AN INVESTIGATION ON CHARACTERIZATION OF BIO-COMPOSITES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF TECHNOLOGY
IN

MECHANICAL ENGINEERING

[Specialization: Production Engineering]

By

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Dedicated to my most loving family

National Institute Of Technology
Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"AN INVESTIGATION ON CHARACTERIZATION OF BIO-COMPOSITES"** *submitted by* **ARPAN KUMAR MONDAL** *in partial fulfilment of the requirements for the award of Master of Technology Degree in* **MECHANICAL ENGINEERING** *with specialization in* **"PRODUCTION ENGINEERING"** *at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.*

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date

PROF. S. S. MAHAPATRA

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Arpan Kumar Mondal

CONTENTS

Abstract

This research work describes the characterization and fabrication of bio-composites as artificial bone implant materials. The fractured bone can be repaired or replaced by artificial bone materials. Many implant materials has been made in the last three decades made of metals alloys ceramics polymers etc. The main problem with the metallic bone implants is the stress shielding and bone regeneration. Polymeric bone implants may overcome these difficulties. This article presents the processing techniques and experimental results of two different bio-composites viz. Hydroxyapatite (HAp)/High density polyethylene (HDPE) bio-composite by micro-injection molding and compression molding technology and Hydroxyapatite (HAp)/High molecular high density polyethylene (HMHDPE) bio-composite by compression molding technology. The initial materials HAp was synthesized by wet chemical precipitation technique, mixed with HDPE granules at 180 ^{0}C in a micro-compounder and also mixed with HMHDPE in a twin screw extruder at 220 ^{0}C, followed by micro-injection and compression molding and compression molding. Testing of different mechanical properties like tensile, compressive, flexural, impact and two body abrasion wear has been carried out. The experimental result provided shows a good mechanical behavior. An artificial neural network (ANN) model and a fuzzy logic (FL) model have been presented, for the prediction of abrasion wear amount of the fabricated bio-composites. Two body abrasive wear testing has done as per the full factorial design approach as well as it helps to construct the fuzzy prediction model based on Mamdani method. 75% of the response data used for training and 25% data used for testing of the artificial neural network (ANN) prediction methodology. The predicted results are in good (for testing) arrangement with the experimental data with an absolute average percentage error of 0.3470 and 1.8224 for ANN and 4.4542 and 2.7104 for fuzzy logic. It was found that both the fuzzy and ANN model are able to predict the abrasion wear rate in operating conditions with a very high degree of accuracy.

Keywords: Bio-composites, hydroxyapatite; abrasion wear; micro-compounder; twin screw extruder; micro-injection molding; compression molding; full factorial design; fuzzy logic; artificial neural network.

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Abbreviations

HA	Hydroxyapatite
HDPE	High density polyethylene
HMHDPE	High molecular high density polyethylene
PEEK	Poly-ether-ether-ketone
ANN	Artificial neural network
ANOVA	Analysis of variance
PMMA	Poly-methyl-methyl-acetate
PHB	Polyhydroxybutyrate
UHMWPE	Ultrahigh molecular weight polyethylene
PLLA	Poly l-lactide
PEMA	Polyethylmethacrylate

Chapter 1

INTRODUTION

1.1 Introduction

At the present time, the life expectancy is two times higher than in the past 100 years. (e.g. in 1900, the world life expectancy was approximately 30 years and in 1985 it was about 62 years, and nowadays is around 75-80 years [1,2]. Old is getting older, therefore, the human body is subjected to higher cumulative stress that results in degradation of the tissues and so new therapies are required to overcome these problems [3, 4]. Bone fractures among the aged mainly among women [5] is a common phenomenon in patients above 40 years. Low back pain and cervical pain is also a big problem in the society [6]. The bone grafts field has been developed to increase the quality of life of a patient who suffers from a bone disease, (e.g. osteoporosis, osteomalacia, osteogenesis, imperfect) or bone defect (e.g. bone fracture) [7]. Bone disease is a serious health condition that directly impacts on the quality of life of sufferers, particularly among the aged [8]. The following Table 1.1 investigated by Cranney et al. [5] showing the hip fractures happens in 1000 patient per year which really a matter of concern among the women.

Table 1.1 Hip Fractures per 1000 Patient per Year [5]

WHO CATEGORY	Age 50-60	Age > 64	Overall
Normal	5.3	9.4	6.6
Oesteopenia	11.4	19.6	15.7
Oesteoporosis	22.4	46.6	40.6

A bone graft should fulfill the required mechanical and biological functions. Bone grafts can be classified according to its origin, autografts if the tissue is obtained from the patient itself; allograft if the tissue is obtained from a different donor, but the same species, xenograft if the tissue is obtained from a different donor and different specie [10, 15] or synthetic bone grafts (alloplastic). The surgical procedures involving autografts require two surgeries, the first one to harvest the bone from one site within the patient and the second one to implant the tissue into the damage site. The problems associated with this type of bone grafts are mainly related with its limited supply and the need to subject the patient to a second surgery, which results in more pain and morbidity at the donor site. The main source for autografts is the iliac crest. It has been reported that harvesting bone tissue from the iliac crest can lead to several problems, namely arterial injury, hernia, chronic pain, and infection [15].

The use of allograft eliminates the need of a second surgery, because tissue from a human donor is harvested and implanted in a different patient. The main source of allografts is cadavers. Allografting procedures are less successful then autograft. The use of allografts eliminates the need of a second surgery, being this fact one of the great advantages of allografting. Although, the processing of allograft tissue does not eliminate the risk of transferring viral contaminants such as HIV, hepatitis B and hepatitis C or also the transmission of potential unknown diseases and the promotion of immunological reactions.

When bone from one species is implanted into a member of different species is designated by xenografts. Due to adverse antigenic responses, xenografts are not considered suitable for bone grafting [10].

The limitations of autografts, allografts and xenografts previously described led to a great advance in the development of synthetic alternatives. Till date a large variety of material has been investigated for the orthopedic applications. Over the last 30 years, ceramics, glasses and glass-ceramics for use in the medical field, which are grouped together and termed ‘‘bioceramics’’. The principal metallic materials used are titanium, aluminium, stainless steel, cobalt-chromium alloys and titanium alloys [9]. But there is big question with the bio-compatibility and bonding characteristics of the metallic materials [9, 46]. The worst problem with metallic implants is stress shielding [11]. Basically, it is a mechanism that protects the skeleton from the natural stresses that the everyday life puts on it. Total hip device and prosthesis exerts such stress shielding effect on the skeleton around it as a. result develops mechanically induced osteopenia. According to the Wolff’s law [12] if loading on a particular bone increases, the bone will remodel itself over time to become stronger to resist that sort of loading. The internal architecture of the trabeculae undergoes adaptive changes, followed by secondary changes to the external cortical portion of the bone, perhaps becoming thicker as a result. The opposite is also true as well. This will result pain in the transplanted region. So that mechanical fracture devices should design accordingly to prevent stress shielding.

Bio-ceramics have the advantage of being compatible with the human body environment. Synthetic hydroxyapatite (HA) is used as a bone graft substitute, due to its similarity in composition to the mineral phase of bone and to its bioactivity. Several reports showed that HA has the ability to form an interface with bone. The interfacial strength between bone and HA is significantly higher when compared to the “bond” between bio-inert surfaces and host tissue [10].

The ideal bone replacement material would have a modulus equal to that of bone. A simple mechanical rule says that in every composite system composed of two materials where one component is stiffer, the stiffer component will sustain the greater part of the load. Because metals are too stiff addition to their other biocompatibility problems, ceramics are too brittle. And polymers are too flexible and weak to meet the mechanical demands, composites of polymers and ceramic materials may offer the desired compromise.

A biomaterial can be defined as “a nonviable material used in a medical device, intended to interact with biological systems” [14]. Hench defined a bioactive material as “a non-toxic, biologically active and that forms an interfacial bond with the host” [3]. The most important characteristic of a biomaterial is its biocompatibility that can be defined as “the ability to perform with an appropriate host response in a specific application” [14]. The medical use of synthetic polymers also has a long history and the success of polymers in medicine. The concept of bioactive polymer matrix particulate reinforced composite as bone analogue was introduced in the early 1980s by Bonfield et al. [26]. Following the pioneering work of Bonfield et al., many other bioactive HA-polymer composites were developed using various polymer matrices. Viz. poly(methyl methacrylate) (PMMA) [20], Poly l-lactide (PLLA)[19], Polyhydroxybutyrate (PHB) [16], high density polyethylene (HDPE), and polypropylene (PP) [11], ultrahigh molecular weight polyethylene (UHMWPE) [21], polyethylmethacrylate (PEMA) [21], Polyetheretherketone (PEEK) [18, 25], Polysulfone [22].

The processing of thermoplastics polymer is quite easy following the conventional plastics processing route [13], which consists of the four steps of compounding, milling, drying and compression or injection molding. Many researchers have done work mainly to determine the mechanical properties and bioactivity of the bio-composites [11, 16-22, 26]. But a very little emphasis has drawn to determine the wear behavior of the bio-composites for bone replacements. Some work on sliding wear, fretting wear has done by Bodhak et al. [23] and Nath et al. [24], but till date none has given any interest on the study of two body abrasion wear properties of the polymer bio-composites. Neither the optimization of wear processes nor the influence of process parameters and also no statistical regression techniques have been constructed to select the proper testing conditions on wear rate of two body abrasive wear has adequately been studied yet. Selecting the optimum operating conditions is always a major concern. Past experience of the engineer or technician does not ensure the maximum quality and also does not confirm optimal performance a particular machine or environment. Therefore, in this situation, it is practical to select optimal input parameters for which we need some statistical techniques, mathematical modeling or design of experiments (DOE) [41] etc. can be applied to get the best optimal cutting parameters and performance. But these required a large number of cutting experiments and required huge amount of time to perform these operations and to build some mathematical model which becomes very much costly in terms of materials, time and labor. In order to optimize such an operation with such restrictions, a more efficient experimental model is required and here fuzzy logic and neural network based prediction technique plays the role. Design of experiment (DOE) and optimization of the processing variables of the bio-composite production and testing is a very important part as the bio-composite production is a very lengthy work to do any may affected by so many noises. Design of experiment is one of the statistical techniques widely used to determine the number experiment to be performed for any process. Optimization of process parameters is also important to improve quality of the product or process by achieving the best process parameters. In the present study the two body abrasion wear experiment has been performed using full factorial design approach and a statistical analysis of variance (ANOVA) has been used to indicate which process parameters are statistically significant. The optimal combination of the process parameters can then be predicted.

The total process consisting of the fabrication and testing of a single sample technique of the polymer matrix bio-composite through classical plastics processing takes approximately more than two weeks. As the bio-composite production and characterization process is a very long process, it can’t be possible to prepare composite by varying all the possible combinations of the matrix and the reinforcement. Design of experiment may take care of this up to a certain extent by organizing the number of experiments. But when we need to characterize all the possible combinations of the matrix and reinforcement, a prediction model based on Fuzzy Inference System (FIS), Artificial Neural Network (ANN) and Adaptive Neuro Fuzzy inference System (ANFIS) can be formed. A properly trained or designed prediction model can be used to predict the outputs for any combinations of the input variables.

1.2 Objective of the research work

The aim of this thesis is to contribute to the understanding of the mechanical as well as tribological properties like abrasion wear rate of the HAp reinforced polymer matrix bio-composites. Two prediction models based on Fuzzy Inference System (FIS) and Artificial Neural Network (ANN) has been designed to predict the three body abrasion wear of the fabricated composite. A brief summary of the objectives are given in the following.

- To prepare bio-ceramics at laboratory scale having bone-like properties through wet chemical precipitation route
- To prepare bio-composites for potential bone replacement
- To characterize mechanical and tribological behavior of bio-composites
- To predict wear characteristics of composites using artificial intelligence technique

Chapter 2

LITERATURE REVIEW

2.1 Literature Review

The purpose of literature review is to provide background information on the issues to be considered in this thesis and to emphasize the relevance of the present study. This treatise embraces various aspects of polymer matrix bio-composites with a special reference to abrasion wear characteristics. The concept of bioactive particulate reinforced polymer composite as bone analogue was introduced in the early 1980s by Bonfield et al. [26]. Hydroxyapatite (HA) reinforced polyethylene (PE) composites were the earliest bioactive particulate reinforced polymer composite developed. Currently, it is commercially known as HAPEX^{TM} and has been used successfully in clinical situation [27]. Following the pioneering work of Bonfield et al., many other bioactive HA-polymer composites were developed using various polymer matrices including among others poly(methyl methacrylate) (PMMA) [20], Poly l-lactide (PLLA)[19], Polyhydroxybutyrate (PHB) [16], high density polyethylene (HDPE), and polypropylene (PP) [11], ultrahigh molecular weight polyethylene (UHMWPE) [17, 21], polyethylmethacrylate (PEMA)[21], Polyetheretherketone (PEEK)[18], Polysulfone [22]. The composite materials were mainly manufactured by injection or compression molding. Mechanical and tribological properties like tensile strength [18], tensile modulus [18], impact strength [11], friction and sliding wear (6, 23, 24), fretting wear [23, 24] and fatigue [18] properties etc. were examined. Evaluation of the material's biological response and tissue in-growth at an early implantation period has investigated by Nath et al. [24] and Abu Bakar et al. [18]. The survivability half-life of prostheses made with current bio-inert materials is approximately 15 years, depending upon clinical applications. Bioactive materials improve device lifetime but have mechanical limitations. Hench et al. [4] proposes that biomaterials research needs to focus on regeneration of tissues instead of replacement. Gingu et al. [6] presents the experimental results concerning the processing of HAP/Ti bio-composites by powder metallurgy technology where the ball-on-disc dry wear tests. The tribological behaviour of the processed bio-composites was appreciated on the basis of the coefficient of friction and wear rate, corroborated with the wear track depth [6]. Kokubo et al. [8] investigated on some novel bioactive materials with different mechanical properties. Botelho et al. [10] has contributed to the understanding of the biological mechanism behind the enhanced bioactivity of silicon-substituted hydroxyapatite (Si-HA). LE THI BANG [9] has done work on synthesis and characterization of hydroxyapatite (HA) and silicon substituted hydroxyapatite (Si-HA) produced by a precipitation method. Robert B. Heimann [46] has reviewed some basic properties and applications of crystalline bioceramics. He has also lighted on the fact that to date, in the United States and in Europe, more than 800,000 hip and knee arthroplasties are being performed annually, with increasing tendency. According to Robert B. Heimann [46] the properties and function of biomaterials, in particular bioceramics are frequently being discussed in the context of hip endoprosthetic implants, hence his review deals with most commonly utilized bioceramic materials such as alumina, stabilized zirconia (Y-TZP, Y-stabilized Tetragonal Zirconia Polycrystal), and calcium phosphates, in particular hydroxyapatite. A. Sendemir and S. Altintag [11] fabricated hydroxyapatite (HA) reinforced polymer composites and evaluated to be used in bone implants. An attempt has done to produce a material that has similar modulus of elasticity (E) and other mechanical properties to those of bone in order to achieve mechanical compatibility in the body [11]. Min Wang [13] has developed bioactive composite materials for tissue replacement. The possible rationale and strategy of developing these composites were explained. Major factors influencing the production and performance of bioactive composites are discussed and some promising composites for tissue replacement and regeneration are reviewed [13]. Roeder et al. [16] has studied mechanical properties of hydroxyapatite whiskers reinforced polymer composites. Whereas Converse et al. [26] also done an investigation on processing and tensile properties of hydroxyapatite-whisker-reinforced Polyetheretherketone, elastic constants were measured using ultrasonic wave propagation and revealed an orthotropic anisotropy also similar to that measured in human cortical bone. Fang et al. [17] has fabricated HA/UHMWPE nanocomposites by compounding mixtures in paraffin oil using twin-screw extrusion and then compression molding and mechanical properties of HA/UHMWPE nanocomposite was also evaluated. Abu Bakar et al. [18] have investigated tensile properties, tension–tension fatigue and biological response of polyetheretherketone–hydroxyapatite composites for load-bearing orthopedic implants. This study presents the mechanical and biological behavior of the composite materials developed. Wang et al. [22] has produced and evaluated hydroxyapatite reinforced polysulfone for tissue replacement. Odhak et al [23] studied friction and wear properties of novel HDPE–HAp–Al_2O_3 bio-composites against alumina counterface. Same type of work is performed by Nath et al. [24] where processing and characterizations of HDPE-Al2O3-HAp composites has done for biomedical applications. Their work is also demonstrate how the stiffness, hardness as well as the biocompatibility property of bio-inert high-density polyethylene (HDPE) can be significantly improved by the combined addition of both bio-inert and bioactive ceramic fillers. A. Binnaz and Y Koca [28] synthesized Nano-sized hydroxyapatite powder by using double step stirring which is a novel method for precipitation of hydroxyapatite. Salma et al. [29] prepared calcium phosphate bio-ceramics from wet chemically precipitated powders. Naruporn MONMATURAPOJ [31] successfully synthesized nano-size hydroxyapatite powders n by wet-chemical precipitation route. There are some methods available to prepare HA chemically like Sol-gel method [47], Freeze-drying method [48], Emulsion method [48] and wet chemical precipitation route [28-31]. Among these methods wet chemical precipitation method is found to be easy and affordable in laboratory grade.

This research will focus on developing a bio-composite as an artificial bone material aiming to be used both in the hip implant and vertebra implant or repair as two body abrasion wear test has been given a major importance. Use of prediction methodologies by applying artificial intelligence is intended to reduce the large time of material fabrication and testing.

Chapter 3

MATERIALS SELECTION

3.1 Materials selection

This chapter describes the materials and methods used for the processing of all the composites under this investigation. It presents the details of the characterization and erosion tests which the composite samples are subjected to. The methodology is related to the design of experiment technique based on Taguchi method and the statistical analyses inspired by artificial neural networks are also presented in this part of the thesis.

3.2 Matrix Material

Selection of matrix materials has done considering the following criteria

- Processing of HDPE and HMHDPE is very easy through conventional plastics processing technique.
- HDPE and HMHDPE is very cheap and readily available in the market
- Low elastic modulus of HDPE and HMHDPE can avoid stress shielding

A commercial grade polymer granule has been supplied by Haldia Petrochemicals Ltd. Two types of polymer matrix are used viz. HDPE (Halen-H B6401) with a density of 0.90 gm/cm^3 and melt flow index 0.40 gm/10 min at 190° C. and HM-HDPE (Halen-H F5400) with a density of 0.954 gm/cm^3 melt flow index 0.09 gm/10 min at 190° C.

3.3 Reinforcement Materials

Bone is the primary mineralized tissue in mammalian bodies whose main function is "load-carrying" [11]. It can be thought of as a composite material, being made up of a collagen fiber matrix stiffened by hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$)crystals which account for 69% of the weight of the bone [11]. It is difficult to impart collagen from the natural bone. There are some methods available to prepare HA chemically. Among these methods wet chemical precipitation method is found to be easy and affordable in laboratory grade.

- Sol-gel method[47]
- Freeze-drying method [48]
- Double step stirring [28]
- Emulsion method [48]
- Wet chemical precipitation route [28-31]

3.3.1 Wet chemical precipitation route for Hydroxyapatite (HAp) preparation

Hydroxyapatite (HAp) is prepared by taking Calcium Hydroxide $Ca(OH)_2$, Ortho Phosphoric acid (H3PO4) as the starting materials through wet chemical precipitation route as shown in

Figure 3.1 [28-31] .Initially, ten grams of Calcium Hydroxide is weighted in a weighing machine (Mettler Toledo, 0.01 g accuracy). It is mixed with water about 40 times. The solution is stirred by a magnetic stirrer (Remi Equipments Pvt. Ltd.) at 50^0C to 60^0C for 3 to 4 hours. Then after, ortho-phosphoric acid is mixed with the solution at the rate of 30 drops/minute through a burette and continuously stirred but heat input to the solution is stopped. Care is taken to reach at pH value of the solution at 8 to 10[28-31]. The synthesis process is prepared by a wet chemical precipitation reaction following the reaction proposed by FERRAZ et al. [30]

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

If pH value of the solution drops below the threshold values, ammonia solution (NH4OH) may be added to increase the pH value. After 5 to 6 hours, magnetic stirrer is stopped and the mixer is keep for 12 hours at room temperature. Then, precipitations are collected using a filter paper. The HAp precipitations are dried at 80ºC in an oven and calcinated at 850^0Cfar below the decomposition temperature of HAP (~1100^0C) for eight hours to get rid of any organic material that might be left and to allow the transformation of amorphous phases to the crystalline structure. After calcination, the material was ground in a ceramic hand grinder to avoid any agglomeration.

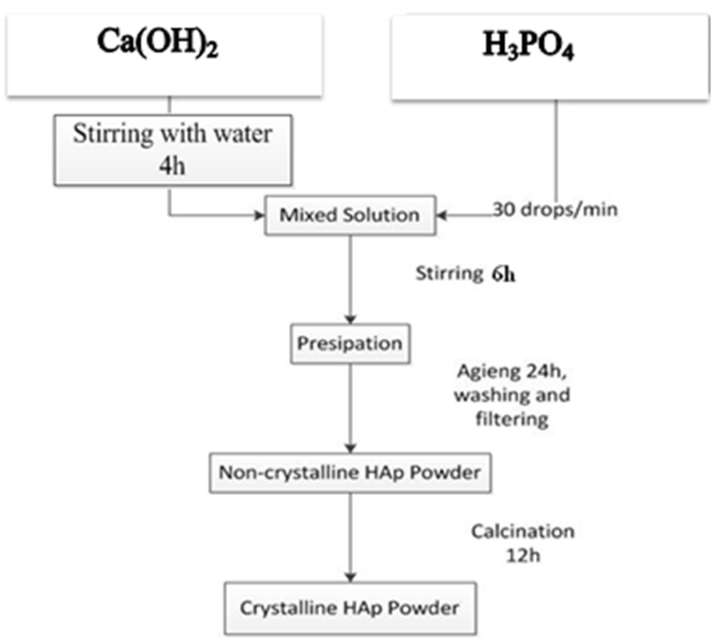


Figure 3.1 Wet chemical precipitation method [31]


a
b
c
d
e
f

Figure 3.2 HAp preparation through wet chemical precipitation route: (a-c) stirring, (d-f) precipitation, (g-j) drying and sintering

All the steps viz. preparation of mixed solution of $Ca(OH)_2$ and H_3PO_4, drying and sintering, for HAp preparation through wet chemical precipitation route is shown in the Figure 3.2 (a-j).

Chapter 4

COMPOSITE FABRICATION

4.1 Composite fabrication

4.1.1 Methods of producing bioactive composites

There are a number of production techniques for making non-porous, bioactive ceramic–polymer composites for tissue replacement, which are summarized below:

Route I: Physico-chemical methods

Method 1: Precipitating mineral crystals in situ in the polymer matrix

Method 2: Dispersing bioceramic particles in the polymer solution with subsequent consolidation

Route II: Thermo-mechanical methods

Method 1: Impregnating a porous bioceramic matrix with a polymer

Method 2: Incorporating bioceramic particles into the polymer matrix using conventional plastics processing technologies (Figure 4.1)

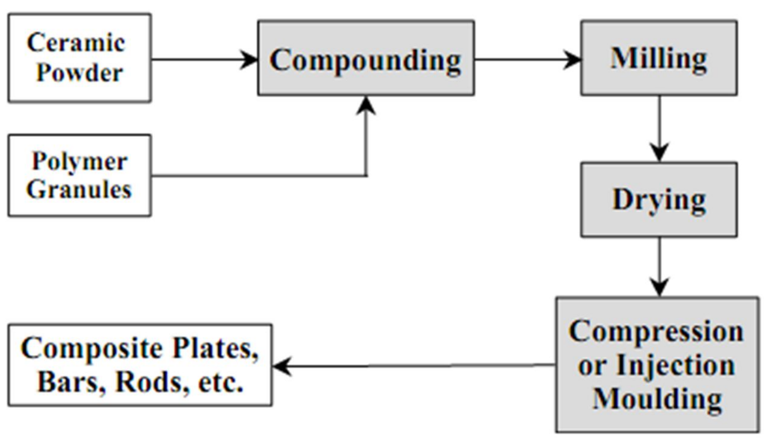
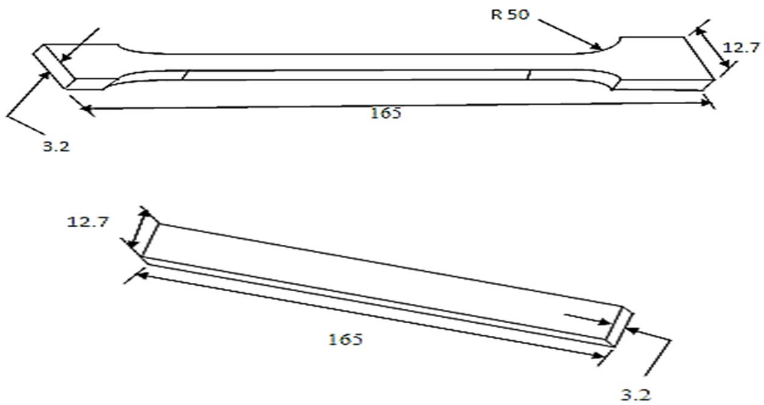


Figure 4.1 Manufacturing of bioactive composites using plastics processing technologies [13]

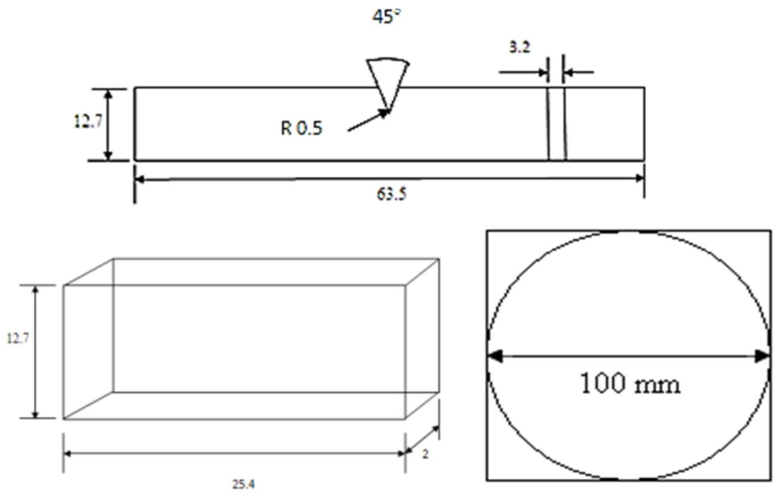
In the thermo-mechanical route for producing bioactive composites, the manufacturing process normally consists of compounding, milling and compression or injection molding. Composites of various geometries can be made. The compounding process is crucial in composite production for achieving a homogenous distribution of bio-ceramic particles in the composite. Compounding particulate bio-ceramics with polymers can be conducted using a compounding extruder, an internal mixer. The specific heat values of ceramics are much lower than those of polymers, which can cause severe oxidation of polymers such as polyethylene during the compounding process if cooling of the compounded material is not rapid and adequate. In the compounding process, processing parameters such as temperature, screw/rotor speed and dwell/processing time should be strictly controlled. The milling process is to palletize strands of the extruded material or to break down large chunks of compounded material into small pieces so that they can be used for compression or injection molding. Prior to compression or injection molding, the milled, compounded materials must be dried, which drives off moisture in the materials. (If drying is not properly done, it is very likely that the molded products will contain micro-voids which have resulted from air bubbles formed at the processing temperature.) With regard to compression or injection molding of bioactive composites, the molding temperature and pressure are two key parameters, which depend on the melting behavior and viscosity of the composite. The molding time, i.e., the dwell time at the molding temperature, should also be kept short.

4.2 Preparation of HA/HDPE bio-composites

Sintered HAp powder and commercial grade HDPE has been used to fabricate HAp-HDPE composite through micro-injection molding. Dog bone shaped tensile specimens with geometric dimension shown in Figure 4.2 (a) were produced for Hap/HDPE bio-composites. Dimensions for impact, compressive and flexural and wear testing are shown in the Figure 4.2 (b), 1(c), 1(d), & 1(e) accordingly. Compounding of HAp/HDPE composites were carried out in a DSM Xplore micro compounder (Figure 4.3 (a)) at a temperature of 180^0C-220^0C and rotor-speed of 40 rpm. Composites with various amounts of HAp (10, 20, 30 and 40 vol. %) were prepared.



(a) (b)



(c) (d) (e)

Figure 4.2 Test specimen, All dimensions are in mm (a) Tensile test specimen; (b) Flexural test specimen; (c) Impact test specimen; (d) Compressive specimen; (f) Abrasion wear specimen

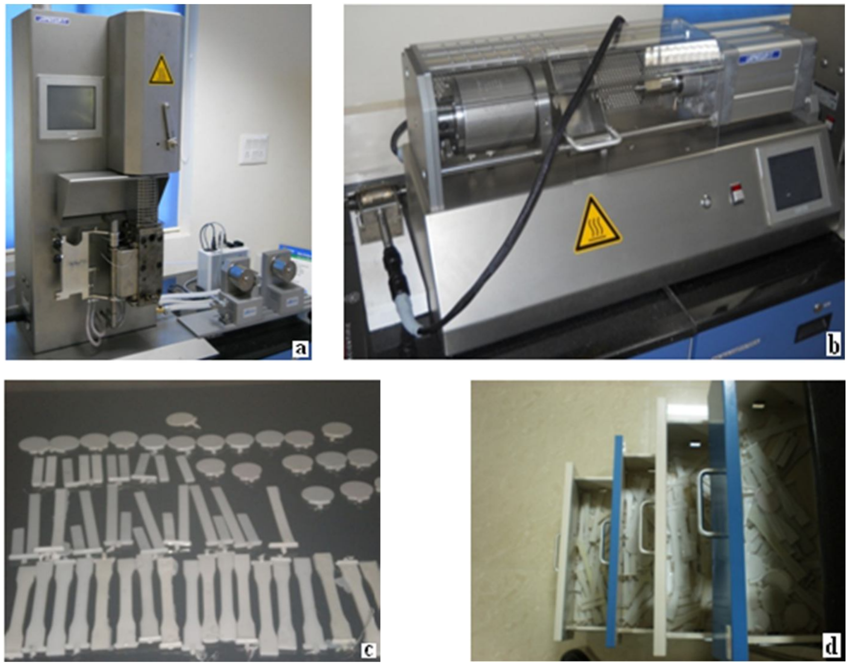


Figure 4.3 (a) DSM Xplore micro compounder (b) and DSM Xplore micro injection molding machine (c-d) Samples for different test of different vol. %

The mixtures were directly sent to micro-injection molding machine. The major micro-injection molding machine (Figure 4.3 (b)) parameters were; barrel temperature at different zones i.e zone 1, zone 2, zone 3, zone 4 were170^{0,} 180^{0}C, 190^{0}C, 200^{0}C subsequently, mold temperature 60^{0}C and injection pressure of 14 MPa. Samples of different dimensions has been prepared as shown in the Figure 5 (c,d). In case of wear testing specimens compression molding techniques were used with mold temperature of 200^{0}C and a compression pressure of 308 MPa was applied using a NEOPLAST hydraulic press (Model no-HP 80T) as shown in Figure 4.4.

Figure 4.4 NEOPLAST hydraulic press (Compression molding machine)

4.3 Preparation of HA/HMHDPE bio-composites

As the melt flow index of HMHDPE is very low (0.09 gm/10 min at 190^0C), so that micro-injection molding is difficult as the screw may fail due to very high load, hence compression molding route has been followed. Sintered HAp powder and commercial grade HM-HDPE are mixed by a Thermo Scientific (TSE 24 MC) twin screw extruder (Figure 4.5 (b-d)) at a temperature of 180^0C-220^0C. After mixing the mixed material has send to grinding machine (Figure 4.5 (f)) for crushing into small granules. After granulation compression molding technique has been applied to get the composite sheets. A NEOPLAST hydraulic press (Model no-HP 80T) as shown in Figure 4.4 has been used at operating temperature of 220 ^{0}C in both the top and the bottom plates and applying a pressure of 308 MPa. A contour cutter (Figure 4.5 (g)) is used to cut the samples into shape according to the ASTM standards for different mechanical tests. Composites with various amounts of HAp (10, 20, 30 and 40 vol. %) were prepared.

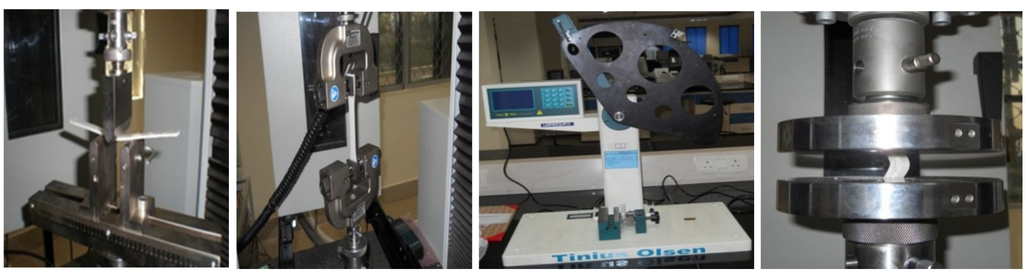
Figure 4.5 Composite preparation through compression molding route: (a) hand mixed HAp and polymer granules, (b-d) mixing in twin screw extruder, (e) mixed composite after mixing in the extruder (f) Grinding Machine (g) contour cutter (h) final shapes of the samples

Chapter 5

CHARACTERIZATION OF MECHANICAL PROPERTIES

5.1 Characterization of Mechanical Properties

Tensile, compressive and flexural testing is carried out in Instron 3382 Universal Testing Machine at a temperature of 23±2˚C, and with relative humidity of 50±5RH. Testing procedures were carried out in ASTM D638 for tensile testing, ASTM D695 for compressive, ASTM D790 for flexural test. Loading arrangement for the entirely performed mechanical testing performed is shown in the Figure 5.1 (a-d). Tinius Olsen high energy pendulum impact tester (Model IT406) for plastics has been used for izod impact testing considering the ASTM D256 standard. For each composition tested, the average of four readings was presented for all type of the testing. Two body abrasion wear test has done in the TABER industries abrasion resistance tester (Figure 5.2 (a)). The difference between the weights before and after testing has been measured in METTER TOLEDO XS204 digital weight balance (Figure 5.2 (b)) with an accuracy of 10^{-4}. Summary of the entire test performed are shown in the Table 5.1.



(a) (b) (c) (d)

Figure 5.1 Loading arrangement of the (a) flexural, (b) tensile, (c) impact, (d) compressive specimens

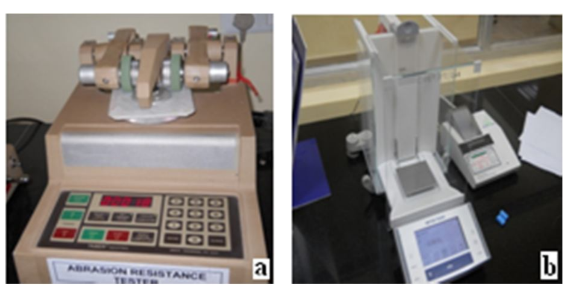


Figure 5.2 (a) Picture of the two body abrasion wear test rig, (b) Digital weight balance

Table 5.1 Summary of all the testing

Testing	Type of Machine Used	Working Variables	No of Specimen Tested	Standard Used
Tensile	Instron 3382 UTM	Load cell : 100 KN Rate : 10 mm/min	12×2	ASTM D638
Compressive	Instron 3382 UTM	Rate: 1.3 mm/min	12×2	ASTM D695
Flexural	Instron 3382 UTM	Rate : 0.77 mm/min	12×2	ASTM D790
Impact	Tinius Olsen Impact Systems IT406	-	12×2	ASTM D256
Two Body Abrasion Wear	Taber Abrasion Resistance Tester	Sliding Distance : 100-300 cycle Load : 500-1500 gm.	4×2	ASTM D4060

Chapter 6

EXPERIMENTAL DESIGN

6.1 Experimental Design

6.2 Full Factorial Design of wear testing

Two body abrasion wear test of the fabricated parts consists of several input control variables. The possible variable parameters of two body abrasion wear are viz. HAp vol%, applied load and sliding distance with having different levels that may influence the wear rate of polymer matrix bio-composites largely. Proper selection and control of the input variables may be done through design of experiment technique. Design of experiments is a powerful tool for modeling and analyzing the influence of control parameters on the performance output. The vital phase in the design of experiment lies in the selection of the control parameters. Hence, a large number of factors are initially involved so that non-significant variables can be recognized and may reject. Full factorial design of experiment has been considered as in a full factorial experiment, responses are measured at all combinations of the experimental factor levels, Each combination of factor levels represents the conditions at which a response measure will be taken. Each experimental condition is a called a "run" and each measure an observation. It gives the lowest error but number of runs may be more, but here the input parameters are only three, so that the number of experimental runs will be only 27. The selected control parameters and their values at different levels are listed in Table 6.1 and other parameters (Table 6.2) are kept at their fixed level.

Table 6.1 Control Parameters and their levels

Control Parameters	Symbol	Level			Unit
		1	2	3	
HAp vol%	A	20	30	40	%
Load	B	500	1000	1500	MPa
Slidig Distance	C	100	200	300	Cycle

Table 6.2 Fixed parameters

Fixed Parameters	Value	Unit
Molding technique used	Compression molding	-
Mixing technique Used	Micro-compounder	-
Compression molding pressure	308	MPa
Batch timer for compression molding	700	sec
HAp calcination temperature	850	^{0}C

All the experiments are conducted as per factor combination shown in Table 6.3. The plan of the experiments based on the classical full factorial design of experiment taking all the factor and level combinations. The experimental observations wear rates (W) are transformed into signal-to-noise (S/N) ratio. The signal to noise ratio (S/N) ratio is used to determine the performance characteristics deviating from the desired values. Generally, there are three categories of performance characteristic in the analysis of the S/N ratio, that is, the lower-the-better, the higher-the-better, and the nominal-the-best. Irrespective of the type of the performance characteristics, the larger signal to noise ratio corresponds to the better performance characteristic. The objective of experimental layout is to minimize the wear rate. Hence, lower-the-better quality characteristic is considered. The signal-to-noise ratio (η_{ij}) of lower-the-better performance characteristic can be expressed as:

$$\eta_{ij} = -10 \log \frac{1}{n} \sum_{k=1}^{n} y_{ijk}^2 \quad (6.1)$$

Where, y_{ijk} is the experimental value of the ith performance characteristic in the jth experiment at the kth observation.

Table 6.3 Experimental layout using full factorial design of experiment along with S/N ratio data of the responses

Exp. No.	A	B	C	HAp-HDPE		HAp-HMHDPE	
				Wear(gm)	Wear (SN ratio)	Wear(gm)	Wear (SN ratio)
1	1	1	1	0.0043	47.33	0.0006	64.43
2	1	1	2	0.0049	46.19	0.0011	59.17
3	1	1	3	0.0092	40.72	0.0011	59.17
4	1	2	1	0.0088	41.11	0.0005	66.02
5	1	2	2	0.0092	40.72	0.0009	60.91
6	1	2	3	0.0099	40.08	0.0007	63.09
7	1	3	1	0.0119	38.48	0.0012	58.41
8	1	3	2	0.015	36.47	0.0013	57.72
9	1	3	3	0.0097	40.26	0.0009	60.91
10	2	1	1	0.0059	44.58	0.064	23.87
11	2	1	2	0.0052	45.67	0.0041	47.74
12	2	1	3	0.0106	39.49	0.0132	37.58
13	2	2	1	0.0078	42.15	0.0059	44.58
14	2	2	2	0.0133	37.52	0.0011	59.17
15	2	2	3	0.0134	37.45	0.0015	56.47
16	2	3	1	0.0095	40.44	0.0084	41.51
17	2	3	2	0.0129	37.78	0.0014	57.07
18	2	3	3	0.0131	37.65	0.0056	45.03
19	3	1	1	0.0075	42.49	0.0249	32.07
20	3	1	2	0.0092	40.72	0.0209	33.59
21	3	1	3	0.013	37.72	0.0093	40.63
22	3	2	1	0.0097	40.26	0.0055	45.19
23	3	2	2	0.0181	34.84	0.0125	38.06
24	3	2	3	0.019	34.48	0.0043	47.33
25	3	3	1	0.0117	38.63	0.0133	37.52
26	3	3	2	0.0160	35.91	0.0109	39.25
27	3	3	3	0.0195	34.19	0.0035	49.11

6.3 Construction of Fuzzy Inference System

6.3.1 Fuzzy logic system

Fuzzy logic system (in this study, Mamdani system considered) **as shown in Figure 6.1** comprises a fuzzifier, membership functions, a fuzzy rule base, an inference engine, and a defuzzifier.

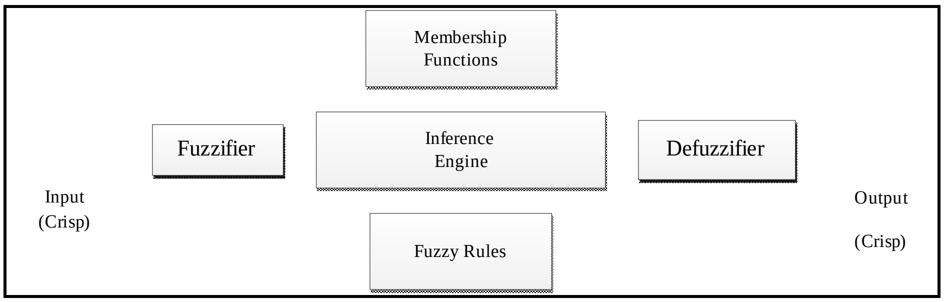


Figure 6.1 Structure of a fuzzy logic system

First, the fuzzifier uses membership functions to fuzzify the signal-to-noise ratios of each performance characteristic. Next, the inference engine (Mamdani fuzzy inference system) performs fuzzy reasoning on fuzzy rules to generate a fuzzy value. Finally, the defuzzifier converts the fuzzy value into a real world output and this can be used for prediction of the wear properties of the HA/HDPE bio-composites.

6.3.2 Development of Mamdani model

Mamdani fuzzy system is to predict or estimate the abrasion rate of HA/HDPE bio-composites. If the fuzzy system is given a set of measured data input and output it can predict the output for any given input even if a specific input condition had not been covered in the building stage. Multi Input and Single Output model (MISO) is considered here. Figure 6.2 represented the proposed Mamdani Fuzzy model for prediction abrasion wear rate.

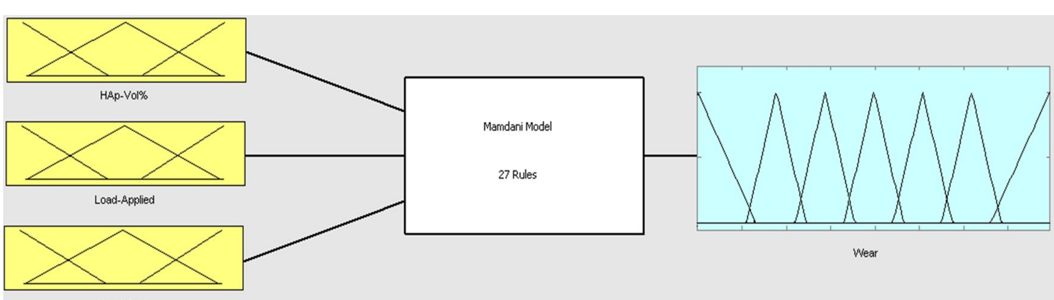
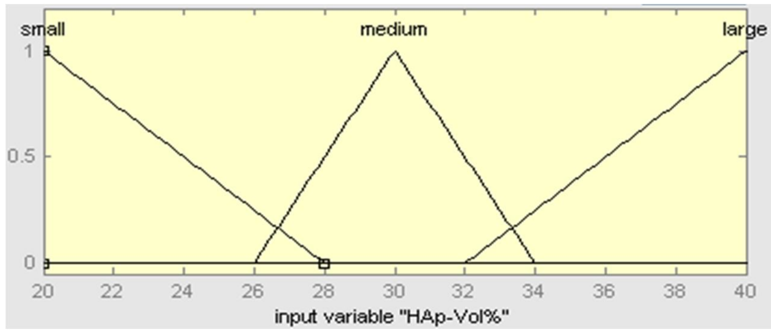
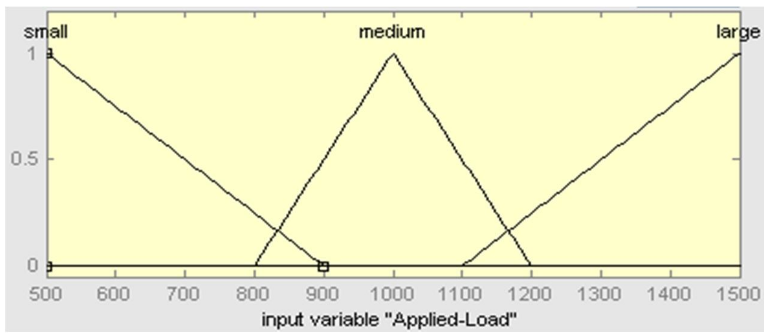


Figure 6.2 Structure of mumdani fuzzy rule base system for prediction of abrasion wear rate

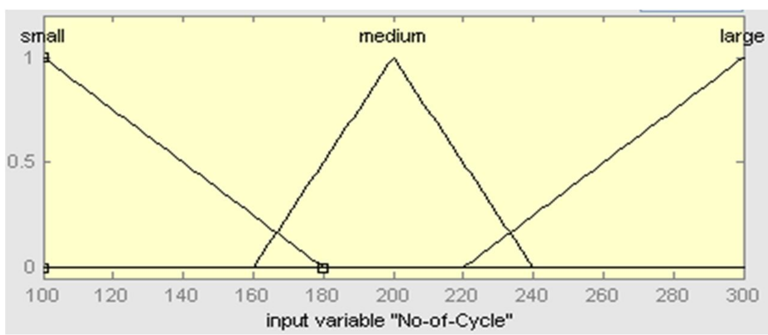
6.3.3 Selection of input and output variables (HA/HDPE)



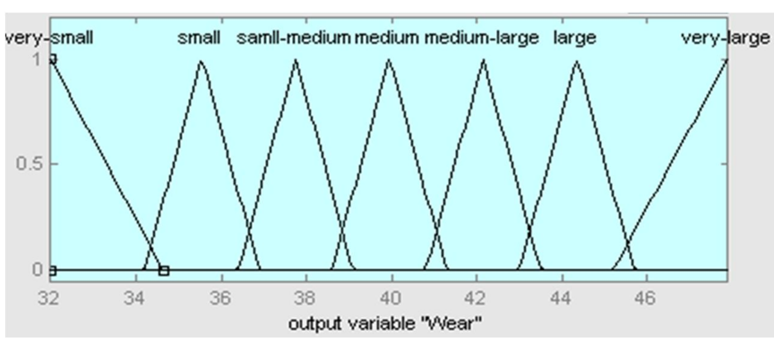
(a)



(b)



(c)



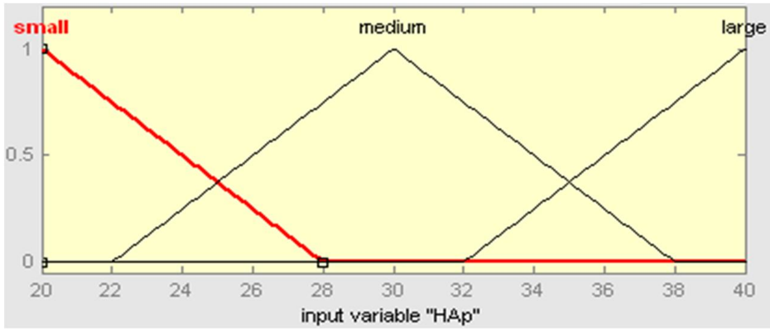
(d)

Figure 6.3 Membeship functions for change in (a)HAp Vol%, (b) Load, (c)Number of cycle, (d)Amount of material removed in abrasion wear test (HA/HDPE)

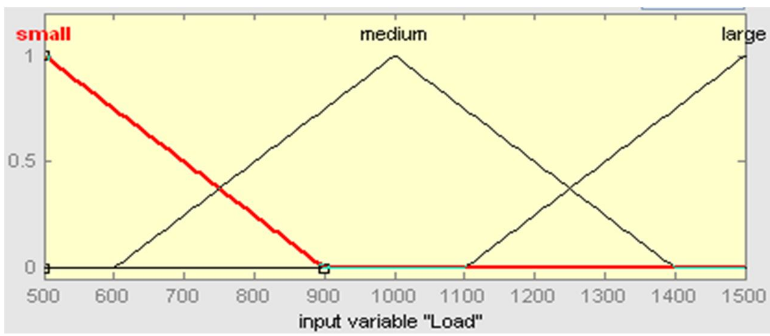
Table 6.4 Inputs and output with their fuzzy and fuzzy intervals of two body abrasion wear test of HA/HDPE bio-composite

Sl. No.	System's linguistic variables	Variables	Linguistic values	Fuzzy interval
1	Input1	HAp Vol%	Low	20-28 (Vol %)
			Medium	26-34 (Vol%)
			High	32-40 (Vol%)
2	Input2	Applied Load	Low	500-900 (gm)
			Medium	800-1200 (gm)
			High	1100-1500 (gm)
3	Input3	No. of Cycle	Low	100-180 (rev)
			Medium	160-240 (rev)
			High	220-300 (rev)
4	Output3		Very Small	32-34.7 (dB)
			Small	34.2-36.9 (dB)
			Small Medium	36.4-39.1 (dB)
			Medium	38.6-41.3 (dB)
			Medium Large	40.8-43.5 (dB)
			Large	43-45.7 (dB)
			Very Large	45.2-47.9 (dB)

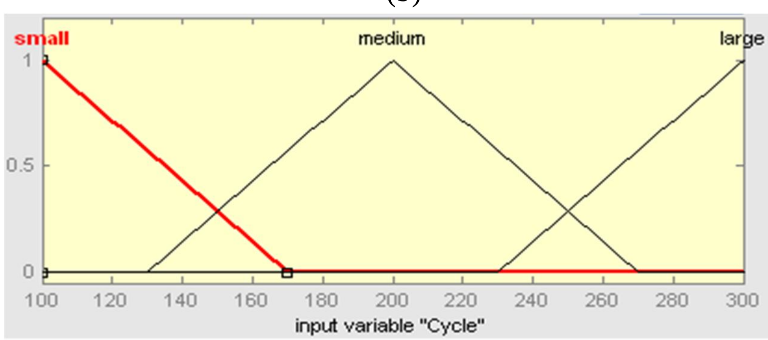
6.3.4 Selection of input and output variables (HA/HDPE)



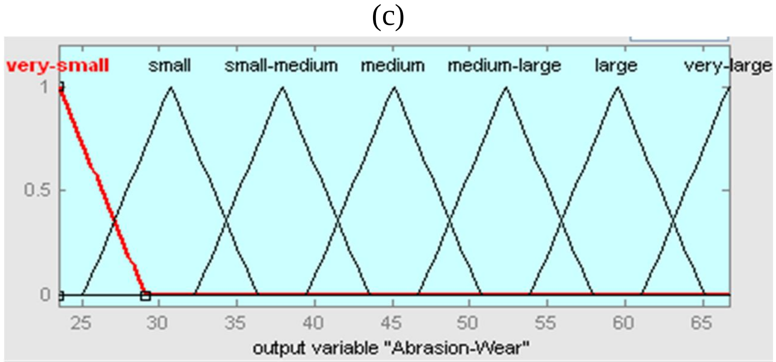
(a)



(b)



(c)



(d)

Figure 6.4 Membeship functions for (a)HAp Vol%, (b)Applied Load, (c)Number of cycle, (d)Amount of material removed in abrasion wear test (HA/HMHDPE)

Table 6.5 Inputs and output with their fuzzy and fuzzy intervals of two body abrasion wear test of HA/HMHDPE bio-composite

Sl. No.	System's linguistic variables	Variables	Linguistic values	Fuzzy interval
1	Input1	HAp Vol. %	Low	20-28 (Vol. %)
			Medium	26-34 (Vol. %)
			High	32-40 (Vol. %)
2	Input2	Applied Load	Low	500-900 (gm.)
			Medium	800-1200 (gm.)
			High	1100-1500 (gm.)
3	Input3	No. of Cycle	Low	100-180 (rev.)
			Medium	160-240 (rev.)
			High	220-300 (rev.)
4	Output3		Very Small	23.5-29.1 (dB)
			Small	25.1-36.3 (dB)
			Small Medium	32.3-43.5 (dB)
			Medium	39.5-50.7 (dB)
			Medium Large	46.7-57.9 (dB)
			Large	53.9-65.1 (dB)
			Very Large	61.1-66.7 (dB)

Figure 6.3 and Figure 6.4 are showing the membership functions taken for the construction of the fuzzy inference system, whereas inputs and output with their fuzzy and fuzzy intervals of two body abrasion wear test of HA/HDPE and HA/HMHDPE bio-composites are listed in the Table 6.4 and Table 6.5 respectively.

6.4 Construction of the Artificial Neural Network (ANN)

6.4.1 Artificial Neural Network Prediction

Manufacturing of bio-composites through conventional plastics processing technique is a long and time consuming method. Sothat after composite fabrication abrasion testing will take more time to get a good result. To save time and resources we need some prediction technique to predict the wear behaviour of the bio-composites taking different input parameters within the domain. This paper aims to develop an artificial neural network (ANN) model for the analysis and prediction of the wear behavior of the HAp-HDPE bio-composite. The input parameters of the Artificial Neural Networks (ANN) model are Hap vol% incorporated in the HDPE matrix, applied load and number of cycle turned in the abrasion wear test. The output parameters of the model is amount of abrasion wear. Nowadays the ANN is one of the models used to solve problems by imitating human neural networks and it has been used for modeling complex manufacturing process due to their learning and generalization capabilities, accommodation of non-linear variables, adaptivity to changing environments and resistance to missing data. Durmus et al. [41] used ANN to predict wear loss and surface roughness of AA 6351 aluminium alloy. Velten et al. [42] used back propagation ANN with Levenberg-Marquardt algorithm to predict and analyze the wear behaviour of short fiber reinforced polymer bearing materials. In this research, A Multilayer neural network is choosen in this study consisting of input layer, hidden layers and output layer. In this study, commonly used sigmoidal function is chosen and ANN model with feed forward and error back propagation is created. The model is illustrated in Figure 6.5.

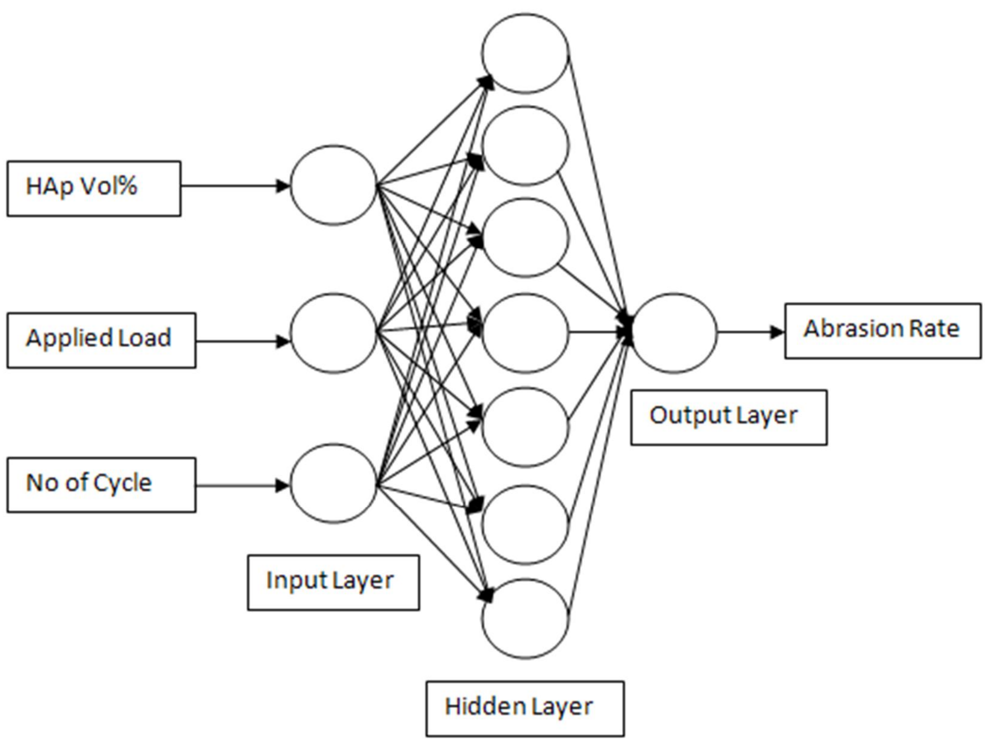


Figure 6.5 The ANN architecture

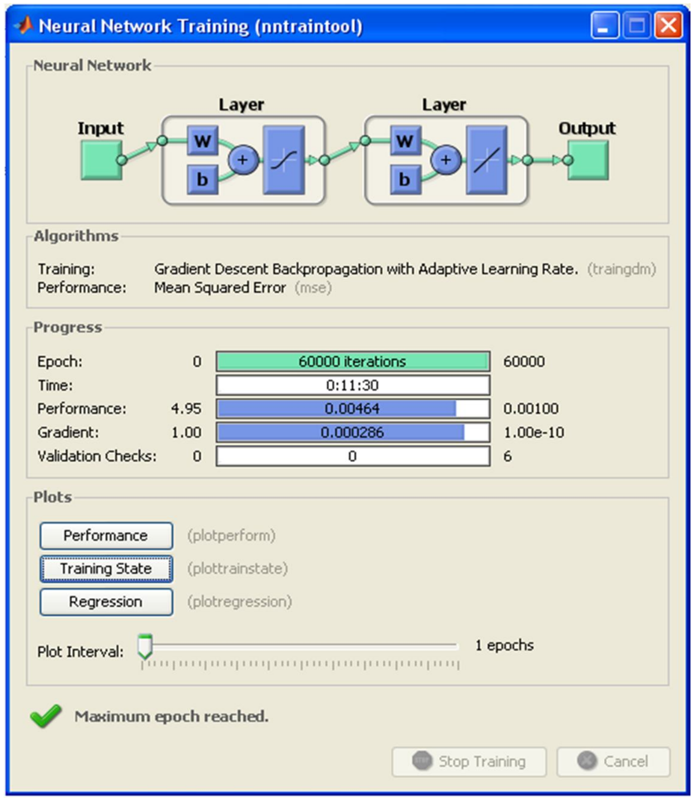


Figure 6.6 ANN Taining model (HA/HDPE)

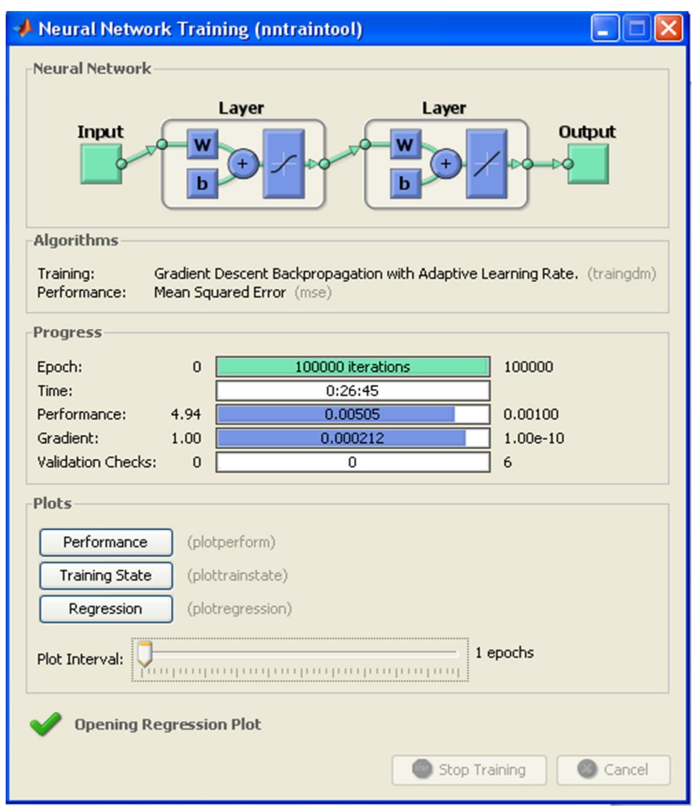


Figure 6.7 ANN Taining model (HA/HMHDPE)

Figure 6.6 and Figure 6.7 displays the graphical user interface of ANN training model. Where Figure 6.8 & Figure 6.9 are showing the regression plot, performance and training state of the ANN model. The regression equation of best linier fit with an R value of 0.99769 and 0.99046 for HA/HDPE and HA/HMHDPE composites respectively as given by the ANN model isshown following.

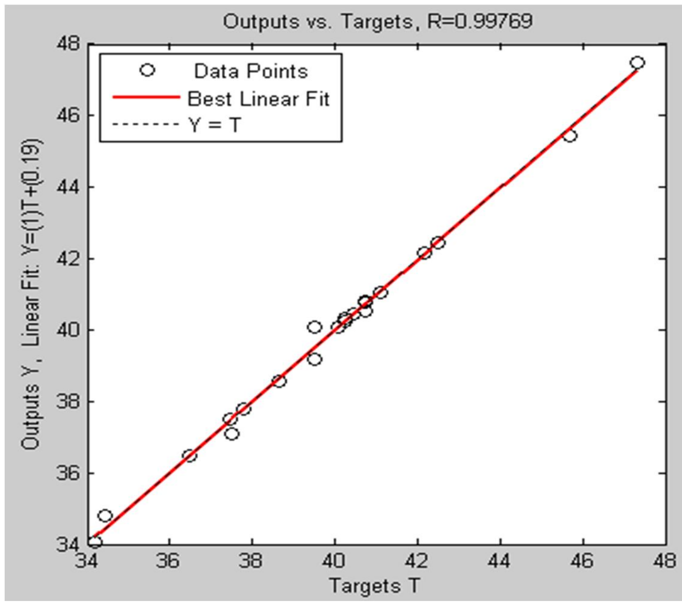


Figure 6.8 Regression plot for training (HA/HDPE)

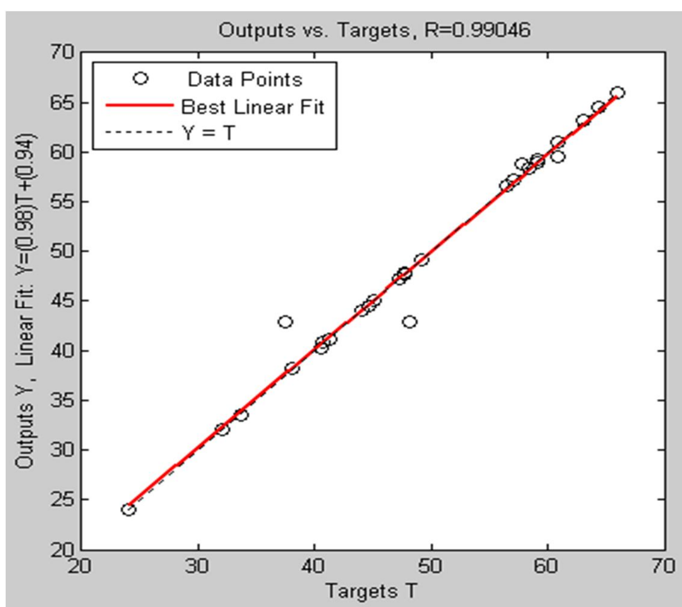


Figure 6.9 Regression plot for training (HA/HMHDPE)

Randomly chosen 75% of data of 27 experiments are used for learning state and remaining 25% of data is used for testing purpose. The sample set is trained by chancing neuron number in hidden layer, The number of neurons in the hidden layer is taken as 7. Training is done with starting iterations over 100000 epoches which is high enough so that the network can be trained rigorously. The details of this methodology are described by Rajasekaran et al.[43].

MATLAB 2009b platform has been used to construct the neural network consists of back propagation algorithm as the prediction tool for abrasion wear rate of the HAp/HDPE and HAp/HMHDPE composites under different test conditions.

Chapter 7

RESULTS AND DISCUSSION

7.1 Results and Discussions

7. 2 Scanning Electron Microscopy

Composites with up to 40% by volume were successfully compounded and SEM images revealed good dispersion of HAp in the HDPE polymer matrix. SEM micrograph of the HAp/HDPE and HAp/HMHDPE composites are shown in the Figure 7.1 (a) and Figure 7.1 (b) which reveals the global dispersion of HAp in both the polymer matrix.

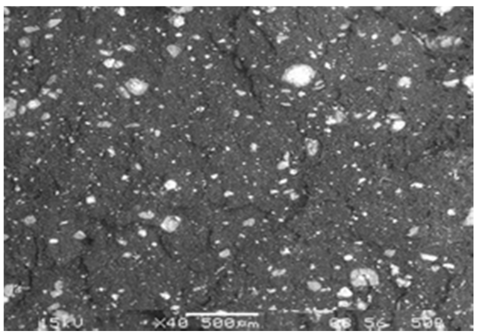


Figure 7.1 (a) SEM micrograph of 40vol% HAp/HDPE composite

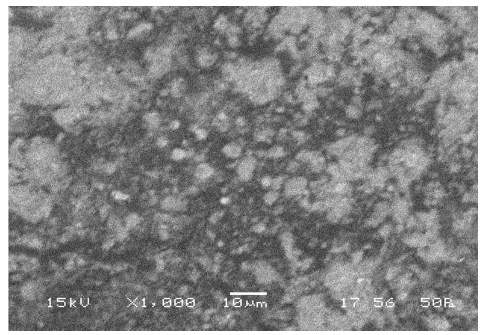


Figure 7.1 (b) SEM micrograph of 40vol% HAp/HMHDPE composite

7.3 XRD analysis

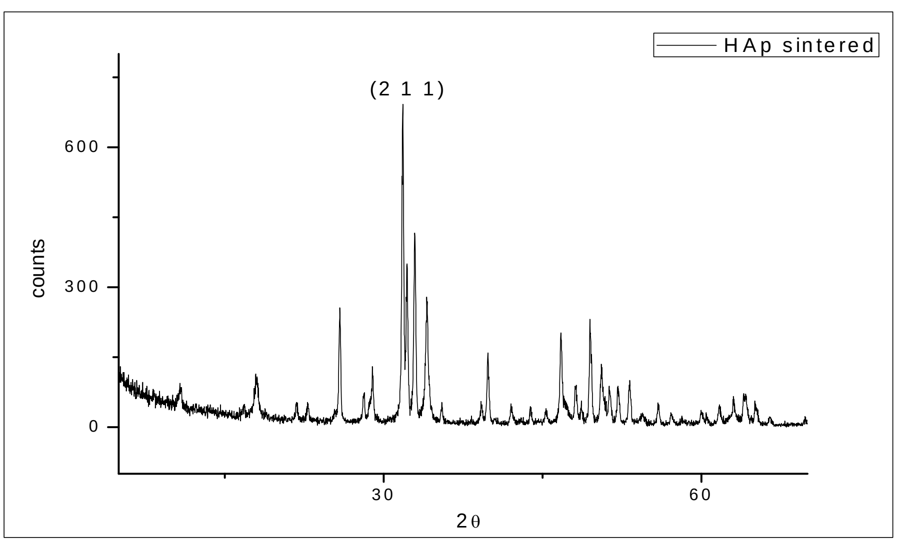


Figure 7.2 (a) XRD pattern of the sintered HAp powder

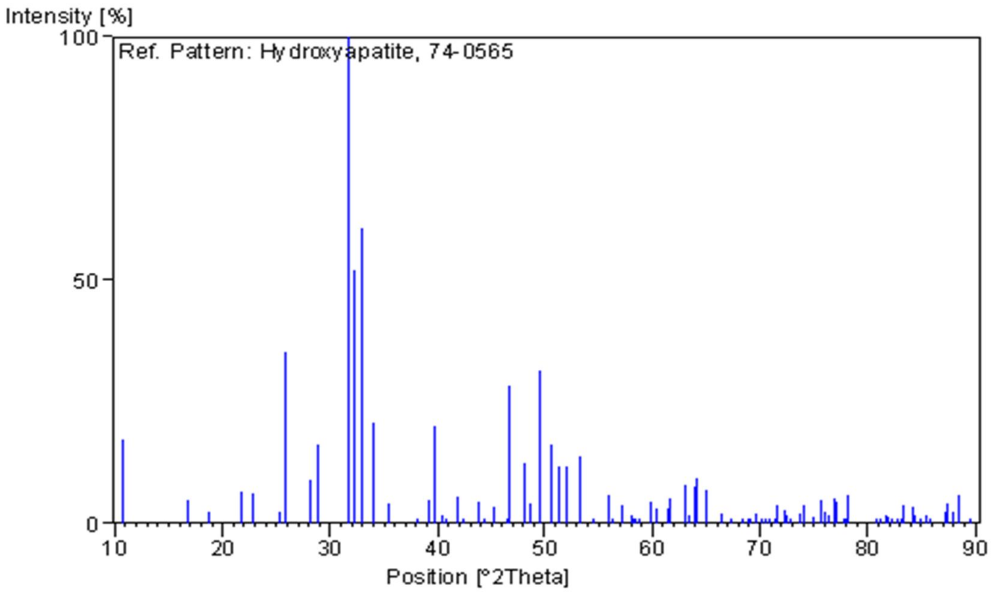


Figure 7.2 (b) XRD Reference pattern of HAp

The analysis of the XRD peaks of HAp phases (Figure 7.2 (a)) reveals the presence of pure HAp. Broad sharp peak of pure HDPE can be identified in the Figure 7.2 (a) at peak no. 10: hkl [2 1 1], d value 2.81468 A and intensity I is 100%. At a lower temperature a longer aging time is needed to avoid the appearance of β -tricalcium phosphate (β- $Ca_3(PO_4)_2$) after calcining treatment over 850 °C. The sample precipitated by wet chemical recipitation technique did not contain any $Ca(OH)_2$ peaks as shown in Figure 20(a). The presence of $Ca(OH)_2$ peaks in the powder structure were attributed to especially weak stirring effect. The XRD pattern obtained is compared with the reference pattern as shown in Figure 7.2 (b) and found to be matched.

7.4 Density and void fraction

The theoretical density of composite materials in terms of weight fraction can easily be obtained as per the following equations given by Agarwal and Broutman [45]

$$\rho_{ct} = \frac{1}{(W_p / \rho_p) + (W_m + \rho_m)} \tag{7.1}$$

Where, W and ρ represent the weight fraction and density respectively. The suffix p, m and ct stand for the particulate, matrix and the composite materials respectively. The actual density (ρ_{ca}) of the composite materials was evaluated by determining the test piece mass using Mettlertoledo weighing machine with the accuracy of $\pm 10^{-3}$gm and its volume basing on the apparent mass loss by immersing in water. The volume fraction of voids (V_v) in the composites is calculated using the following equation:

$$V_v = \frac{\rho_{ct} - \rho_{ca}}{\rho_{ct}} \tag{7.2}$$

Table 7.1 Measured and Theoretical densities of the composites

Composites	Theoretical Density(gm/cm^3)	Measured Density(gm/cm^3)	Volume fraction of voids (%)
10vol%HAp/HDPE	1.125	1.114	0.97
20vol%HAp/HDPE	1.35	1. 340	0.74
30vol%HAp/HDPE	1.575	1.498	4.88
40vol%HAp/HDPE	1.80	1.76	1.66
10vol%HAp/HMHDPE	1.17	1.165	042
20vol%HAp/HMHDPE	1.38	1.377	0.21
30vol%HAp/HMHDPE	1.60	1.59	0.625
40vol%HAp/HMHDPE	1.81	1.78	1.65

It is clear from the Table 7.1 that void fraction of the 20 vol.% HAp/HDPE bio-composite is much more around 4.88%. Hence, it may affect the mechanical properties of the 30vol% HA/HDPE bio-composite. In case of HA/HMHDPE composites amount of void present is very less, hence the mechanical properties of the composite will not be affected by void fraction.

7.5 Characterization of the mechanical properties

7.5.1 Characterization of HA/HDPE composites

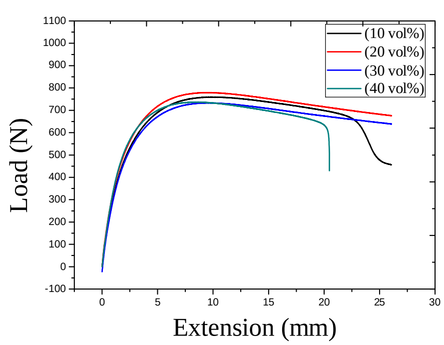


Figure 7.3 (a) Typical load-extension curves for HA/HDPE

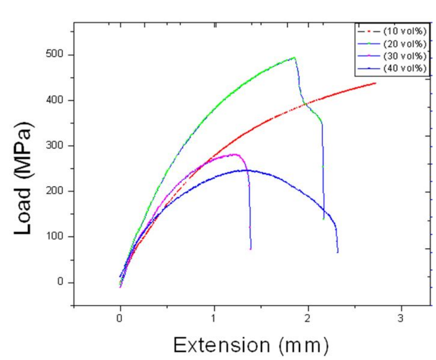


Figure 7.3 (b) Typical load-extension curves for HA/HMHDPE

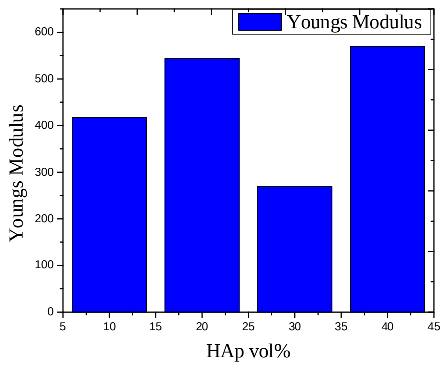


Figure 7.4 Plot of Young's modulus versus HAp vol%

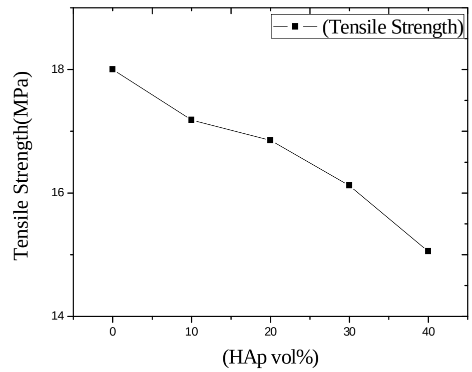


Figure 7.5 Effect of HAp contents on the tensile strength

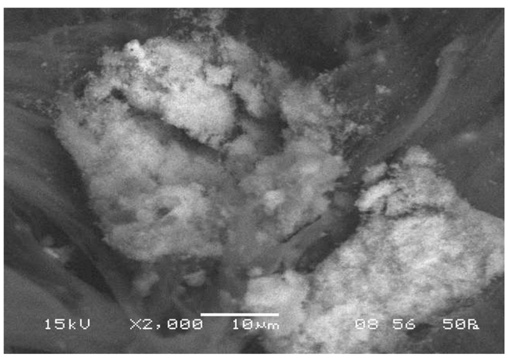


Figure 7.6 (a) Fracture mechanism of the 30vol% HA/HDPE bio-composite

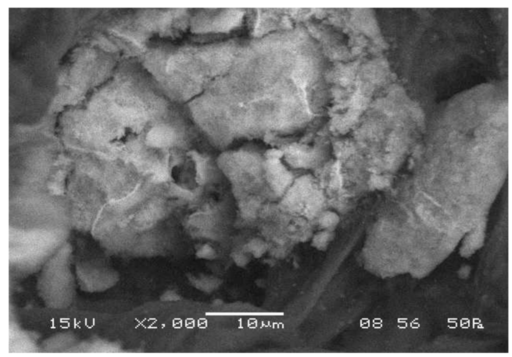


Figure 7.6 (b) Fracture mechanism of the 40vol% HA/HDPE bio-composite.

Figure 7.3 (a) and Figure 7.3 (b) shows the plot for tensile load/displacement in different HA volume percent for the bio-composite developed. Notably, it can be seen that the HA/HDPE-composite materials exhibited both ductile and brittle behavior, depending on the amount of HA incorporated into the HDPE and HMHDPE polymer matrix. It can be seen that increasing the amount of HA resulted in the composite losing its ductility as seen from the composite brittle mode failure occurring in the elastic region. Figures 7.4 and Figure 7.5 are revealing the increase in Young's modulus and decrease in tensile strength with respect to the increasing amount of HA of HA/HDPE bio-composite, respectively. It can be seen that the tensile properties of HA/HDPE composites were dependent on the HA content. In Figure 7.5 (a) & Figure 7.5 (b), it is shown that the main fracture mechanism of the 30 vol% HA/HDPE and 40 vol% HA/HMHDPE bio-composites occurred during tensile test, suggesting poor interfacial interaction between HA and both the polymer matrix and denotes a brittle type fracture.

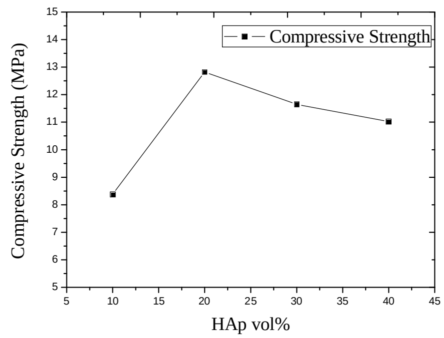


Figure 7.7 Effect of HAp content on the Compressive strength

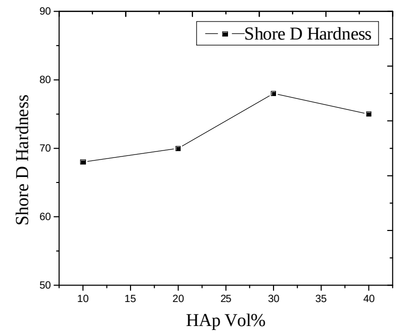


Figure 7.8 Effect of HAp content on hardness

Hence, the drop in tensile strength with increasing HAp content is clearly evident. Comparing the Young's modulus of the natural bone, it was found that the modulus of (10-40%) HA/HDPE composite is less than the low to medium range of the natural bone modulus which ranges from 3 to 30GPa [9], which may not fulfill the requirement.

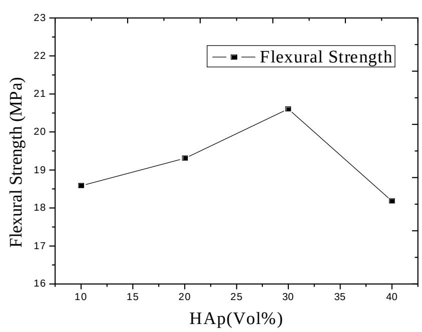


Figure 7.9 Effect of HAp content on Flexural Strength

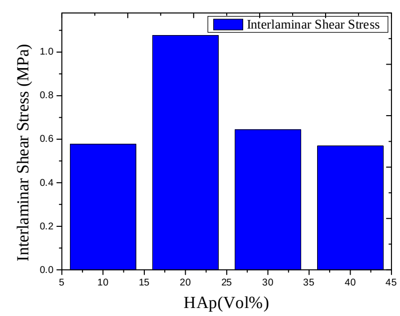


Figure 7.10 Reinforcement effect of HAp on ILSS

Effect of HAp reinforcement in the composite compressive strength plotted in the Figure 7.7 upto 20 vol% of HAp incorporation in the HDPE matrix shows an increase in compressive strength of the HA/HDPE bio-composite, but a sharp fall can be seen in 30 and 40 vol% of HAp due to lack of global dispersion of Hap content in the 30 vol% composite but in case of 40 vol% due to uneven bonding among HAp and HDPE matrix and because of brittle nature of the HAp compressive strength decreases.

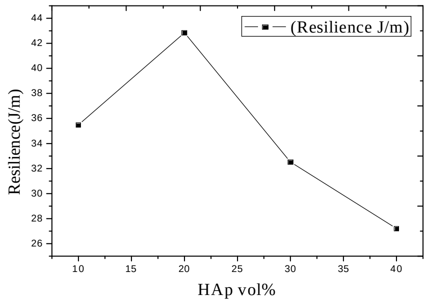


Figure 7.11 Effect of resilience with respect to HAp vol%

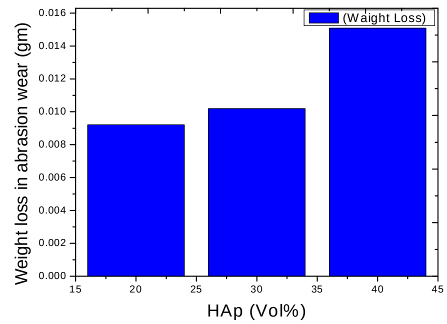


Figure 7.12 Effect of HAp vol% on abrasive wear

Shore-D hardness test has been carried out which prompts the hard and brittle nature of the HAp as a ceramic material. A plot between HApvol% and Shore-D hardness (Figure 7.8) Shows 30 vol% HA/HDPE composite shows the maximum hardness. Flexural testing is carried out in an instron 3382 universal testing machine system as per ASTM D790 standard at a rate of 0.77 mm/min. The loading arrangement is shown in the Figure 5.1 (a) the dimension of sample specimen is 3.2mm x 12.7mm x 125mm. The Flexural strength (FS) of the specimen is calculated as follows.

$$FS = \frac{3P.L}{b.t^3} \qquad (7.3)$$

Where, P is maximum load, b is width, t is the thickness and L is length of the specimen. The data recorded in the flexural test is also used to determine the inter-laminar shear stress (ILSS) values, calculated as follows

$$ILSS = \frac{3P}{4b.t} \qquad (7.4)$$

The flexural properties are of great importance for any structural element. Bio-Composite used in hip joints may fail in bending loads and therefore the development of new composites with improved flexural characteristics is very essential. From the results it may now be suggested that HAp/HDPE bio-composites to be used in bio-medical applications making high flexural strength bio-composites. The flexural strength of the HAp/HDPE bio-composites shows an approximately linier increase with the HAp vol% (Figure 7.9).The inter-laminar shear strength values of the particulate filled bio-composites are shown along with the flexural strength. It can be seen (Figure 7.10) that with increase in filler content from 30 wt% to 40 wt% there is sharp drop in the inter-laminar shear strength. The stresses acting on the interface of two adjacent laminas are called inter-laminar shear stress. The stresses cause relative deformation between the lamina and if these are sufficiently high, they may cause failure along the common plane between the laminas. It is therefore, of considerable interest to evaluate inert-laminar shear strength through tests in which failure of laminates initiates in a shear (delaminating) mode. Tinius Olsen High Energy Impact System - IT406 Pendulum Impact Tester was used to do the pendulum type impact testing. ASTM D256 is the standard used impact strength determination. It can be suggest from the Figure 7.11 that the 20 vol% HA/HDPE bio-composite shows very high resilience. High strain rates or impact loads may be expected in bone structures in case of running or accidental conditions. The suitability of a bio-composite for such applications should therefore be determined not only by usual design parameters, but by its impact or energy absorbing properties. Thus, it is important to have a good understanding of the impact behavior of composites for both safe and efficient design of artificial bone structures and to develop new composites having good impact properties. 20 vol% HA/HDPE bio-composite system is exhibiting minimum weight loss in two body abrasion wear test shown in Figure 7.12.

7.5.2 Characterization of HA/HMHDPE composites

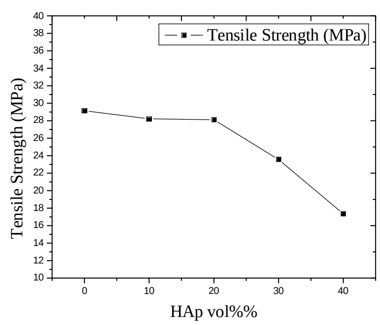


Figure 7.13 Plot of tensile Strength vs. HAp vol%

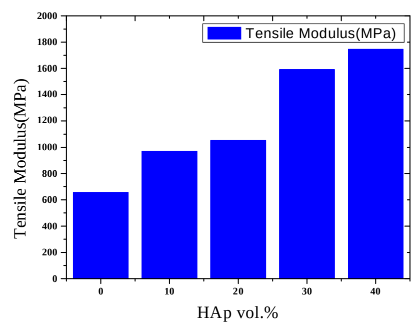


Figure 7.14 Plot of tensile Modulus vs. HAp vol%

Figure 7.13 showed the typical tensile strength vs. HAp vol. % curves of the HAP/HMHDPE composites. The Young's modulus of the composite specimens decreased almost linearly with the HA volume percentage and reached about three times that of pure HMHDPE when the HA volume percentage was 40%. Generally, the brittle ceramic fillers damage the fracture resistance of composites. The tensile fracture strain somehow decreased with HAp content, but it still reached over 300% with 20 vol% HAp. This demonstrated one of the advantages of using HMHDPE as the matrix. Compressive strength of the composite is also affected with the brittleness associated with the HAp reinforcement. Flexural and inter-laminar shear strength come out very low at 40 volume percent but 20 percent composites possess a moderate strength. Impact test of all the composite specimens have shown good resilience characteristics. 10 volume percent composite gives the lowest amount of abrasion wear as tested in the two body abrasion test.

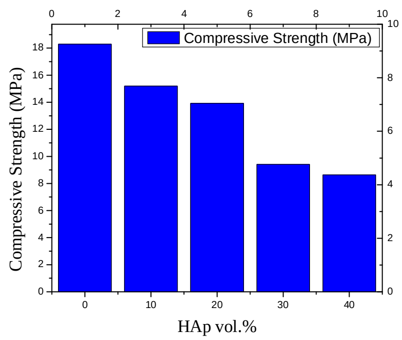


Figure 7.15 Plot of compressive strength vs. HAp vol%

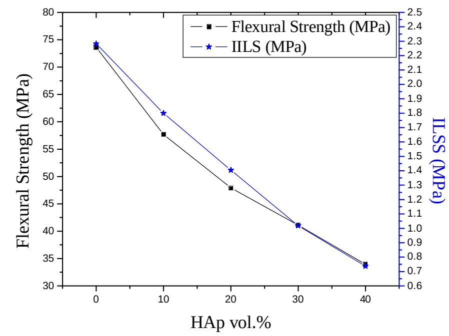


Figure 7.16 Plot of flexural and ILSS vs. HAp vol%

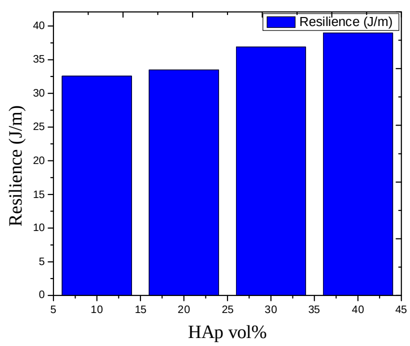


Figure 7.17 Resilience vs. HAp vol%

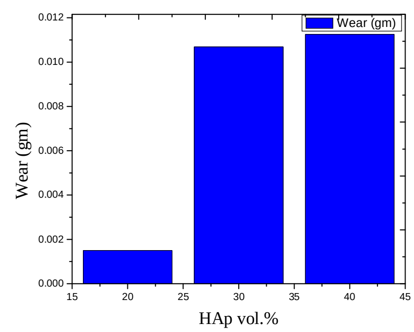


Figure 7.18 Amount of abrasion wear vs. HAp vol%

7.6 Comparison of mechanical properties of HA/HDPE and HA/HMHDPE composites with human cortical bone

The tensile properties of HA/HDPE and HA/HMHDPE composites were compared with some well-studied bone-analogue **composites [16, 17, 35-38] and** cortical bone [39, 40] as shown in Table 7.2. With the same HAp content (20 vol %), the Young's modulus of HA/HMHDPE composite was comparable to that of the HA/PEEK [37] and HA/PMMA [38] composite, but it was higher than that of HDPE matrix composite [16, 32, 33, 36] except the highly oriented HA/HDPE composite processed by SCORIM [34]. The composite would have had an elastic modulus similar upto the low-mid region of cortical bone (7-30GPa) [39, 40].

Table 7.2 The mechanical properties of bone-analogue composites and human cortical bone

Material	Author	Processing Method	Modulus (GPa)	Tensile Strength(MPa)
HA/HDPE (20 vol %)	Wang et al. [32,33]	Twin-screw extrusion Compression molding	1.55-1.81	17. 65-19.97
HA/HDPE (50wt %)	Reis et al. [34]	Twin-screw extrusion Injection molding	4.0	39
HA/HDPE (50wt %)	Reis et al. [34]	Twin-screw extrusion SCORIM	7.5	91
HA/HDPE (20 vol %)	Roeder et al. [16]	Ultrasonic mixing Compression molding	3.0-4.2	25.77-29.67
BG/HDPE (20 vol %)	Bonfield et al. [35]	Twin-screw extrusion Compression molding	1.21	12.69
AW/HDPE (20 vol %)	Juhasz et al. [36]	Twin-screw extrusion Compression molding	1.4	5.57-5.67
HA/PEEK (20 vol %)	Abu Bakar et al. [37]	Shear mixing Injection molding	7.0	32
HA/PMMA (20 vol %)	Cheang et al. [38]	Shear mixing Injection molding	6.23	38.9
HA/UHMWPE (20 vol %)	Fang et al. [17]	Twin-screw extrusion Compression molding	6.87	26.67
HA/HDPE (20 vol%)	Mondal et al. (This work)	Micro-compounder Micro-injection molding	0.543	17.18
HA/HMHDPE (20-40 vol%)	Mondal et al. (This work)	Twin screw extruder Compression molding	1.05-1.74	28.21
Cortical bone (50 vol %)	[39-40]		7-30	50–150

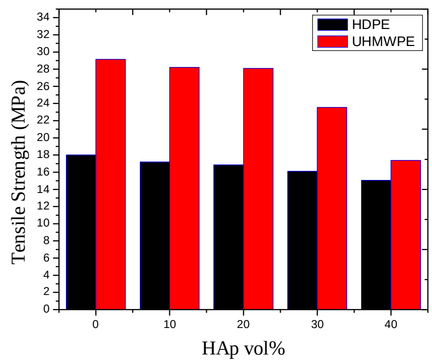


Figure 7.19 Plot of Tensile Strength vs. HAp vol%

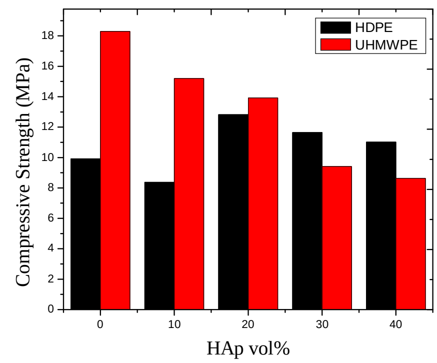


Figure 7.20 Plot of compressive strength vs. HAp vol%

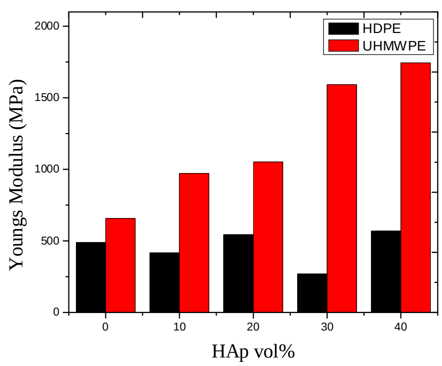


Figure 7.21 Plot of Young's modulus vs. HAp vol%

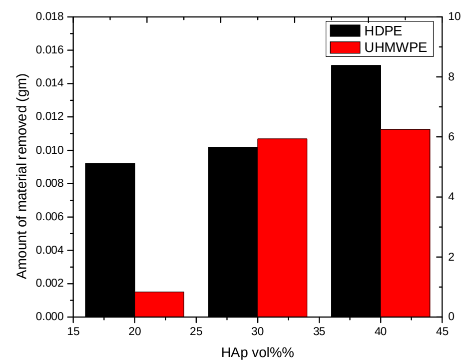


Figure 7.22 Amount of material removal (two body abrasions wear) with respect to HAp vol%

Minimum amount material removal as a measure of wear is shown by 10 vol% of both the composites as 0.00921 gm and 0.0015 gm for HDPE and UHMWPE composites respectively (Figure 7.22). It has been observed that tensile strength of the composite decreases with increase in HAp volume percent. The virgin HDPE sample has strength of 18 MPa in tension but this value drops rapidly with increase in HAp amount, but in case of HA/HMHDPE composite (20 vol %) maximum tensile strength 28.214 MPa (Figure 7.19). Maximum compressive strength is 18.3 MPa and 14.18 MPa given by 10 vol% HA/UHMWPE and 20 vol% HA/HDPE composites respectively (Figure 7.20). Youngs modulus of both the composite found to be lies between the ranges of 0.269 to 1.745 GPa (Figure 7.21). Comparing the Young's modulus of the natural bone, it was found that the modulus of (10-

40%) HA/HDPE composite is fall in the low to medium range of the natural bone modulus which ranges from 3 to 30GPa [9], which may partially fulfill the requirement.

7.7 Characterization of the two body wear test

Full factorial design method has been successfully implemented in this work to identify statistically significant factors and their interactions responsible for improving wear behaviour of ceramic particulate(HAp) filled composites. To characterize the morphology of as-received and abrased surfaces and to identify the mode of material removal, the abrased samples are observed under scanning electron microscope (Model JEOL JSM-6480LV). Figure 7.23 (a) and Figure 7.23 (b) shows the surface of the HAp reinforced composites at different testing conditions are HAp vol%-30, Applied Load 1500gm, number cycle turned 300 for both the HDPE and HMHDPE matrixces.

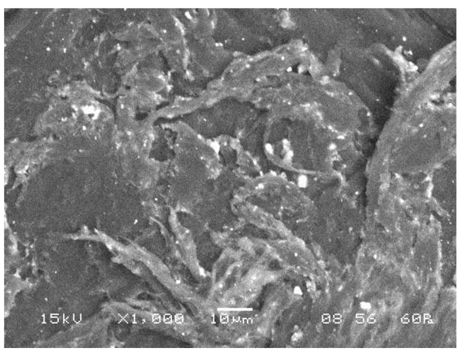


Figure 7.23 (a) SEM micrograph of the abrasion wear specimen (HA/HDPE)

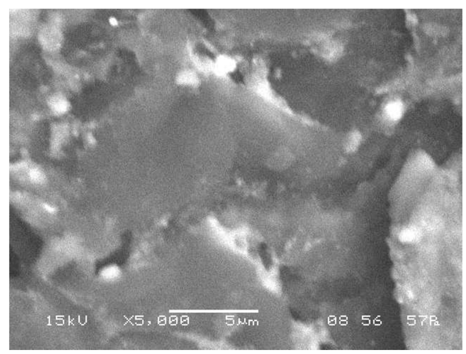


Figure 7.23 (b) SEM micrograph of the abrasion wear specimen (HA/HDHDPE)

In this micrograph, the crack formation and propagation are clearly visible along with groove formation, which implies the removal of bulk mass of materials from the surface. Here, a relatively large amount of the material is seen to be removed from the surface along with formation of large amount of grooves are visible. At the same time, the ceramic reinforcement, made of HAp, crashes and is pulled out under the normal load. and, hence, it is distributed along the wear track as white spots, over the grey polymer matrix.

7.8 ANOVA of two body abrasion wear test

7.8.1 HA/HDPE composite system

Main effect plots for S/N ratio of the response as shown in **Figure 7.24** gives the optimum factor setting which gives minimum abrasion wear are HAp=10 vol%, load=500gm and sliding distance=100cycles.The significant factors and interactions are identified using ANOVA shown in **Tables 7.3** for the abrasion wear rate.

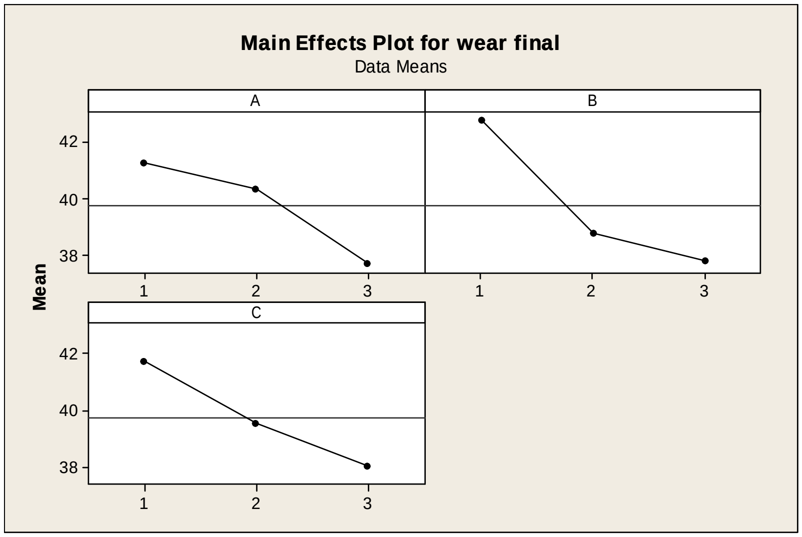


Figure 7.24 Main effect plots

Table 7.3 ANOVA for abrasion wear (HA/HDPE)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	2	61.406	61.406	30.703	14.24	**0.002**
B	2	127.005	127.005	63.503	29.44	**0.000**
C	2	62.725	62.725	31.363	14.54	**0.002**
A*B	4	5.289	5.289	1.322	0.61	0.665
A*C	4	8.205	8.205	2.051	0.95	0.483
B*C	4	28.374	28.374	7.094	3.29	**0.071**
Error	8	17.254	17.254	2.157		
Total	26	310.258				
S = 1.46861		R-Sq = 94.44%		R-Sq(adj) = 81.93%		
DF =degree of freedom		SS = sum of square		MS = mean sum of square		

The overall mean for the S/N ratios of composites reinforced with HAp is found to be 34.19 dB. The analyses are made using MINITAB R14. Before using this model as a predictor for measuring performance, the possible interactions must be analyzed. The analysis of variances for the factors is shown in Table 7.3 which clearly indicates that all the factors are important and influencing the wear amount. It has been found that the applied load is the most influencing among all the factors. The interaction plot is shown in (Figure (7.25)). The interaction between the factor load and sliding distance shows a significant interaction effect and other interactions are not so significant.

Figure 7.25 Interaction plots

7.8.1.1 Model Analysis of abrasion wear

The coefficients of model for S/N ratios for wear are shown in Table 7.4. The parameter R^2 describes the amount of variation observed in wear is explained by the input factors. R^2 = 94.44% indicate that the model is able to predict the response with high accuracy. Adjusted R^2 is a modified R^2 that has been adjusted for the number of terms in the model. If unnecessary terms are included in the model, R^2 can be artificially high, but adjusted R^2 (=81.93 %.) may get smaller. The standard deviation of errors in the modeling, S= 1.46861 . Comparing the p-value to a commonly used α-level = 0.05, it is found that if the p-value is less than or equal to α, it can be concluded that the effect is significant (shown in bold), otherwise it is not significant.

Table 7.4 Estimated Model Coefficients for SN ratios (HA/HDPE)

Term	COEF1	F	P
Constant	39.7530		
A	1.5093	14.24	**0.002**
B	0.5504	29.44	**0.000**
C	3.0148	14.54	**0.002**

A*B	-1.0185	0.61	0.665
A*C	1.9659	0.95	0.483
B*C	-0.2174	3.29	**0.071**
S = 1.46861	R-Sq = 94.44%	R-Sq(adj) = 81.93%	

The coefficient of determination (R^2) which indicates the goodness of fit for the model so the value of R^2 =94.44% which indicate the high significance of the model. With the above analysis we found the following regression equation:-

Wear (SN ratio) = 39.7530+1.5093A+0.5504B+3.0148C+-0.2174(B*C)

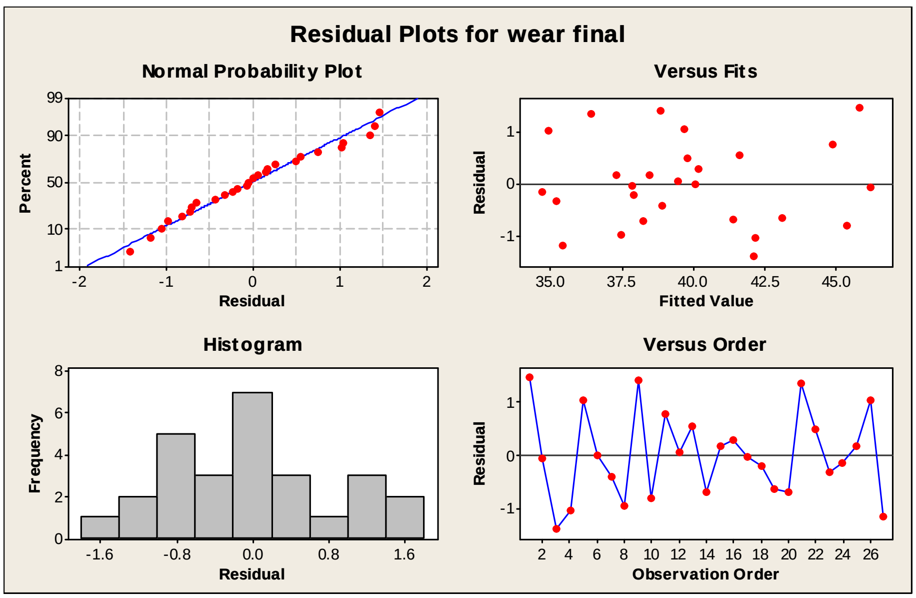


Figure 7.26 Residual plots for two body abrasion wear

The residual plots of abrasion wear are shown in Figure 7.26. This layout is useful to determine whether the model meets the assumptions of the analysis. The residual plots in the graph and the interpretation of each residual plot indicate below:

a. Normal probability plot indicates the data are normally distributed and the variables are influencing the response. Outliers don’t exist in the data, because standardized residues are between -2 and 2.

b. Residuals versus fitted values indicate the variance is constant and a nonlinear relationship exists as well as no outliers exist in the data.

c. Histogram proves the data are not skewed and not outliers exist.

d. Residuals versus order of the data indicate that there are systematic effects in the data due to time or data collection order.

7.8.2 HA/HMHDPE composite system

The analysis of variances for the factors is shown in Table 7.5, which clearly indicates that the number of cycle is less important for influencing the amount of wear but all the three factors are significant enough and have effect on the abrasion wear. The optimal factor setting for minimum wear by using lower the better signal to noise ratio is determined from main effect plot. Optimal parameter setting are HAp=10vol%, load=1000gm, cycle=300.

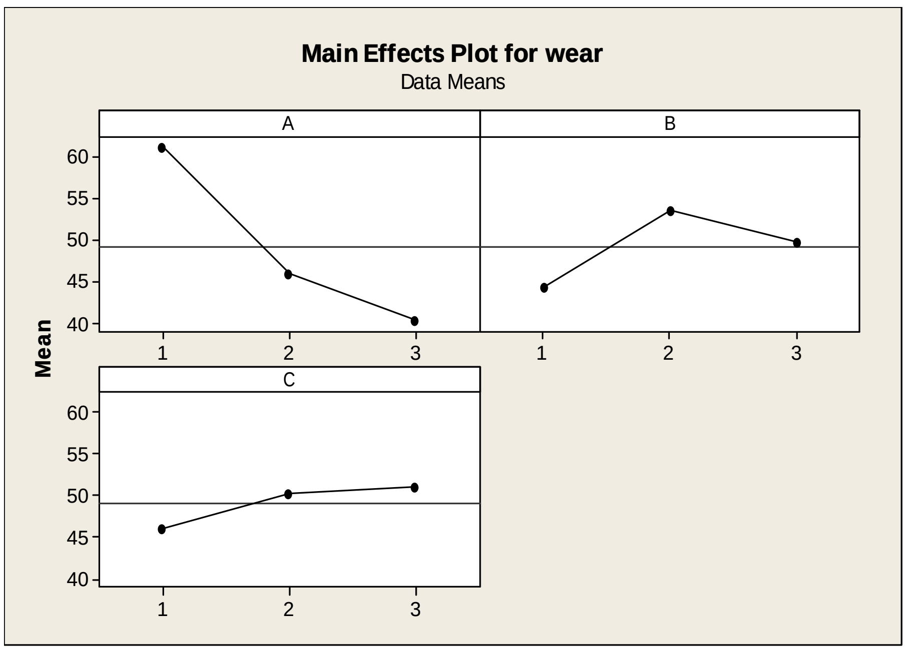


Figure 7.27 Main effect plots for abrasion wear

Table 7.5 ANOVA for abrasion wear (HA/HMHDPE)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
A	2	2083.07	2083.07	1041.54	113.30	**0.000**
B	2	382.39	382.39	191.20	20.80	**0.001**
C	2	135.62	135.62	67.81	7.38	**0.015**
A*B	4	208.10	208.10	52.03	5.66	**0.018**
A*C	4	505.10	505.10	126.27	13.74	**0.001**

B*C	4	30.64	30.64	7.66	0.83	0.540
Error	8	73.54	73.54	9.19		
Total	26	3418.46				
S = 3.03196		R-Sq = 97.85%		R-Sq(adj) = 93.01%		
DF =degree of freedom		SS = sum of square			MS = mean sum of square	

It has been found that the HAp vol% is the most influencing among all the factors. The interaction plot is shown in (Figure (7.27)). The interaction between the factors HAp vol% & load and HAp vol% & sliding distance shows a significant interaction effect and the interaction between load and sliding distance is not so significant as shown in the Figure 7.28.

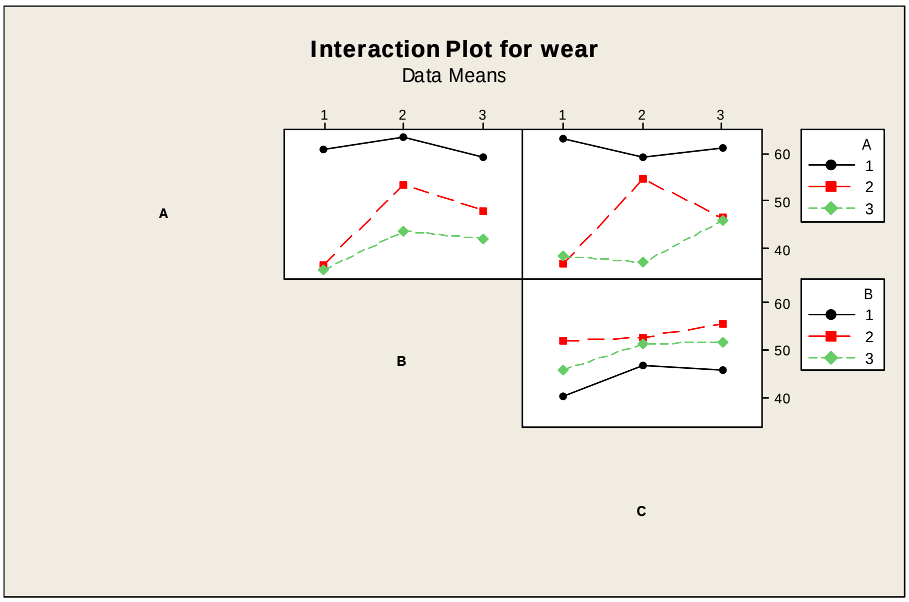


Figure 7.28 Interaction plots for wear test

7.8.2.1 Model Analysis of abrasion wear

The coefficients of model for S/N ratios for wear are shown in Table 7.6. The parameter R^2 describes the amount of variation observed in wear is explained by the input factors. R^2 = 97.85% indicate that the model is able to predict the response with high accuracy. Adjusted R^2 is a modified R^2 that has been adjusted for the number of terms in the model. If unnecessary terms are included in the model, R^2 can be artificially high, but adjusted R^2 (=93.01%) may get smaller. The standard deviation of errors in the modeling, S= 3.03196. Comparing the p-value to a commonly used α-level = 0.05, it is found that if the p-value is less than or equal to α, it can be concluded that the effect is significant (shown in bold), otherwise it is not significant.

Table 7.6 Estimated Model Coefficients for SN ratios (HA/HMHDPE)

Term	COEF	F	P
Constant	49.0963		
A	11.9959	113.30	**0.000**
B	-3.2052	20.80	**0.001**
C	-4.8463	7.38	**0.015**
A*B	4.3281	5.66	**0.018**
A*C	-3.1407	13.74	**0.001**
B*C	1.2015	0.83	0.540
S = 3.03196	R-Sq = 97.85%	R-Sq(adj) = 93.01%	

The coefficient of determination (R^2) which indicates the goodness of fit for the model so the value of R^2 =97.85% which indicate the high significance of the model. With the above analysis we found the following regression equation:-

Wear (SN ratio) = 49.0963+11.9959A-3.2052B-4.8463C+4.3281(A*B)-3.1407 (A*C)

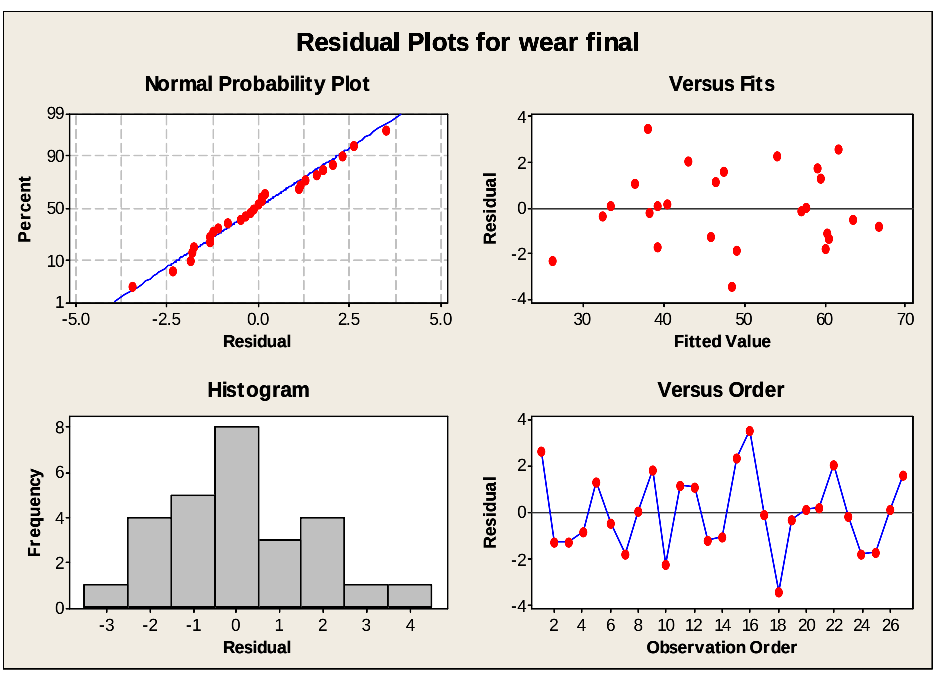


Figure 7.29 Residual plots for abrasion wear

The residual plot of wear is shown in Figure 7.29. This layout is useful to determine whether the model meets the assumptions of the analysis. The residual plots in the graph and the interpretation of each residual plot indicate below:

a. Normal probability plot indicates the data are normally distributed and the variables are influencing the response. Outliers don't exist in the data, because standardized residues are between -2 and 2.

b. Residuals versus fitted values indicate the variance is constant and a nonlinear relationship exists as well as no outliers exist in the data.

c. Histogram proves the data are not skewed and not outliers exist.

d. Residuals versus order of the data indicate that there are systematic effects in the data due to time or data collection order.

7.9 Prediction using Fuzzy logic and artificial neural network

Table 7.7 (a) Comparison of Experimental, ANN and Fuzzy Results (Training)

Exp. No.	HA/HDPE			HA/HMHDPE		
	Wear Exp.(SN ratio)	Wear ANN	Wear Fuzzy	Wear Exp.(SN ratio)	Wear ANN	Wear Fuzzy
1	47.33	47.3612	47.0529	64.43	64.5363	64.9766
3	40.72	40.7528	39.95	59.17	58.6428	59.4996
4	41.11	41.1496	42.1501	66.02	65.9214	64.9766
5	40.72	40.6222	42.1501	60.91	62.1319	59.4996
7	38.48	38.4803	39.95	58.41	58.3533	59.4996
8	36.47	36.4352	35.55	57.72	58.1936	59.4996
9	40.26	40.3101	39.95	60.91	60.4845	59.4996
11	45.67	45.2396	47.0529	47.74	46.2004	45.1
12	39.49	39.4736	39.95	37.58	38.4218	37.8996
13	42.15	42.1551	42.1501	44.58	43.6732	45.1
14	37.52	37.3864	37.7499	59.17	61.8954	59.4996
15	37.45	37.6955	37.7499	56.478	54.4488	59.4996
16	40.44	40.4374	39.95	41.4789	41.9010	37.8996
17	37.78	37.7854	37.7499	57.077	55.8612	59.4996
19	42.49	42.6641	42.1501	32.076	32.1403	30.7004
20	40.72	40.7891	39.95	33.597	33.2275	30.7004
21	37.72	37.7962	39.95	40.63	40.9233	37.8996
22	40.26	39.45	39.95	45.178	41.3135	45.1
24	34.48	34.3908	35.55	47.33	47.0262	45.1
25	38.63	39.45	37.7499	37.523	41.3135	37.8996
26	35.91	35.9051	35.55	39.209	39.0827	37.8996
Absolute average percentage error		Training 0.3771	1.95		Training 2.1578	3.11

Table 7.7 (b) Comparison of Experimental, ANN and Fuzzy Results (Testing)

Exp. No.	HAp/HDPE			HAp/HMHDPE		
	Wear Exp.(SN ratio)	Wear ANN(SN ratio)	Wear Fuzzy(SN ratio)	Wear Exp.(SN ratio)	Wear ANN(SN ratio)	Wear Fuzzy(SN ratio)
2	46.19	46.2727	47.0529	59.17	60.4922	59.4996
6	40.08	40.0572	37.7499	63.09	61.2682	64.9766
10	44.58	44.6444	44.35	23.87	24.4063	25.2234
18	37.65	37.8349	37.7499	45.036	46.0232	45.1
23	34.84	34.5592	35.55	38.061	38.5746	37.8996
27	39.19	35.9096	32.8317	49.118	49.1299	52.3004
Absolute average percentage error		0.3470	4.4542	Absolute average percentage error	1.8224	2.7104

The wear testing of the HAp-HDPE bio-composites conducted as per full factorial design approach to get the abrasion wear rate as the output. Abrasion wear rate has been predicted by using two predictive models based on fuzzy logic and ANN, have been proposed for abrasion rate prediction are validated using simulation studies. The experiments conducted as per the full factorial design layout is used for prediction purpose. In fuzzy model, full factorial desigh layout is used for developing inference engine whereas in case of ANN entire data is splited into training and testing sets. Both the studies were carried out by using MATLAB simulation environment. The prediction is done by selecting 25 % of the experiments randomly and predicting their values and found to be exact with the experimental values. The Comparison between the experimental result and the pridcted result (both Fuzzy and ANN model) for training is shown in Table 7.7(a). From the table, it can be observed that the proposed Mamdani model provides absolute average percentage error of 1.95 and 3.11 respectively, whereas ANN model provides an absolute average percentage error of 0.3771 and 2.1578 respectively. Athough it is clear from the study that the ANN model gives better result than the Mamdani fuzzy system but the main advantage of the fuzzy model lies in the fact that it does not need any training data set as required for

ANN system. As both the model shows a very minimum amount error of less than 2.5 %, hence, these proposed model can be easily implemented. Six experiments conducted with different factor combinations not included in the training set (randomly selected). The results are shown in Table 7.7 (b). It can be observed that the proposed Mamdani model provides av absolute average percentage error of 4.4542 and 2.7104 and for ANN model which is 0.3470and 1.8224 respectively.

Chapter 8

Conclusions and Future works

8.1 Conclusions

Based on the research presented in this paper the following conclusions are drawn:

- Two new bio-composite was developed with a high amount of HA upto 40 vol%. The bio-composite having 20 vol.% HAp has shown the highest mechanical characteristics with having tensile strength 18.7 MPa, Compressive strength 14.18 Mpa, Young's Modulus in tension is 543.64. Flexural and Inter Laminar Shear Strength are 19.30 Mpaand 1.07Mpa. Resieliance in the impact test was 46.81 J/m for HAp/HDPE. Where 20 vol.% HA/HMHDPE composites shows much better performance of tensile strength 28.214 Mpa, Compressive strength 15.2 Mpa, Young's Modulus in tension 1052 Mpa and 1592 Mpa for 20 vol% and 30 vol% accordingly. Flexural and Inter Laminar Shear Stress are 47.92 Mpa and 1.40 Mpa. Resilience in the impact test was 33.49 J/m and 36.91 J/m for 20 vol5% and 30 vol% composites respectively. During daily activities bones are subjected to a stress of approximately 4 Mpa whereas the tendons and ligaments experience peak stresses in the range 40-80 Mpa [45]. The mean load on a hip joint is up to three times body weight and peak load during jumping can be as high as 10 times body weight. More importantly these stresses are repetitive and fluctuating depending on the activities such as standing, sitting, jogging, stretching, and climbing. Hence the HA/HDPE composite developed may only fulfill the stress requirement in static portion of the body or in the low load region.
- The amount of material removed in two abrasion wear test of HAp-HDPE and HA/HMHDPE bio-composite increases (Figuere 7.22) with the incorporation of particulate fillers (HAp).
- Full factorial design layout makes it convenient to develop predictive models based on fuzzy logic and ANN. When data set is limited and process is not completely characterized, the rule base can be efficiently developed with less number of experiments. Further, the method provides a systematic approach for rule base development rather than completely depending on expert's reasoning.
- Two predictive models- one based on fuzzy approach and the other on ANN approach are proposed. It is demonstrated that these models well reflect the effects of various factors on the erosion loss and their predictive results are consistent with experimental observations. The maximum absolut average percentage error between experimental and fuzzy model is found to be 0.3470 & 4.4542 (HA/HDPE and HA/HMHDPE composites respectively) and the same for ANN is 1.8224 & 2.7104 (HA/HDPE and HA/HMHDPE

composites respectively). Therefore, the results obtained are satisfactory and can be used to investigate abrasion wear loss of any composites.

8.2 Scope for Future works

- In future, this study can be extended to new bio-composites using different matrix-particulate combinations and the resulting experimental findings can be likewise studied.
- Thermosetting polymers like epoxy with carbon fibre and HA may be used to develop some new bio-composites.
- Biological response can be determined by 'in vivo' and 'in vitro' test, using simulated body fluid (SBF) or in the actual implant conditions.

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