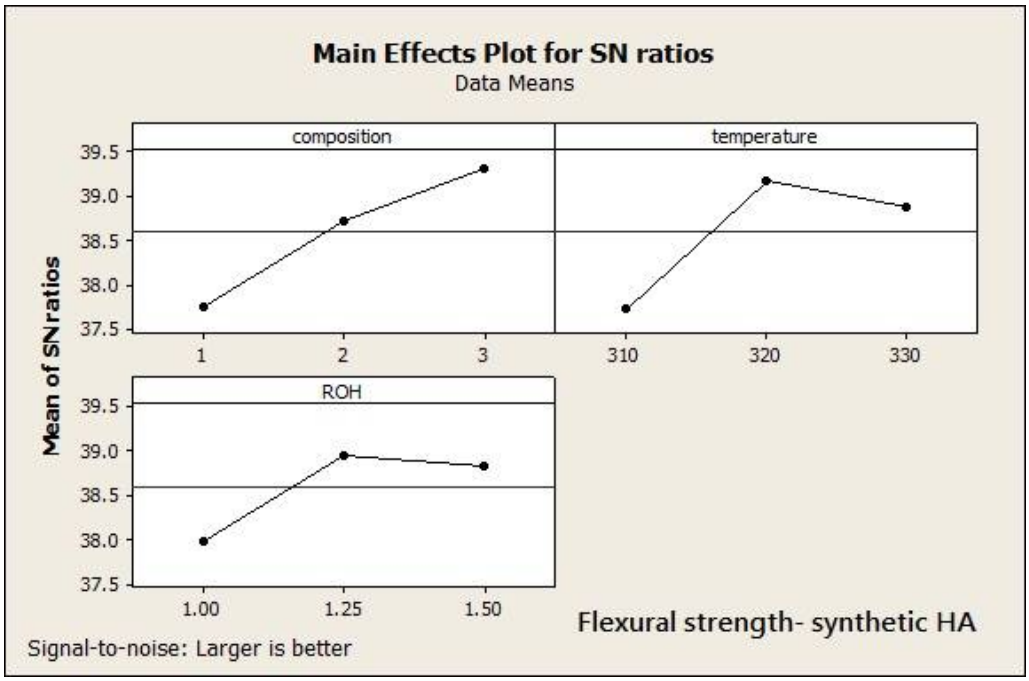


Fig. 5.15 Main effects plot- influence of process parameters on flexural strength of composite with synthetic HA

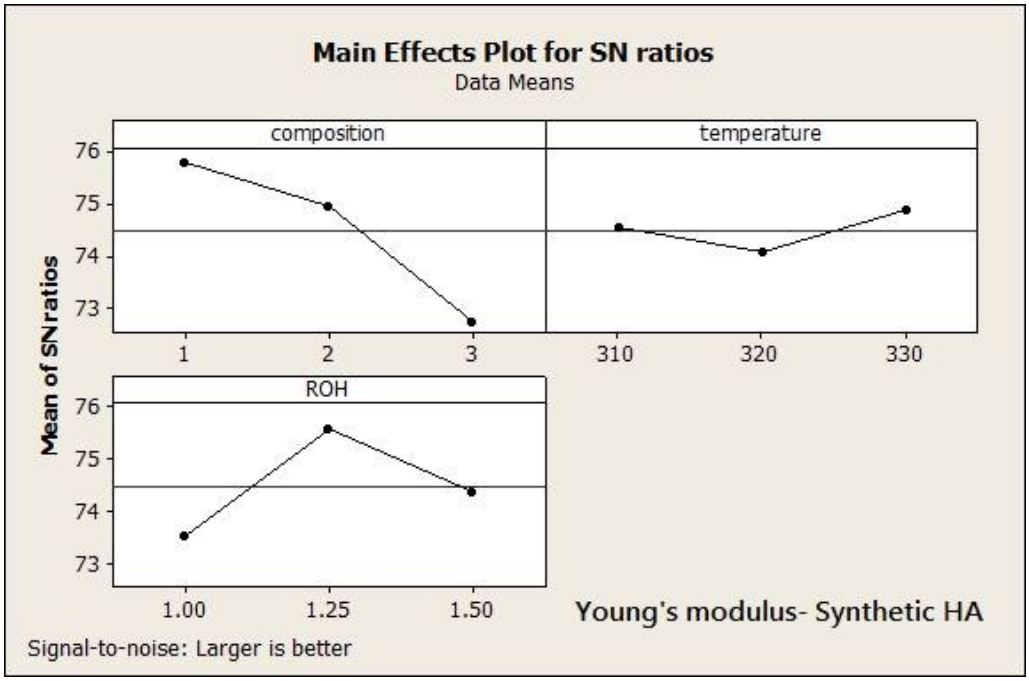


Fig. 5.16 Main effects plot- influence of process parameters on Young's modulus of composite with synthetic HA

However, the interaction between process parameters alters the preferred process parameter levels for better response or the output. Table 5.4 comprehends the preferred process parameter levels for optimum response.

Table 5.4 Interpretation of main effects plots

Response to be optimized (Fig number)	Highly influencing parameter- level		
	Composition %(PEEK, HA)	Rate of Heating ^{0}C/ min	Sintering temperature, ^{0}C
Flexural strength- Natural HA (Fig 5.13)	80,20	1.5	320
Young's Modulus - Natural HA (Fig 5.14)	70,30	1.5	320
Flexural strength- Synthetic HA (Fig 5.15)	80,20	1.25	320
Young's Modulus - Synthetic HA (Fig 5.16)	70,30	1.25	330

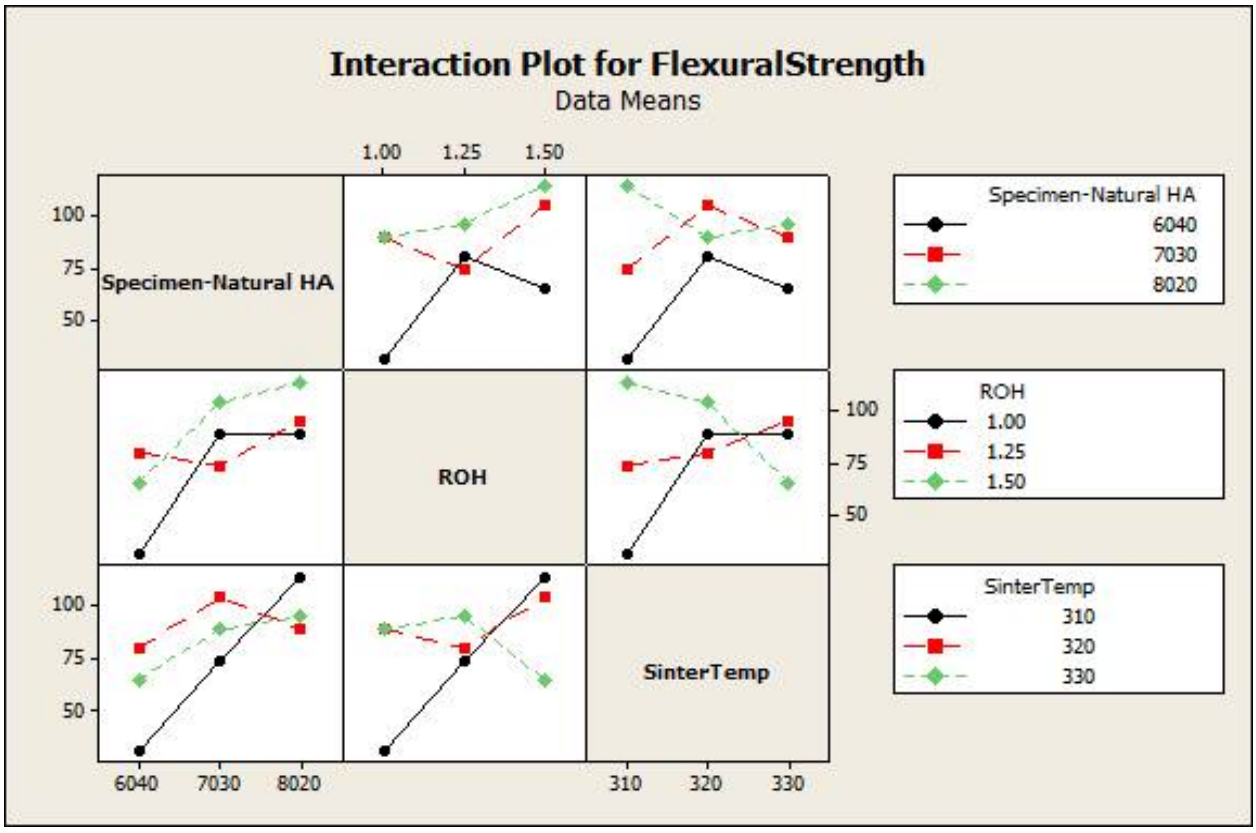


Fig. 5.17 Interaction plot for the flexural strength of the composite with Natural HA reinforcement

Flexural strength of the composite with natural HA reinforcement would depend on several combinations of composition, ROH and sintering temperature. Referring to Fig 5.17, for better flexural strength PEEK/ HA composition 80/20, ROH =1.5^{0}C/ min at 310^{0}C sintering temperature were suggested. Similar the way PEEK/ HA composition 70/30, ROH and sintering temperatures were 1.5^{0}C/ min at 320^{0}C respectively. And finally for PEEK/ HA composition 60/40, ROH and sintering temperatures were 1.25^{0}C/ min at 320^{0}C respectively.

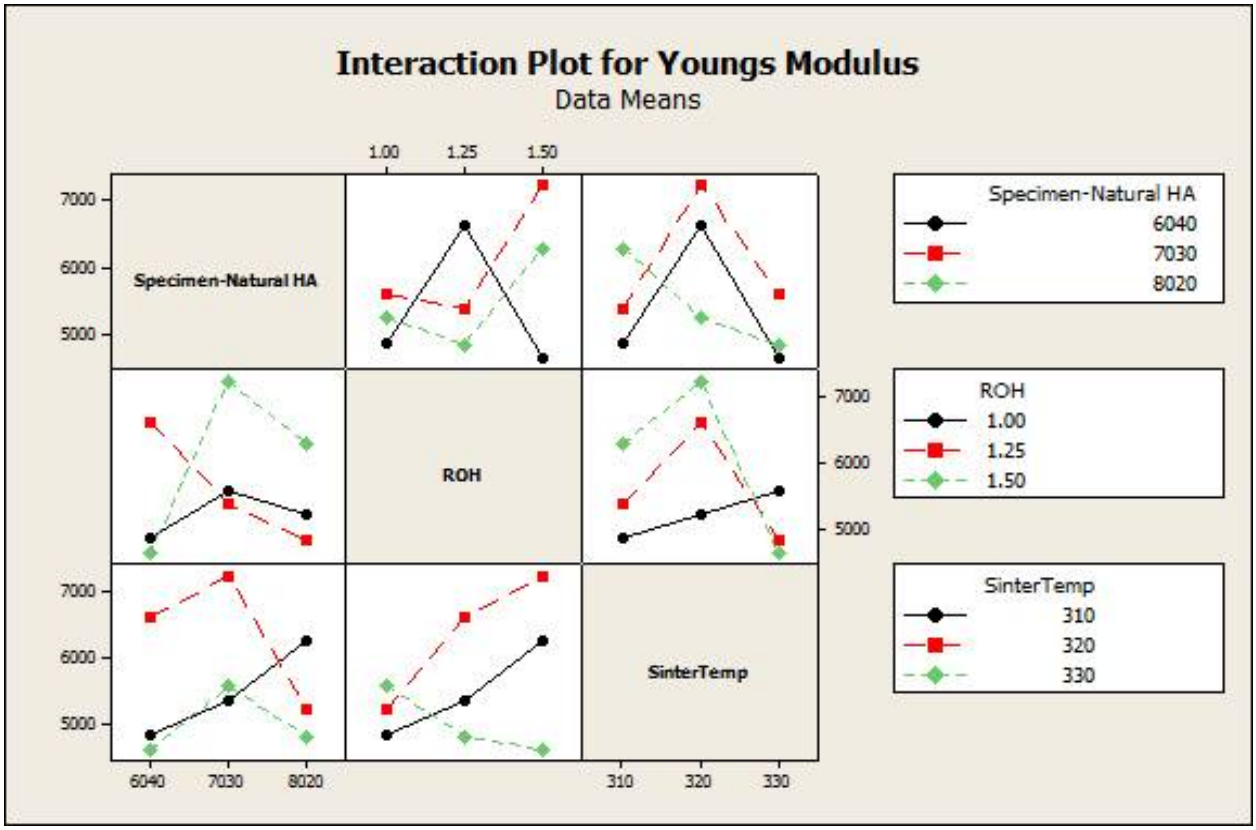


Fig. 5.18 Interaction plot for Young's modulus of the composite with Natural HA reinforcement

Young's modulus of the composite with natural HA reinforcement would attain its maximum value in combinations of composition, ROH and sintering temperature as presented in Fig 5.18 and in similar lines of explanation with regard to Fig 5.17. For better Young's modulus, PEEK/ HA composition 80/20, ROH =1.25^{0}C/ min at 310^{0}C sintering temperature were suggested. Similar the way, for PEEK/ HA composition 70/30, ROH and sintering temperatures were 1.5^{0}C/

min at 320^{0}C respectively. And finally for PEEK/ HA composition 60/40, ROH and sintering temperatures were 1.25^{0}C/ min at 330^{0}C respectively.

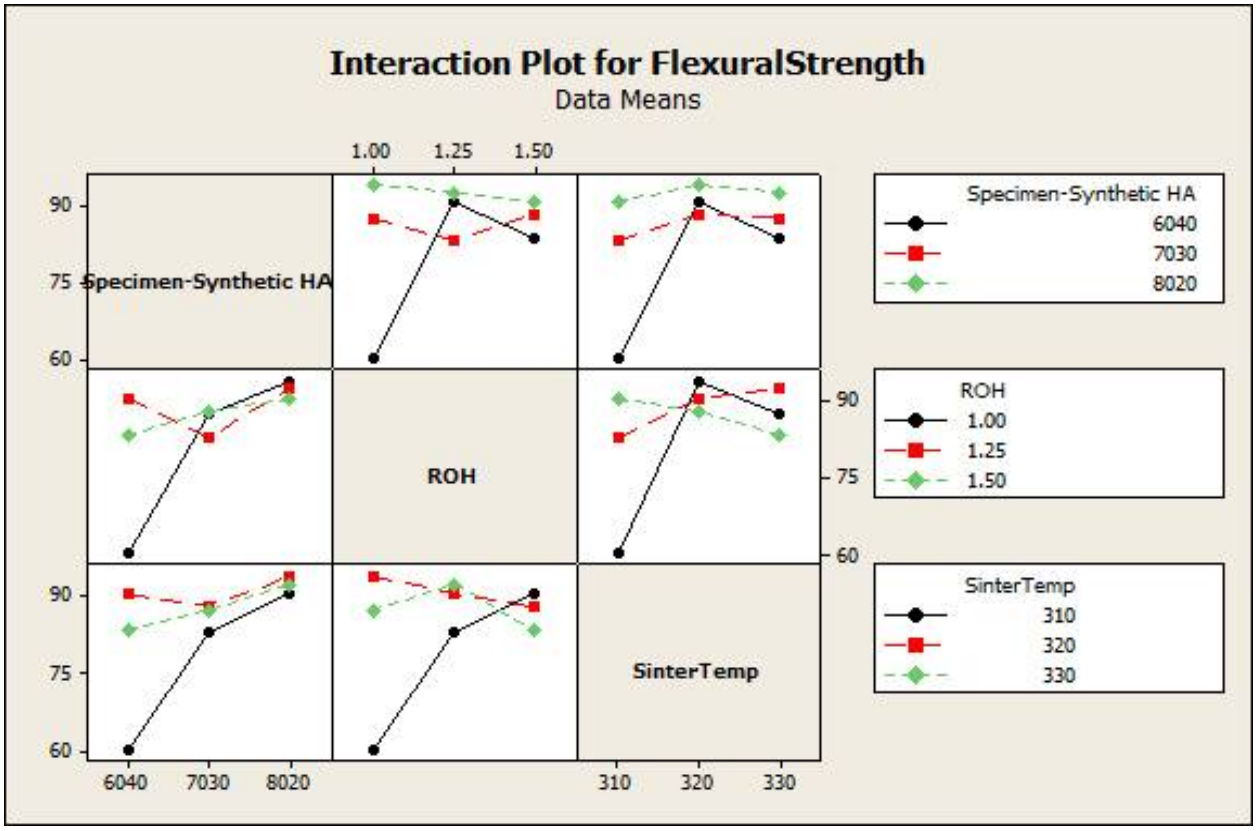


Fig. 5.19 Interaction plot for flexural strength of the composite with synthetic HA reinforcement

Referring to Fig 5.19, flexural strength of the composite with synthetic HA reinforcement would attain its maximum values for PEEK/ HA composition 80/20 at ROH =1.0^{0}C/ min and 320^{0}C sintering temperature. Similar the way PEEK/ HA composition 70/30, ROH and sintering temperatures were 1.5^{0}C/ min at 330^{0}C respectively. And finally for PEEK/ HA composition 60/40, ROH and sintering temperatures were 1.25^{0}C/ min at 320^{0}C respectively.

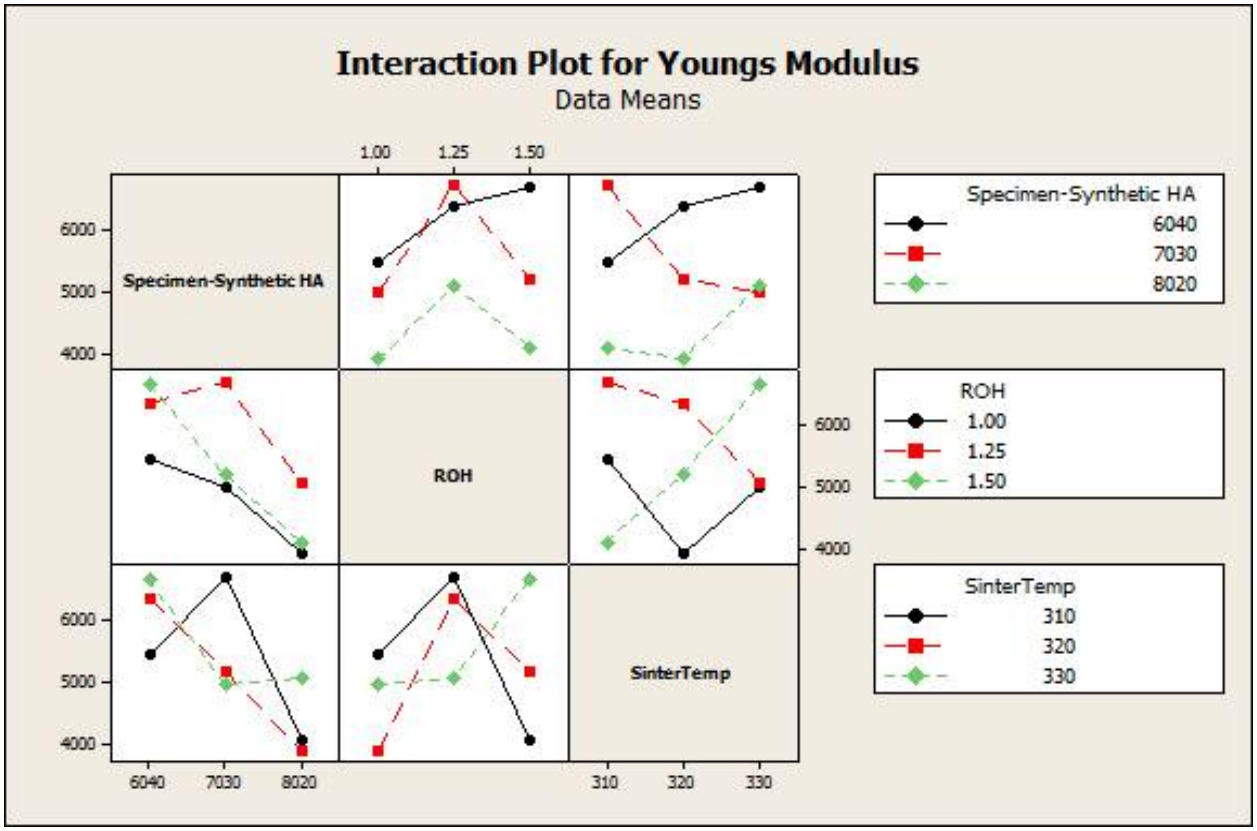


Fig 5.20 Interaction plot for Young's modulus of the composite with synthetic HA reinforcement

Young's modulus of the composite with synthetic HA reinforcement would attain its maximum value in combinations of composition, ROH and sintering temperature as presented in Fig 5.20 and in similar lines of earlier explanations. For better Young's modulus PEEK/ HA composition 80/20, ROH =1.25^{0}C/ min at 330^{0}C sintering temperature were suggested. Similar the way PEEK/ HA composition 70/30, ROH and sintering temperatures were 1.25^{0}C/ min at 310^{0}C respectively. And finally for PEEK/ HA composition 60/40, ROH and sintering temperatures were 1.5^{0}C/ min at 330^{0}C respectively.

5.4.2 Regression analysis

For regression analysis, MINITAB 15 was used. The project window data is reproduced for interpretation.

NATURAL HA Reinforcement:

i) Regression Analysis: Flexural strength versus Composition, Sintering Temperature (TEMP), Rate of Heating (R.O.H)

```
The regression equation is
STRESS, MPa = 37 + 6.77 COMPOSITION - 0.156 TEMP + 49.3 R.O.H

Predictor       Coef  SE Coef      T      P
Constant        37.1    210.8   0.18  0.867
COMPOSITION    6.772    2.090   3.24  0.023
TEMP         -0.1559   0.6608  -0.24  0.823
R.O.H          49.35    25.08   1.97  0.106

S = 15.3559   R-Sq = 75.1%   R-Sq(adj) = 60.1%

Analysis of Variance

Source          DF      SS      MS     F      P
Regression       3  3552.8  1184.3  5.02  0.057
Residual Error   5  1179.0   235.8
Total            8  4731.9
```

Results for: Worksheet 1

Taguchi Design

```
Taguchi Orthogonal Array Design

L9(3**3)

Factors:  3
Runs:     9

Columns of L9(3**4) Array
1 2 3
```

Taguchi Analysis: STRESS versus composition, temperature, ROH

Response Table for Signal to Noise Ratios

Larger is better

Level	composition	temperature	ROH
1	34.80	36.15	36.00
2	38.92	39.18	38.37
3	39.94	38.33	39.29
Delta	5.14	3.02	3.29
Rank	1	3	2

Response Table for Means

Level	composition	temperature	ROH
1	59.16	73.14	70.07
2	89.22	91.47	83.37
3	99.79	83.57	94.74
Delta	40.63	18.33	24.67
Rank	1	3	2

Taguchi Analysis: STRESS versus composition, temperature, ROH

Response Table for Signal to Noise Ratios

Larger is better

ii).Regression Analysis: MODULUS versus COMPOSITION, TEMP, R.O.H

The regression equation is

MODULUS, MPa = 11708 + 14 COMPOSITION - 25.6 TEMP + 1646 R.O.H

Predictor	Coef	SE Coef	T	P
Constant	11708	13793	0.85	0.435
COMPOSITION	13.8	136.7	0.10	0.923
TEMP	-25.63	43.24	-0.59	0.579
R.O.H	1646	1641	1.00	0.362

S = 1004.74 R-Sq = 21.5% R-Sq(adj) = 0.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	1378763	459588	0.46	0.725
Residual Error	5	5047491	1009498		
Total	8	6426254			

SYNTHETIC HA Reinforcement:

i). Regression Analysis: STRESS versus COMPOSITION, TEMP, R.O.H

The regression equation is

STRESS, MPa = - 25 + 2.38 COMPOSITION + 0.254 TEMP + 13.7 R.O.H

Predictor	Coef	SE Coef	T	P
Constant	-24.6	108.6	-0.23	0.830
COMPOSITION	2.380	1.077	2.21	0.078
TEMP	0.2540	0.3406	0.75	0.489
R.O.H	13.70	12.92	1.06	0.338

S = 7.91392 R-Sq = 62.5% R-Sq(adj) = 40.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	521.50	173.83	2.78	0.150
Residual Error	5	313.15	62.63		
Total	8	834.65			

ii) Regression Analysis: MODULUS versus COMPOSITION, TEMP, R.O.H

The regression equation is

MODULUS, MPa = - 6494 - 301 COMPOSITION + 37.6 TEMP + 1077 R.O.H

Predictor	Coef	SE Coef	T	P
Constant	-6494	10922	-0.59	0.578
COMPOSITION	-300.9	108.3	-2.78	0.039
TEMP	37.64	34.24	1.10	0.322
R.O.H	1077	1299	0.83	0.445

S = 795.652 R-Sq = 62.9% R-Sq(adj) = 40.6%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	5359737	1786579	2.82	0.146
Residual Error	5	3165311	633062		
Total	8	8525048			

The regression equations for PEEK/ HA natural and PEEK/ HA synthetic obtained from MINITAB 15 were picked up and the same were used to assess the error in Young's modulus and flexural strength. Results of regression analysis are presented in Table 5.5 thru Table 5.8. Regression equations mentioned in regression analysis above are useful in interpreting/ interpolating the composite behaviour.

Table 5.5 Regression analysis- % error in Flexural strength- Natural HA reinforced composite

Specimen	Parameters and levels			Flexural strength, MPa -Natural HA			
	Composition, PEEK- HA	Sintering Temperature, ^{0}C	R.O.H , ^{0}C/min	From Experiment	from Regression equation	Difference	%error
1	60-40	310	1.0	31.4	44.71	13.31	42.39
2	60-40	320	1.25	80.49	62.245	-18.245	-22.67
3	60-40	330	1.5	65.59	79.78	14.19	21.64
4	70-30	310	1.25	73.85	77.345	3.495	4.73
5	70-30	320	1.5	104.46	94.88	-9.58	-9.17
6	70-30	330	1.0	89.35	75.44	-13.91	-15.57
7	80-20	310	1.5	114.17	109.98	-4.19	-3.67
8	80-20	320	1.0	89.45	90.54	1.09	1.22
9	80-20	330	1.25	95.76	108.08	12.315	12.86

Table 5.6 Regression analysis- % error in Young's modulus- Natural HA reinforced composite

Specimen	Parameters and levels			Young's modulus, MPa -Natural HA			
	Composition, PEEK- HA	Sintering Temperature, ^{0}C	R.O.H , ^{0}C/min	From Experiment	from Regression equation	Difference	%error
1	60-40	310	1.0	4861.06	5432	570.94	11.75
2	60-40	320	1.25	6624.63	5601.5	-1023.1	-15.44
3	60-40	330	1.5	4636.59	5771	1134.41	24.47
4	70-30	310	1.25	5376.51	5885.5	508.99	9.47
5	70-30	320	1.5	7238.05	6055	-1183.1	-16.34
6	70-30	330	1.0	5593.44	4990	-603.44	-10.79
7	80-20	310	1.5	6288.86	6339	50.14	0.79
8	80-20	320	1.0	5240.32	5274	33.68	0.64
9	80-20	330	1.25	4841.6	5443.5	601.9	12.43

Table 5.7 Regression analysis- % error in Flexural strength -synthetic HA reinforced composite

Specimen	Parameters and levels			Flexural strength, MPa -Synthetic HA			
	Composition, PEEK- HA	Sintering Temperature, ^{0}C	R.O.H , ^{0}C/min	From Experiment	from Regression equation	Difference	%error
1	60-40	310	1.0	60.34	69.82	9.48	15.71
2	60-40	320	1.25	90.76	78.165	-12.595	-13.88
3	60-40	330	1.5	83.57	86.51	2.94	3.52
4	70-30	310	1.25	83.13	80.385	-2.745	-3.30
5	70-30	320	1.5	88.28	88.73	0.45	0.51
6	70-30	330	1.0	87.59	86.8	-0.79	-0.90
7	80-20	310	1.5	90.77	90.95	0.18	0.2
8	80-20	320	1.0	94.14	89.02	-5.12	-5.44
9	80-20	330	1.25	92.6	97.365	4.765	5.15

Table 5.8 Regression analysis-% error in Young's modulus-Synthetic HA reinforced composite

Specimen	Parameters and levels			Young's modulus, MPa -Synthetic HA			
	Composition, PEEK- HA	Sintering Temperature, ^{0}C	R.O.H , 0C/min	Composition, PEEK- HA	Sintering Temperature, ^{0}C	Difference	Composition, PEEK- HA
1	60-40	310	1.0	5470.3	5938	467.7	8.55
2	60-40	320	1.25	6370.46	6282.25	-88.21	-1.38
3	60-40	330	1.5	6676.91	6626.5	-50.41	-0.75
4	70-30	310	1.25	6720.85	5304.25	-1416.6	-21.08
5	70-30	320	1.5	5201.86	5648.5	446.64	8.59
6	70-30	330	1.0	4986.94	5185	198.06	3.97
7	80-20	310	1.5	4104.96	4670.5	565.54	13.78
8	80-20	320	1.0	3910.9	4207	296.1	7.57
9	80-20	330	1.25	5084.85	4551.25	-533.6	-10.49

5.5 Thermal stability analysis of PEEK/ HA natural composite

Thermal stability analysis of PEEK/ HA natural composite was carried out to examine the stability of the composite while in application in human body i.e. 37^0C and for the processing of the composite beyond its melting point and up to 600^0C. Thermal gravimetric analysis (TGA), Derivative thermo gravimetric analysis (DTG) and Differential Scanning Calorimetry (DSC) were the sources of analysis. TGA, DTG and DSC were used to find percentage of weight loss, peak degradation temperature and melting temperature respectively. TGA, DTG and DSC test results in graphical form for PEEK are presented in Fig 5.21, Fig 5.22 and Fig 5.23respectively. Similar data of the PEEK/ HA composite are consolidated and presented in Table 5.9. Inferences could be drawn on the thermal behavior of the composite with a variation of HA component and the rate of heating during manufacturing processes.

Table 5.9 Summary of TGA, DTG and DSC of PEEK, PEEK/ HA composite

S No	Sample details*	T_m	IDT	PDT	T_5	T_{10}	T_{20}	%weight loss at 600^0C
1	100% PEEK	338.2	566.6	590.8	564.2	574.69	586.16	33.9
2	60-40 -310-1	342.1	505.7	542.5	519.01	538.35	585.19	21.3
3	60-40 -320-1.25	353.6	512.2	544.6	523.31	540.79	582.79	21.5
4	60-40-330-1.5	341.8	513.0	544.4	524.63	541.76	588.79	20.9
5	70-30 -310-1.25	348.5	516.6	546.8	524.43	540.32	567.91	24.6
6	70-30 -320-1.5	340.2	509.1	543.9	518.72	535.77	565.95	24.5
7	70-30 -330-1	341.1	509.2	542.5	517.44	534.37	563.19	25.3
8	80-20 -310-1.5	341.7	518.9	549.9	523.69	538.86	561.16	27.9
9	80-20 -320-1	340.4	514.3	547.2	519.11	534.68	556.87	28.7
10	80-20 330-1.25	340.6	518.1	549.0	523.32	538.36	560.72	27.8
11	100%HA	1150	-	-	-	-	-	-

*Sample specification 60-40-310-1stands for PEEK-60%, HA-40%, sintering temperature 310^0C, and ROH 1^0C/ min

T_m- Melting temperature, ^0C

IDT- Initial degradation temperature, ^0C

PDT- Peak degradation temperature, ^0C

T_5- Temperature in ^0C corresponding to 5% weight loss

T_{10}- Temperature in ^0C corresponding to 10% weight loss

T_{20}- Temperature in ^0C corresponding to 20% weight loss

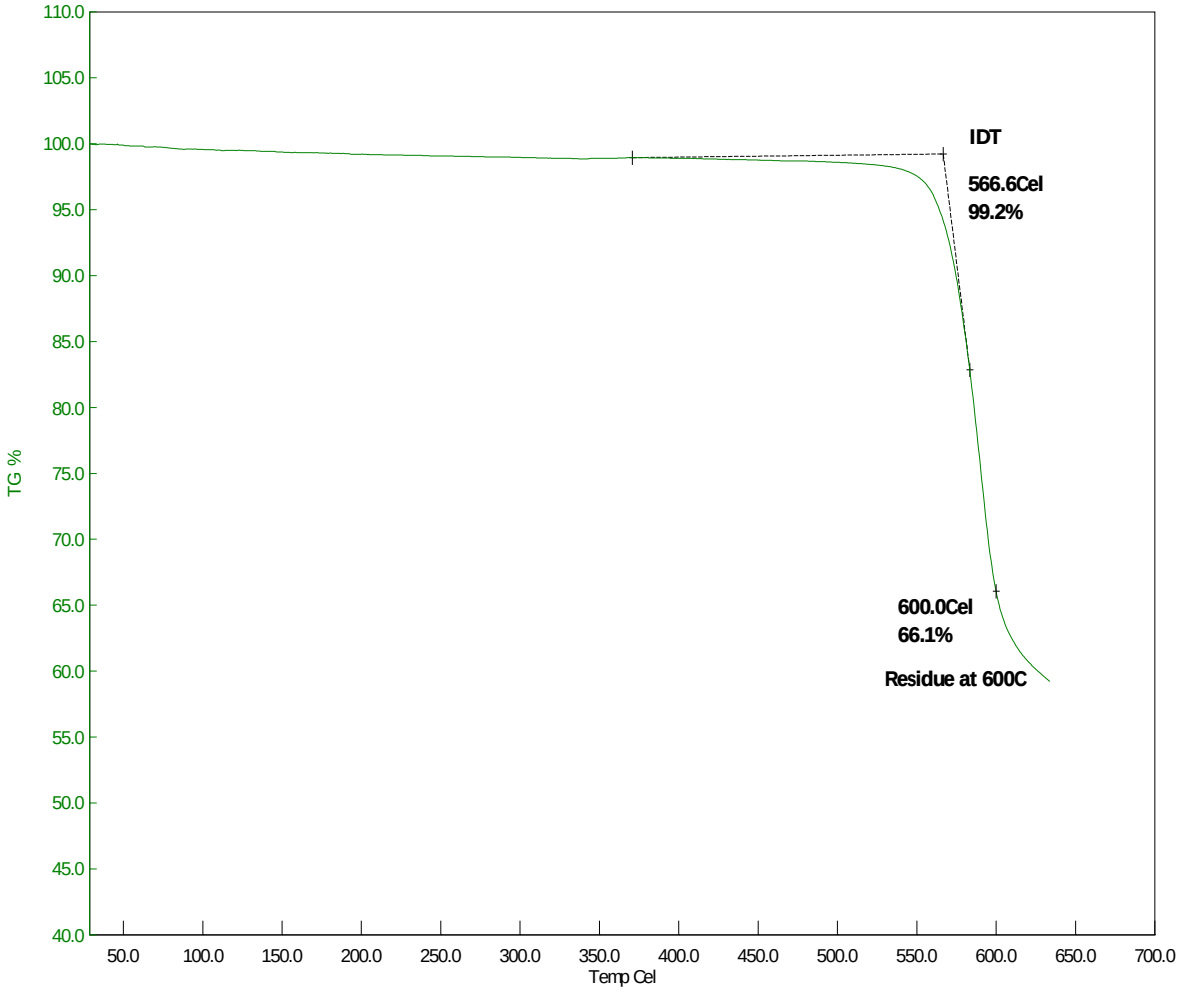


Fig. 5.21 Thermal Gravimetric Analysis of PEEK powder

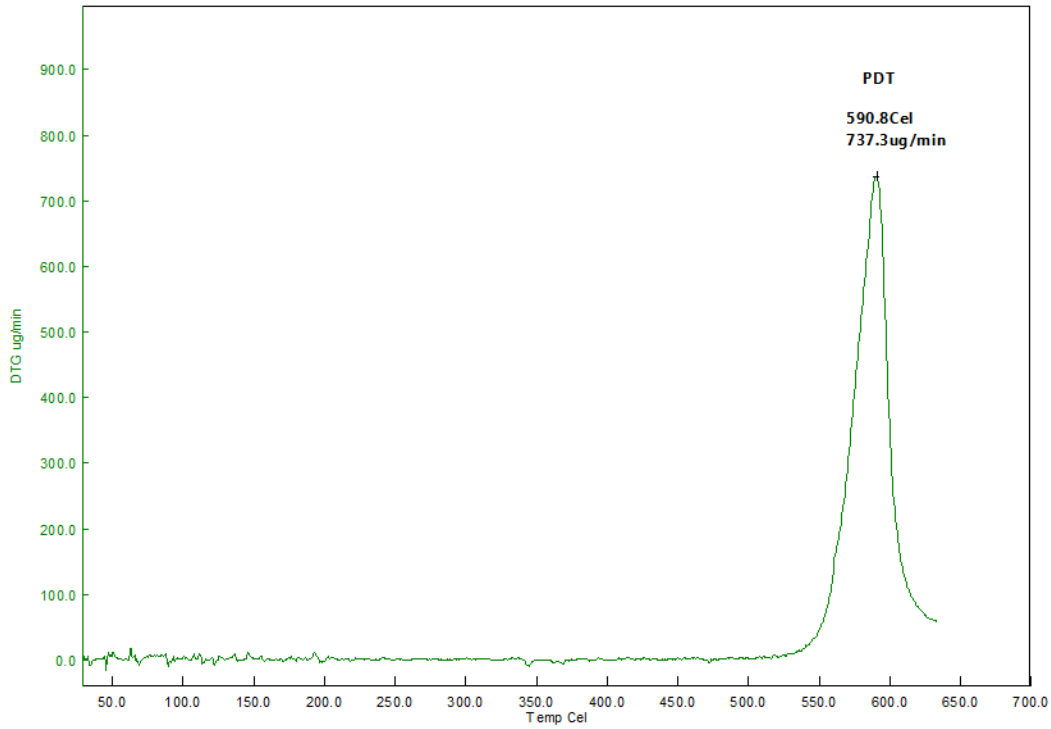


Fig. 5.22 Derivative Thermal gravimetric Analysis of PEEK powder

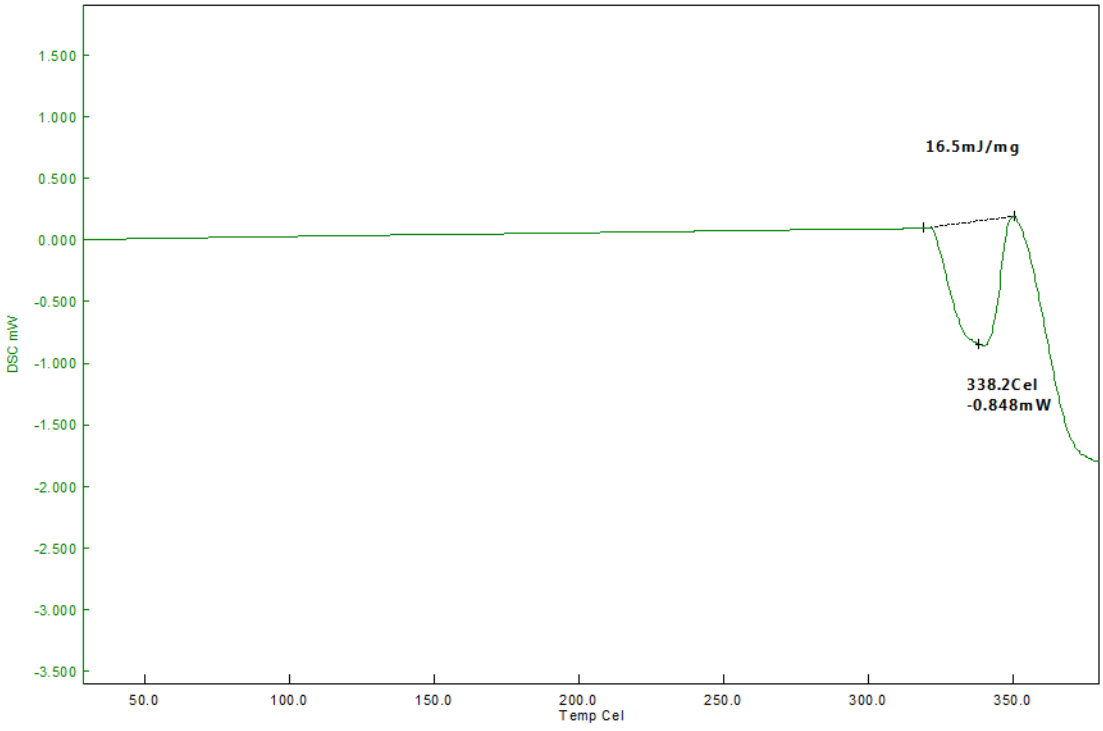


Fig. 5.23 Differential scanning calorimetry of PEEK

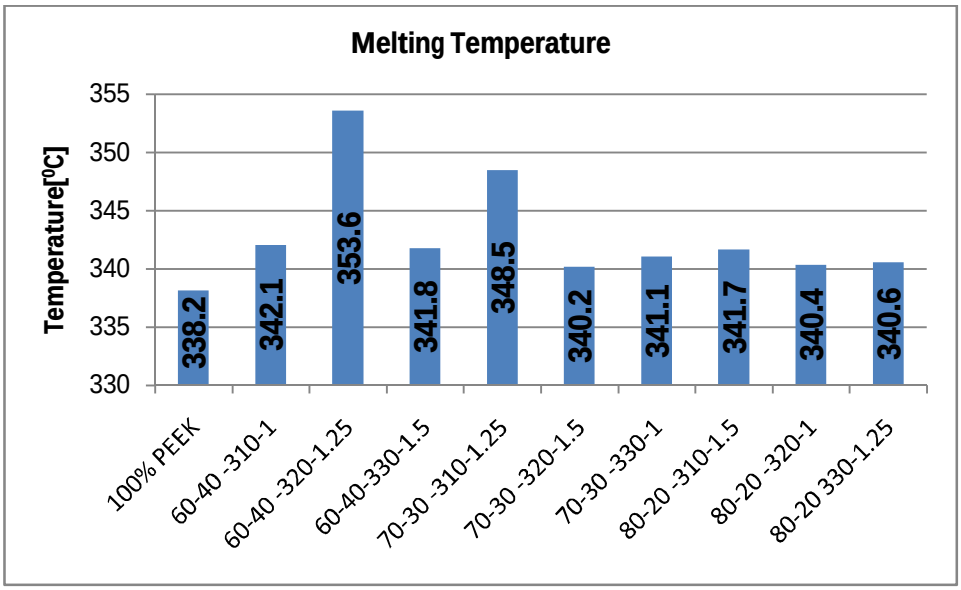


Fig. 5.24 Effect of HA on melting temperature of PEEK/ HA composite

Referring to Fig 5.24 and Table 5.9, melting temperature (T_m) of the PEEK/ HA composite was found increasing with the addition of HA in to PEEK matrix as compared to pure PEEK. The rise in T_m was sharp in composites with a ROH of 1.25^{0}C among the same group of PEEK/ HA compositions at higher values of HA.

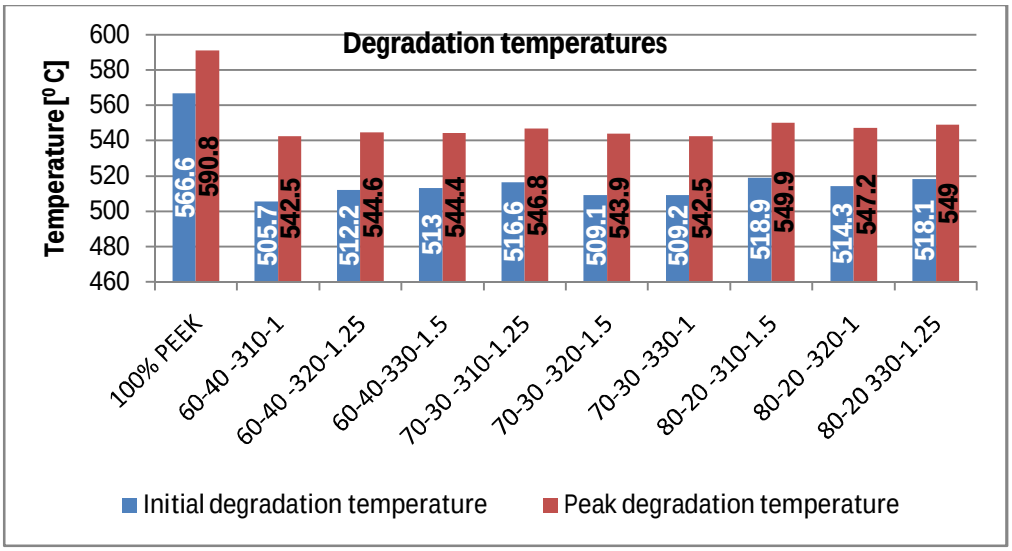


Fig. 5.25 Effect of HA on degradation temperature of PEEK/ HA composite

Referring to Fig 5.25, degradation of PEEK/HA composite was found advanced with an increase in HA and reached peak degradation at lower temperatures than pure PEEK. A down trend was found in degradation temperatures with an increase in HA component.

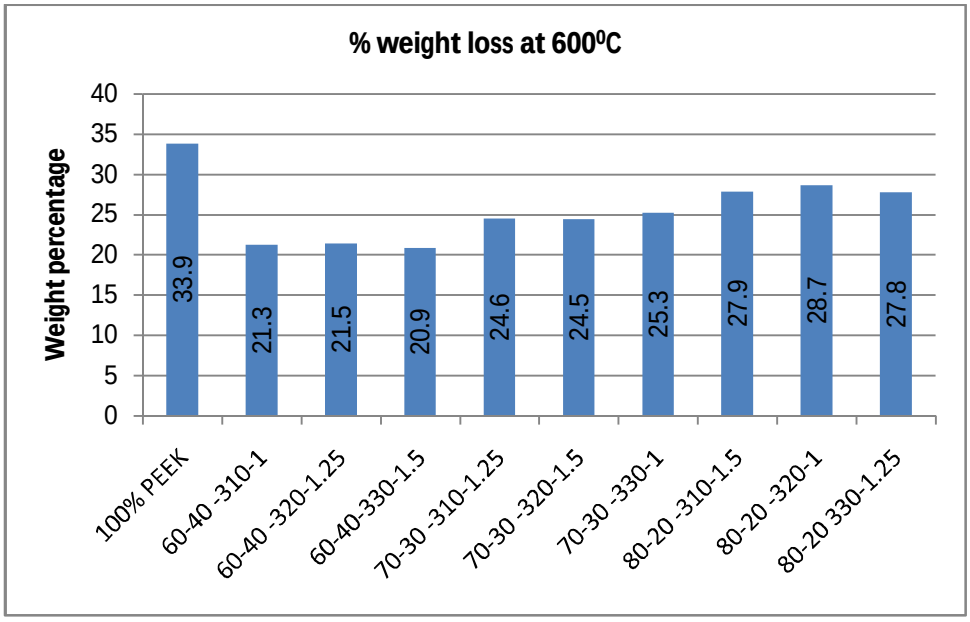
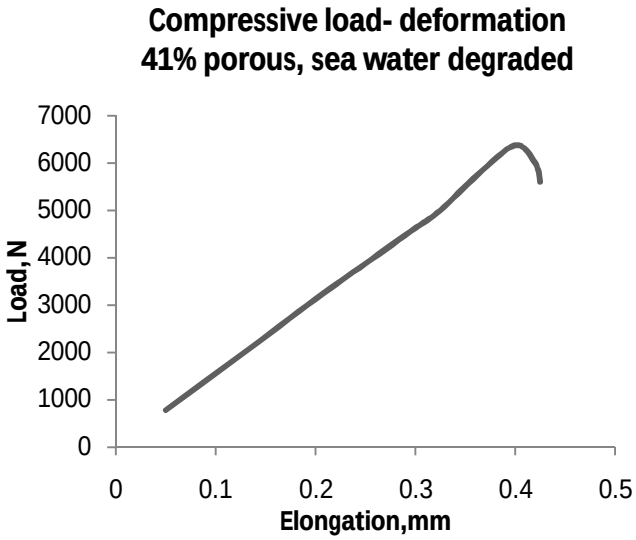


Fig 5.26 Effect of HA on % weight loss of PEEK/ HA composite

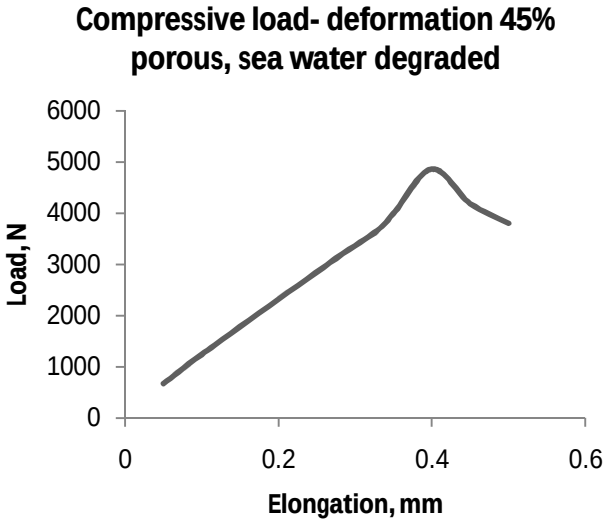
Fig 5.26 depicts the percentage of PEEK/HA composite weight loss at 600^0C. Addition of HA was found to reduce degradation rate and percentage of weight loss as HA is more stable than PEEK. Low rate of heating in composite formation was found resulting in higher percentage of weight loss.

5.6 Mechanical properties of PEEK/ HA 70/30 composite porous specimens

In view of optimum mechanical properties obtained from dense specimen PEEK/HA 70/30 composite, porous specimens were prepared from the slurry of PEEK/HA 70/30. Two sets of specimens were tested in unconstrained state of simple compression- i) the specimens as sintered and ii) the specimens exposed to artificial sea water invitro for 25 days. The load - contraction behaviour of specimens exposed to artificial sea water degradation is presented in Figs 5.27 a, b and c. The results presented in Table 5.10 are derived from stress strain behaviour corresponding to Load- Contraction curves Fig 5.27.



(a)



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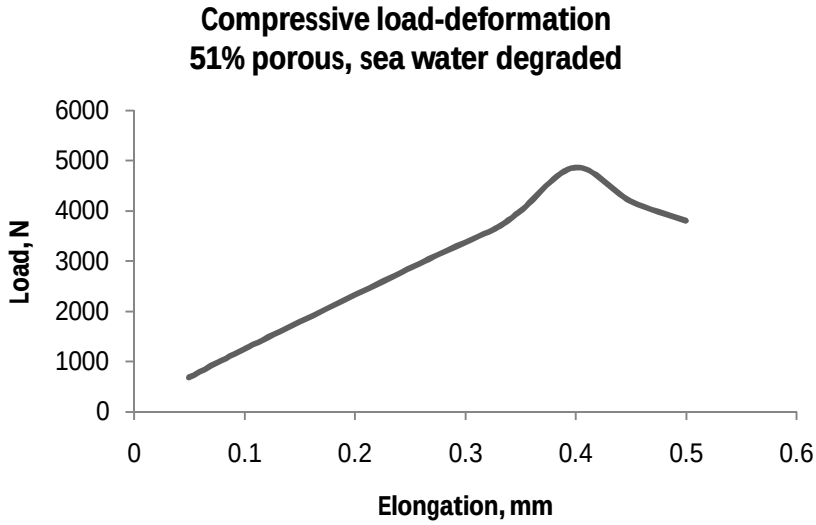


(c)

Fig. 5.27 Load – contraction behaviour of porous specimens in unconstrained compression a) 41% porous specimen, b) 45% porous specimen and c) 51% porous specimen

Table 5.10 Mechanical properties of PEEK/HA 70/30 porous specimens

S No	% porosity	Compressive strength MPa		Young's modulus MPa	
		As sintered	Sea water degraded	As sintered	Sea water degraded
1	41	11.2	10.2	682	621
2	45	8.7	7.8	529	474
3	51	4.9	3.7	412	301

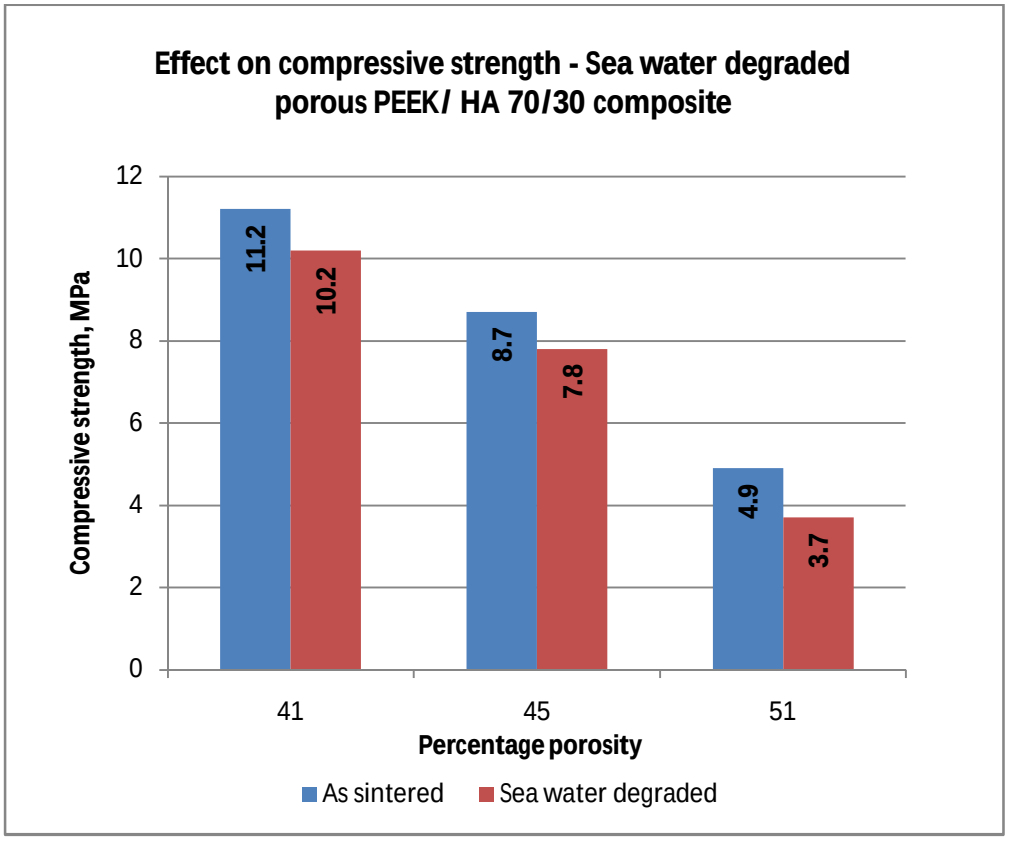


Fig. 5.28 Effect of porosity on compressive strength of as sintered and sea water exposed 70/30 PEEK/ HA composite

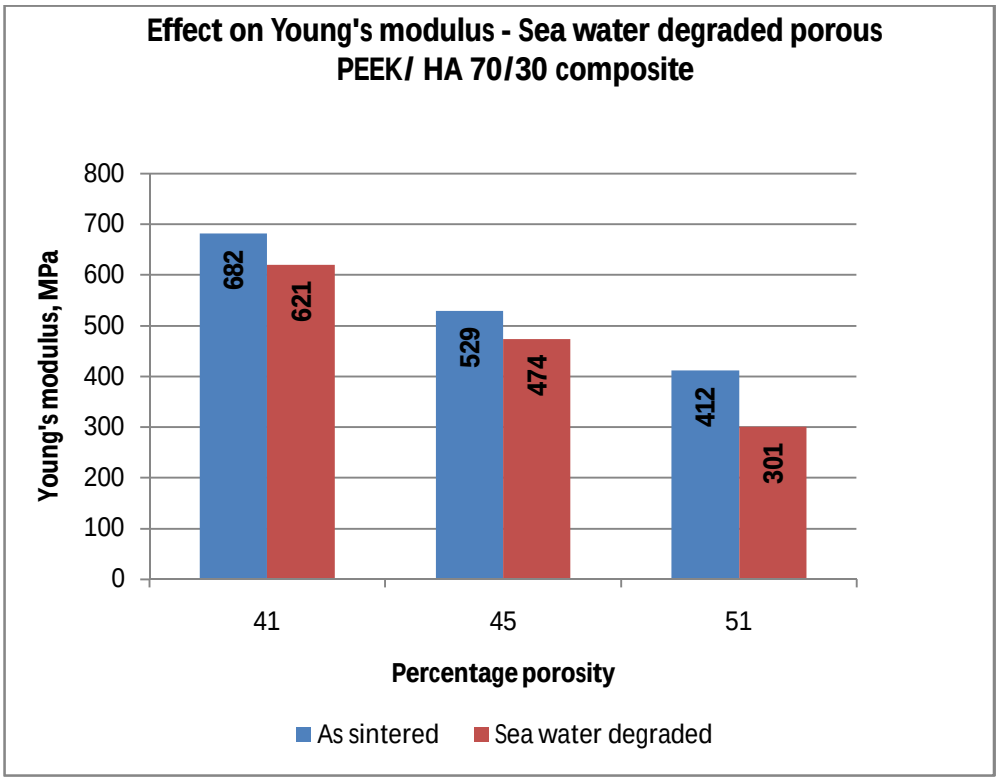


Fig 5.29 Effect of porosity on Young's modulus of as sintered and sea water exposed 70/30 PEEK/ HA composite

Referring to Fig 5.28, a huge drop in compressive strength of the specimens was observed in comparison to dense specimens. With a rise in porosity, the compressive strength was reduced both in as sintered and sea water degraded composite specimens. There was an insignificant fall observed in compressive strength due to sea water degradation compared to as sintered specimen as PEEK was a proven hydrophobic material. This effect was understood due to superior hydrophobic properties of PEEK in composite.

Similar were the results from Fig 5.29 with regard to Young's modulus. A significant fall in Young's modulus was seen in porous structure exposed to degradation media as compared to dense specimen. The Young's modulus was decreasing with an increase in porosity. Invitro tests were establishing a slight decrease in Young's modulus compared to as sintered specimens.

5.7 Load bearing predictions of porous scaffolds using DEFORM 3D software

Load- contraction behavior of porous specimens was assessed using DEFORM 3D (JNTU, Hyderabad) software. Results shown in Fig 5.29 thru Fig 5.33 are the conceptual values extracted from the deformation behavior of porous structure with attributed strength and Young's modulus values of dense specimen applied to strut elements. Average strength and Young's modulus were calculated from the nominal size of the scaffold. Elemental strength and Young's modulus were calculated using FEM at material nodes. Table 5.11 details the consolidated results of two optimum compositions of PEEK/ HA for three different porosities each. The average results presented in Table 5.11 would be higher than practical values, as strut mechanical properties were fed from dense specimen optimum results.

Table 5.11Predictive mechanical properties of porous scaffolds

S No	PEEK/ HA (% Porosity)	Fracture strength, MPa		Young's modulus, MPa	
		Average	Elemental	Average	Elemental
1	70/30 (75)	6.4	209.85	8.33	51
2	70/30 (83)	4.0	197.17	5.29	51
3	70/30 (89)	2.5	111.75	4.02	51
4	80/20 (75)	4.42	130.92	6.00	38.65
5	80/20 (83)	3.55	125.41	3.86	38.65
6	80/20 (89)	1.62	97.2	2.96	38.65

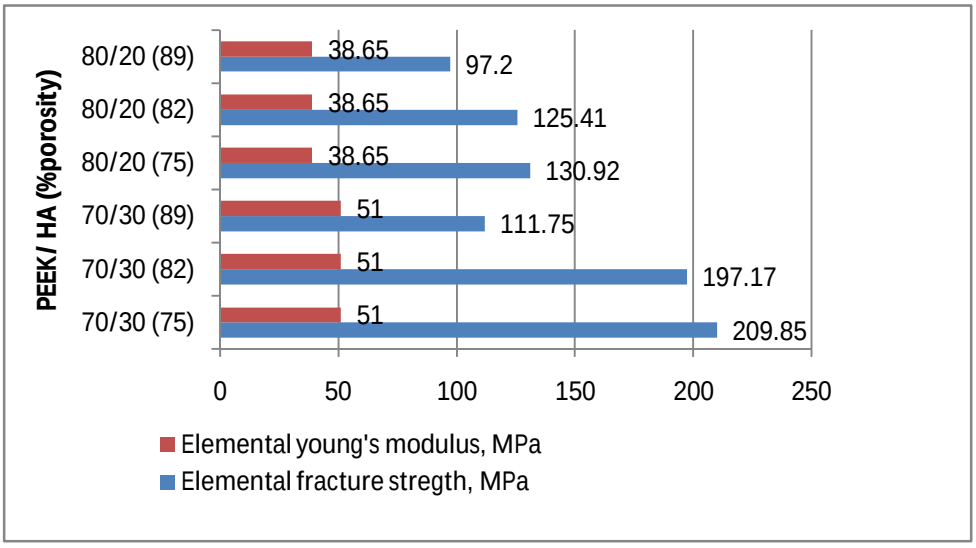


Fig. 5.30 Predictive elemental fracture strength and Young's modulus of porous scaffold

Referring to Fig. 5.30, elemental Young's modulus was found dependant on stress-strain behaviour of dense specimens, and remains same for a given component ratio of PEEK/ HA but varies with the porosity percentage even within the same composite. Elemental fracture strength was found varying with porosity and composition. Higher Young's modulus was found with higher percentage of HA in the composite. Flexural strength was found high at low porosity.

Referring to Fig. 5.31, the average fracture strength and Young's modulus were found decreasing with an increase in porosity for a given composition of PEEK/HA. The drop was sudden at higher porosities. Average fracture strength and Young's modulus were found better in PEEK/HA 70/30 for all the three porosities tested.

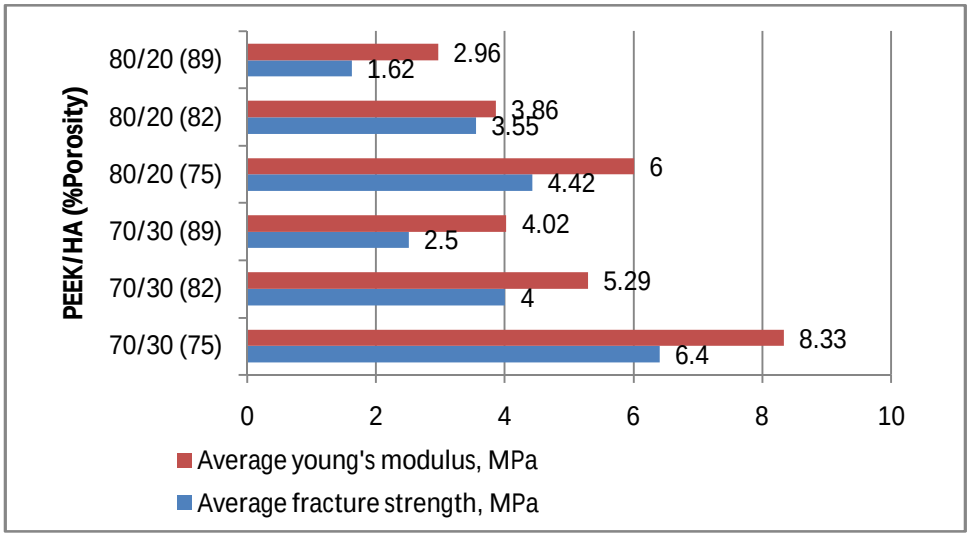


Fig 5.31 Predictive average fracture strength and Young's modulus of porous scaffold

The data comprehended in Table 5.11 was elaborated from the output of DEFORM 3D; the detailed graphical data is presented in the Figs 5.32 thru 5.36.

Figs. 5.32 is the output of DEFORM 3D finite element software, showing the bulging of the specimens in compression. Load deformation curves shown in the Fig 3.1 (a) are the response of porous specimens upon loading axially.

Fig. 5.33(a), 5.34(a), 5.35(a), 5.36(a), and 5.37(a) were drawn from the extracted load versus deformation data using nominal geometry of the specimen. Where, average stress is the ratio between instantaneous load and the nominal cross sectional area. And the average strain is the ratio between the net contractions over the nominal specimen height.

Fig 5.33 (b), 5.34 (b), 5.35 (b), 5.36 (b), and 5.37 (b) were the FEM data presentations of stresses and strains at element levels.

In all cases, Young's modulus was approximated from the linear portion of stress-strain using MS-excel built in regression. Non linear portion of the deformation curve was also treated for Young's modulus through regression. The results of Figs 5.33 thru 5.37 are presented in Table 5.11 and plotted in Fig 5.30 and Fig 5.31

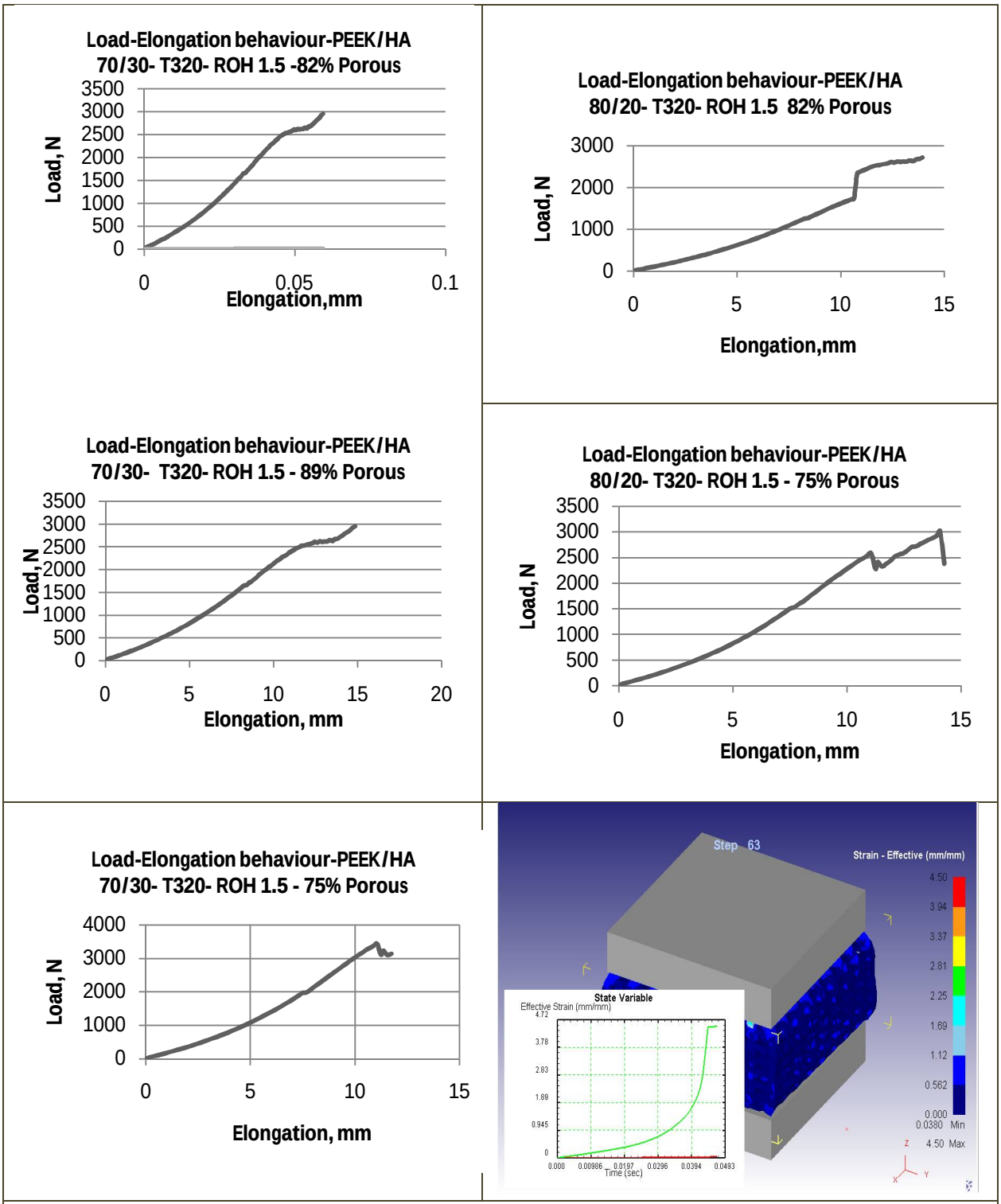


Fig. 5.32 Load- Elongation plots of PEEK/ HA 70/30 porous scaffoldsas predicted through DEFORM 3D

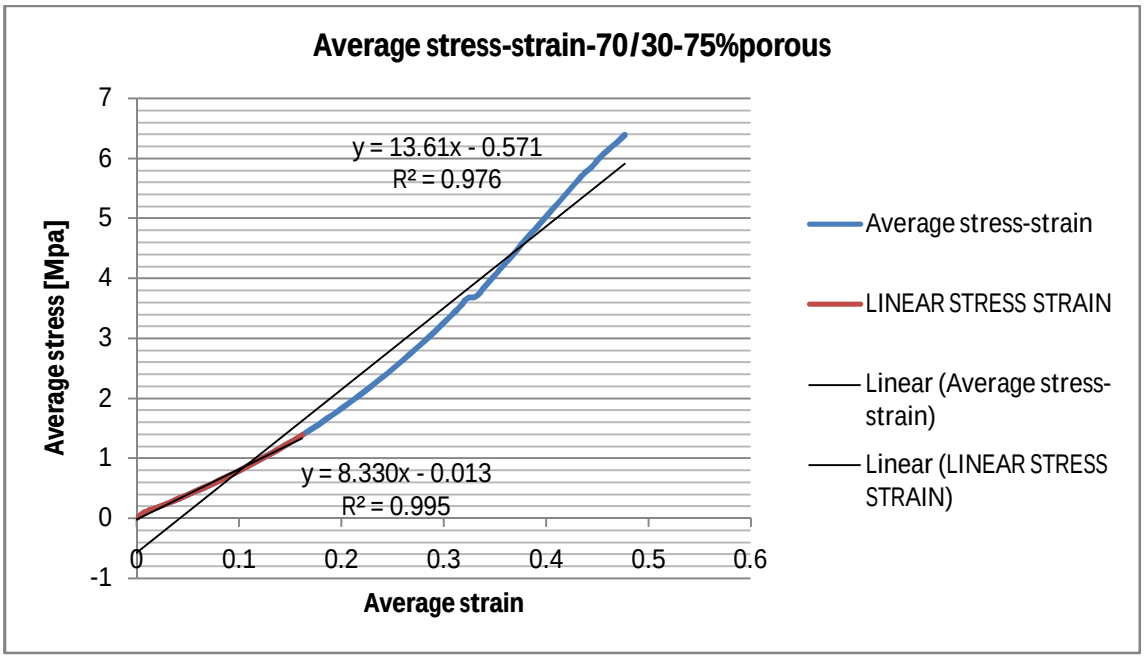


Fig.5.33 a) Average stress-strain behaviour of PEEK/ HA 70/30-75%porous specimen

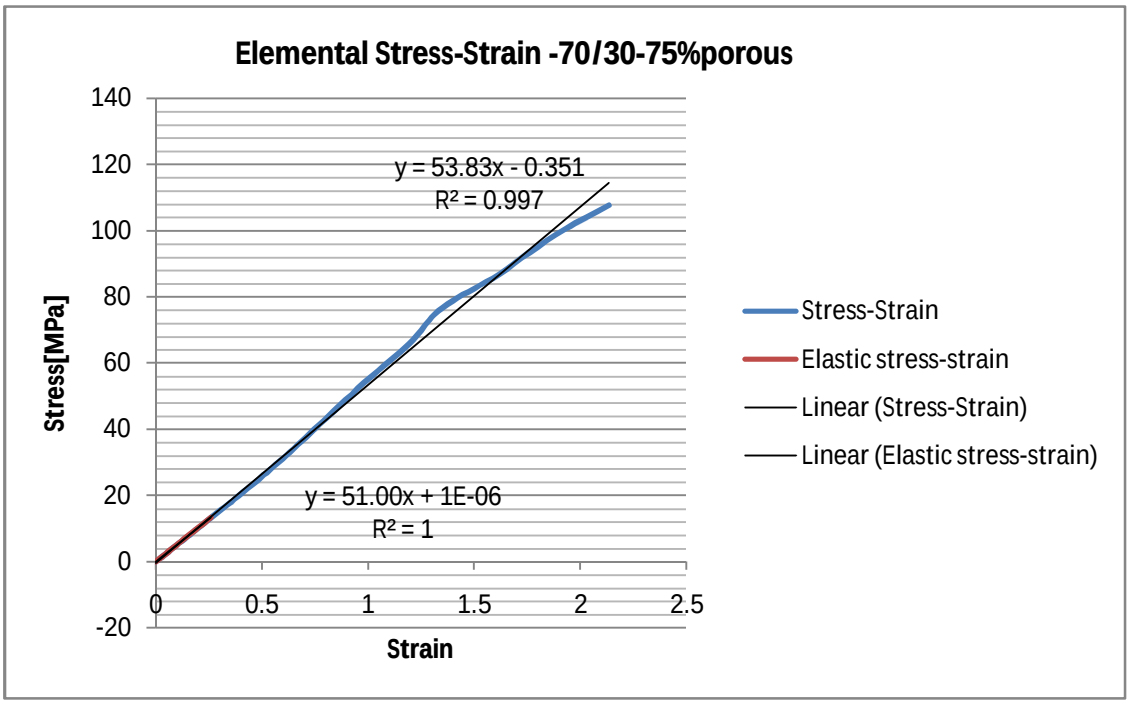


Fig.5.33 b) Elemental stress-strain behaviour of PEEK/HA 70/30-75%porous specimen

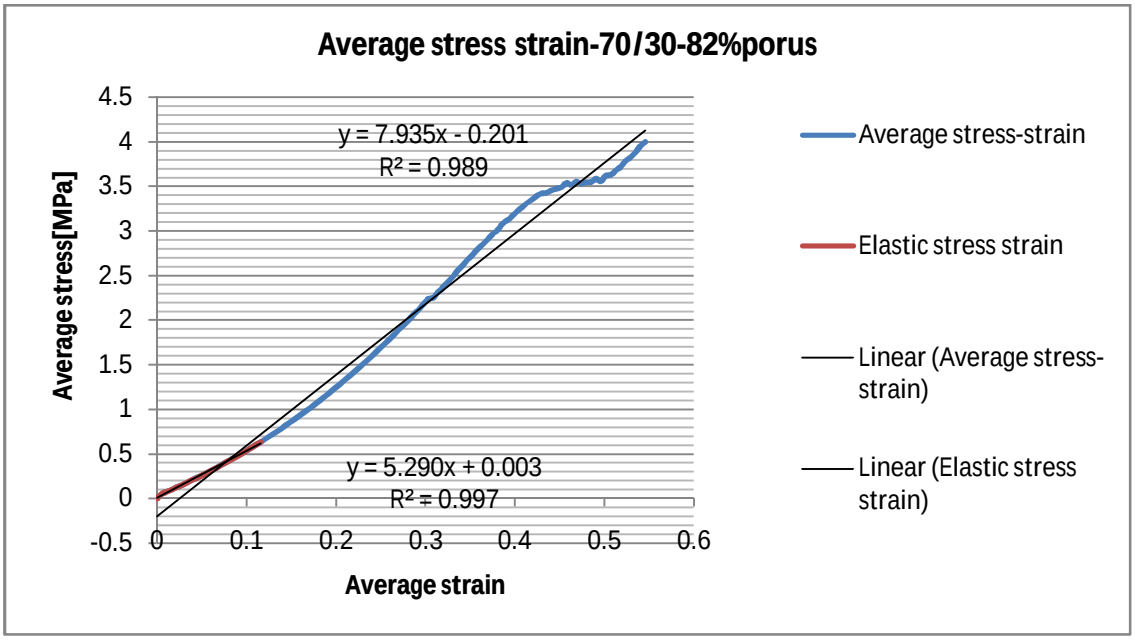


Fig.5.34 a) Average stress-strain behaviour of PEEK/HA 70/30-82%porous specimen

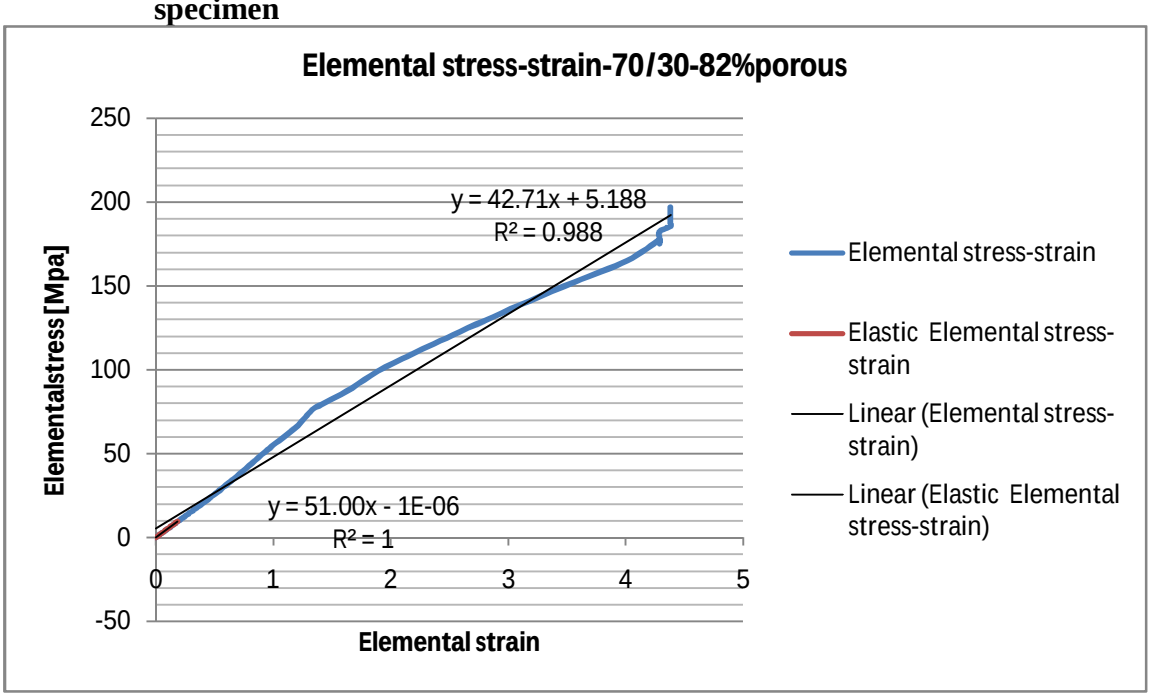


Fig.5.34 b) Elemental stress-strain behaviour of PEEK/HA 70/30-82%porous specimen

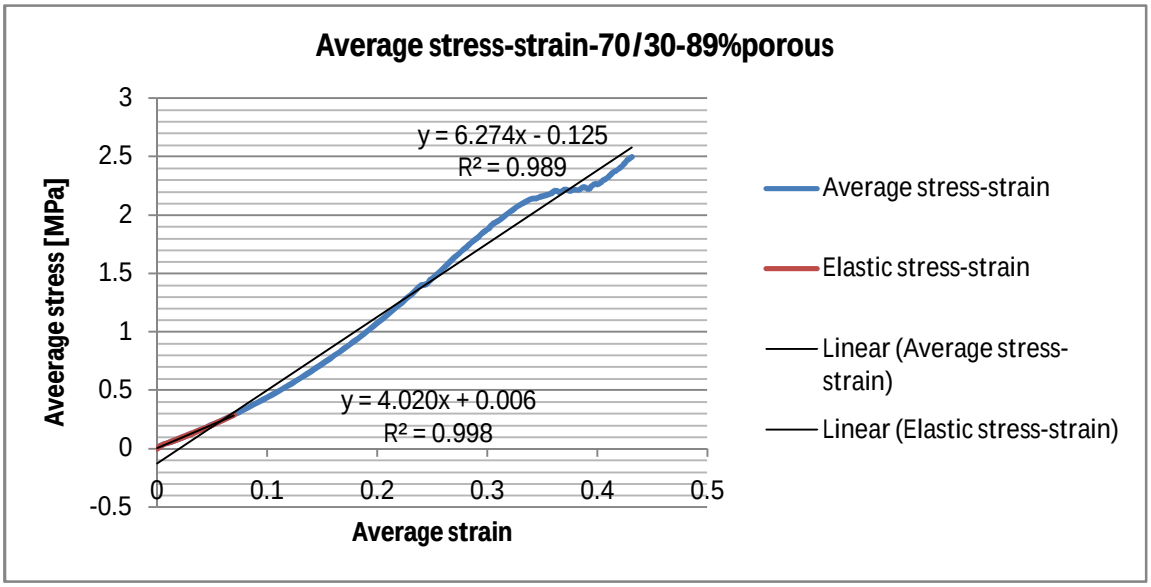


Fig.5.35 a) Average stress-strain behaviour of PEEK/HA 70/30-89%porous specimen

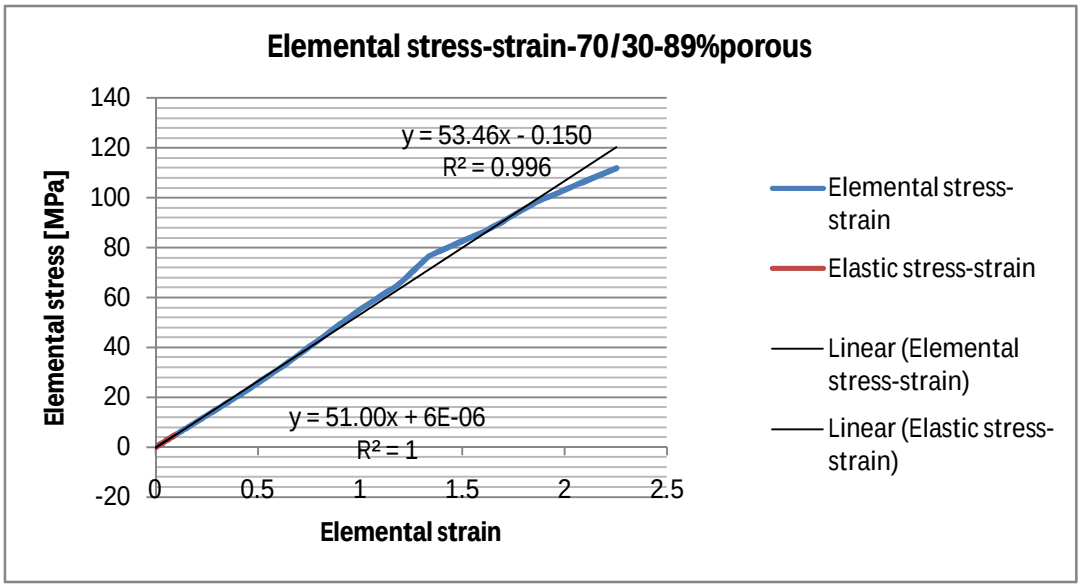


Fig.5.35 b) Elemental stress-strain behaviour of PEEK/HA 70/30-89%porous specimen

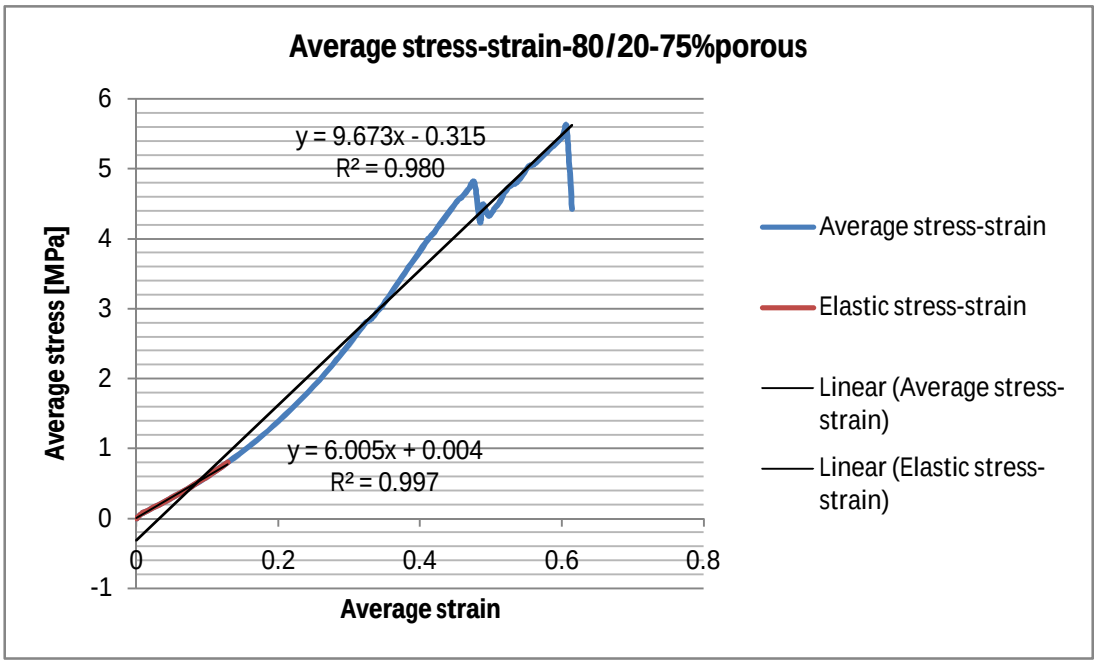


Fig. 5.36 a) Average stress-strain behaviour of PEEK/HA 80/20-75%porous specimen

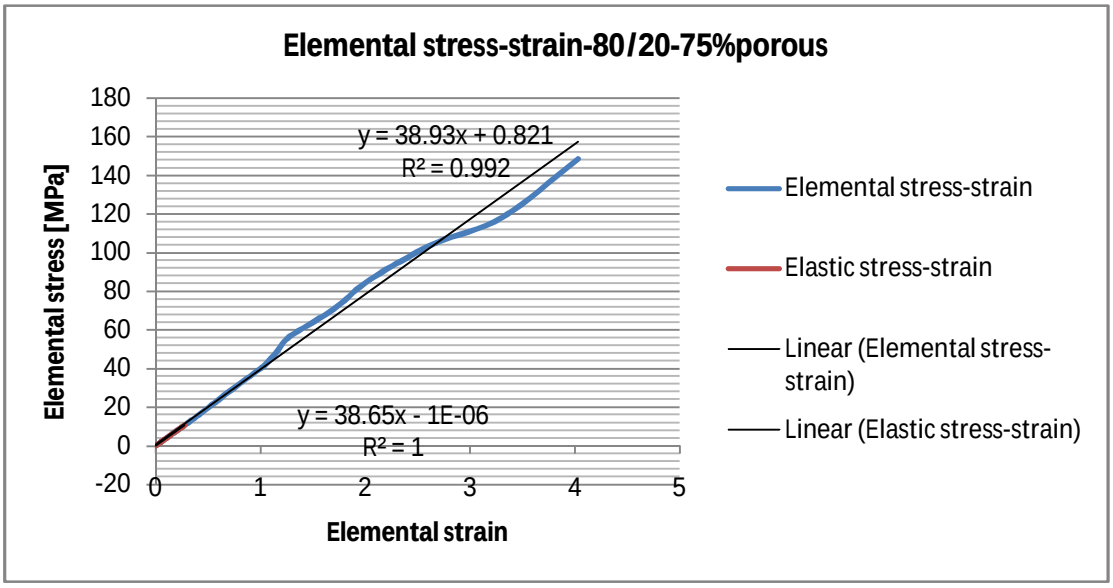


Fig.5.36b) Elemental stress-strain behaviour of PEEK/HA 80/20-75%porous specimen

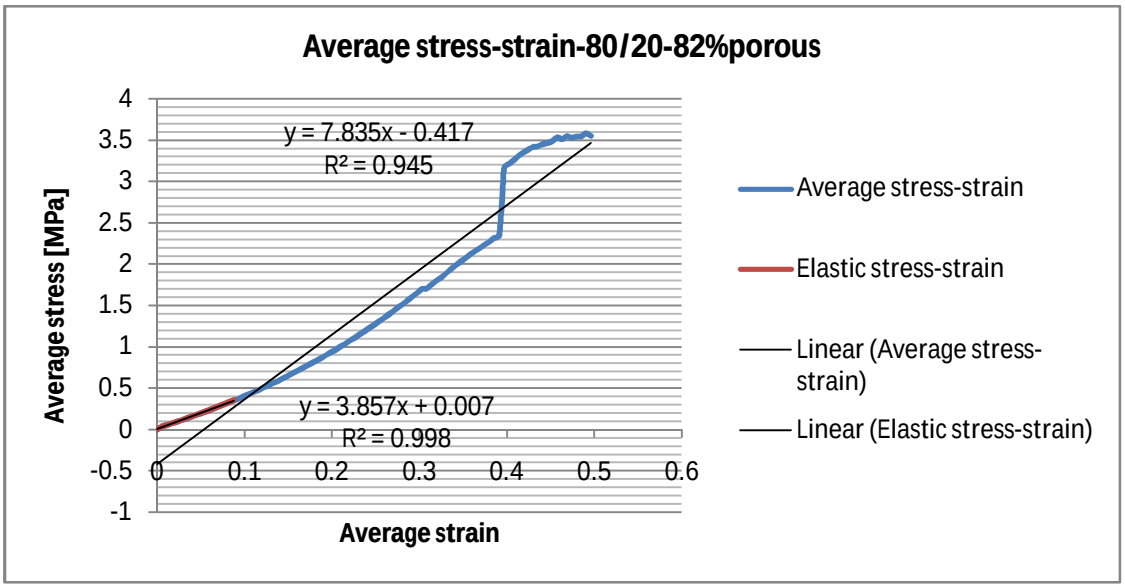


Fig.5.37 a) Average stress-strain behaviour of PEEK/HA 80/20-82%porous specimen

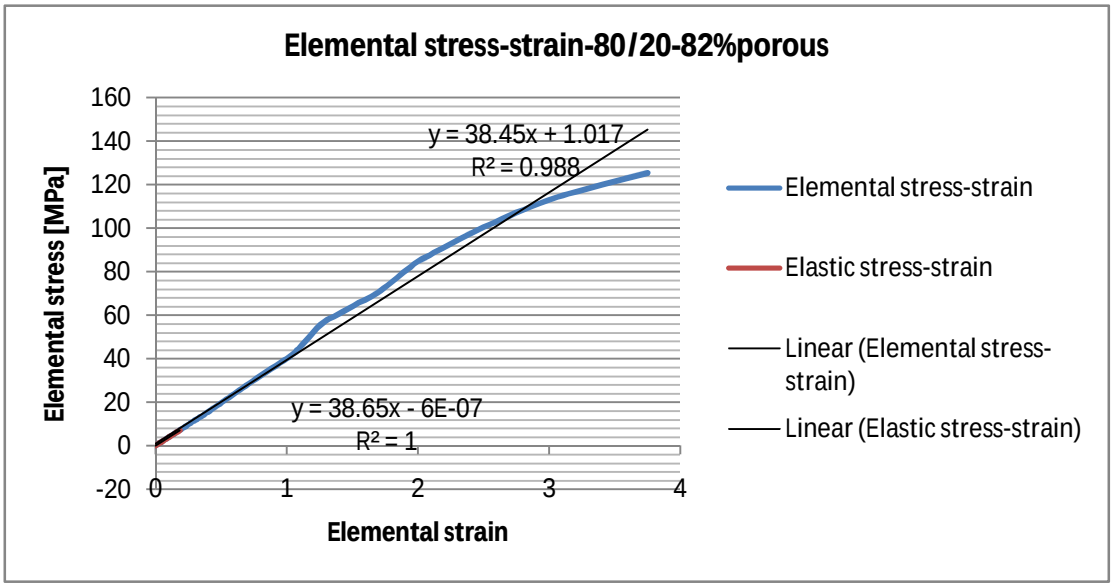
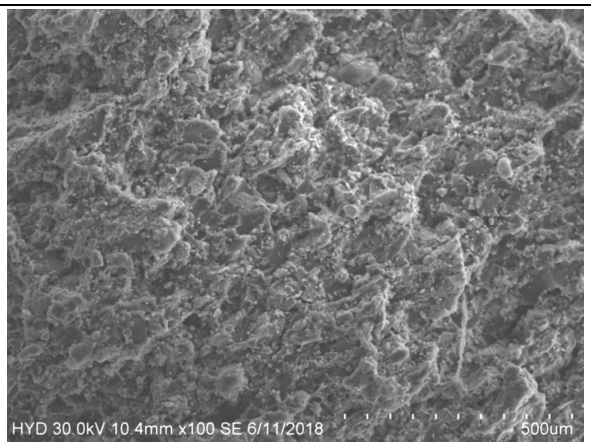


Fig.5.37 b) Elemental stress-strain behaviour of PEEK/HA 80/20-82%porous specimen

SEM of fractured dense specimens are presented in Fig. 5.38a. Specimen with 80/20 composition shows a delaminated fracture surface. Fig 5.38b shows SEM of fractured porous specimens, at sites beyond pores.



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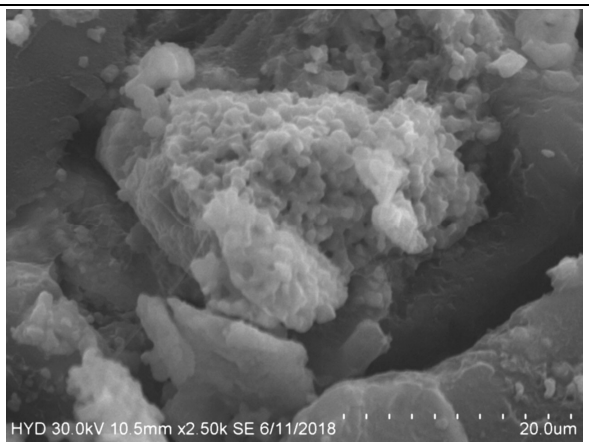

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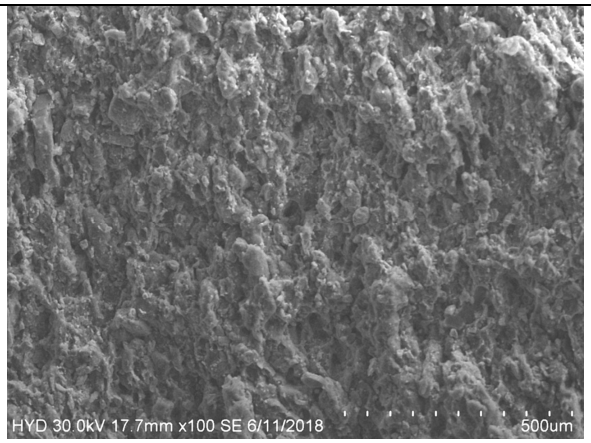

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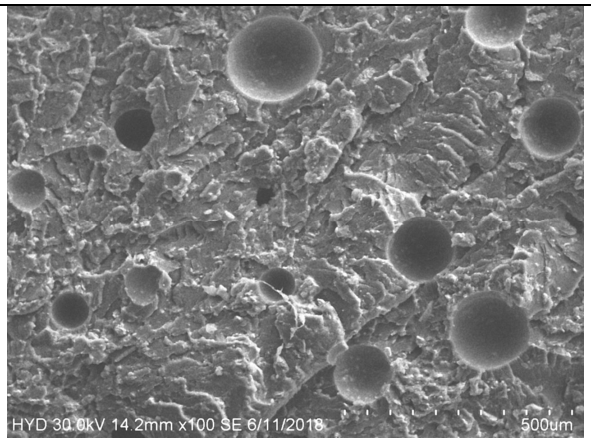

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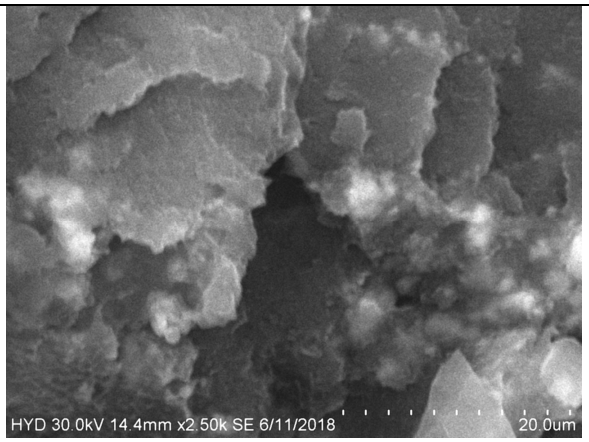
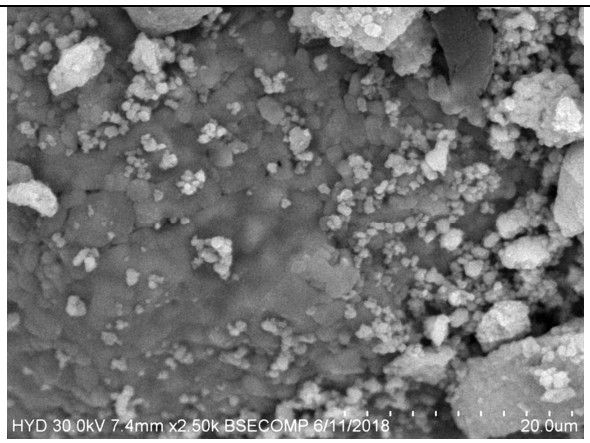


vi

Fig. 5.38a SEM images of fractured dense specimens i) PEEK/HA 60/40-100x ii) PEEK/HA 60/40-2500x iii) PEEK/HA 70/30-100x iv) PEEK/ HA 70/30-2500x v) PEEK/ HA 80/20-100x vi) PEEK/ HA 80/20-2500x



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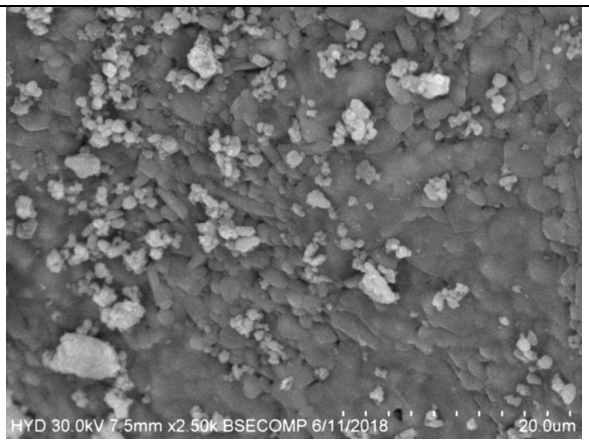

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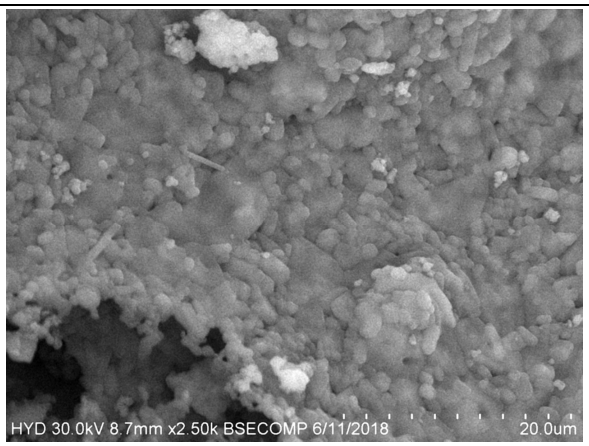

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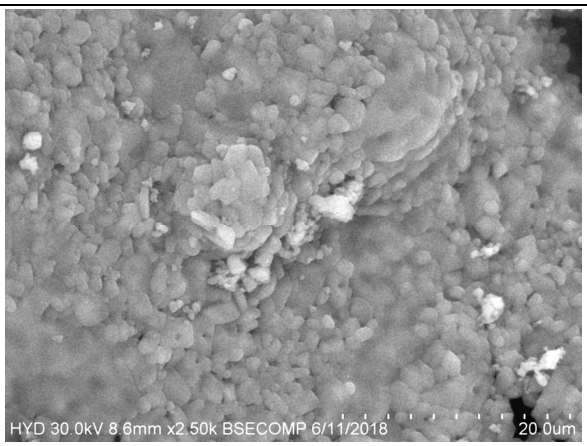

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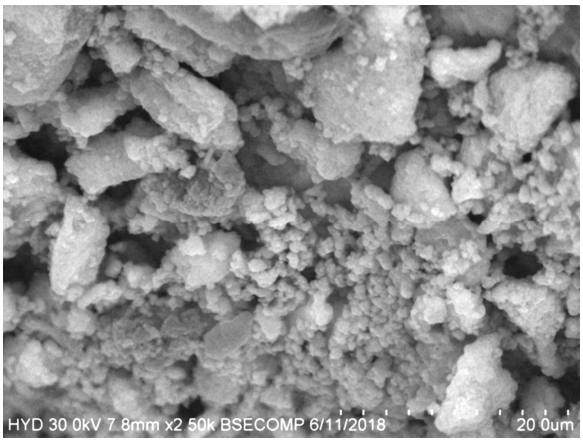
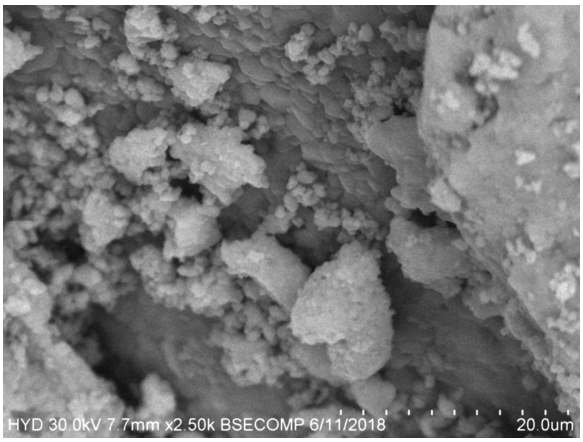


v



vi

Fig.5.38b SEM images of fractured PEEK/HA 70/30 porous specimens tested after degradation in artificial sea water: i &ii – 41% porous; iii & iv – 45% porous; v & vi – 51% porous (all images at 2500x)

Chapter 6 CONCLUSION AND FUTURE SCOPE OF WORK

6.1 Conclusion

PEEK/HA combination is found justified through thermal stability studies in processing perspective i.e. below 338^0C. Further, thermal degradation of the composite (560^0C +) was proven to be very high compared to human body in-situ application (37^0C)

Highest flexural strength exhibited by PEEK/HA 80/20 composite was 114 MPa, 14% more than PEEK's strength due to the presence of HA reinforcement phase. The Young's modulus reached to a highest value of 7238 MPa in PEEK/HA 70/30 composite. The maximum Young's modulus attained by present composite is well comparable with PEEK/synthetic nano HA composite in literature 7850 MPa [139].

Natural HA was found superior over synthetic HA as a reinforcement phase in PEEK/HA composite. Highest Young's modulus in natural HA reinforced composite was found to be 7.75% more than that of synthetic HA reinforced composite. Interestingly, the natural HA reinforcement exhibited 17.42% higher flexural strength than synthetic HA reinforcement. Natural HA could be concluded exhibiting superior coordination with its matrix phase. One of the possible reasons of better coordination of natural HA could be its smaller average particle diameter 4.5µ as against 45µ in synthetic HA.

Microwave sintering failed due to non responsiveness of PEEK to microwave heating and lower percentages of HA.

The highest Young's modulus and highest flexural strength in PEEK/HA 70/30 dense specimens respectively were 7238 MPa and 104 MPa. In contrast, the specimens of same composition but with 41% porosity were exhibiting only 9.4% of the Young's modulus of dense specimens. There was a substantial 43.4% drop in compressive strength in porous specimens with an increase in porosity from 41% to 51%. Also seen was 44.1% drop in Young's modulus due to increased porosity from 41% to 51%. Hence porosity was found seriously affecting the mechanical properties.

Upon exposure to artificial sea water (pH value 8.2+) for 25 days at 370^0 C, porous specimens could marginally loose compressive strength and Young's modulus as compared to unexposed specimens. The loss in Young's modulus recorded was ranging between 9-27% (for porosities 41%-51%) and the loss in compressive strength was ranging between 9-25%. Higher losses at 51% porosities were understood due to more pore space exposed to degradation media.

Deform 3D finite element models applied for load - deformation predictive studies reveal an increase in porosity from 75% to 89% in PEEK/ HA70/30 composite was resulting in a drop of compressive strength by 61% and a drop in Young's modulus of 52% .

Similar studies on PEEK/ HA 80/20 revealed a drop of 64% compressive strength and a 50% drop in Young's modulus with the porosity increased from 75% to 89%.

Finally, PEEK/HA could be concluded as prospective composite at load bearing sites with these observations:

i. PEEK/HA dense composite is found suitable to replace Cortical bone as the flexural strength 114 MPa is very close to the natural bone strength 130 MPa. But rigidity point of view, additional reinforcement (CF/GF) is required.
ii. The mechanical properties of Cancellous bone could be delivered by 70/30 PEEK/ natural HA with a porosity of 45% to replace the Cancellous bone sites with 75% and above porosities.

6.2 Scope for future work

i) It is suggested to carry out this work in future with medical grade polymers, nano sized HA extracted from egg shells, and appropriate biomedical acceptability tests on egg shell extractions. Direct printing of user specified materials should evolve to ease out the complications involved in indirect processing methods of composites. Control on reinforcement dispersion and fiber orientation in polymer matrix could be another area expected to come up.

ii) Another prominent area under explored is the synthesis of biodegradable composite materials with concurrent service and degradation at load bearing sites.

iii) Finally, it is wished to develop new materials, patient centric design approaches, precise and accurate processing methods and advanced clinical studies to avoid multiple replacement surgeries to raise human life expectancy.

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