EXPERIMENTAL INVESTIGATION OF GLASS MICROBALLOON/HDPE SYNTACTIC FOAM COMPOSITE

Thesis

Submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

by

JAYAVARDHANA M. L.

DEPARTMENT OF MECHANICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY KARNATAKA,

SURATHKAL, MANGALORE – 575025

JUNE, 2018

DECLARATION

I hereby *declare* that the Research Thesis entitled **"EXPERIMENTAL INVESTIGATION OF GLASS MICROBALLOON/HDPE SYNTACTIC FOAM COMPOSITE"** which is being submitted to the **National Institute of Technology Karnataka, Surathkal** in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** in **Department of Mechanical Engineering** is a *bonafide report of the research work carried out by me*. The material contained in this Research Thesis has not been submitted to any University or Institution for the award of any degree.

Register Number : **145023ME14F07**

Name of the Research Scholar : **JAYAVARDHANA M. L.**

Signature of the Research Scholar :

Department of Mechanical Engineering

Place : **NITK, Surathkal**

Date :

CERTIFICATE

This is to *certify* that the Research Thesis entitled **“EXPERIMENTAL INVESTIGATION OF GLASS MICROBALLOON/HDPE SYNTACTIC FOAM COMPOSITE”** submitted by **Mr. JAYAVARDHANA M. L.** (**Register Number: 145023ME14F07**) as the record of the research work carried out by him, is *accepted as the Research Thesis submission* in partial fulfillment of the requirements for the award of degree of **Doctor of Philosophy.**

Research Guide

Dr. Mrityunjay Doddamani
Assistant Professor
Department of Mechanical Engineering
NITK, Surathkal

Chairman–DRPC
Date:

ACKNOWLEDGEMENT

I would like to extend my gratitude to Dr. Mrityunjay Doddamani, Assistant Professor, Mechanical Engineering, National Institute of Technology Karnataka (NITK), Surathkal for the invaluable constructive guidance and encouragement extended throughout my study. Sincere gratitude is expressed to Prof. Nikhil Gupta of New York University, USA for the encouragement and the help provided.

I would like to thank my Research Progress Assessment Committee members Dr. Ramesh M. R. and Dr. Raviraj H. M. for their valuable inputs. Useful discussions and suggestions of Dr. R. R. N. Sailaja, Dr. Keshav Prabhu, Ms. Deepthi and Mr. Puneeth are deeply appreciated.

I would like to thank Prof. S. Narendranath, Head of the Mechanical Engineering and all the members of faculty, Mechanical Engineering, NITK for their support throughout this research work.

Constant encouragement of my family to pursue higher studies has made it possible for me to reach at this stage. I wish to thank all my family members for love, help and encouragement provided. Special note of thanks to all my friends and well-wishers for their constant help, encouragement and understanding.

ABSTRACT

Polymer matrix composites inherit good specific values and reduced structural weight making them more promising in automobiles and aerospace applications. Thermoplastic polymers are moldable into different shapes, recyclable and reusable leading to wide usage in semi-structural and engineering applications. These materials are widely used in consumer products and industrial components. Reducing weight of thermoplastic components has been always a high priority in transportation, aerospace, consumer products and underwater vehicle structures. Their current and future potential are driven by processing flexibilities using variety of industrial scale manufacturing techniques and material innovations therein like in foams.

Foams are lightweight cellular materials that are widely used in applications such as packaging, thermal insulation, sound absorption, underwater vehicle structures and as the core in sandwich structures used in aircraft. Rapid production of such high quality foam components for industrial applications reduces matrix material requirement and the associated cost. The present study is focused on developing an industrial scale compression molding based processing method for glass microballoon/high density polyethylene (GMB/HDPE) syntactic foams and studying their mechanical properties to develop structure-property correlations. Although glass hollow particle filled lightweight syntactic foams with thermoset matrices have been studied in detail, studies on thermoplastic syntactic foams are scarce. Despite continued interest in developing lightweight thermoplastic syntactic foams, they have not been studied extensively with focus on volume fraction and wall thickness variations.

Matrix material used in the present investigation is high density polyethylene (HDPE) and the filler is glass microballoon (GMB), both in as received conditions. Syntactic foam (SF) developed by glass microballoons have benefits like low density, good dimensional stability, high stiffness, material saving and reduced component cost without compromising the specific properties. Blending of GMB in HDPE is carried out using a Brabender mixer with processing parameters optimized for minimal filler breakage. The optimized parameters are used for manufacturing HDPE syntactic foam lumps (brabender output) with 20, 40 and 60 volume % glass microballoon. SF lumps

are processed through compression molding route to form SF sheets that are used for mechanical characterization. In total NINE types of syntactic foams are prepared with three different GMB true particle densities (200, 270 and 350 kg/m^3) varying by 20, 40 and 60 volume % in HDPE resin. Different density particle resemble varying wall thickness of GMBs. Lower and higher density values represent thin and thick walled GMBs. Neat HDPE samples are also prepared with similar processing condition as that of foams for comparative analysis. Minimum of five replicates are tested and average values are used for analysis. Uniform distribution of GMBs is observed through micrography affirming the good quality of GMB/HDPE syntactic foam sample processed through the adopted compression molding route.

Experimental and theoretical densities of developed syntactic foams are computed. Measured density of all the syntactic foams is lower than neat HDPE resin. Weight saving potential of 10-36% is observed by using GMBs in HDPE matrix. For all particles types, GMB failure is observed to be the highest for syntactic foams containing 60 vol. % GMBs. Increasing glass microballoon content increases particle to particle interaction during processing resulting in particle breakage. Additionally, increasing wall thickness makes GMBs stronger resulting in reduced particle fracture. Particle failure forms glass debris that gets embedded in HDPE matrix. Although fractured particles do not provide reduction in density as planned, they still help in replacing more expensive HDPE resin.

Tensile test is conducted at a constant strain rate of 5 mm/min strain rate on trimmed GMB/HDPE foam samples as per ASTM D638-14. Tensile modulus is observed to be highest for the thick walled microballoon having highest filler content as compared to neat resin. Increasing filler content and the wall thickness increases modulus, effect of volume fraction being more prominent. Ultimate tensile strength is seen to be decreased by 32-66% with increasing filler content as compared to neat HDPE. The fracture strength of all the GMB/HDPE foams is 1.3-2.9 times lower than that of the neat HDPE. Neverthless, specific modulus is highest for syntactic foam with thick walled microballoon at 60 vol. % filler loading as compared to neat resin and other foams. Specific strength of GMB/HDPE foams is less compared to neat resin. Higher values of specific tensile modulus affirm the use of these syntactic foams for weight sensitive applications demanding higher modulus in molded components. Further, tensile test is carried out for lower strain rates (1.6×10^{-5}, 1.6×10^{-4} and1.6×10^{-3} s^{-1}). Highest tensile modulus is observed in foams with thin walled microballoons at highest filler loading as compared to neat HDPE at 1.6×10^{-3} s^{-1} strain rate. The effect of wall thickness on the modulus of syntactic foams with the same GMB volume fraction is greater at lower strain rates compared to higher ones. Tensile modulus is found to be relatively insensitive to GMB wall thickness variations. Ultimate tensile strength decreases with increasing filler content. Compared to neat HDPE, syntactic foams fracture at lower strain. The fracture strength of all the developed syntactic foams is 1.5-3 times lower than that of the neat HDPE. No clear trend is observed for specific tensile strength.

GMB/HDPE foams samples are subjected next to flexural test as per ASTM D790-10. Foams exhibited higher flexural modulus as compared to neat HDPE. Flexural modulus increases while strength decreases with increasing filler content. Additionally, increase in wall thickness increases the flexural modulus. Specific flexural modulus and strength of SF with 350 kg/m^3 particle density having 60 vol. % GMB and 200 kg/m^3 GMB having 60 vol. % are observed to be 147 and 8% higher compared to neat HDPE samples. Flexural properties are sensitive to volume fraction variations as compared to wall thickness variation.

Two theoretical approaches, Porfiri-Gupta and Bardella- Genna model are used to estimate tensile and flexural modulus of syntactic foams. Bardella-Genna model predicts values closer with experimental results for all GMB/HDPE foams tested under tensile (except lower strain tests) and flexural conditions. Outcome of existing literature on tensile and flexural studies is compared with the experimental results of the present work is presented in the form of property maps which helps in material selection for the material scientist/design engineer based on the suitable application.

Quasi-static compressive behavior of GMB reinforced HDPE syntactic foams are investigated next. Compression molded GMB/HDPE sheets are subjected to 0.001, 0.01 and 0.1 s^{-1} strain rates. Compressive modulus of foams is higher compared to neat HDPE. Increasing strain rates and decreasing filler content increases yield strength for all the foams investigated compared to neat HDPE. Yield strain and energy absorption of GMB/HDPE foams increases with an increasing strain rate and wall thickness. Specific compressive modulus and strength of GMB/HDPE foams are superior and are comparable to neat HDPE. GMB/HDPE foam achieved high stiffness to weight ratio making them suitable for wide variety of applications. Porfiri-Gupta model based on differential scheme predicts a good estimate of compressive modulus for all the type of GMB/HDPE foams. Property maps are exhibited to present comparative studies of quasi-static compression with existing literature.

Further, GMB/HDPE foams are characterized for viscoelastic properties by dynamic mechanical analysis. Test is ramped from 35-150°C at a rate of 5°C/min with the deformation occurring at a constant frequency of 1 Hz. With increase in temperature, storage and loss modulus decreases while tanδ increases with increase in filler loading and wall thickness. Storage modulus and loss modulus increases with increasing wall thickness and volume fraction of GMBs. Damping factor (tanδ) shows an increasing trend with increase in GMB content and wall thickness. Damping factor is less sensitive to glass microballoon content as compared to storage and loss modulus.

Structure-property correlations of all the investigated properties are presented with the help of exhaustive SEM images to understand underlying mechanisms. Finally the behavior of material is analyzed using the crystallinity measurement. Crystallinity is observed to be highest for the HDPE as compared to GMB/HDPE foams. Inclusion of GMB decreases the crystallinity signifying stiffness rise of the polymer backbone resulting in ductile to brittle behavioral change.

Developed GMB/HDPE syntactic foams achieved better physical and mechanical properties as compared to other thermoplastic foams studied in recent past as exhibited by property maps. Consumption of expensive matrix is reduced by dispersing GMBs leading to lower cost of these syntactic foams. GMB/HDPE foams developed in the present work have a weight saving potential of 36% with better

specific mechanical properties making them candidate material in weight sensitive and buoyant applications.

Keywords: *Syntactic foam; Compression molding; High density polyethylene; Glass microballoon; Theoretical modeling; Mechanical properties*; *Crystallinity*.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

ASTM	: American Society for Testing and Materials
BG	: Bardella-Genna
CM	: Compression Molding
DMA	: Dynamic Mechanical Analysis
DSC	: Differential Scanning Calorimetry
GMB	: Glass Microballoon
HDPE	: High Density Polyethylene
PMC	: Polymer Matrix Composite
PG	: Porfiri-Gupta
SEM	: Scanning Electron Microscopy
SF	: Syntactic Foam
UTS	: Ultimate Tensile Strength
WAXD	: Wide Angle X-ray Diffraction

NOMENCLATURE

ρ	: Density	kg/m^3
w	: Wall thickness	µm
η	: Radius ratio	-----
T_g	: Glass transition temperature	◦C
$Tan\delta$	: Damping factor	-----
ρ_g	: Density of glass	kg/m^3
ρ_{TPD}	: True particle density of GMBs	kg/m^3
r_o	: Outer radius of GMBs	µm
E_f	: Flexural modulus	MPa
L	: Span length	mm
m	: Slope	-----
b	: Width	mm
d	: Thickness	mm
ρ_{fM}	: Flexural stress	MPa
P	: Load	N
$\%X_c$	: % of crystallinity	%
I_c	: Crystalline phase of HDPE	-----
I_a	: Amorphous phase of HDPE	-----
d'	: Interplanar distance	nm
λ	: Wavelength	Å
θ	: X-ray incidence angle	degrees
n	: Integer (n=1)	-----
ΔH_m	: Enthalpy of fusion	J g^{-1}
ΔH_m^*	: Enthalpy of fusion per gram for 100% crystallinity of HDPE	J g^{-1}
V_{mp}	: GMB Porosity	%
ρ_t	: Theoretical density	kg/m^3

ρ_m	: Measured density	kg/m^3
E_T	: Tensile modulus	MPa
σ_y	: Yield strength	MPa
σ_{uT}	: Ultimate tensile strength	MPa
E_f	: Flexural modulus	MPa
σ_{uf}	: Ultimate flexural strength	MPa
ε_{uf}	: Strain at ultimate flexural stress	%
σ_{ff}	: Flexural fracture strength	MPa
ε_{ff}	: Flexural fracture strain	%
E_i	: Young's modulus of microballoon	MPa
v_i	: Poisson's ratio of microballoon	-----
E_m	: Young's modulus of matrix	MPa
v_m	: Poisson's ratio of matrix	-----
Φ_f	: Microballoon volume fraction	%
Φ_m	: Maximum packing factor of particles	-----
K	: Bulk modulus of syntactic foams	MPa
K_m	: Bulk modulus of matrix resin	MPa
K_i	: Bulk modulus of GMB material	MPa
G	: Shear modulus of syntactic foams	MPa
G_m	: Shear modulus of matrix resin	MPa
G_i	: Shear modulus of GMB material	MPa
E	: Elastic modulus of syntactic foam	MPa
E'	: Storage modulus	MPa
E''	: Loss modulus	MPa
T_m	: Melting temperature	◦C

1 INTRODUCTION

1.1 Composite Materials

Development of innovative materials is increasing rapidly in the field of engineering applications. Material innovations are evident as early as Stone Age. Today the development of any country is based on the amount of steel and concrete used. Revolution in industry, sports, medical, aerospace and marine applications is due to the advancement of materials. Unique properties of advanced materials help to define the area of application. Versatile application areas trigger advancement in materials which could be achieved by combining two materials of different constituents forming a composite material. Composite material is defined as material systems consisting of mixture of or combination of two or more micro constituents insoluble in each other and differing in form and or material composition (Mueller and Krobjilowski 2003).

A formal definition of composite materials given by ASM Handbook (ASTM D3878) is, macroscopic combination of two or more distinct materials, having a recognizable interface between them. In other words, a composite is one, which satisfies the following conditions (Chawla 2012):

- It is manufactured or man-made (synthetic).
- It consists of two or more physically and/or chemically distinct, suitably arranged or distributed phases with an interface separating them.
- It has characteristics that are not depicted by any of the constituents examined in isolation.

Composites are multifunctional materials having unprecedented mechanical and physical properties which can be tailored to meet the requirements of a particular application (Kutz 2015). Nevertheless, these materials offer the possibility of exciting new solutions to difficult engineering problems (Harris 1986). However the society has become more energy conscious of late. This has led to an increasing demand for lightweight yet strong and stiff structures in all walks of life. They are increasingly providing the answers (Chawla 2012). Composite materials are widely used to enhance the properties of materials to sustain higher service loads. These materials can strengthen the properties like strength, stiffness, and corrosion and wear resistance, weight reduction, fatigue life, temperature dependent behavior and thermal properties (Manoj et al. 2008). These materials provide unique combination of properties, which cannot be obtained from any of the constituent material used individually. Composite materials are widely used in aeronautics and space sector as they can be made lightweight and possess high specific properties (Sachinkumar et al. 2018, Santhosh and Hiremath 2014).

Composites are classified based on matrix and reinforcement. Matrix is a continuous phase and reinforcement is a discontinuous or dispersed phase. Interface between matrix and the reinforcement is a third phase in these materials. Based on the matrix material, composites can be further classified into Metal Matrix Composite (MMC), Ceramic Matrix Composite (CMC) and Polymer Matrix Composite (PMC). PMCs are becoming promising materials for variety of structural and automotive applications since these possess favorable combinations of mechanical properties (Benchekchou et al. 1998). Due to the difficulty in processing and cost involved, metal and ceramic matrix composites are least used compared to polymer matrix composites.

PMCs are extensively used because of their relative ease of processing, low density, desirable electrical/thermal properties and excellent chemical/corrosion resistance (Guru et al. 2015). Hence, these find applications in aerospace, structural, marine, automotive and electronics engineering. Classification of composites on the nature of reinforcement is presented in Figure 1.1 (Agarwal and Broutman 1980). PMCs comprise of a polymer (resin) matrix combined with a fibrous or particulate dispersed phase. These composites can be molded into a variety of shapes and sizes. Matrix can be either thermoplastic or thermoset resin. Thermoset and thermoplastic are the two types of polymeric resins that are being widely explored for variety of applications. Thermoset polymers are insoluble on heating and infusible after curing. This is due to the cross linking of molecules forming a strong covalent bond. Epoxies, polyesters, phenolics and polyamides are examples of thermoset polymers. Thermoplastic polymers are reusable and remoldable into different shapes on heating. Typical examples of thermoplastics include polyethylene, polystyrene, polyether-ether-ketone (PEEK) and polyphenylene sulfide (PPS). Reinforcing these polymers provides great strength and stiffness along with corrosion resistance (Benchekchou et al. 1998, Patnaik et al. 2009, Satapathy et al. 2010).

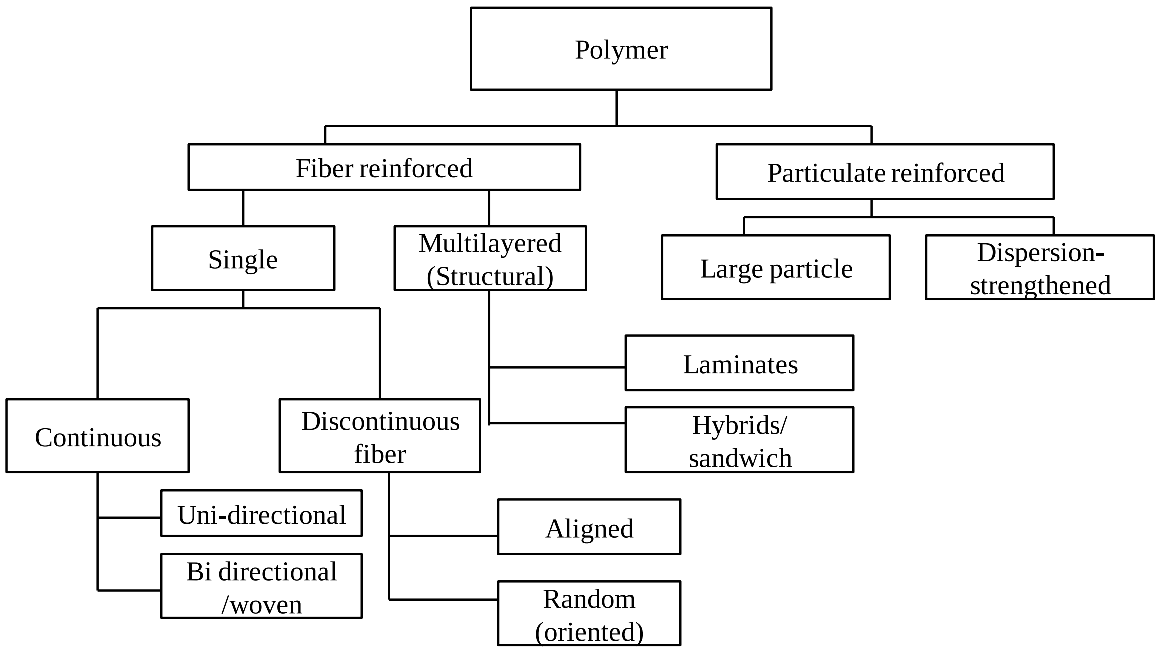


Figure 1.1 Classification of composites based on the nature of reinforcement.

PMCs often exhibit excellent specific properties owing to constituent’s lower density. Secondly, PMCs can be processed at low pressure and temperature. Degradation of the reinforcement during processing is less significant for PMCs than for composites with other matrices. These composites require relatively simpler equipments and easier fabrication route. Reducing weight of most commonly used polymers processed using conventional industrial scale machines demands development of new lightweight composites such as syntactic foams (SFs).

Syntactic foams are lightweight composites wherein hollow microballoons are dispersed in matrix resin. In the present scenario, syntactic foams (Bardella et al. 2012), a special class of structural composite have become very popular due to high specific strength and bending stiffness. Low density of these materials makes them especially suitable for use in aeronautical, space, marine and sports applications (Gupta et al. 2002). These closed cell foams find wide applications in marine structures, aerospace, automotive and thermal insulation of pipelines. In marine structures the SFs can be used as buoyant and low absorption material. Lightweight feature of SFs is beneficial in automobile sector by increasing the fuel consumption with a reduced weight. Combination of material selection, hollow particle volume fraction and hollow particle wall thickness tailors the mechanical and thermal properties of these materials. Methods have been developed to tailor the mechanical and thermal properties of syntactic foams independent of each other over a wide range, which is a significant advantage over other traditional particulate and fibrous composites (Gupta et al. 2005).

1.2 Syntactic foam composites

The term "syntactic" comes from the Greek word "syntaktikos," which means "to arrange together" and term "foams" is used because of the cellular nature of the material (John and Nair 2014). Syntactic foams are hollow particulate filled composites (Karthikeyan et al. 2001, Maharsia 2005, Wouterson et al. 2005). These foams possess lower density, high specific strength and low thermal conductivity (Gupta et al. 2005, Rugele et al. 2017, Shahapurkar et al. 2018). SFs are widely used in weight sensitive applications. Due to its light weight, high compressive strength, modulus and lower moisture absorption it makes suitable for fabricating flotation devices and submarine buoyancy systems (Grosjean et al. 2009, Hobaica and Cook 1968). The thermal insulation properties of syntactic foams are utilized in space shuttle applications by the United States and also it is used as insulation for the external fuel tank and solid rocket boosters (Gupta et al. 2013). In 1960s these materials are introduced as buoyancy aid materials, for deep sea applications. Further these materials are being used in aircraft, spacecraft and ship structures (Gupta and Woldesenbet 2002). Syntactic foam comprised of hollow microballoon and matrix resin as constituent materials. Matrix resin (thermoplastic and thermoset) is chosen based on service and the microballoon of polymer, ceramic or metal are chosen based on the target properties and availability (Gupta et al. 2013).

These foams are classified into two and three-phase structures. They are classified as closed pore/cell foams, due to the existence of enclosed porosity within the microballoons (Gupta 2007). The schematic representation of two, three and multi-phase structure of syntactic foams are presented in Figure 1.2. Two- phase structure of syntactic foams consists of microballoons and matrix. These foams are formed by embedding microballoons in matrix with negligible levels of voids in the final structure. During fabrication of syntactic foams, entrapment of air or void is inevitable in the matrix which leads to three-phase syntactic foams. Syntactic foams reinforced with fibers result in multi-phase structure. Two-phase structure has good mechanical properties and low moisture absorption as compared to the three-phase structure. Though three-phase structure syntactic foams have lower mechanical properties due to voids present in matrix, they possess low dielectric and loss coefficients compared to two phase foams (Calahorra et al. 1987, Sankaran et al. 2006).

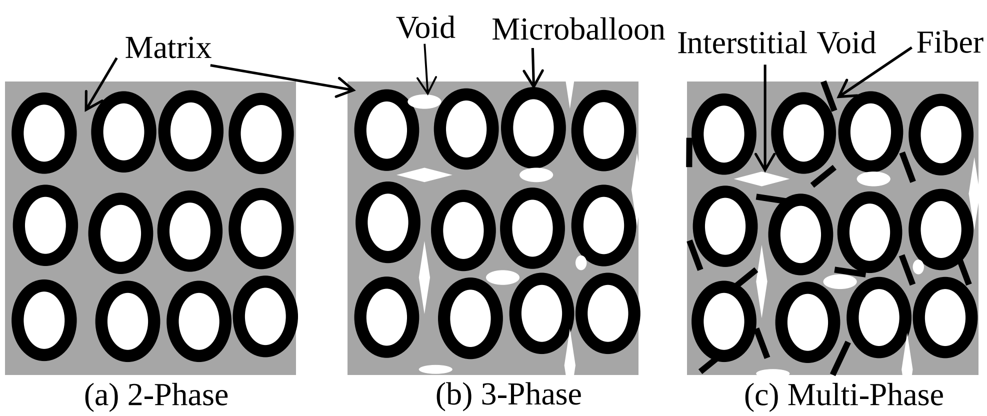


Figure 1.2 Schematic representation of two, three and multi-phased structured syntactic foams.

Interest in utilizing the advantage of low density of syntactic foams in variety of applications has made it necessary to characterize these materials for mechanical behavior. Though SFs are widely used, thrust on developing these with variety of hollow particulate fillers is overgrowing.

1.2.1 Filler/Reinforcement

Wide varieties of fillers are available to be used as reinforcements in matrix. These fillers when incorporated with matrix improve tensile and compressive strength, toughness, tribological characteristics, dimensional and thermal stability. Selection of filler material is primarily dependent on the requirements expected in the end product, the interface compatibility, shape, size and packing factor. The particles of minerals, metals, ceramics, polymers and some industrial wastes are some of the materials being used or selected as filler for polymers (Shaikh and Channiwala 2006). Particles of Alumina, silica, hollow and solid particles of glass, wood chips, fly ash and carbon black are some of the common examples of filler materials. Filler particles are selected based on the desired properties of the composite. The property of composite is dependent on the shape of the filler. Spherical particulate fillers are more popular and have higher advantage compared to the other shapes (Ferrigno et al. 1978):

- Low surface area to volume ratio
- Regularity of shape
- Control of surface properties
- High crush strength
- Closely controlled particle size
- Better rheology

Glass microballoon (GMB) is widely used because of the strength of glass and the substantial difference between the elasticities of glass and polymer (Shutov 1986). It is a free flowing powder with particle sizes of 10-200 μm and densities of 200 to 400 kg/m^3. Density of GMBs mainly depends on the wall thickness. Wall thickness increases the density of the GMB when outer particle diameter is same. These hollow microballoons are developed in the 1960s as an outgrowth from the manufacture of solid glass beads. GMBs are commercially made in several ways. The process technology and raw material sources for making glass microspheres are well established in many countries and hence glass microspheres are cheaper than polymeric ones (Shutov 1986).

GMBs are manufactured in vertical tube furnaces which are heated up by the gas (propane-butane mixture). A powder containing glass and a porofore is sprayed at the bottom of the tower. The porofore is a chemical blowing agent evolves gas at the melting point of the glass and inflates the partially fused monolithic particles. The microspheres thus formed are carried by the hot gas to the top of the tower where they are cooled. They are then treated with acid to improve their chemical resistance and raise their softening temperature and finally washed with water to remove defective microspheres (Shutov 1986). Defect free microspheres are considered and can be utilized as reinforcements in matrices. Sodium borosilicate microballoons are synthesized by mixing sodium silicate with ammonium pentaboratea followed by spray–drying to form hollow microballoons (Lee 1992).

GMBs are engineered particles with good surface finish and crushing strength. The structure of GMB is presented in Figure 1.3. GMBs have unique properties like spherical shape, lower density, controllable size, good thermal conductivity, high compression strength, dielectric property, low moisture absorption, good acoustic insulating property. These microspheres are cheaper and readily available hence it is used as filler in preparing composites with variety of thermosetting polymers. Glass microballoon polymer based thermosetting syntactic foam exhibits multifunctional properties such as low density, high specific compressive strength, thermal conductivity, low moisture absorption (Calahorra et al. 1987, Gupta and Nagorny 2006, Kim and Khamis 2001, Wouterson et al. 2005) which are suitable for the structural application of aerospace, automobile body parts , marine etc.

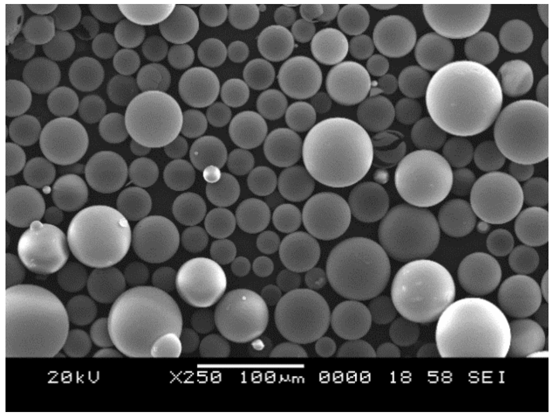


Figure 1.3 SEM of glass microballoons showing its structure.

Presently, glass microballoon/ polymer composites have significant opportunities in basic science and technology and pose significant challenges for future work in polymer composite field. Such glass microballoon filled polymer composites possess attractive mechanical, thermal, electrical properties, with better dimensional stability at lower cost. Glass microballoon reinforced thermoset foams are well explored with desirable properties (Gupta and Nagorny 2006, Swetha and Kumar 2011). Nevertheless, GMB infused thermoplastics are yet to be explored.

GMBs when used with well-established matrix materials, help in reducing the cost and either retain or improve desirable and specific mechanical properties (Scheetz and Earle 1998). The feature of inbuilt porosity in glass microballoon is of considerable significance in weight specific applications. As the fillers are of near spherical shape, the resin spread is also better. Developing newer and utilitarian thermoplastic systems using glass microballoon displaying near isotropic properties should be an interesting and challenging task.

1.2.2 Matrix

Polymers are referred to as macromolecules, which are formed by joining of repeating structural units on a large scale. The repeating structural units are monomers and are linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerisation. Polymers have desirable properties such as high ductility, ease of forming and non-corrosiveness (Srinivasan 1983).

A wide variety of such materials are available in the market for a materials designer. Polymers are generally classified as thermoplastic and thermoset. Thermoset polymers are polymeric materials that have cross link between the molecules upon heating. This cross linking process is the formation of chemical bonds between the long carbon chains (John and Nair 2014). The irreversible cross link process and Van der Waals force makes the material stronger and brittle. Thermoset polymer remains rigid on heating (Arzamasov 1989). Thermoplastic are polymeric materials that soften upon heating and harden upon cooling. On heating the Van der Waals forces acting between the molecules of thermoplastic polymers are relatively weak. Thus bond between the molecules weaken substantially and the material becomes soft and yieldable. On the other hand, during reheating, thermoset remains rigid till they are converted into char. Thermoplastic polymer process is reversible and the material can be remolded by repeated reheating and cooling without losing its properties (Arzamasov 1989).

Polyethylene, polypropylene, polystyrene, nylons, etc. are some of the thermoplastics readily available been accepted as engineering plastics. These plastics can be a substitute of metal and ceramic in structures with low mechanical properties. Plastics are used in developing high performance composites which possess advantages like high stiffness, high strength to weight ratio and increased chemical and atmospheric inertness compared to conventional materials (John and Nair 2014).

Polymer matrix composites are widely used in composite materials, because of its inherent characteristics. PMCs cost can be reduced by reinforcing plastic with the low cost filler like glass microballoons. Usage of plastic products in the day today lives has created an increased demand of plastics in India. The plastic products developed from many industries such as automotive, packaging, agriculture and infrastructure etc. are of good quality and are used in various applications. In 1997 A.D the per capita demand on plastic in India was 0.800 kgs, which is one among the lowest in Asia (Burgiel et al. 1994, Burgueño et al. 2004, Scott 2000, Shah and Rajaram 1997). Later in the year of 2000A.D the projected demand was 2.16 kg/capita (KSSPMA 1992). A boom in the consumption of plastic in India is experienced with the economic liberalization since 1991. Plastic consumption in India has more than doubled from 0.85 million tons during 1990-91 to 1.79 million tons during 1995-96. Demand for commodity plastics is growing at the rate of 15% per year.

According to the survey of All India Plastic Manufacturers Association, the total capacity to produce PE, PVC, PP and PS is 1.39 million mega tonne (MMT) against the estimated demand of 1.55 million mega tonne MMT in 1995 and increased to a value of 1.8-1.9 MMT for 1996-97. This is in concern with three major sectors as per Plastic India survey: infrastructure (power, roads, bridges, telecommunications and construction) which is 30% of the total, packaging is 25% of the total and 25% is for agriculture and water (Nanavaty 1997). In the year 2015 the polymer consumption is 13 MMT in India which is 15 times higher than 1990 and is estimated to grow up to 22 MMT by 2020 (Figure 1.4) (Shekhar 2012).

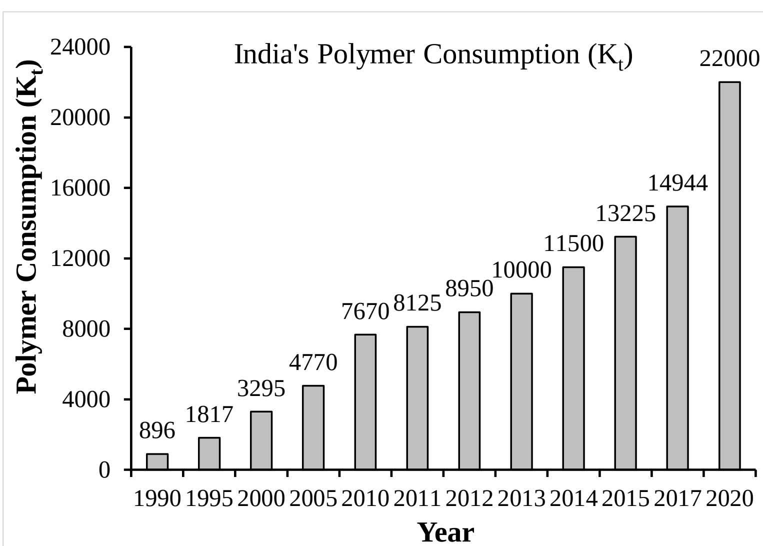


Figure 1.4 Polymer consumption in India. Note: K_t denoted Kilo tones.

With such a drastic growth prevailing in the consumption of plastic, thermoplastic syntactic foam composites with filler such as glass microballoons maybe an essential requirement to avoid issues in plastic management and cost saving problems. Further, when matrix is reinforced with such fillers, role of interface bonding between them and filler breakage issues need attention.

1.3 Processing of Syntactic foams

Numerous manufacturing routes are available for composite fabrication. Selection of a method for a material to produce particular part will depend on the material characteristics, part design and end use or application. PMCs are the fast growing composite in a worldwide market. Advantage of PMCs made the material to spread and replace over the product in automotive, marine, aerospace and structural applications. Such widespread growth in product applications mandated corresponding growth in materials technology, design approaches and fabrication processes.

In case of syntactic foam composites the processing method is to be designed properly with careful attention towards void formation, uniform dispersion and integrity of the constituent materials. Additionally, type of resin, microballoon, microballoon concentration and breakage of microballoon are found to be crucial to ease of manufacturing syntactic foams (Bunn and Mottram 1993).

The commonly used processing route for the fabrication of thermosetting polymer based reinforced syntactic foam is hand layup process as illustrated in Figure 1.5. In this method, initially, reinforcement is mixed with resin and mixed thoroughly for uniform dispersion of reinforcement in matrix. Later, this mixed proportion is added up with hollow particles and stirred thoroughly until slurry of consistent viscosity is obtained. Finally hardener is added to the resin and stirred slowly. The mixture is cast in molds and cured as per the requirements of the resin. Additional rigorous mixing of reinforcement before hollow particles helps in reducing the possibility of hollow particle breakage during processing (Arza 2012).

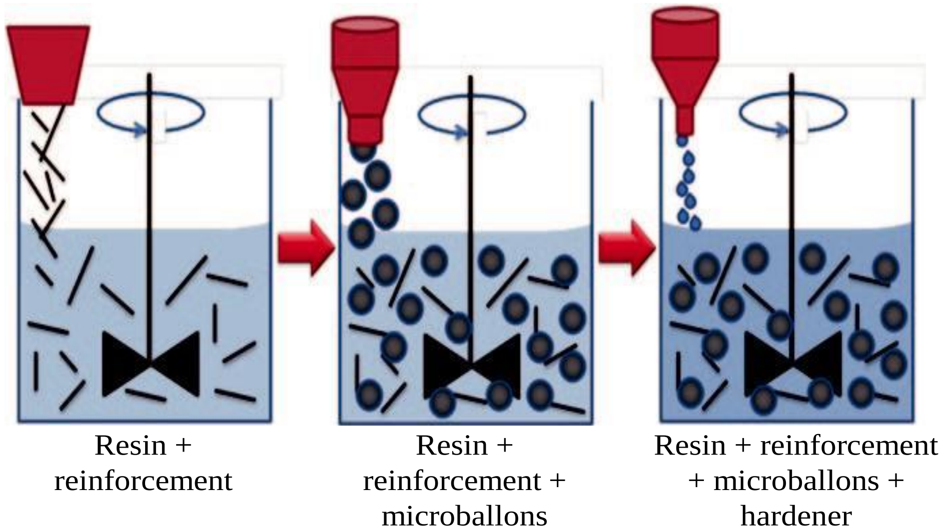


Figure 1.5 Illustration of reinforced syntactic foam fabrication method (Gupta et al. 2013).

Some of the fabrication processes utilised for processing polymer based material systems are:

- Open molding process : Hand layup, autoclave, press cure oven cure process.
- Closed molding process: Compression molding, injection molding, transfer molding and thermostamping.

The processing routes used for the thermoset and thermoplastic materials with variety of reinforcement are presented in Figure 1.6 (Reinhart 1998).

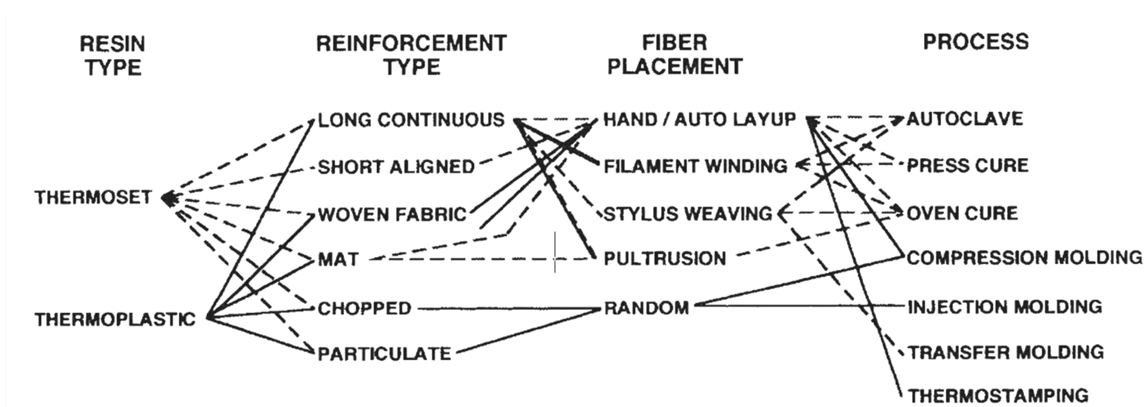


Figure 1.6 Constituents of PMCs and manufacturing options.

From the Figure 1.6 it is observed that the particulate reinforced thermoplastics are processed using injection and compression molding routes.

1.3.1 Polymer injection molding

Polymer injection molding (PIM) is one of the most widely used manufacturing methods to develop thermoplastic products. PIM consists of hopper, screw, barrel, heater and sprue. The input of the PIM is in the form of pellets. Pellets fed into the hopper enter the heated screw conveyor chamber and are pushed in to a split mold cavity. Material is filled in the spilt mold through the feeding system with sprue gates and subsequently part is removed. This process completes at a shortest time hence is used for rapid production.

The advantages of PIM are low material consumption, improved dimensional stability, shorter cycle time, lower injection pressures and clamp forces. Due to the rapid cycle time, low material cost and variety of material options, it is considered as the promising alternative technique for mass-fabrication of the polymer micro/nano engineered surface materials. The PIM products offers better thermal, acoustic insulation and mechanical properties. Low Density Poly Ethylene (LDPE) and High Density Poly Ethylene (HDPE), polymethyl methacrylate and polylactic acid (Bachmatiuk et al. 2010) are thermoplastic materials which are widely used in PIM. High precise plastic parts of various shapes and complex geometries are manufactured by PIM at low cost. Use of these resins in fabricating syntactic foams (Bunn and Mottram 1993, Gupta et al. 2004) can provide opportunities of saving weight in existing applications and also in developing new material systems.

Bharath Kumar et al. (2016) developed the cenosphere/HDPE foams using the PIM and investigated their physical and mechanical properties. Though this approach of using PIM to develop fly ash cenosphere/HDPE syntactic foams was successfully demonstrated, owing to higher particle failures during processing intended weight reduction is not achieved. Higher particle failures within the matrix resin compromised few of the mechanical properties. Further, naturally available cenospheres have numerous surface defects on exterior surface along with shell wall thickness variations and in-situ porosities within the cenosphere wall. These facts make usage of high pressurised techniques with higher shear forces due to screw in PIM not feasible in developing SFs with hollow GMBs. Finer GMB particles settle at the bottom of hopper in PIM making the process to seize. Thereby techniques like compression molding are suitable in developing lightweight GMB thermoplastic foams.

1.3.2 Compression molding

Compression molding machine is a kind of press which is oriented vertically with two molding halves (top and bottom). It is high-pressure method suitable for molding complex, high strength fiber glass reinforcements.

Compression mold consists of two components namely male and female plate. Male plate is fixed and the female plate is movable. Thermoplastics blended with filler are placed inside the mold which is preheated to a set temperature depending on the materials requirement. Pressure is applied through hydraulic means to the preheated mold to form the required shape. Advanced composite thermoplastics can also be compression molded with unidirectional tapes, woven fabrics, randomly oriented fiber mat or chopped strand. Materials such as polystyrene, polypropylene and polythene are used with this method.

Compression molding is a cost effective process when compared to the injection molding and stamping. It is the oldest and unique process for molding of plastic components that produce parts of near net shape (Chanda and Roy 2006). In compression molding of thermosets, the mold remains hot throughout the cycle. As soon as a molded part is ejected, a new charge of molding powder can be introduced. On the other hand, unlike thermosets, thermoplastics must be cooled to harden. Compression molding of HDPE composites was prepared and characterized for impact and wear performance (Chand et al. 2010). They observed considerable improvement in both the properties. Multi walled carbon nanotubes reinforced cenosphere/HDPE syntactic foam sheets at 15 MPa pressure and 160°C temperature using compression molding is investigated for mechanical properties (Divya et al. 2015). Further, Deepthi et al. (2014) developed HDPE reinforced with silicon nitride and nanoclay using compression molding at 15 MPa pressure and 130°C temperature and dealt with mechanical characterization.

Increasing market demand can be met by production of quality syntactic foam components with sufficient service life and strength, different geometries and shapes. CM is one such technique to produce syntactic foam components at low tooling cost with better strength. The present work deals with utilization of industrial scale compression molding to synthesize glass microballoon/HDPE syntactic foam composites.

1.4 Literature survey

Syntactic foams are one of the widely used composites in weight saving applications because of its lightweight characteristic. However, the extent to which these can be altered to produce a target mechanical performance such as design of SF, strongly depends on the resultant effective properties as and more importantly, on how these properties relate to its microstructure. Therefore investigating mechanical, thermal and or other relevant properties for a given microstructure and its spatial distribution plays a significant role in the design and development of SF.

A number of reviews dealing with various aspects of syntactic foams under different loading conditions have been published in recent years and are presented in tabular form herewith.

Notations used while presenting the summary of literature is as below:

$d_{\mu m}$	Particle diameter	µm
Φ_w	Filler content	wt. %
Φ_v	Filler content	vol. %

Table 1.1 Literature review on Tensile behavior.

Author	Reinforcement	Matrix	Remarks
Rizzi et al. (2000)	*Glass microballoon (K1)* ρ : 0.125 $d_{\mu m}$: 70 w : 0.58 Φ_w : 11.89	SP Ampreg Epoxy Ultra slow hardener	• Tensile modulus is observed to be higher by 35% than as compared to compression modulus. • The average tensile strength (15.63 MPa) for syntactic foams is 55% lower than the compression strength (28.39 MPa).
Wouterson et al. (2005)	*Glass microballoons* *(K15 and K46)* *Phenoset (BJO-093)* *phenolic microspheres.* ρ : 0.15, 0.46 and 0.25 $d_{\mu m}$: 70, 43.6 and 71.5 w : 0.70, 1.37 and 1.84 Φ_v : 0, 10, 20, 30, 40 and 50	Epicote 1006 epoxy resin	• For 10% volume fraction of syntactic foams, tensile strength increases by 23.48% compared to neat resin. • Tensile strength is decreased by 53.24, 46.33 and 62.04% with increase in filler content by 10-50 vol. % for K15, K46 and BJO-093 foams respectively. • K46 foams exhibits a highest modulus of 3.78 GPa compared to all other foams. • In K46 foams, as the filler content increases by 10-50 vol. % modulus increases by 34.04%. • Specific tensile strength is observed to increase for 10 % filler content which later gets reduced with the increase in filler content.

Kishore et al. (2005)	*Glass microballoon* ρ : 0.25 $d_{\mu m}$: 82 Φ_v : 25.9, 34.9, 39.8 and 43.9	Epoxy (LY-556) with HT-972 hardener.	• Decrease in microballoon content increases the tensile strength by 23.8-41.9 MPa. • Tensile modulus is increased linearly from 2-2.47 GPa with decrease in microballoon content.
Maharsia and Jerro (2007)	*Glass microballoons (K22, K32, K38 and K46)* ρ : 0.22, 0.32, 0.38 and 0.46 η : 0.9703, 0.9561, 0.9474 and 0.9356 $d_{\mu m}$: 40 *Nanoclay particles* Φ_v : 2 and 5	Epoxy (D.E.R. 332) with D.E.H 27 hardener.	• Tensile strength is increased with an increase in volume percentage of nanoclay. • Addition of 5% nanoclay particles results in strength enhancement between 6 and 22%. • Syntactic foams have increased the damage tolerance substantially due to the addition of nanoclay particles. • Increasing the density from 0.22-0.46 g/cm^3 increases the tensile strength and the modulus.
Gupta and Nagorny (2006)	*Glass microballoons* ρ : 0.22, 0.32, 0.38 and 0.46 η : 0.9703, 0.9561, 0.9474 and 0.9356 $d_{\mu m}$: 40 and 35 Φ_v : 30, 40, 50 and 60 w : 0.52, 0.88, 1.05 and 1.29	Epoxy resin (DER 332) with hardener DEH 24	• All syntactic foam shows 60-80% decrease in the tensile strength compared to neat resin. • Increase in percentage of filler from 30-60 vol. % decreases the strength by 25-60% for all types of GMB/epoxy foams. • Modulus of the foams is increased with the increase in the filler content and the density of the microballoon.

John et al. (2007)	*Glass microballoon* (K25 and K37) ρ : 0.25 and 0.37 Φ_v : 62.6 - 89.1	BACY (2,2-bis (4-cyanatophenyl) propane) with Zinc octate, nonyl phenol and co-catalyst	• As volume percentage of filler increases from 62.6-89.1 vol. % tensile strength is decreased by 81.25 and 61.05% for K37 and K25 foams respectively. • Syntactic foams with K-37 showed a higher value of tensile and specific tensile strength compared to those with K-25 except at higher volume fractions of microballoon. • Specific tensile strength is decreased by 73.68 and 42.85% for K37 and K25 foams for varying filler content 62.6-89.1 vol. %.
Mae et al. (2008)	*Microballoon (092-120)* Φ_v : 0, 20, 30, 40 and 50	Polypropylene (PP) with ethylene propylene rubber (EPR) at 30 wt. %	• Modulus and yield stress of foams are high strain rate sensitive. Relative elastic modulus increases drastically at the relative density ranged from 0.9 to 1.0. • Increase in strain rate in all the microballoon blended polypropylene drastically decreases the rupture strain.
Patankar et al. (2009)	*Glass microballoon (iM30K)* ρ : 0.66 Φ_w : 10, 20 and 30	High density polyethylene with 1wt. % Polyethylene-graft-maleic anhydride (PE-g-MAH)	• For 10-30 wt. % increase of filler the tensile strength is increased by 20.12%. • Tensile modulus is increased by 50% with an increase in filler weight percentage by 10-30%. • Addition of PE-g-MAH compatibilizer increases the tensile strength by 11.67%.

Dimchev et al. (2010)	*Glass microballoon (S22, S32, K37 and K46)* ρ : 0.22, 0.32, 0.38 and 0.46 $d_{\mu m}$: <25 to 90> Φ_v : 30, 40 and 50 *Carbon nanofibers*; Φ_v : 0.25	Epoxy resin (DER 332) with hardener DEH 24	• Tensile modulus and strength shows 10-20% and 20-50% increase for most foam compositions due to the presence of nanofibers. • Tensile modulus and strength are increased with the increase in filler content and the wall thickness of the filler.
Gupta et al. (2010)	*Glass microballoon* ρ : 0.22, 0.32, 0.37 and 0.46 Φ_v : 30, 40, 50 and 60. $d_{\mu m}$: 40 η : 0.9703, 0.9561, 0.9474 and 0.9356 w : 0.52, 0.88, 1.05 and 1.29	Vinyl ester resin and methyl ethyl ketone peroxide catalyst	• Tensile Modulus is increased with decrease in microballoon volume fraction. • The specific moduli of VE320, VE370 and VE460 type syntactic foams containing over 40 vol. % microballoons are 50-75% higher compared to neat vinyl ester resin. • Tensile modulus is 15-30% higher than the compressive modulus for the same syntactic foam type.
Colloca et al. (2012)	*Glass microballoon* ρ : 0.22 and 0.46 η : 0.9703 and 0.9356 $d_{\mu m}$: 35 and 40 Φ_v : 30 and 50 w : 0.52 and 1.29 *Carbon nanofibers*	Epoxy resin (DER 332) with hardener DEH 24	• The specific tensile modulus increases with density of the microballoon and the volume fraction of filler. • Tensile modulus is increased by 55 and 100% with an increase in density of the microballoon for 30 and 50 vol. % of filler. • Tensile strength is achieved to be highest (26.5 MPa) for CNF/epoxy foam compared to other foam.

Hu et al. (2013)	*Glass microballoon* ρ : 0.3753	107 silicon rubber with curing agent TEOS (tetraethoxysilane) and catalyst DD (dibutyltin dilaurate)	• As percentage of broken HGM increases from 0-100% the tensile strength and elongation at break % increased by 81.66 and 131.25%.
Kulkarni and Mahanwar (2014)	*Fly ash* ρ : 0.65 $d_{\mu m}$: 100 Φ_w : 0, 10, 20, 30 and 40	PP with 3% PP-g-MAH compatibilizer	• Increasing filler content, modulus increases by 33.43% and strength is decreased by 35%. • The values of yield stress (52.7%) and breaking strength (25.4%) of compatibilized PP-g-MAH/FA-based PP composites showed higher values as compared untreated FA-filled PP composites at corresponding filler content.
Singh and Siddhartha (2015)	*Cenospheres* ρ : 0.67, 0.65 and 0.64 d_{nm} : 900, 600 and 300 Φ_w : 10	Polyester resin with Methyl ethyl ketone peroxide catalyst	• Strength increases to the tune of 11% with decreasing particle size. Strength for 300 nm particle reinforced composite is observed to be 16% higher as compared to neat polyester.
Bharath Kumar et al. (2016)	*Cenospheres (CIL-150)* Φ_w : 20, 40 and 60 ρ : 0.800 2 vol. % of 3-Amino propyl tri ethoxy silane for surface	High density Polyethylene (HD50MA180)	• Failure strain over 120%, whereas the composite specimens fracture at 8-11% strain. Modulus is increased by 8.5% and 24.9 % for 20 and 60 wt. % cenospheres compared to HDPE. • Ultimate strength (19.9 MPa) is highest for neat HDPE as compared to HDPE foams. Increase in cenospheres content

	treatment		decreases the ultimate tensile strength. Surface modification of constituents results in rise in strength with increasing filler content.
Zhang et al. (2016)	*Glass Microballoon(K1)* ρ : 0.125 $d_{\mu m}$: 65 Φ_v : 0, 5, 10, 15 and 20 *w :* 0.58 η : 0.991	Epoxy Epolam 5015 and Hardener	• Tensile strength exhibits strain rate sensitivity, increase in strain rate increases the strength value. • Tensile strength is decreased rapidly with the increase in filler content at constant strain rate. • Tensile strength (90MPa) exhibits highest for 0% filler content at 0.2 s^{-1} strain rate compared to other foams.
Kang et al. (2017)	*Glass Microballoon* ρ : 0.66, $d_{\mu m}$: 18 µm Φ_w: 0-20 ; *Single-walled carbon nanotubes;* Φ_v : 1.4	Polypropylene resin HF 429	• Tensile strength is decreased with the increase in glass microballoon. • Up to 10 wt. % of HGMs addition foam shows higher tensile strength as compared to neat PP resin (35.00 ± 1.84 MPa).
Kumar et al. (2017)	*Glass microballoon (iM16K)* ρ : 0.46 *Bamboo fiber*	Polypropylene (H110MA)	• Addition of 10 wt. % glass microballoon in to the matrix decreases the tensile strength by 8% as compared to BM. • At 20 wt. % fiber the tensile strength and modulus of composite is enhanced by 14.38% (up from 42.49 to 48.60 MPa) and 65.55% (up from 0.90 to 1.49 GPa) as compared to BM.

Table 1.2 Review of Flexural studies.

Author	Reinforcement	Matrix	Remarks
Kim and Khamis (2001)	*Glass microballoon (K1)* ρ : 0.125; $d_{\mu m}$: 70, 43.6 and 71.5; w : 0.70, 1.37 and 1.84 Φ_v: 0-0.65	Epoxy 105 with slow hardener	• Specific flexural modulus is increased by 53.57 % for varying filler content from 0-0.65 vol. %. • As the volume percentage of filler increases from 0-0.65 vol. % the specific flexural strength is decreased by 70.58%.
Wouterson et al. (2005)	*Glass microballoons (K15 and K46) and Phenoset (BJO-093) phenolic microspheres* ρ : 0.15, 0.46 and 0.25 $d_{\mu m}$: 70, 43.6 and 71.5 w : 0.70, 1.37 and 1.84. Φ_v : 0, 10, 20, 30, 40 and 50	Epoxy resin (Epicote 1006)	• Flexural strength of K15, K46 and BJO-093 foams is decreased by 27.98-71.36, 32.17-56.76 and 23.07-65.37 % for varying filler content 10-50 vol. % in comparison to neat resin. • Increase in volume percentage of filler by 10-50 vol. % reduces the flexural strength by 60.23, 36.25 and 54.98 % for K15, K46 and BJO-093 foams. Specific strength is decreased with the increase in filler content.
Kishore et al. (2005)	*Glass microballoon* ρ : 0.25; $d_{\mu m}$: 75-90 Φ_v: 38.5, 50.2, 54.5 and 57.7	Epoxy (LY-556) with HT-972 hardener	• Strength increases from 3.87 to 5.79 MPa decreases the glass microballoons content by 57.7 to 38.5 vol. %.
Maharsia et al. (2006)	*Glass microballoons (K22, K32, K38 and K46)* ρ : 0.22, 0.32, 0.38 and 0.46	Epoxy (D.E.R. 332) with D.E.H 27 hardener	• Addition of 2% nanoclay particles resulted overall reduction in flexural strength of the syntactic foams to the tune of 11%. • Addition of 5% nanoclay particles has resulted in an increase

	η : 0.9703, 0.9561, 0.9474 and 0.9356 $d_{\mu m}$: 40 *Rubber particles* $d_{\mu m}$: 40 and 75 *Nanoclay particles* Φ_v : 2 and 5		in strength of low density syntactic foams by around 22%. However a reduction in strength is observed in syntactic foams. • Flexural stiffness and modulus of foams are observed to increase by 7% with decrease in η. With decrease in rubber particle diameter, strength increases by 16%.
John et al. (2007)	*Glass microballoons* (K25 and K37) ρ : 0.25 and 0.37 Φ_v : 62.6-89.1	BACY (2,2-bis (4cyanatophenyl) propane) with Zinc octate, nonyl phenol and co-catalyst	• As volume percentage of filler increases from 62.6-89.1 vol. % the tensile strength decreased by 78.12 and 80 % for K37 foams and for K25 foams. • Specific flexural strength is decreased by 68.75 and 40% for K37 and K25 foams for varying filler content 62.6-89.1 vol. %.
Gupta et al. (2008)	*Glass microballoons (S22, S32, S37, K46)* ρ : 0.22, 0.32, 0.37 and 0.46 Φ_v : 30, 40, 50 and 60 $d_{\mu m}$: 35 and 40 η : 0.9703, 0.9561, 0.9457 and 0.9356	Epoxy DER332 with DEH24 Hardener	• In volume fraction based functionally graded syntactic foams (FGSFs), flexural modulus and strength is decreased by 39.5 and 34.18% with the reduction in radius ratio. • The radius ratio type FGSFs shows that increase in microballoon volume fraction decreases the strength and modulus by 52 and 13% respectively.

Ferreira et al. (2010)	*Glass microballoon (K20)* ρ : 0.125 Φ_v : 0, 10, 19, 26, 33, 39, 43 and 50 *Glass and Carbon fiber of 3mm length*	Epoxy 520 with hardener 523	• For filler content of 10 and 43% the addition of glass fiber shows a slight improvement in flexural stiffness whereas the addition of carbon fiber shows an improvement in stiffness by 40%. • The specific stiffness obtained for 50% microspheres is about 17% higher than that for 10% filler content.
Tagliavia et al. (2010)	*Glass microballoons* ρ : 0.22 and 0.46 Φ_v : 30 and 60	Vinyl ester and methyl ethyl ketone peroxide (MEKP) initiator	• Flexural modulus of water exposed vinyl ester is 3.46 and 3.61 GPa for DIW and SW environments, higher as compared to 3.21 GPa for virgin resin. • The flexural strength is decreased from 104 MPa to 88 and 83 MPa for neat resin at Deionized water and salt water (SW) environment. • For a set 30 vol. % of filler, flexural strength increases as wall thickness of particles is increased in DIW and SW environments. • Moisture absorption generally increases the flexural strength of exposed syntactic foams and this effect is more evident for SW environments and thick hollow particles. • As particle volume fraction increases, virgin specimens exhibit an increase or a decrease in the Young’s modulus

			depending on the particle wall thickness. • Moisture exposed syntactic foams exhibit a Young's modulus reduction that can be as large as 35% and 30% for DIW and SW environments.
Das and Satapathy (2011)	*Cenospheres (CS-300)* ρ : 0.45-0.80 Φ_w : 0, 5, 10, 15 and 20.	Polypropylene Homopolymer (REPOL H110MA)	• Flexural modulus is increased by 38.7% with the increase of cenospheres content from 0-20 wt. %. • Flexural strength is decreased by 8.9% with the increase of cenospheres content from 0-20 wt. %.
Tagliavia et al. (2012)	*Glass microballoons* ρ : 0.22, 0.32, 0.37 and 0.46 Φ_v : 30, 40, 50 and 60	Vinyl ester and methyl ethyl ketone peroxide (MEKP) initiator	• Flexural modulus is increased by 19.44% with the increase in wall thickness. Additionally flexural modulus is reduced by 18.96% for a varying filler content 30-60 vol. %. • Specific flexural modulus is increased by 26.31-34.48% compared to neat resin for varying filler content and wall thickness. • Flexural strength of neat resin is highest compare to GMB/vinyl ester based foams. • Flexural strength of foams is decreased with the increase in filler content due to the presence of brittle material.

Wang et al. (2014)	*Glass microballoon (K25)* ρ : 0.250 $d_{\mu m}$: 55 Φ_w : 15 *Glass fiber (HP3540) of 3 mm length.* Φ_w : 0, 0.5 and 1.5	Epoxy resin (E-51) with hardener polyamide 651	• Fiber weight ratio increases from 0-1.5 wt. % increase in strength by 25% and modulus by 16.6%. • Flexural modulus increases with increase in layers of fiber glass mesh excepting that the mesh is placed at the middle of specimens. • The flexural strength and modulus increased further by 2.5 and 2 times in addition of two-layer fiber glass mesh to the glass fiber reinforced syntactic foams. • The strength of the foams is increased due to the increase in the number of fiber glass mesh layers, unless the fiber glass mesh is far away from the stress surface.
Kulkarni and Mahanwar (2014)	*Fly ash* ρ : 0.65 $d_{\mu m}$: 100 Φ_w : 0, 10, 20, 30 and 40	PP with 3% PP-g-MAH compatibilizer	• The flexural strength values of the compatibilized PP/PP-g-MAH/FA composites showed comparable performance with that of PP up to 40% and followed by gradual reduction to 16.8% at higher filler contents.
Singh and Siddhartha (2015)	*Cenospheres* ρ : 0.67, 0.65 and 0.64 d_{nm} : 300, 600 and 900 Φ_w : 10	Unsaturated polyester resin with methyl ethyl-ketone peroxide hardener	• Flexural strength of polyester composites gradually increases (10-25%) with decrease in the practical size. • Composite with particle size of 300 nm shows the highest flexural strength (25%) among all the studied samples.

Bharath Kumar et al. (2016)	*Cenospheres (CIL-150)* ρ : 0.800 Φ_w : 20, 40 and 60 2 vol. % of 3-Amino propyl tri ethoxy silane for surface treatment	High density Polyethylene (HD50MA180) mixed with Dibutyl maleate (DBM)	• Flexural modulus and strength are found to be the highest for specimens blended by brabender mixing before injection molding. • Flexural modulus (660MPa) and strength (21MPa) achieved to be highest for 60 wt. % cenospheres processed by brabender mixing. Above values are 70 and 41% higher than the corresponding values for the HDPE resin.
Kumar et al. (2017)	*Glass microballoon (iM16K)* ρ : 0.46 *Bamboo fiber (BM)*	Polypropylene (H110MA)	• Glass microballoon content increases the flexural strength by 8.5% (up from 42.10 to 45.70 MPa) compared to BM and 16.94% (up from 39.08 to 45.70 MPa) with respect to PP. • Addition of 10 wt. % of glass microballoon modulus is increased by 17.6% (up from 1.30 to 1.54 GPa) and 25.05% (up from 1.23 to 1.54 GPa) as compared to BM and PP respectively.
Ozkutlu et al. (2018)	*Glass microballoons (K37 and iM30K)* ρ : 0.12, 0.37 and 0.60 $d_{\mu m}$: 18, 45 and 70 Φ_w : 5, 10 and 15	Poly methyl meth acrylate (PMMA)	• The flexural strength is observed to be enhanced with increasing HGM density. • The flexural modulus of matrix PMMA is improved with GMB addition. • Flexural strength is increased by 12% for 15% PMMA coated HD-HGM compared to that of uncoated HD-HGM.

Table 1.3 Review on Quasi- static compression.

Author	Reinforcement	Matrix	Remarks
Gupta et al. (1999)	*Glass microballoon* ρ : 0.25; Φ_w : 35; $d_{\mu m}$: 10-100 *E-glass fibers*: 6 mm length Φ_w : 9.7	Epoxy Araldite LY5052 with HY5052 Hardener	• Compressive strength of unreinforced system is higher by 20.86 MPa as compared to the reinforced system. • The void content in reinforced foam is 11.1% as compared to 8.4% in unreinforced foam.
Gupta et al. (2005)	*Glass microballoons (S22, S32, S38 and K46)* ρ : 0.22, 0.32, 0.38 and 0.46 Φ_v : 63 η : 0.922, 0.907, 0.888 and 0.863 *Rubber particles* ρ : 1.12-1.15; Φ_v : 2	Epoxy DER332 with DEH24 Hardener	• Compressive modulus decreases by 50%, whereas a reduction of approximately 10% is observed in the compressive strength due to the incorporation of rubber particles by 0.02 vol. %. • Compressive toughness and damage tolerance of these high-strength foams is increased by 11%. • The effect of microballoon η is found to be similar in hybrid and syntactic foams. Decrease in η, corresponds to increase in strength.
Wouterson et al. (2005)	*Glass microballoons (K15, K46)* ρ : 0.25, 0.15 and 0.46 Φ_v : 0, 10, 20, 30, 40 and 50	Epoxy Epicote 1006	• K46 microspheres (10, 20 and 30%) exhibit higher compressive yield strengths (84.61, 80.64 and 76.63 MPa) and modulus (0.95, 1.14 and 1.14 GPa) compared to K15 and phenolic microspheres. • Strength and modulus decreases by 10-70% and 8-50% with increasing filler content (0-50 vol. %).

Saha et al. (2008)	*Carbon nanofibers* ρ : 1.95; d_{nm} : 0.2 TiO_2 ρ : 3.95–4.2; d_{nm} : 0.030 *Nanoclay (Montmorillonite)* ρ : 3–3.7; Φ_w : 1	Polyurethane Foam (PUR)	• Addition of 1 wt. % of CNFs into the PUR foam increases its compressive modulus and strength by 40% and 57% respectively as compared to neat resin. • The compressive modulus and strength of PUR/Clay and PUR/TiO2 system are 20%, 38% and 12%, 16% higher as compared to neat resin.
Gupta et al. (2010)	*Glass microballoons* ρ : 0.22, 0.32, 0.37 and 0.46 Φ_v : 30, 40, 50 and 60 η : 0.970, 0.956, 0.947 and 0.936	Vinyl ester with methyl ethyl ketone peroxide Hardener	• Compressive modulus of syntactic foams increases with decreasing η. The specific moduli for composites are found to be 10-47% higher than the neat resin tested for 30, 40, 50 and 60 vol. %. The compressive strength increases by 7-11% with increase in filler content as compared to neat resin.
Shunmugasamy et al. (2010)	*Glass microballoons* *(S22 and K46)* ρ : 0.22 and 0.46 Φ_v : 30, 60 $d_{\mu m}$: 35 and 40 w : 0.521 and 1.289	Vinyl ester with methyl ethyl ketone peroxide	• In quasi-static compression, the strength is decreased by 45.09 % with an increase in filler content from 30-60 vol. %. • Compressive strength is increased with the increase in wall thickness and strain rate. • Thick walled microballoon with higher filler loading shows modulus 16.5% higher as compared to lower filler loading.
Swetha and Kumar (2011)	*Glass microballoons* *(K15, S22 and K46)* ρ : 0.15, 0.22 and 0.46	Epoxy (Araldite GY257) resin with Aradur (HY951)	• Increase in filler content from 0-60 vol. %, the strength value decreases from 105 to 25.9 MPa, 105 to 25 MPa and from 105 to 51 MPa for K15, S22 and K46 foams respectively.

	$d_{\mu m}$: 60, 35 and 40 Φ_v : 0, 10, 20, 30, 40, 50 and 60 w : 0.60, 0.52 and 1.29 *η: 0.98, 0.9 and 0.94*	curing agent	• Energy absorption capacity of the foams is higher compared to neat resin. Increase in the microballoon content increases the energy absorption capacity of the foams whereas strength is decreased. • Modulus is decreased with an increase in volume fraction of filler, whereas it increases with microballoon wall thickness.
Luong et al. (2013)	*PVC foams (HP60, HP100, HP 200, and HP250)* ρ : 0.60, 1, 2 and 2.5		• Compressive strength increases with strain rate and foam. • The peak and plateau strength are dependent on the compressive strain rates.
Poveda and Gupta (2013)	*Glass microballoons* ρ : 0.22 and 0.46 Φ_v : 30 and 50 w : 0.52 and 1.29 $d_{\mu m}$: 35 and 40 *Carbon Nanofibers(CNF)* Φ_w : 1	Epoxy DER332 with DEH24 Hardener	• CNF/epoxy composites show higher modulus in wet condition than in dry condition. At quasi static compression the compression strength of all foams is decreased by 25-35% due to the moisture exposure compared to dry specimens. • Moisture exposure does not affect the quasi-static compressive modulus of CNF/syntactic foams but decreased the strength by about 30%. • High strain rate strength is found to be 1.3 to 2.2 times higher for both wet and dry syntactic foams depending on thin and thick walled glass microballoons and volume fraction (30-50%).

Huang and Li (2015)	*Glass microballoon (S60)* ρ : 0.6 $d_{\mu m}$: 10-60 Φ_v : 10, 20, 30 and 40 w : 2	Epoxy Epicote 1006	• Young's modulus is increased by 13.63% with the increase in microballoon volume fraction from 10-40 vol. %. • Predicted young's modulus is 8.31-10.46% higher compared to measured values. • Failure mode of syntactic foams in macroscopic scale is significantly influenced by the microballoon volume fraction.
Singh and Siddhartha (2015)	*Cenospheres* ρ : 0.67, 0.65 and 0.64 Φ_w: 10; d_{nm} : 900, 600 and 300	Polyester resin with methylethyl-ketone peroxide Hardener	• Composite B300 shows the highest flexural strength (244%) compared to B900 (133%) and B600 (177%) composites.
Bharath Kumar et al. (2016)	*Cenospheres (CIL-150)* ρ : 0.800 Φ_w : 20, 40 and 60	High density Polyethylene (HDPE) (HD50MA180)	• At all strain rates, the yield strength of neat HDPE is less compared to cenospheres/HDPE foam composites. • Modulus and yield strength values of HDPE and its foams increases with strain rates in the quasi-static strain rate regime.
Zhang et al. (2016)	*Glass microballoon (K1)* ρ : 0.125 $d_{\mu m}$: 65 Φ_v : 0, 5, 10, 15 and 20 *w : 0.58* η : 0.991	Epoxy Epolam 5015 and Hardener	• Compressive strength decreases with the increase in filler content and modulus increases with strain rate. • At quasi-static compression, as filler content increases from 5-20 vol. % compression modulus decreases by 12%. • Varying filler content from 0-50 vol. % decreases the compression strength by 44.44% for constant quasi-static strain rate.

Ren et al. (2017)	*Glass microballoons* *(K46, S60HS, iM16K and iM30K)* ρ : 0.46 and 0.60 Φ_w : 45 w : 1.46, 1.28, 1.34 and 1.20. η : 0.936, 0.914, 0.933 and 0.907	*Borosilicate Glass* with Tert-butyl alcohol	• Foam samples sintered at 700°C exhibited higher specific compressive strength as compared to the ones sintered at 650°C and 750°C. • Compressive strength achieved to be highest for all foam samples sintered at 750°C. • Increase in sintered temperature from 600-750 °C increases the modulus by 0.231-1.655 GPa for all syntactic foams. • Composite composed of the iM30K HGMs with small mean particle size exhibited high compressive strength of 25.04 MPa and Young's modulus of 1.66 GPa, respectively.
Zhang et al. (2018)	*Glass cenospheres* ρ : 0.38 Φ_v : 63 w : 1.05	Aluminium alloy 5A03	• Increase in strain rate, peak strength and plateau strength is increased by 43.3 and 38% respectively. • In quasi-static compression, the syntactic foam exhibited 110.5 MPa in peak strength with a stress plateau region about 90.6 MPa. • Densification strain is observed to be 15.87% higher for lower strain rate 0.001.

Table 1.4 Review on Dynamic mechanical analysis.

Author	Reinforcement	Matrix	Remarks
Sankaran et al. (2006)	*Glass microballoon* ρ : 0.45 Φ_v : 62.12, 68.33 and 71.70	DGEBA Epoxy with cycloaliphatic amine and aromatic amine Hardeners	• Modulus decreases with temperature rise which is much higher in neat resins than the corresponding foams. • T_g of syntactic foam is 1.7-24.9% higher over the neat resin. • Cycloaliphatic amine based syntactic foam has highest Tan δ at room temperature.
Tagliavia et al. (2009)	*Glass microballoon (K20)* ρ : 0.22, 0.32, 0.37 and 0.46 Φ_v : 30, 40, 50 and 60 $d_{\mu m}$: 35 and 40 η : 0.970, 0.956, 0.947 and 0.936	Vinyl ester resin with Methyl ethyl ketone peroxide catalyst	• Storage modulus increases with GMB wall thickness. • Storage modulus of thin walled GMB decreases with increase in filler content, while opposite trend is observed for thick-walled GMB.
Lefebvre et al. (2009)	*Glass microballoon (S38)* ρ : 0.38	Epoxy, Polypropylene and Polyurethane resin	• Storage modulus for Epoxy, Polypropylene and Polyurethane foam decreases by 6 and 12%, 10 and 36%, 67 and 51% respectively for 2,000 and 10,000 h of aging. • In Epoxy, Polypropylene and Polyurethane foam temperature for maximum Tanδ changed from 157 to 155 and 163°C, 36 to -34 and -30°C and 30 to 18 and 23°C. • Aging effect in seawater is exhibited at 40°C and 300 bar.

John et al. (2010)	*Glass microballoon (K37)* ρ : 0.37 Φ_v : 70 *Nano clay* Φ_v : 2 and 4	BACY with Zincoctate Nonyl phenol catalyst	• Glass transition temperature is decreased with the addition of 4 vol. % nanoclay. • Nanoclay addition increases storage modulus by 10%. • Storage modulus is decreased by 90% with temperature increase in the range of 100-350°C.
Capela et al. (2010)	*Glass microballoon (K20)* Φ_w : 2, 6 ,13 $d_{\mu m}$: >55 *Glass fiber* *E 3313 average length of 3 mm.* Φ_w: 1 and 3	Epoxy 520 with Hardener 523	• Storage modulus decreases by 44% at 25°C for 13 wt. % GMB as compared to neat resin. • Addition of 3 wt. % of glass fiber and 13 wt. % of GMB increases the storage modulus by 30% with respect to plain foams. • Tanδ reduced by 41% at 13 wt. % GMB and 3 wt. % glass fibers. • Addition of fiber reinforcements increases the loss modulus. Loss modulus increases only marginally till reaching the maximum temperature use (T_{max}) after which increases sharply with temperature.
Ferreira et al. (2011)	*Glass microballoon (K20)* Φ_w : 2, 6, 13 and 17 $d_{\mu m}$: >55 *Glass fiber E 3313 average*	Epoxy 520 with Hardener 523	• Storage modulus of syntactic foams is 56% lower as compared to neat resin at 25°C. • Storage modulus is increased by 39 and 28% at 3 and 2 wt. % of glass and carbon fibers in 13 wt. % GMB-reinforced syntactic

	length of 3 mm. Φ_w : 1 and 3 *Carbon fiber* *T300 average length of 3 mm.* Φ_w : 1 and 2		foam in comparison to the plain foam at 25°C. • Loss modulus decreased by 35% for foams with 17% of filler when compared with 2% filled foams.
Das and Satapathy (2011)	*Cenospheres (CS-300)* ρ : 0.45-0.80 Φ_w : 0, 5, 10, 15 and 20.	Polypropylene Homopolymer (REPOL H110MA)	• Enhancement in the energy dissipation ability of the composite with 10 wt. % of cenospheres and an increase in the storage modulus up to 30% in the composites relative to the soft PP-phase. • At lower temperatures (-25 to 0°C) the storage modulus is relatively higher with increasing cenospheres content up to 10 wt. %.
Shunmugasamy et al. (2013)	*Glass microballoons (S22, S32 and K46)* ρ : 0.22, 0.32 and 0.46 Φ_v : 30, 40, 50 and 60 η : 0.970, 0.956 and 0.9363	Vinyl ester resin with Methyl ethyl ketone peroxide Hardener	• After T_g, storage modulus for neat resin is 76–96 % lower as compared to syntactic foam. • Increase in filler content by 30-60 vol. % decreases the loss modulus and T_g by 28-74% and 14-66% respectively.
Poveda et al. (2014)	*Glass microballoons* ρ : 0.22 and 0.46 $d_{\mu m}$: 35 and 40	Epoxy DER 332 with Hardener DEH 24	• In CNF/epoxy composites, as CNF content increases the storage and loss modulus is increased (14.6 and 22.6%) as compared to neat resin at room temperature.

	Φ_v : 15 and 30 *Carbon nanofibers* Φ_w : 1, 2, 5 and 10		• At room temperature loss modulus of CNF/syntactic foams is increased by 25.3% compared to neat epoxy. • A glass transition temperature of CNF/syntactic foams is increased by 27.1 and 25% compared to neat resin.
Ghamsari et al. (2015)	*Glass microballoons (S38)* ρ : 0.38 $d_{\mu m}$: 40 Φ_v : 30 *Sisal fibers* Φ_v : 1, 2.5 and 3.5	Epoxy DER 332 with Hardener DEH 24	• Increasing sisal fiber loading in syntactic foam decreases the T_g. • Storage modulus and loss modulus is increased with the increase in volume fraction of sisal fiber in syntactic foams. • Tan δ is decreased by 32.61-35.19% for varying sisal fiber content 1-3.5% as compared to plain foam.
Zeltmann et al. (2017)	*Cenospheres (CIL-150)* ρ : 0.800 Φ_w : 20 and 40	High density Polyethylene (HD50MA180)	• Addition of cenospheres is observed to be significant in improving storage modulus at all temperatures. • The loss modulus of HDPE foams is greater than the neat resin at all temperatures. • Damping increases with increasing temperature.

From the existing literature, it is very clear that engineered glass microballoons have not been exploited well to synthesize and develop thermoplastic based syntactic foams using industrial scale compression molding technique. Hence, present work deals with the development and characterization of GMB/HDPE syntactic foam composites.

1.5 Objectives and Scope of the present work

From the foregoing literature survey, it is clear that the research reports on development of GMB/HDPE syntactic foam composites using compression molding technique is not available. Development of a low cost glass microballoon filled HDPE is proposed in the present investigation. The perusal of literature review on syntactic foams prompted a thorough and systematic study on these composites by performing experimental characterization for physical and mechanical behavior. Thereby the work undertaken pursues the following objectives:

1. Synthesize GMBs (same outside diameter and varying wall thickness) filled high density polyethylene (HDPE) using brabender mixing with as received constituents and develop through compression molding technique.
2. Optimize the blending parameters based on the experimental density estimations and filler breakage.
3. Investigate the effect of GMB volume fraction and wall thickness on tensile (different strain rate), flexural, quasi-static compression (different strain rate) and dynamic mechanical analysis.
4. Comparison of experimental results with theoretical models (Porfiri-Gupta and Bardella-Genna) for modulus of selected properties. Existing literature outcome comparison with experimental results for tensile, flexural and quasi-static compression in the form of property maps.
5. Perform micrography of as cast and fractured samples for structure-property correlations and to study the effect of crystallinity on neat HDPE and GMB/HDPE syntactic foams.

In thermoplastic syntactic foams, the materials process under controlled condition provides high quality foam (Bharath Kumar et al. 2016). However processing of materials with any manufacturing technique may not give the similar quality; thereby the effect of such manufacturing environment needs to be studied and is the focus of present work. Increasing market demands can be met by production of components with low cycle time, sufficient service life and strength, complex geometries and large components. Compression molding is one such technique to produce large components at low tooling cost with high strength. The present work deals with utilization of compression molding, with optimized temperature and pressure to synthesize glass microballoon/HDPE syntactic foam composites.

Scope of the present work includes, compression molding of glass microballoon reinforced HDPE syntactic foam composites with glass microballoon varying as 20, 40 and 60% by volume and wall thickness by 0.716, 0.925 and 1.080 μm. Blending parameters are optimized to get quality samples, this work being an attempt of using industrial scale compression molding machine to fabricate eco-friendly and lightweight syntactic foam composites. Optimization is carried out based on the density estimation of the prepared samples. Based on the optimized screw speed, glass microballoon/HDPE samples are fabricated using brabender mixing, prior to loading the blend in compression molding machine. Such cast samples are tested under tensile and flexural conditions to investigate the effect of glass microballoon loading, glass microballoon breakage and wall thickness of the glass microballoon. Theoretical models are used to estimate the effectiveness of glass microballoon in reinforcing syntactic foams.

Further glass microballoon/HDPE samples are tested for quasi-static compressive response and dynamic mechanical analysis. Finally, crystallinity effect on the neat resin and glass microballoon/HDPE foams is analyzed.

1.6 Outline of the thesis

The systematic study conducted with respect to above objectives is presented in the thesis. A brief skeletal structure of the thesis is detailed as below.

- Chapter 1 aims at providing necessary details of the research in syntactic foam composites along with an exhaustive literature survey followed by objective and scope of the work.
- Chapter 2 focuses on the constituents used for thermoplastic syntactic foam composites, processing route adopted and testing methodology.
- Chapter 3 presents the performance evaluation of glass microballoon/HDPE syntactic foam composites prepared and tested as mentioned in Chapter 2. The results of the tests conducted on these samples are presented here. Further, the

results of the experimental investigation of tensile, flexural and quasi-static compressive behavior are compared with theoretical models.

- Chapter 4 highlights the significant conclusions drawn from the results presented earlier.

2 MATERIALS AND METHODS

2.1 Constituents

In the present work, glass microballoons are used as filler and HDPE matrix is utilized to prepare lightweight thermoplastic syntactic foam composite. Details about these constituents are dealt with in the section to follow.

2.1.1 Glass microballoon

Glass microballoon (GMB) of SID200, SID270 and SID350 grades, supplied by Trelleborg Offshore, USA, are used as hollow fillers (Figure 2.1a). GMBs are used in as received condition. Table 2.1 presents the basic properties of three different types of GMBs used in this work. These particles differ in density due to variation in wall thickness for nearly the same mean outer diameter (Table 2.1). The average diameters of GMBs are noted to be 53, 50 and 45 μm respectively for SID 200, SID 270 and SID 350 grades, which are in a close range, eliminating particle size as a study parameter. The radius ratio for the GMBs is computed by assuming uniform fully dense walls using equation as outlined in Ref. Shunmugasamy et al. (2014) and is given by,

$$\eta = (1 - \frac{\rho_{TPD}}{\rho_g})^{\frac{1}{3}} \tag{2.1}$$

where, ρ_g is taken as 2540 kg/m^3 (Tagliavia et al. 2010). The wall thickness of the GMBs is estimated using (Gupta et al. 2008),

$$w = r_o\,(1\text{-}\eta) \tag{2.2}$$

where, w varies between 0.716 - 1.080 μm for the GMBs utilized in the present work.

Table 2.1 Basic properties of glass microballoon*.

Microballoon Type	Collapse Pressure[a] (psi)	Theoretical thermal conductivity (K/mK)	Average microballoon size (μm)	True particle density (kg/m^3)	Wall thickness [b] (μm)	Radius ratio [b] (η)
SID200	1000	0.08	53	200	0.716	0.973
SID270	5000	0.10	50	270	0.925	0.963
SID350	6500	0.12	45	350	1.080	0.952

[*]As specified by supplier
[a]Isostatic collapse pressure (80% survival) - (ASTM D3102-78)
[b] Calculated value

2.1.2 HDPE

HDPE of grade 180M50 (melt flow index 20 g/10 min) procured from Indian Oil Corporation Ltd., Mumbai, India, is used as the matrix material. The resin is in granular form (3mm diameter) having molecular weight of 97500 g/mol. Table 2.2 presents the details about the matrix used. HDPE (Figure 2.1b) is used in as received condition.

Table 2.2 Basic properties of HDPE grade 180M50*.

Properties	Test Method	Value	Unit
Melt flow index	ASTM D1238	20	g/10 min
Density @ 23°C	ASTM D1505	950	kg/m^3
Tensile yield strength	ASTM D638	22	MPa
Elongation at yield	ASTM D638	12	%
Flexural Modulus	ASTM D790	750	MPa
Hardness	ASTM D2240	55	shore D
Vicat Softening Point	ASTM D1525	124	°C

* As supplied by Indian Oil Corporation Ltd., Mumbai, India.

(a) (b)

Figure 2.1 (a) Glass microballoons and (b) HDPE matrix used in the present work.

2.2 Sample preparation

Figure 2.2a presents the material flow and the test plan is presented wherein block diagram of the methodology adopted for preparing GMB/HDPE syntactic foams is depicted by Figure 2.2b. A Brabender (Plasticoder, Western company Keltron CMEI, MODEL-16CME SPL) as shown in Figure 2.3a is used for preparing GMB/HDPE blends. The blend is then compression molded to form sheets. Specifications of the brabender and compression molding machine are presented in Table 2.3. The cast specimens are named according to the convention HYYY-ZZ, where H denotes the HDPE matrix, YYY and ZZ are the true particle density in kg/m^3 and GMB volume %, respectively. Nine types of syntactic foams having three types of GMBs with filler loadings of 20, 40 and 60 volume % are fabricated.

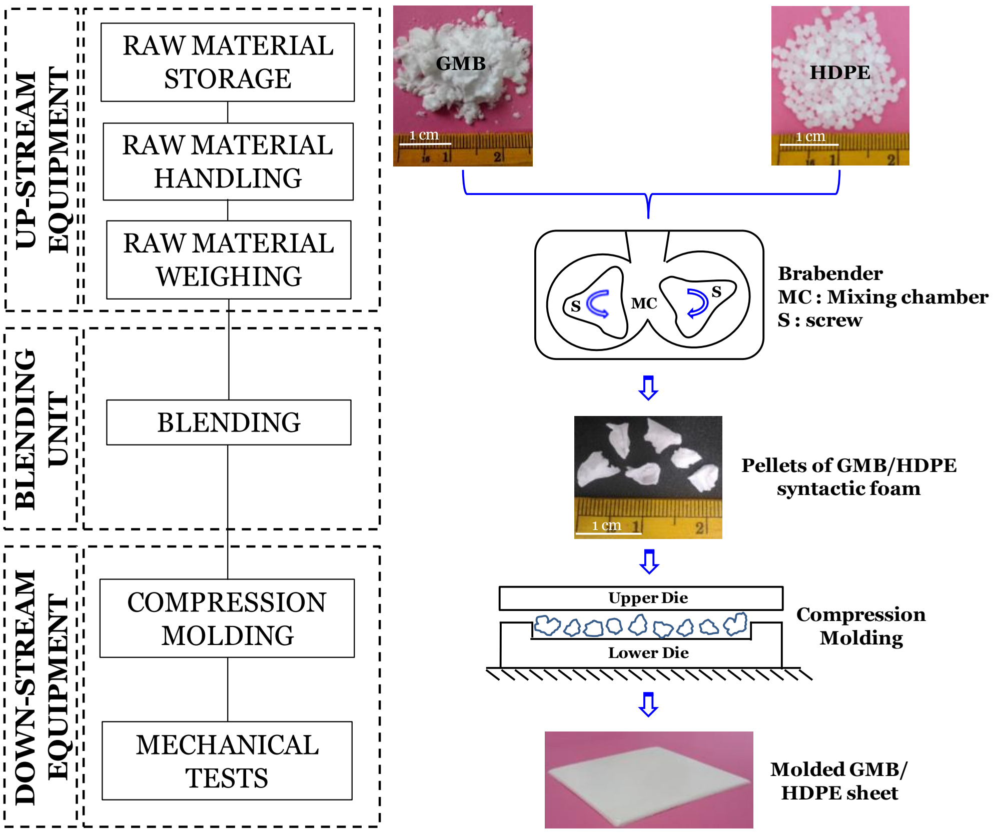
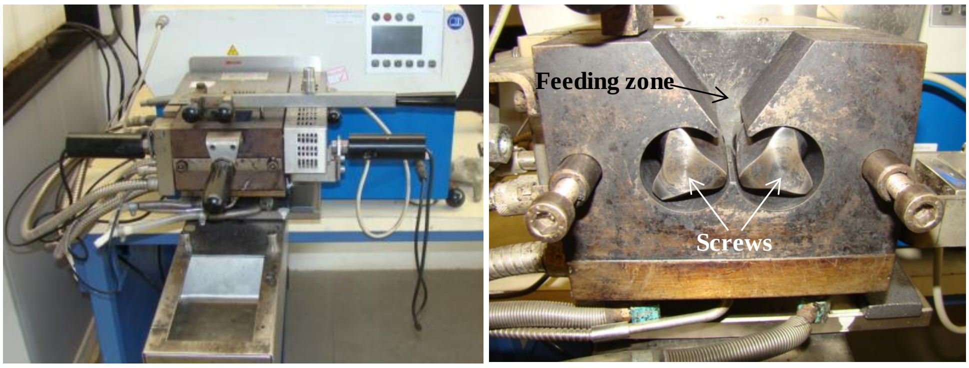


Figure 2.2 (a) Material flow and test plan (b) block diagram of methodology adopted.

Table 2.3 Brabender and Compression molding machine specifications.

Details	Brabender	Compression molding
Make	Western Company Keltron, Germany	Santec Automation Pvt. Ltd., India
Model	16 CME SPL	SP - 30
Product	Mixer 50 HT	SAIPL
Voltage (V)	240+PE	415
Frequency (Hz)	50/60	-----
Power (kW)	3.88	3.7
Current (A)	16.2	-----
Max. pressure (bar)	-----	200

During syntactic foam fabrication, HDPE is first plasticized at 160°C (Bharath Kumar et al. 2016) in the brabender (Figure 2.3a) for 5 min. GMB are added to the melt in the mass ratio of 4:1 (HDPE:GMB) and mixed for two more minutes. This process is repeated until the entire quantity of GMBs is mixed thoroughly in HDPE. Mixing takes place in the confined chamber comprising of two screws (Figure 2.3b). Screw rotation speed needs to be optimized to minimize the GMB breakage by high shear mixing. The published literature utilizing Brabender blending has not reported screw speed optimization (Deepthi et al. 2010). An optimization study is first conducted for the screw rotation speed, which is then fixed for fabricating all nine types of foams. Neat HDPE samples are also prepared under the similar processing conditions for comparison. GMB/HDPE syntactic foam pellets from Brabender are shown in Figure 2.3c.



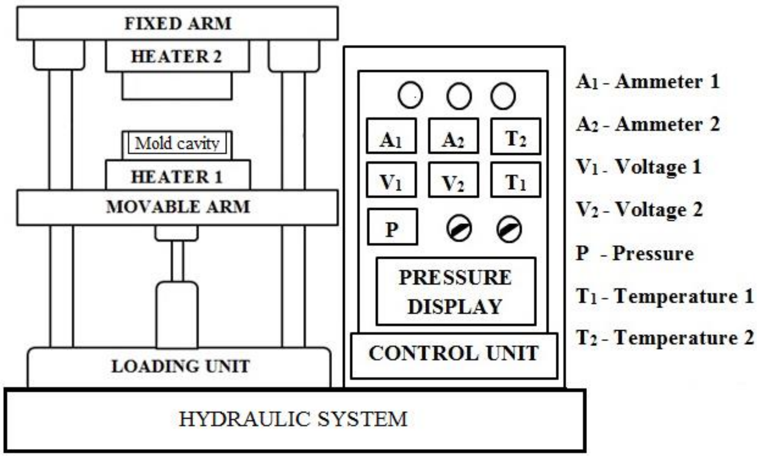
(a) (b)

(c)

Figure 2.3 (a) Brabender (b) blending mechanism and (c) pellets of GMB/HDPE syntactic foam.

GMB/HDPE pellets in desired proportions are hot pressed in compression molding machine (SP30, Santec automation Pvt. Ltd., Delhi, India) to form sheets. Compression molding machine utilized in the present work is presented in Figure 2.4a. Schematic representation for better clarity is shown by Figure 2.4b. A polyethylene sheet is laid into the compression mold cavity initially for easier removal of the cast sheet. Weighed GMB/HDPE lumps (80 g) are loaded into the mold cavity of 165×165×3.2 mm^3 dimension (Figure 2.4b-c) and are covered by another polyethylene sheet from above.

(a)



(b)

(c) (d)

Figure 2.4 (a) Compression molding machine utilized in the present work (b) Schematic diagram for better clarity (c) upper plate and (d) bottom plate that forms compression mold cavity.

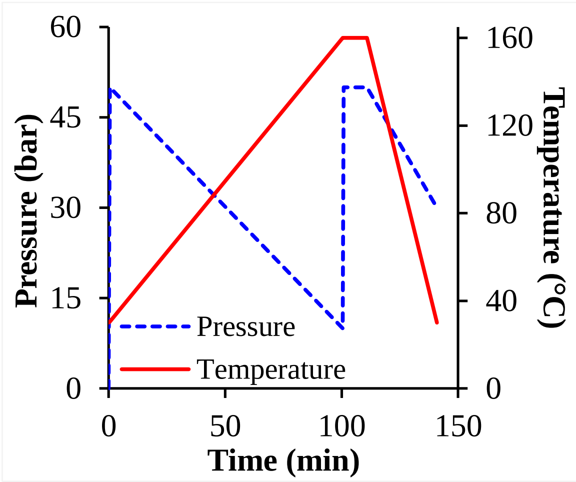
The pressure-temperature cycle used in compression molding is presented in Figure 2.5a. At the start of the pressure temperature cycle, pressure is set at 50 bar to disperse the GMB/ HDPE lumps uniformly into the mold cavity and then the cycle is executed as presented in Figure 2.5a (Deepthi et al. 2010). Once the temperature reaches the peak value of 160°C, pressure is re-applied to consolidate the blend in sheet form. This condition is held for 10 min, after which a 30 min cooling cycle is initiated. Finally, cast sheets of GMB/HDPE are removed from the mold.

Processing conditions of brabender and compression molding process for GMB/HDPE syntactic foams fabrication are presented in Table 2.4. Nine GMB/HDPE sheets are fabricated having varying GMB content (20, 40 and 60 vol. %) and wall thickness (Table 2.1). Neat HDPE sheets are also fabricated for comparison. Figure 2.5b shows a GMB/HDPE sheet, which is sectioned to produce specimens for the flexural, tensile, quasi-static compression and dynamic mechanical analysis tests.

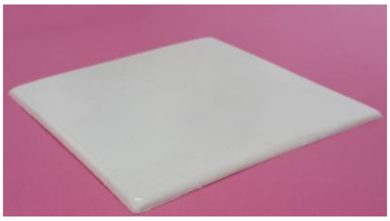
Table 2.4 Processing conditions for brabender and compression molded syntactic foam composites.

Parameters	Brabender	Compression molding
Mold temperature (°C)	------	165
Heating zone temperature (°C)	190	165
Screw speed (RPM)	10	------
Pressure (bars)	------	50
Holding time (min)	5	10
Cooling time (min)	2	30
Total cycle time (min)	10	135

An overview in the form of flow chart is presented in Figure 2.6, used for casting GMB/HDPE samples to characterize developed lightweight thermoplastic syntactic foams for mechanical properties as detailed in the next section.



(a)



(b)

Figure 2.5 (a) Pressure-temperature cycle utilized to prepare samples and (b) a molded GMB/HDPE sheet.

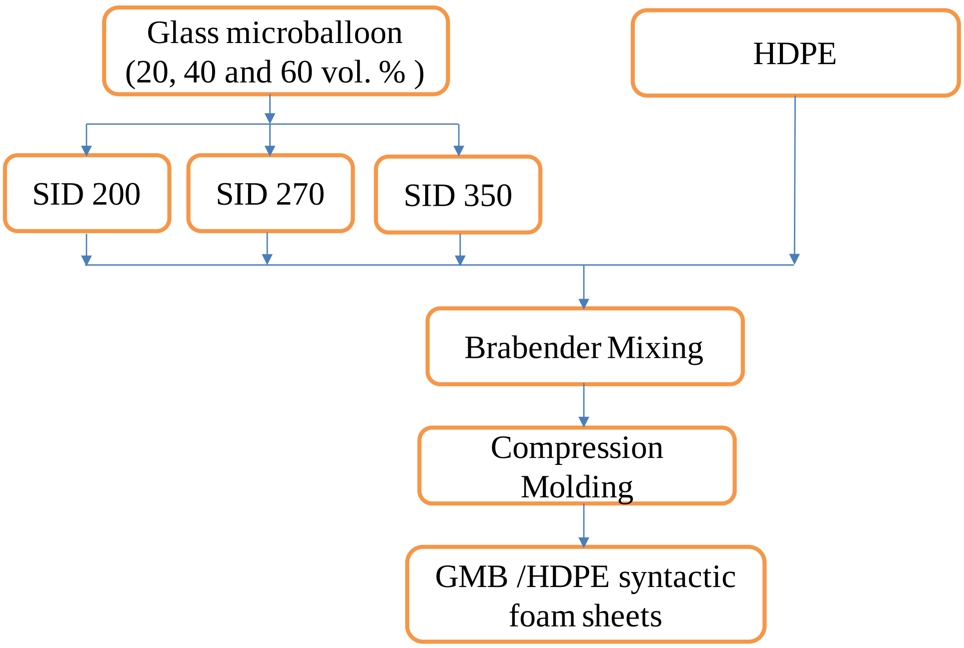


Figure 2.6 Flow chart of fabrication route and types of GMB/HDPE syntactic foams synthesized in the present work.

2.3 Testing

2.3.1 Particle size analysis

Particle size analysis is conducted using a Sympatec (Pennington, NJ) QICPIC high speed image analysis system. The particles are dispersed using the RODOS and VIBRI systems, which aerosolize a stream of particles in a jet of compressed air. A pulsed laser illuminates the particles as they pass a camera that images the particles at 175 frames/sec. For each particle imaged, the equivalent diameter is calculated as the diameter of a sphere having a projected area equal to the projection captured by the camera. Five runs of each particle type are conducted and the values presented are averaged from these runs, with weight according to the number of particles in each run.

2.3.2 Density measurement

ASTM D792-13 standard is used to estimate densities of all fabricated specimens. Densities of five specimens for neat HDPE and their syntactic foams are measured and the average values with standard deviations are reported. The density of neat HDPE is measured to be 0.959 ± 0.002 g/cm^3, which is used in rule of mixtures to calculate theoretical density of syntactic foams.

2.3.3 Tensile testing

Z020 ZwickRoell (USA) with a 20 kN load cell computer controlled universal test system is used to conduct tensile test confirming (ASTM D638-14) standard. Crosshead displacement rate of 5 mm/min is maintained constant throughout the test. The acquired load and displacement data are used to calculate the stress and strain, respectively. Test is also conducted for different strain rates of 1.6×10^{-5}, 1.6×10^{-4} and 1.6×10^{-3} s^{-1}. An Instron 4467 Universal Testing Machine with a 30 kN load cell is used to perform low strain rate tensile test. The strain is captured using a clip-on Instron extensometer of gauge length 50.8 mm (2 inch). The load data is acquired by Bluehill 2.0 software which is then used to calculate stress values. Five specimens for each sample type are tested and average values are reported.

2.3.4 Flexural testing

A computer controlled Zwick universal testing machine (ZwickRoell Z020, USA) having a load cell capacity of 20 kN is utilized for flexural testing in three-point bend configuration. ASTM D790-10 standard is adopted with specimen dimensions of 127×12.7×3.2 mm^3.The crosshead displacement rate is maintained at 1.54 mm/min and a pre-load of 0.1 MPa is applied before the test. Specimens have a span length of 52 mm to maintain 16:1 span length/thickness ratio. Five specimens each are tested and the average values of the measured properties are presented.

Tests are terminated at 10% strain if the specimen does not fracture. The flexural modulus (E_f) is calculated using,

$$E_f = \frac{L^3 m}{4bd^3} \tag{2.3}$$

The flexural stress (σ_{fM}) is estimated by,

$$\sigma_{fM} = \frac{3PL}{2bd^2} \tag{2.4}$$

2.3.5 Quasi-static compression

Z020 ZwickRoell (USA) computer controlled universal test system with a 20 kN load cell is used for quasi-static compression test. The test is conducted for 0.001, 0.01 and 0.1s^{-1} strain rates. The end of test criteria is set at 20 kN load. Flat wise load is applied on all the samples under investigation. Bluehill 2.0 software is used for data acquisition. The data is analyzed using in-house developed MATLAB code to estimate yield strength and modulus for all the samples. Average of five samples for each configuration is reported for analysis.

2.3.6 Dynamic mechanical analysis

DMA 8000 (Perkin Elmer, USA) is used for Dynamic mechanical analysis (DMA). The test is conducted in dual cantilever configuration mode with a span length of 35 mm. Specimen dimensions of 50×10×3 mm^3 are subjected to DMA in strain control mode with a maximum displacement of 25 μm.

Dynamic mechanical analysis is conducted in temperature sweep mode. In the temperature sweep, the behavior of the syntactic foams at high temperature is studied at constant frequency. Temperature is ramped from 35 to 150°C at a rate of 5°C/min with deformation occurring at a constant frequency of 1 Hz. Testing is halted once the storage modulus reaches a value of 20 MPa to prevent total melting of the specimen. Storage modulus, loss modulus and damping factor (Tan δ) values are noted for minimum of five samples and average values are presented for analysis. Crystallinity is a crucial parameter in polymers and is investigated hereafter.

2.3.7 Wide angle x-ray diffraction (WAXD)

Wide angle x-ray diffraction (WAXD) (Rigaku 5thminiflex, USA) measurements are carried out to study the influence of glass microballoon in HDPE matrix. The crystallinity, interplanar distance and characteristic peaks of HDPE are determined for neat HDPE and their syntactic foams. WAXD test is carried out with scan speed of 1°/min in the 2θ range of 10-50° with accelerating power of 600 W and 1.5406Å wavelength. The % crystallinity (%X_c) is determined using,

$$\% X_c = \frac{I_c}{I_a + I_c} \tag{2.5}$$

The interplanar distance (d') is calculated using,

$$d' = \frac{n\lambda}{2sin\theta} \tag{2.6}$$

2.3.8 Differential Scanning Calorimetry (DSC)

Heat of fusion, crystallinity and melting point of HDPE and their foams is carried out by Differential scanning calorimetry (DSC 6000, Perkin Elmer, USA). For each measurement a sample of 5 mg is taken in hermitically sealed aluminium pan having volume of 10 μL. Test is carried out in the temperature range of 0-180°C at a ramp rate of 10°C/min in nitrogen atmosphere. Crystallinity of all the samples is determined using,

$$X_c = \frac{\Delta H_m}{\Delta H_m^*} \times 100 \tag{2.7}$$

where, ΔH_m^* is 293 J g^{-1} (Xiang et al. 2017).

2.3.9 Imaging

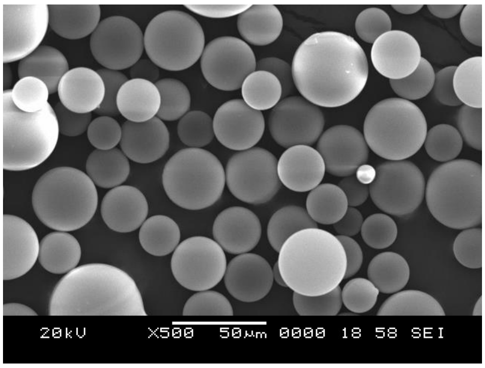
Micrography is carried out by scanning electron microscope (JSM 6380LA, JEOL (Japan). All the samples are sputter coated using JFC-1600 auto fine coater (JEOL, Japan). Nikon D7000 camera with Nikon 35 mm F1.8G lens is used for optical imaging.

Results and discussions therein of the tests envisaged are elaborated in the section to follow.

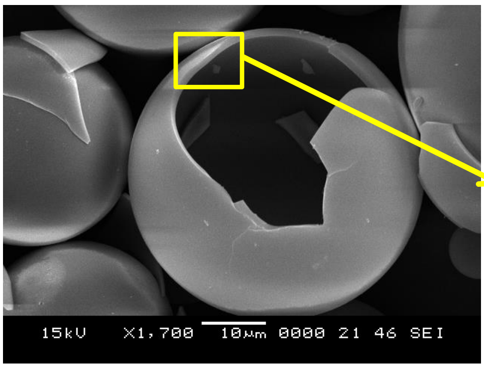
3 RESULTS AND DISCUSSION

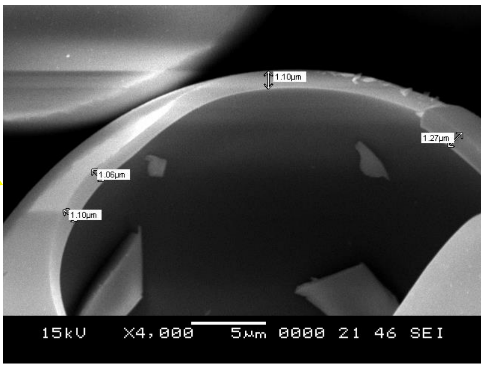
3.1 Particle size analysis

Micrograph of as received glass microballoon is shown in the Figure 3.1a. Glass microballoons are engineered particles with good surface finish and are spherical in shape (Figure 3.1a). Glass microballoons with three different true particle densities and crushing strength are used in the study. The variation in particle density is due to the change in wall thickness as the mean outer diameter of all the three different particles is almost the same. One such broken GMB particle is presented in Figure 3.1b at higher magnification. These engineered GMBs are spherical in shape with perfect smooth exterior surface. Wall thickness variations for the given particle are seen to be varying in very narrow range as shown in Figure 3.1c as against naturally available fly ash cenospheres (Bharath Kumar et al. 2016). Wall thickness for different density particles vary with a wide range as mentioned in Table 2.1.



(a)





(b) (c)

Figure 3.1 Micrograph of (a) as received GMB (b) one such broken particle and (c) marked area in (b) at higher magnification.

Particle size analysis of the GMBs is presented in Figure 3.2. The size distribution is monomodal and less than 1% of particles are observed to be larger than 125 μm for all GMB types used in this work. These particles differ in density due to variation in wall thickness for nearly the same mean outer diameter (Table 2.1). The volume-weighted mean particle size for SID200, SID270 and SID350 are 52.97, 49.98 and 45.05 μm respectively. These measured values are in very close agreement with the ones provided by the supplier in their datasheet. The tail end of the particle distribution for all the three particles is very narrow (absence of extended tail) signify clusters of particles are not formed in as received condition which is an indication of possible uniform dispersion of particles in HDPE matrix during processing. Particle sphericity is observed to be in the range of 0.77-0.89 from the particle size analysis, compared to '1' for perfectly spherical particles.

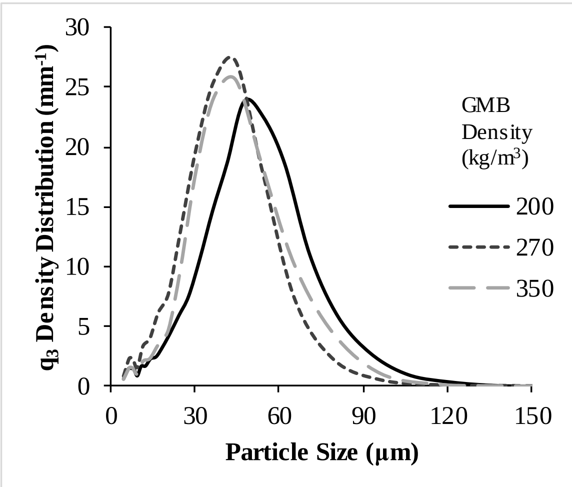


Figure 3.2 Particle size analysis of GMBs used in the present study.

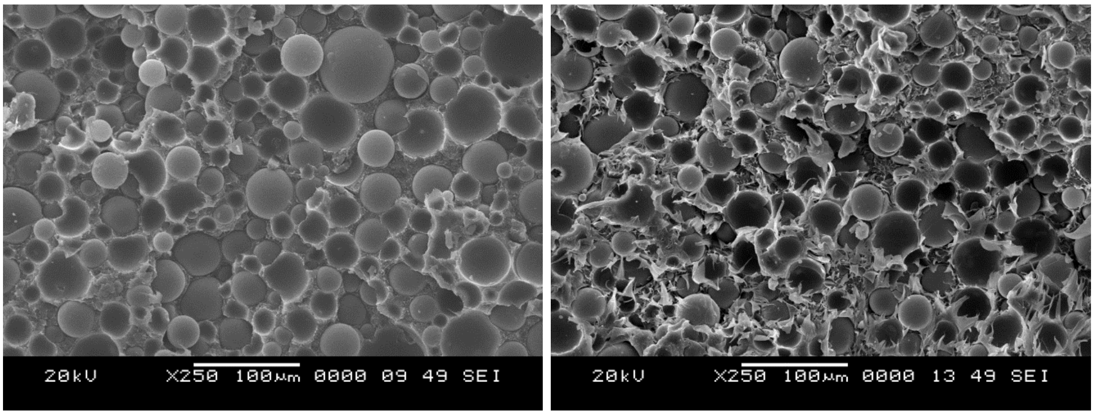
3.2 Brabender process optimization and specimen manufacturing

A pilot study is conducted for finding the optimal screw speed in the brabender to minimize GMB breakage. HDPE reinforced with 60 vol. % of thin walled GMBs (H200-60) is chosen for this study as thin walled particles in high volume fraction results in increased fracture due to particle-particle interaction under shear in brabender and compressive forces in compression molding. It is expected that the conditions optimized for this composition would be useful for other less sensitive compositions. The brabender screw speed is gradually decreased from 40 to 10 rpm as per the results obtained in Table 3.1. Density is a strong indication of foam quality as particle fracture leads to higher density than expected. It is observed that the density trend starts to saturate between 20 and 10 rpm. Therefore, 10 rpm is selected for processing syntactic foams. Slower speeds may further reduce the GMB breakage but such benefit is expected to be very small based on this trend and the processing time would increase drastically.

Table 3.1 Density of H200-60 syntactic foam used in pilot study of screw rotation optimization.

Syntactic foam type	Screw rotation speed (rpm)	Density (g/cm^3)
H200-60	40	0.713±0.007
	30	0.651±0.006
	20	0.625±0.004
	10	0.608±0.002

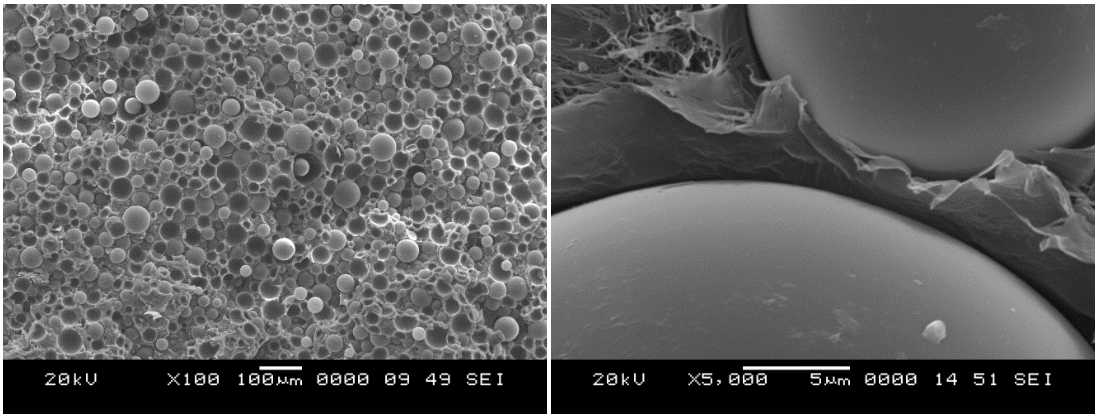
Further observations of specimen quality are presented in Figure 3.3, where specimen micrographs processed at 10 and 40 rpm are compared. Higher particle fracture is observed at 40 rpm screw speed in this figure, whereas most particles appear to be intact for the specimen processed at 10 rpm. Density based estimates show 42.6 vol. %. GMB fracture at 40 rpm speed compared to only 17.8 vol. % GMB fracture at 10 rpm. It is expected that GMBs with thicker walls would fracture less because of their higher strength.



(a) (b)

Figure 3.3 Scanning electron micrograph of as molded freeze fractured H200-60 syntactic foam for (a) 10 and (b) 40 rpm screw rotation acquired at same magnifications. Higher GMB failure is seen in the syntactic foam developed at higher screw speed.

A micrograph of a freeze fractured surface of molded H200-60 syntactic foam is presented in Figure 3.4. Natural surface compatibility between GMB and HDPE is seen to be poor. Tensile and flexural properties strongly depend on the interfacial bonding characteristics to transfer load from the matrix to the particle. Though improvement in the GMB-HDPE interfacial bonding is desired for practical applications, such surface treatment of constituents can adversely affect the flow characteristics of HDPE around GMB, increasing localized stresses leading to greater particle fracture during syntactic foam fabrication (Bharath Kumar et al. 2016). Further, any inconsistency in surface treatment will affect the mechanical property, making the effect of wall thickness difficult to interpret in the present study (Bharath Kumar et al. 2016, Porfiri and Gupta 2009).



(a) (b)

Figure 3.4 Freeze fractured surface of as molded (a) H200-60 at lower magnification showing a large number of intact particles with uniform distribution in HDPE matrix and (b) higher magnification image showing poor interfacial adhesion between the constituents.

Table 3.2 presents experimental and theoretical densities of developed syntactic foams. For all particles types, GMB failure is observed to be the highest for syntactic foams containing 60 vol. % GMBs. Particle failure forms glass debris, which are embedded in the matrix. Although fractured particles do not provide the reduction in density as planned, they still help in replacing more expensive HDPE resin. Figure 3.4a shows uniform distribution of GMBs affirming the good quality of GMB/HDPE syntactic foam sample processed through the adopted route.

3.3 Density

H200, H270 and H350 syntactic foam samples are blended in brabender with optimized screw speed of 10 rpm is used followed by compression molding. Experimentally measured densities, along with theoretical estimates (rule of mixtures), are presented in Table 3.2. Difference between theoretical and experimental density values is attributed to the GMB breakage during processing since no porosity is observed in the matrix resin (Figure 3.3a). The value of GMB breakage during manufacturing is estimated by,

$$V_{mp} = \frac{\rho_t - \rho_m}{\rho_t} \tag{3.1}$$

Negative porosity values indicate GMB breakage. Thermoplastics are processed using high shear mixing. Though, processing parameters are optimized for quality syntactic foams, particle breakage is inevitable. During the fabrication of syntactic foam, some GMB particles are fractured during blending in brabender. The matrix resin fills the cavity exposed due to GMB fracture, increasing the density of the syntactic foam. Some of the previous studies have shown measured density of syntactic foams to be higher than their theoretical densities despite the presence of matrix porosity, which leads to a conclusion that there is fracture of hollow particles in those foams during synthesis (Huang and Gibson 1993). In the present case, experimental density is higher than the theoretical density values, implying particle breakage.

Table 3.2 Composition, nomenclature, density, GMB failure and weight saving potential in fabricated syntactic foams.

GMB density (g/cm^3)	GMB (vol. %)	Syntactic foam nomenclature	Theoretical density (g/cm^3)	Measured density (g/cm^3)	GMB failure (vol. %)	Weight saving potential (%)
0.200	20	H200-20	0.800	0.847±0.008	5.55	10.84
	40	H200-40	0.650	0.712±0.014	8.71	25.05
	60	H200-60	0.500	0.608±0.002	17.76	36.00
0.270	20	H270-20	0.814	0.845±0.003	3.67	11.05
	40	H270-40	0.678	0.727±0.001	6.74	23.47
	60	H270-60	0.542	0.642±0.003	15.58	32.42
0.350	20	H350-20	0.830	0.853±0.003	2.70	10.21
	40	H350-40	0.710	0.741±0.004	4.18	22.00
	60	H350-60	0.590	0.672±0.005	12.20	29.26

The particle fracture is low in composites containing 20 vol. % of GMB. However, as the GMB content is increased in the syntactic foam, the proportion of GMB breakage also increases, likely because of particle to particle interaction and reduction of mix viscosity. Highest GMB breakage is observed in H200-60 syntactic foam. GMB failure at 60 vol. % for all the three particles (200, 270 and 350 kg/m^3) varies within the close range of 12.2-17.76% as seen from Table 3.2. This observation signifies, shear forces developed in HDPE matrix are independent of wall thickness at higher filler loadings. Particle failure opens up the void space within the intact GMB, allowing HDPE matrix to occupy the space along with particle debris if any. Although fractured particles do not provide the reduction in density as planned, they still help in replacing more expensive HDPE resin and make the component cheaper. Freeze fractured surface of H200-60 at lower magnification (Figure 3.4a) show a large number of intact particles with uniform distribution affirming the good quality of GMB/HDPE syntactic foam sample. Absence of matrix porosity is clearly evident. Further, large numbers of intact microballoons are also seen. The intact particles will be useful in density reduction as well as energy absorption under compression.

Filler breakage adversely affects the mechanical properties of the syntactic foam. However even with the failed particles, fabricating syntactic foam components that are non-load-bearing can provide a substantial saving of expensive HDPE resin. Secondly, density of all foams is far lower than the neat HDPE matrix signifying weight saving potentials of these developed foams. As seen from Table 3.2, significant weight reduction (10-36%) is possible by using GMBs in HDPE matrix. Lower densities of foams as compared to neat HDPE matrix makes it worth investigating for mechanical properties.

Significant reduction in density is observed for 60 volume % GMB/HDPE foams having thin walled particles. 36% weight saving potential is achieved as compared to neat HDPE. Such scenarios will be beneficial for applications demanding weight savings and reduction in consumption of HDPE.

3.4 Tensile behavior

A representative set of tensile stress-strain curve for HDPE and their syntactic foams are presented in the Figure 3.5. HDPE specimens show failure strain up to 13.06% (Figure 3.5a), whereas the foams fracture at 6.18-2.12% strain (Figure 3.5b-d). Fracture strain of foams is decreased with the increase in wall thickness and filler content. Effect of filler content is observed to be more prominent as compared to wall thickness variation. The stress strain curve of all HDPE foams show substantial linear region followed by smaller non-linear zone. The failure of syntactic foams appears to be relatively brittle with only a little plastic deformation as seen in Figure 3.5b-d. This behavior might be due to the presence of stiff GMBs in ductile HDPE matrix.

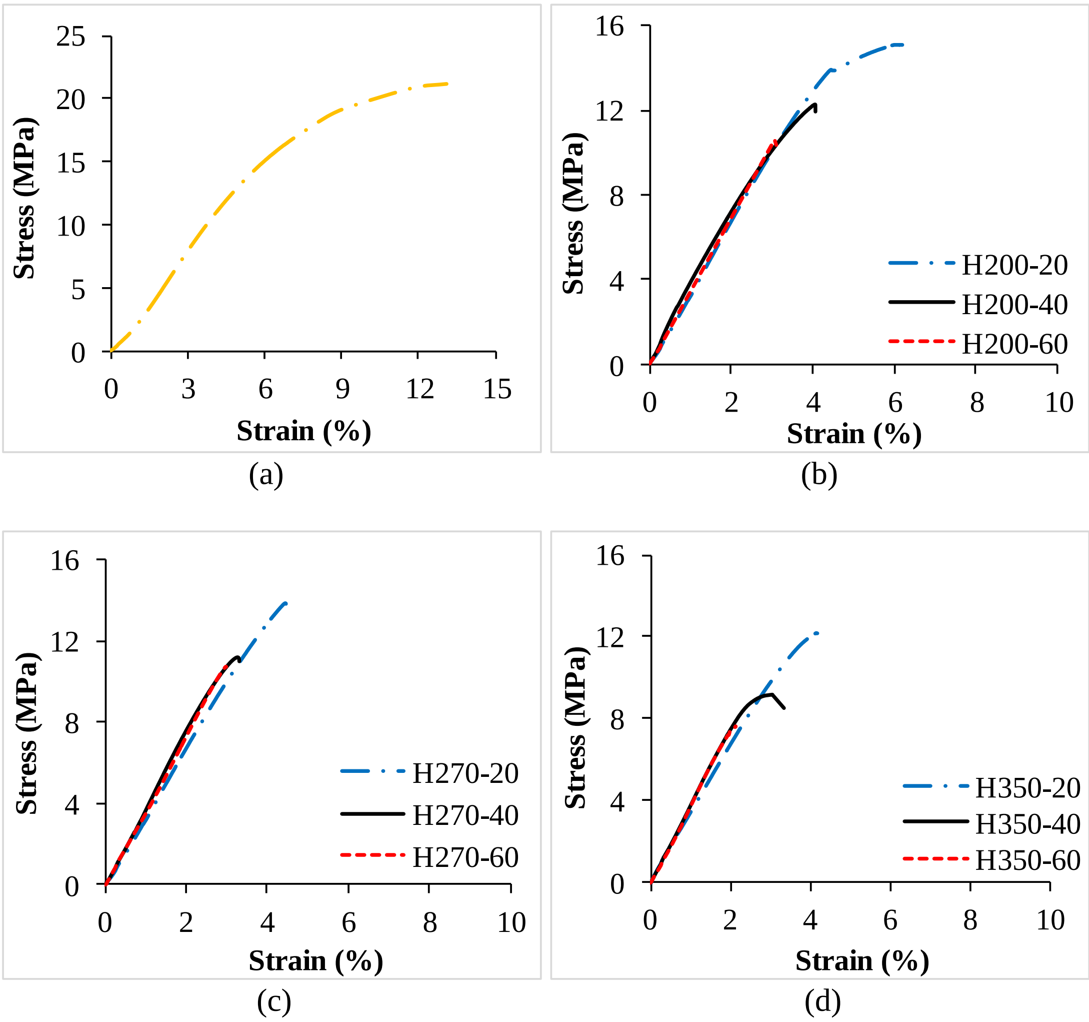


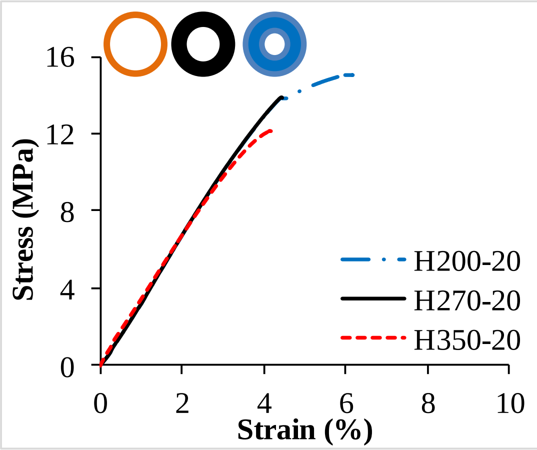
Figure 3.5 Representative tensile stress-strain curves of (a) Neat HDPE (b) H200 (c) H270 and (d) H350 syntactic foam samples with varying GMB content by vol. %. Note: X and Y scales are different in plot (a).

Effect of wall thickness on stress-strain behavior is shown in Figure 3.6. The tensile properties of HDPE foam composites are presented in Table 3.3. Modulus is increased with increase in wall thickness and filler content. This trend is due to the increase in stiffness of GMB in foam composites. Ultimate tensile strength is decreased with increase in filler content and wall thickness. At high filler loading the matrix content (effective load carrying element) is reduced which results in low tensile strength. Elongation at UTS is also decreased with an increased filler loading. No clear trend is observed for wall thickness variation at the same filler loading for strength and elongation values. It would be worthwhile to look into the specific tensile strength trend.

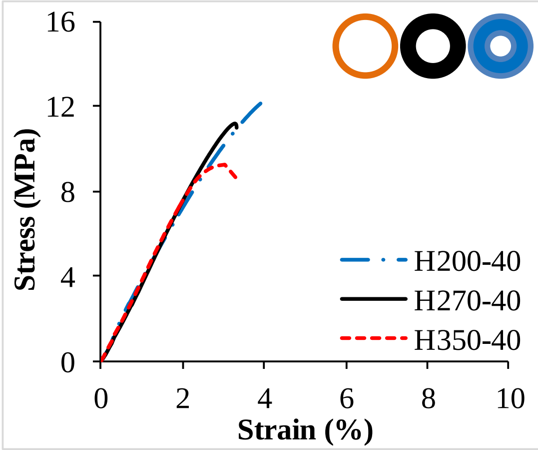
Table 3.3 Tensile properties of neat HDPE and their syntactic foams.

Foam type	Tensile Modulus (MPa)	Ultimate Strength (MPa)	Elongation at UTS (%)	Fracture Strength (MPa)	Fracture strain (%)
H	285.36±14.26	22.19±0.58	13.80±0.31	22.19±0.33	13.06±0.28
H200-20	334.71±16.73	15.08±0.23	6.01±0.25	15.08±0.26	6.18±0.15
H200-40	472.32±23.61	12.29±0.46	3.82±0.42	11.95±0.38	4.08±0.33
H200-60	535.71±26.78	10.57±0.49	2.91±0.09	10.33±0.46	3.11±0.42
H270-20	348.52±17.42	13.90±0.22	4.47±0.15	13.87±0.21	4.46±0.18
H270-40	508.14±25.41	11.15±0.38	3.27±0.47	10.96 ±0.31	3.32±0.28
H270-60	588.43±29.42	10.71±0.45	2.87±0.44	10.70±0.36	2.99±0.14
H350-20	375.43±18.77	12.15±0.37	3.91±0.30	12.14±0.40	4.17±0.31
H350-40	593.15±29.65	9.20±0.52	3.03±0.33	8.54±0.51	3.32±0.13
H350-60	603.95±31.39	7.59±0.67	2.09±0.24	7.59±0.62	2.12±0.11

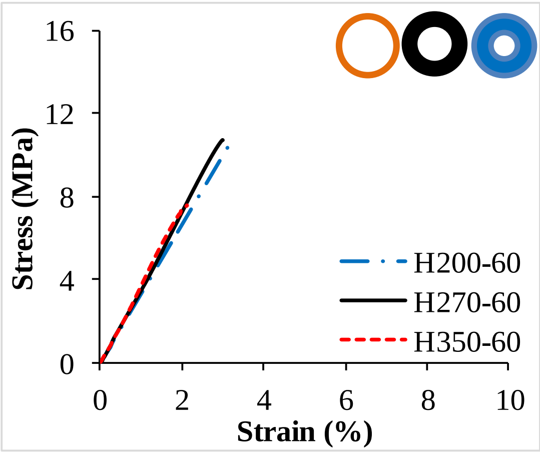
The fracture strength of all the GMB/HDPE foams is 1.45-2.9 times lower than that of the neat HDPE. GMBs are brittle in nature. Under the applied load, these particles fracture into multiple fragments as seen in Figure 3.7a. These fragments acts as stress concentrators and tear apart more compliant matrix resulting in progressive reduction of strength, more prominently in thick walled particles at higher filler loadings. Matrix filling in the void space created due to fracture of particles is seen in lower wall thickness particles Figure 3.7b. The combination of tensile modulus and fracture strength should be carefully analyzed. All the samples developed using compression molding, fracture close to their UTS.



(a)

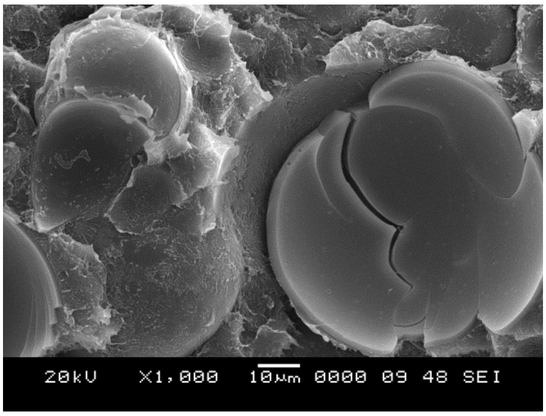


(b)

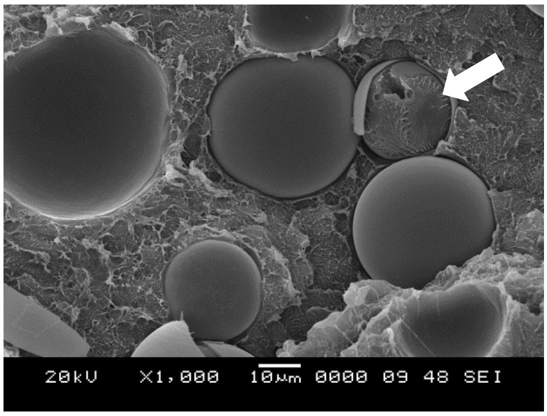


(c)

Figure 3.6 Representative tensile stress–strain curves for syntactic foams with varying wall thickness at (a) 20 (b) 40 and (c) 60 vol. % GMBs.



(a)



(b)

Figure 3.7 Micrographs showing (a) multiple fragments of broken shell and (b) HDPE matrix occupying the space (shown by arrow mark) of the fractured shell revealed by tensile failure.

Figure 3.8 presents specific tensile properties which are crucial in materials selection for weight sensitive applications. Increasing trend is observed for specific modulus for all the three particles in the range of 0.39-0.93 (MPa/kg/m^3) as the GMB content increases. These values are higher than that of HDPE, which is 0.30 (MPa/kg/m^3). Highest specific modulus observed for H350-60 is 0.93 (MPa/kg/m^3). Increasing wall thickness increases specific modulus for a given GMB content. Specific strength decreases with increasing filler loading and wall thickness in the range of 11.25–17.65×10^{-3} (MPa/kg/m^3) for all the three particles. These values are lower than that for HDPE, which is 23.35×10^{-3} (MPa/kg/m^3). Higher specific tensile modulus values affirm that the use of syntactic foams can lead to substantial weight savings in molded components. Fracture of GMBs in syntactic foams increases their density and reduces the specific strength and modulus particularly at higher filler loadings (Table 3.2).

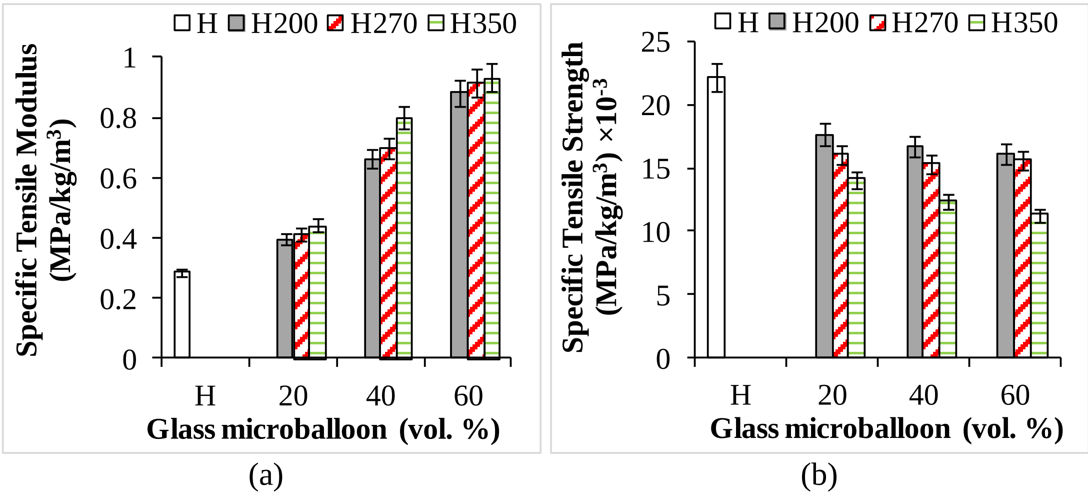


Figure 3.8 Experimentally measured specific tensile (a) modulus and (b) strength of neat HDPE and their syntactic foams.

Fractography at the same magnification level of tensile tested samples of thin walled (H200) and thick walled (H350) particles at lower and higher filler loadings are presented in Figure 3.9. More intact GMBs are seen at higher filler loadings (Figure 3.9b and Figure 3.9d) as compared to syntactic foams with lower GMB contents. This fact confirms higher modulus values exhibited by foams having higher GMB content. Further, higher plastic deformation is seen in foams with thicker walled particles at higher filler contents (Figure 3.9c-d) reducing tensile strength in those composites.

Overall, volume fraction and wall thickness variation has given a clear trend in GMB/HDPE thermoplastic syntactic foam composites. These observations help material developers to choose carefully the GMB/HDPE composition depending on the application.

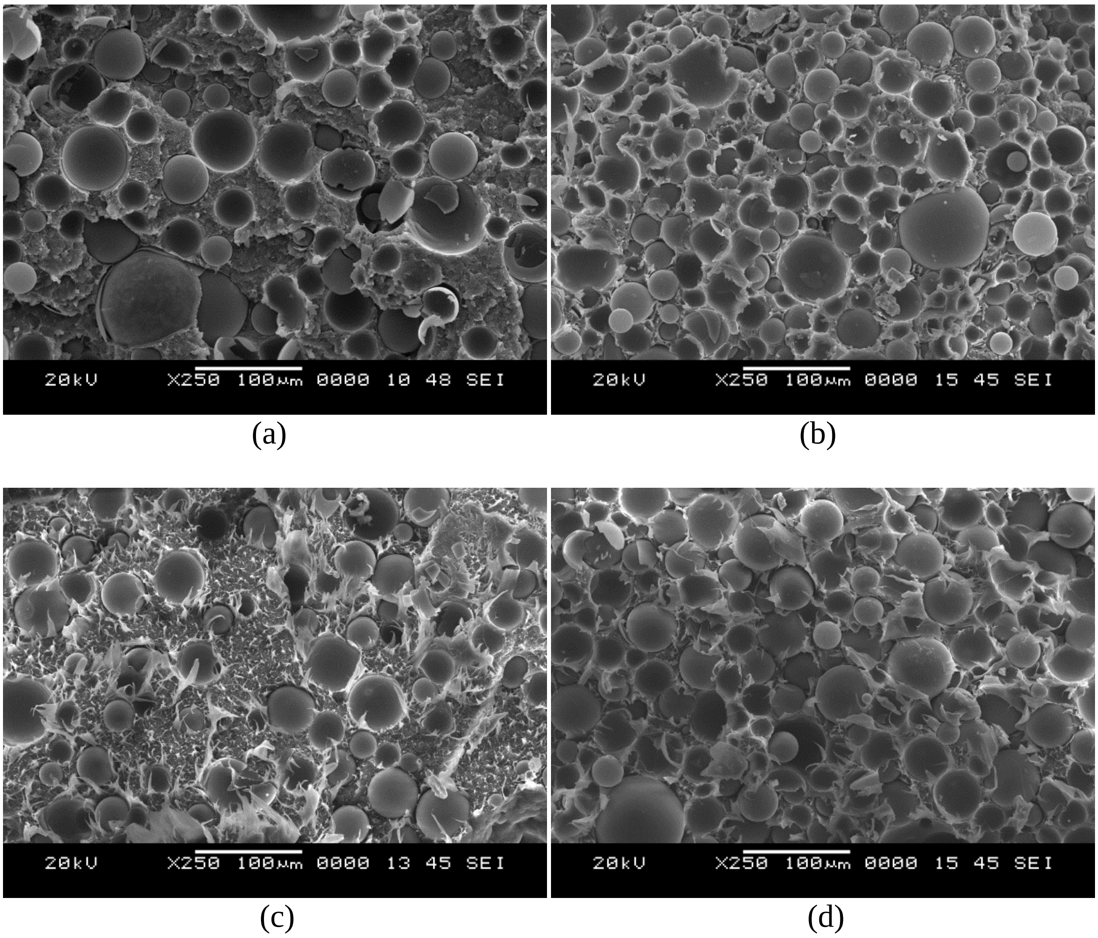


Figure 3.9 Fracture features of (a) H200-20 (b) H200-60 (c) H350-20 and (d) H350-60 syntactic foams post tensile test.

3.4.1 Tensile behavior at low strain rates

The stress-strain behavior of HDPE resin at different strain rates is presented in Figure 3.10. Modulus, yield strength and ultimate tensile strength extracted from the stress-strain graphs are presented in Table 3.4 and Table 3.5. HDPE specimens show failure strains of 9.3, 8.3 and 4.4% for strain rates of 1.6×10^{-5}, 1.6×10^{-4} and 1.6×10^{-3} s^{-1}, respectively. The syntactic foams have lower fracture strains for all GMB volume fractions and strain rates. Failure strain reduces with increasing filler content but no clear trend in fracture strain is observed with change in wall thickness. Ultimate tensile strength for foams is lower than the neat resin and decreases with increasing filler content at all strain rates (Table 3.5). Higher filler content reduces the matrix content (effective load bearing constituent) resulting in lower tensile strength. Foams exhibit higher UTS with increasing strain rate for same wall thickness and volume fraction, which is attributed to the strain rate sensitivity of the matrix resin. Increase in filler content in H200, H270 and H350 foams at 1.6×10^{-5}, 1.6×10^{-4} and 1.6×10^{-3} s^{-1} strain rates decreases the ultimate strength to the tune of 27.33-67.33%, 27.74-61.27% and 30.65-70.85% respectively as compared to neat resin (Figure 3.11).

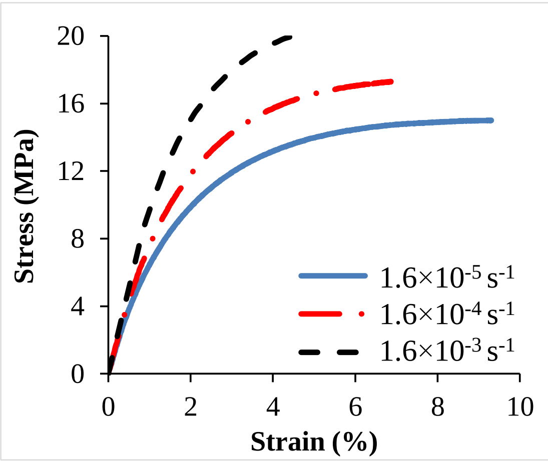


Figure 3.10 Representative stress strain curves of neat HDPE for varying strain rates.

Table 3.4 Tensile properties of neat HDPE and their syntactic foams at varying strain rates.

Foam type	E_T (MPa)			σ_y (MPa)		
	1.6×10^{-5} s^{-1}	1.6×10^{-4} s^{-1}	1.6×10^{-3} s^{-1}	1.6×10^{-5} s^{-1}	1.6×10^{-4} s^{-1}	1.6×10^{-3} s^{-1}
H	762±15	889±46	988±131	7.0±0.4	8.4±0.2	12.4±0.9
H200-20	825±29	755±50	1050±210	7.3±0.7	9.9±0.3	10.8±0.4
H200-40	726±71	918±38	962±11	7.5±0.3	8.3±0.7	11.0±0.8
H200-60	678±58	923±47	1130±12	7.2±1.2	9.5±0.1	9.2±0.9
H270-20	784±70	921±63	1056±79	7.9±0.6	9.6±0.2	11.6±0.5
H270-40	824±50	842±57	1051±89	8.0±0.5	10.9±0.7	12.9±0.2
H270-60	968±114	1019±35	1505±146	5.7±0.7	7.0±0.4	6.0±0.7
H350-20	923±85	1453±161	1062±17	8.0±0.6	9.4±0.7	12.7±0.6
H350-40	1195±59	985±63	1160±55	7.4±0.8	7.7±0.2	9.7±0.8
H350-60	1369±104	1072±102	1299±155	6.6±1.1	7.3±0.7	9.3±0.4

Effect of wall thickness on the modulus of syntactic foams with the same GMB volume fraction is greater at lower strain rates compared to higher ones (Table 3.4). For 1.6×10^{-5} s^{-1} strain rate, variation in modulus due to hollow particle wall thickness is 7, 22 and 28% for 20, 40 and 60% volume fractions, respectively. In contrast, it is found to be 29, 6 and 6% for 1.6×10^{-4} s^{-1} strain rate and 0, 8 and 12% for 1.6×10^{-3} s^{-1}. A general increasing trend is seen in the specific modulus of syntactic foams with GMB wall thickness at all strain rates.

For higher strain rates, the variation in specific modulus with GMB wall thickness is not high enough to prescribe the use of any particular wall thickness for an application. Although there is no apparent trend in specific yield strength with wall thickness, syntactic foams showed better specific properties than the neat resin. The fracture strength of all the syntactic foams is up to 3.1, 2.6 and 3.4 times lower than that of the neat HDPE at strain rates 1.6×10^{-5}, 1.6×10^{-4} and 1.6×10^{-3} s^{-1}, respectively.

Table 3.5 Ultimate tensile strength of neat HDPE and their syntactic foams at varying strain rates.

Foam type	σ_{uT} at strain rate(MPa)		
	1.6×10^{-5} s^{-1}	1.6×10^{-4} s^{-1}	1.6×10^{-3} s^{-1}
HDPE	15.0±1.6	17.3±1.6	19.9±1.6
H200-20	10.9±1.2	12.5±1.1	12.0±1.2
H200-40	9.3±0.2	10.2±0.5	11.6±1.5
H200-60	7.4±1.3	9.9±0.2	9.4±1.1
H270-20	10.3±0.3	12.3±0.3	13.8±1.2
H270-40	9.0±0.6	11.2±0.6	12.9±0.2
H270-60	4.9±0.4	6.7±0.6	5.8±0.5
H350-20	9.9±3.0	12.5±0.4	13.5±1.3
H350-40	7.1±0.1	7.9±0.1	10.1±0.5
H350-60	7.3±1.1	7.4±0.6	9.3±0.4

Failure patterns of neat HDPE and H200 specimens after tensile testing are presented in Figure 3.12. Similar features are observed for other lower strain rates and at 5 mm/min (Section 3.4) as well. H270 and H350 syntactic foams exhibited a similar failure pattern. Compression molded neat HDPE specimens fracture in brittle mode with no measurable necking. This behavior is different than that observed for injection molded neat HDPE samples (Bharath Kumar et al. 2016, Bharath Kumar et al. 2016). Since HDPE is a partially crystalline polymer, the dual pressure-temperature cycle over a longer period of time (Figure 2.5a) in compression molding as compared to very short cycle time in injection molding likely affects crystallinity.

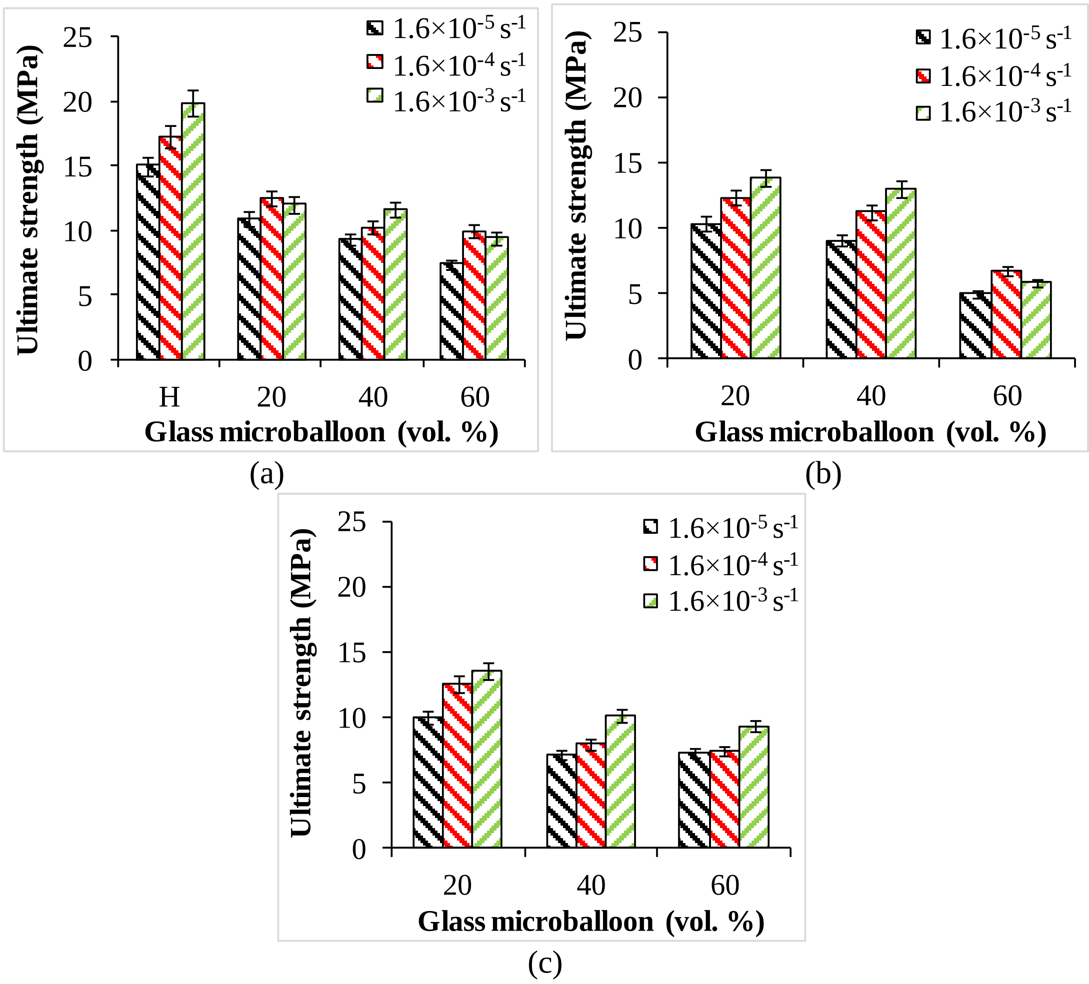


Figure 3.11 Ultimate strength values for (a) neat HDPE and H200 (b) H270 and (c) H350 foams at different strain rates.

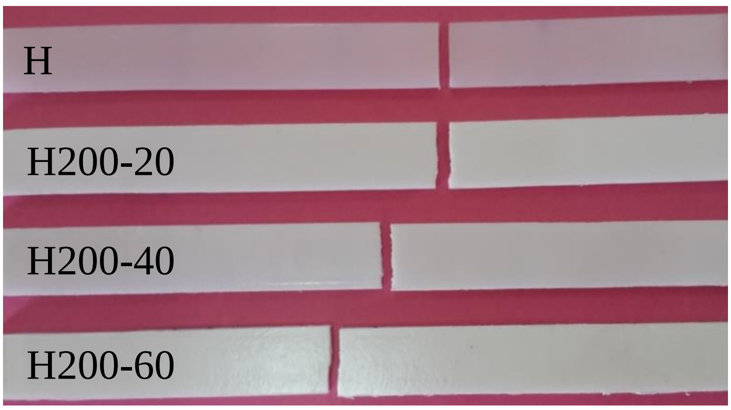


Figure 3.12 Representative specimens of neat HDPE and syntactic foams after tensile test at $1.6 \times 10^{-3}\ s^{-1}$ strain rate.

Fracture surfaces of four types of syntactic foams are shown in Figure 3.13. In all cases, no significant particle crushing is observed, only matrix deformation is visible. Higher plastic deformation is obtained in foams with thicker walled particles at higher filler contents (Figure 3.13d).

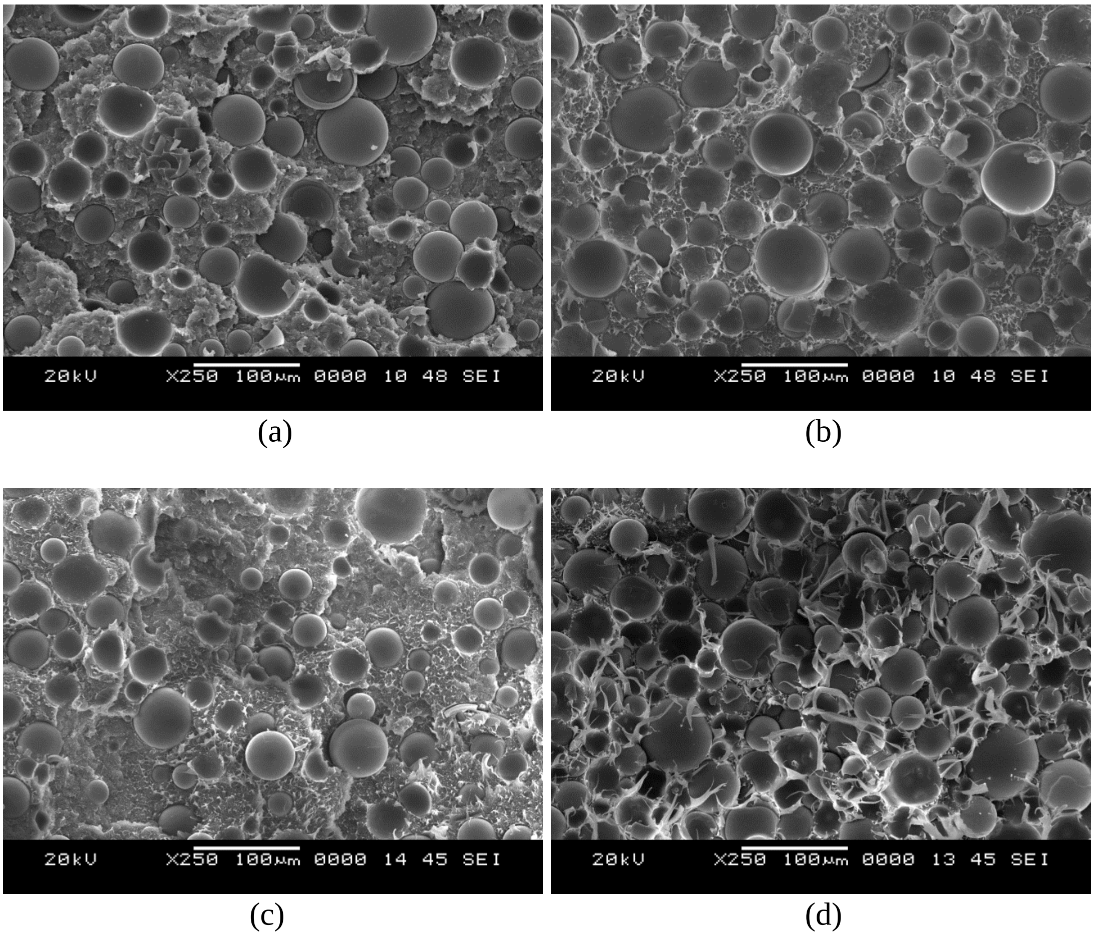


Figure 3.13 Fracture features of (a) H200-20 (b) H200-60 (c) H350-20 and (d) H350-60 syntactic foams after tensile test at 1.6×10^{-3} s^{-1} strain rate.

3.5 Flexural behavior

A representative stress-strain curve for neat HDPE is presented in Figure 3.14a. The test is stopped because the specimen did not fail before 10% strain. The flexural modulus of HDPE is measured to be 672 MPa. The measured properties of syntactic foams are compared with the HDPE resin properties to observe the effect of presence of GMBs in syntactic foams.

Figure 3.14b-d presents a set of representative stress-strain graphs of GMB/HDPE syntactic foams. The plastic strain of HDPE resin helps in obtaining plastic deformation in the syntactic foam specimens. As the particle volume fraction increases, the fracture strain is also observed to decrease.

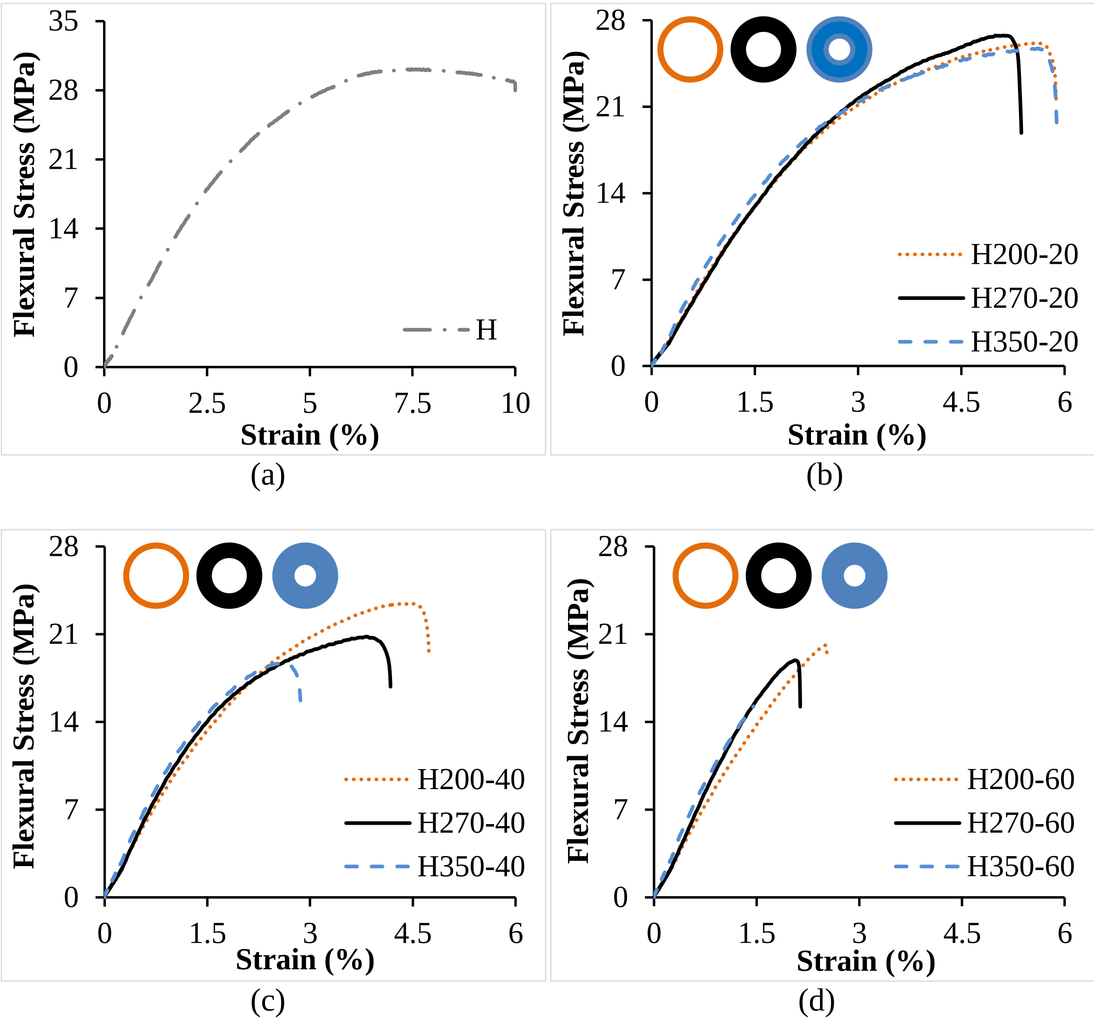


Figure 3.14 Representative stress-strain curves of syntactic foams with varying wall thickness having (a) 20 (b) 40 and (c) 60 vol. % GMBs. Note that (a) has different X and Y-scales than the other parts of the figure.

The mechanical properties calculated from these graphs are presented in Table 3.6. It is observed that for the syntactic foams containing the same type of particles, modulus increases, while strength and failure strength decrease as the GMB volume fraction is increased. Thicker walled GMBs exhibit higher modulus for all filler loadings (Table 3.6). Modulus for H200, H270 and H350 syntactic foams is observed to be 5-42%, 15-45% and 16-73% respectively higher than HDPE with varying filler content (Figure 3.15a).

Table 3.6 Flexural properties of neat HDPE and their syntactic foams.

Foam type	E_f (MPa)	σ_{uf} (MPa)	ε_{uf} (%)	σ_{ff} (MPa)	ε_{ff} (%)
HDPE	672.12± 20.2	30.66±0.70	7.62±0.42	-----	-----
H200-20	707.51± 23.8	27.47±0.36	5.87±0.25	21.55±0.41	5.97±0.02
H200-40	798.49± 28.8	23.21±0.59	4.17±0.24	19.71±0.59	4.72±0.03
H200-60	951.32± 39.9	21.01±0.67	2.51±0.06	18.62±0.71	2.53±0.04
H270-20	769.77± 20.6	27.09±0.42	5.34±0.16	18.78±0.51	5.35±0.03
H270-40	864.93± 32.4	21.35±0.46	3.04±0.21	16.82±0.63	4.28±0.02
H270-60	972.51± 35.4	16.19±0.61	2.39±0.19	15.17±0.55	2.09±0.04
H350-20	781.32± 19.6	25.63±0.43	5.17±0.29	18.68±0.98	5.87±0.03
H350-40	1091.78± 20.9	19.42±1.09	2.91±0.11	15.82±0.94	2.83±0.03
H350-60	1165.73± 39.9	15.23±1.15	1.28±0.15	14.46±0.78	1.27±0.02

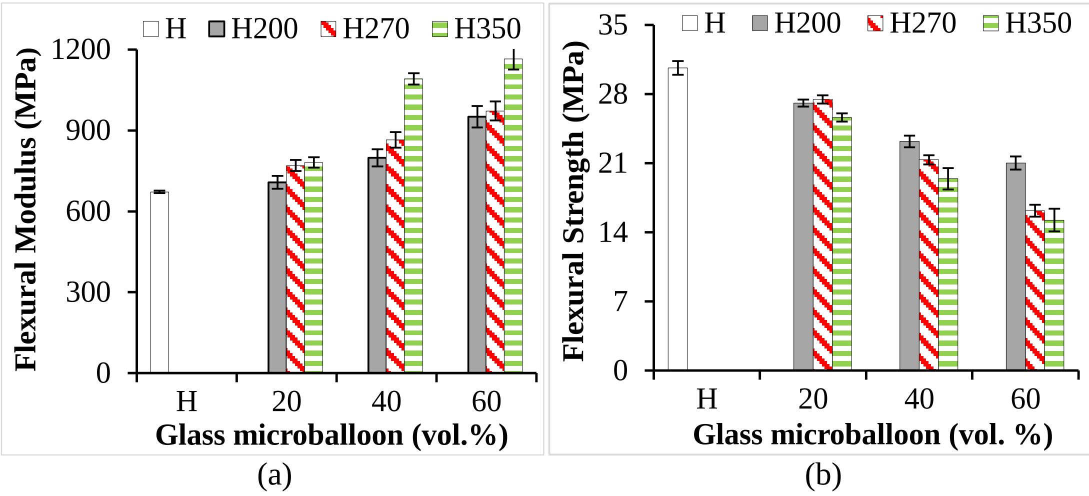


Figure 3.15 Experimentally measured flexural (a) modulus and (b) strength of HDPE and their syntactic foams.

Specific modulus for H350-60 is observed to be 147% higher compared to neat HDPE (Figure 3.16a), implying a weight and cost saving potential from these materials. Flexural strength is found to decrease with increasing GMB content and wall thickness. Specific strength (Figure 3.16b) of syntactic foams containing H200 GMBs was higher than that of the neat resin. Other types of particles showed decreasing specific strength with increasing GMB content. It is likely that fracture of thin walled GMBs in H200 syntactic foams results in stress relaxation and delays failure.

Volume fraction is more influential than wall thickness variation in affecting the flexural response of GMB/HDPE syntactic foams as per the experimental results. Effective load transfer between the constituents is a function of interfacial bonding which is observed to be poor between HDPE and GMBs (Figure 3.4b). Due to the poor interfacial bonding, the matrix tends to flow around particles and provides large deformation. The four types of syntactic foams presented in Figure 3.17 show no signs of particle crushing on the fracture surface during flexural failure.

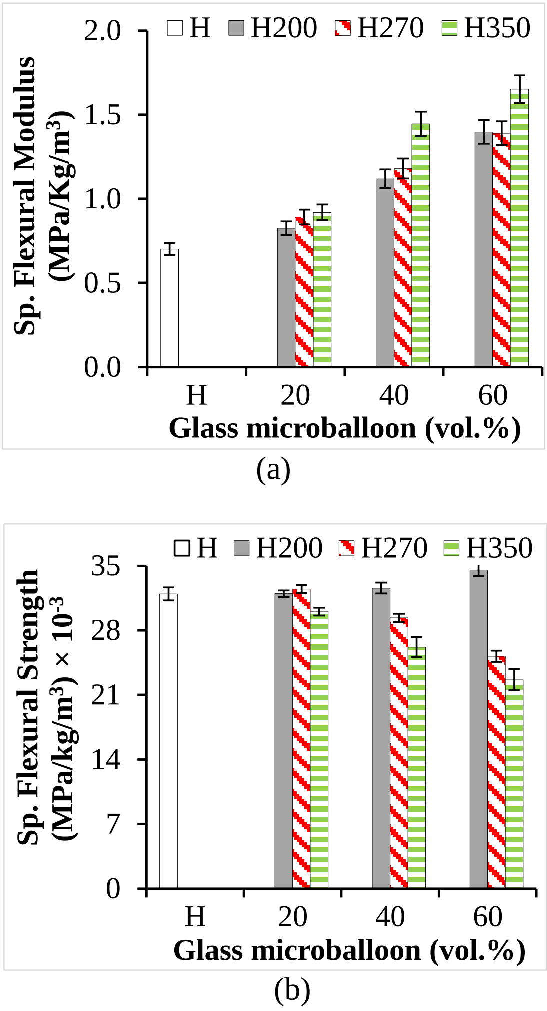
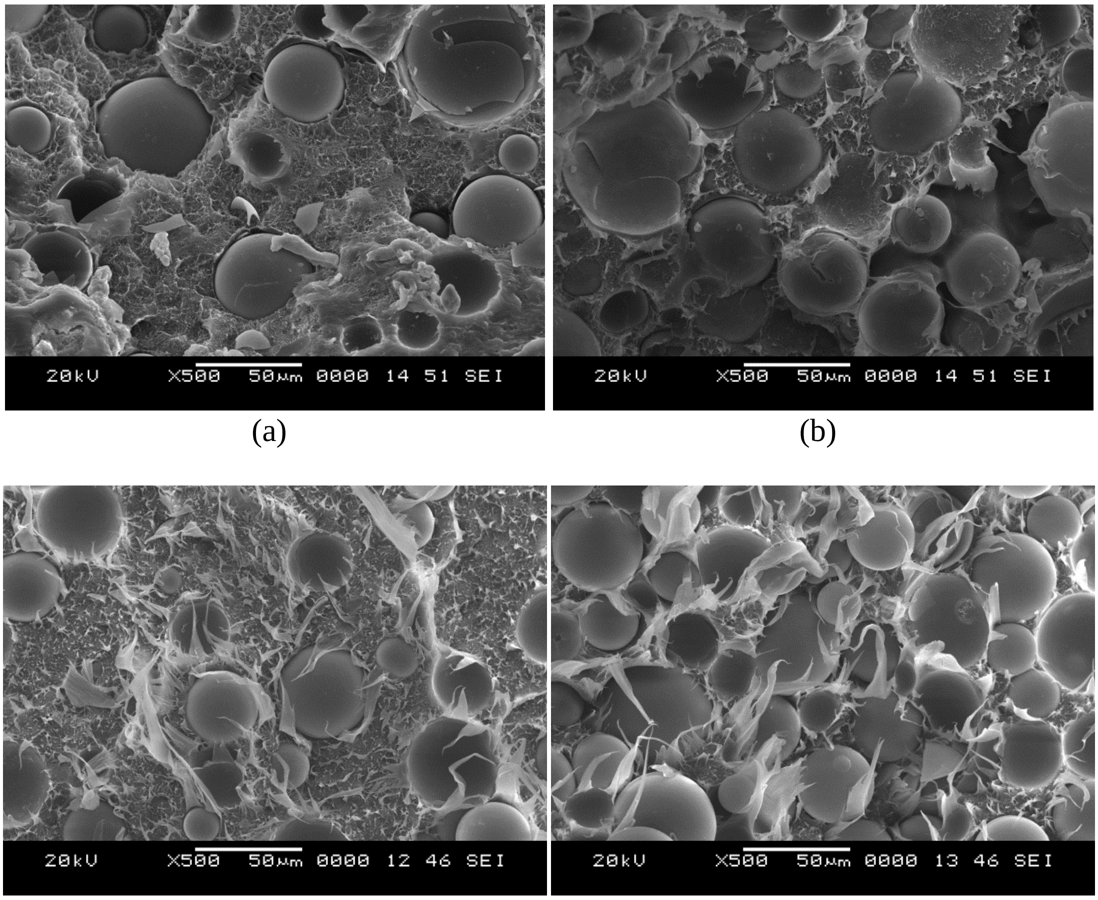


Figure 3.16 Experimentally measured specific flexural (a) modulus and (b) strength of HDPE and their syntactic foams.



(a) (b)

(c) (d)

Figure 3.17 Fracture features of (a) H200-20 (b) H200-60 (c) H350-20 and (d) H350-60 syntactic foams after flexure test. Particles are not broken or crushed on the fracture surface. Large deformation of matrix resin is evident in these micrographs.

3.6 Theoretical Modeling for tensile and flexural properties

Theoretical models available in literature are analyzed for GMB/HDPE syntactic foam composite to estimate the elastic modulus of syntactic foams. Many theoretical approaches are adopted for homogenization of particulate composite (Gupta et al. 2010) wherein elastic behavior of syntactic foam filled with hollow inclusion is studied (Porfiri and Gupta 2009). The two most commonly used theoretical approaches used to estimate elastic modulus are Porfiri-Gupta and Bardella-Genna model. For both these models modulus of the matrix material is taken from the experimental data and the Poisson’s ratio is assumed to be 0.425 (Bharath Kumar et al. 2016). Modulus of the microballoon is assumed to be 60 GPa with a Poisson’s ratio 0.21 (Tagliavia et al. 2010). Theoretical model takes into account GMB failure and actual particles survived (Table 3.2) are considered for estimation of tensile and flexure modulus.

3.6.1 Porfiri-Gupta (PG) model

Differential scheme based Porfiri-Gupta (PG) model measures the elastic properties of syntactic foam considering volume fraction, particle density and Poisson's ratio (Tagliavia et al. 2010). In this approach effective elastic properties of syntactic foam of an infinitely dilute dispersion of microballoon in a matrix medium are first computed by solving dilation and a shear problem (Tagliavia et al. 2010). Effective elastic modulus is calculated by using the differential equation,

$$\frac{dE}{E} = f_E(E_i, \upsilon_i, E_m, \upsilon_m, \eta)\,\frac{d\Phi_f}{1-\Phi_f/\Phi_m} \tag{3.2}$$

where, Φ_m assumed to be 0.637 (Torquato 2013). The parameter radius ratio (η) of the hollow particles is estimated by the Equation 2.1 and the computed values are presented in Table 2.1. Microballoon of three different wall thickness are used (Table 2.1), keeping the outer radius same, change in the inner radius affects modulus of the syntactic foam. Using differential scheme, tensile and flexural modulus is estimated for all types of GMB/HDPE syntactic foams by varying Φ_f and η.

3.6.2 Bardella-Genna (BG) model

Bardella-Genna (BG) model is a four phase theoretical approach that is used to measure the elastic properties of syntactic foams (Bardella and Genna 2001). This model uses a homogenization scheme to estimate the bulk modulus and shear modulus of the composite. The bulk modulus of syntactic foam is determined by,

$$K = K_m\,\frac{\delta(1+\Phi\gamma)+\kappa(1-\Phi)\gamma}{\delta(1-\Phi)+\kappa(\gamma+\Phi)} \tag{3.3}$$

where, $\gamma = \frac{4G_m}{3K_m}$, $\delta = \frac{4G_i}{3K_m}(1-\eta^3)$ and $\kappa = \frac{4G_i}{3K_i} + \eta^3$.

K and G are the bulk and shear modulus of material derived from radius ratio, young's modulus and Poisson's ratio. Radius ratio is already estimated in equation shown above. *m* and *i* represents the matrix and inclusion. Shear modulus is calculated using equations presented in Ref. Bardella and Genna (2001). The elastic modulus of syntactic foam is determined by,

$$E = \frac{9KG}{3K + G} \tag{3.4}$$

Figure 3.18 presents comparison of experimental values of tensile and flexural modulus with both PG and BG model predictions. Both the theoretical approaches reveal an increasing trend in modulus with increasing GMB content and decrease in radius ratio for both tensile (5 mm/min) and flexure modes.

PG model predictions displayed 2-37% and 6-30% deviations when compared with experimental results of tensile and flexural modulus respectively for all three different density particles. Such higher prediction differences make the PG model to be not suitable in predicting elastic modulus of these lightweight compression molded GMB/HDPE syntactic foams. BG model predictions are in close agreement with the experimental results as observed from Figure 3.18. Difference in theoretical and experimental values is in the range of 4-12% and 2-17% for tensile and flexural modulus respectively for all GMB/HDPE syntactic foams.

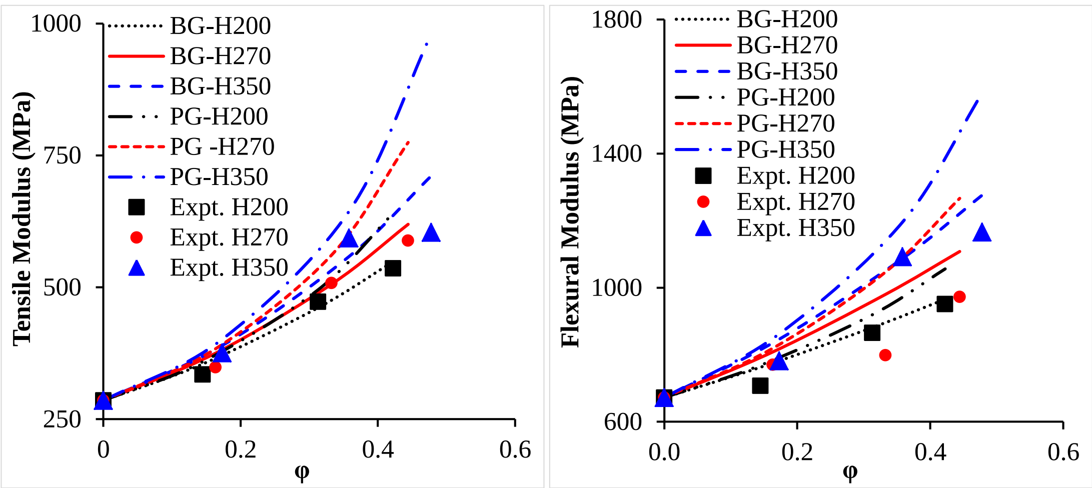


Figure 3.18 Comparison of experimental values with theoretical models for (a) tensile and (b) flexural modulus.

Porfiri-Gupta and Bardella-Genna are the two theoretical models used for the estimation of elastic modulus of tensile and flexural behavior as mentioned earlier. BG model is suitable based on the closer agreement between the predictions and the experimental results for estimating elastic modulus of compression molded GMB/HDPE syntactic foams. Such model helps in predicting the values prior to expensive and time consuming experimentations.

3.7 Property Map for Tensile and Flexural properties

Tensile and flexural properties are plotted with respect to density for HDPE composites containing different reinforcements in Figure 3.19 (Adhikary et al. 2011, Bharath Kumar et al. 2016, Homaeigohar et al. 2006, Khalaf 2015, Liu et al. 2008, Ou et al. 2014, Sim et al. 1997, Yuan et al. 2010) and Figure 3.20 (Adhikary et al. 2011, Ayrilmis 2013, Bharath Kumar et al. 2016, Chen et al. 2006, Gwon et al. 2012, Liu et al. 2008, Liu et al. 2009, Singh et al. 2014, Yuan et al. 2010) respectively.

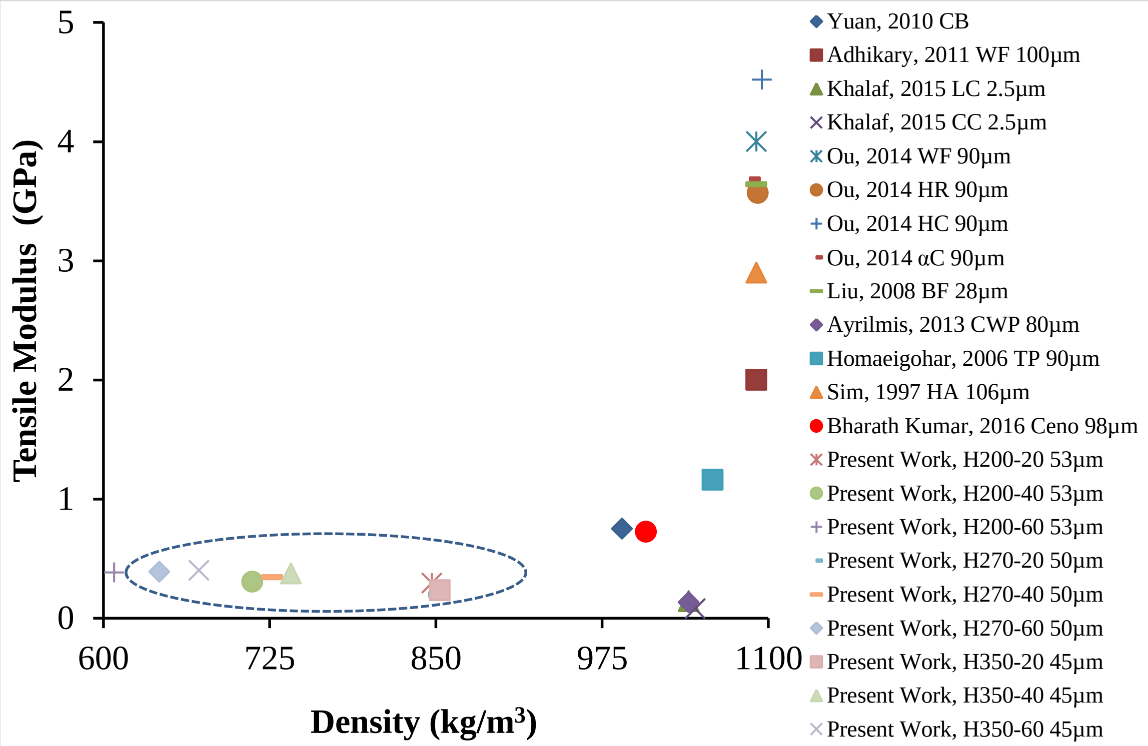
Data are extracted from published literature and are plotted with respect to density in these figures to compare with the results obtained in the present study. It can be observed from the figures that composites with higher modulus also have higher density as a general trend for solid particle filled composites. However, the advantage of hollow particle filler is evident from these figures.

H350-60 has much lower density with higher tensile modulus compared to wood, lignocellulose and calcium carbonate HDPE composites (Figure 3.19a). Tensile strength for H350-20 is higher than cenosphere, b-tricalcium phosphate, scrap rubber powder and comparable to lignocellulose with 1.18-1.3 times lower density as seen from Figure 3.19b.

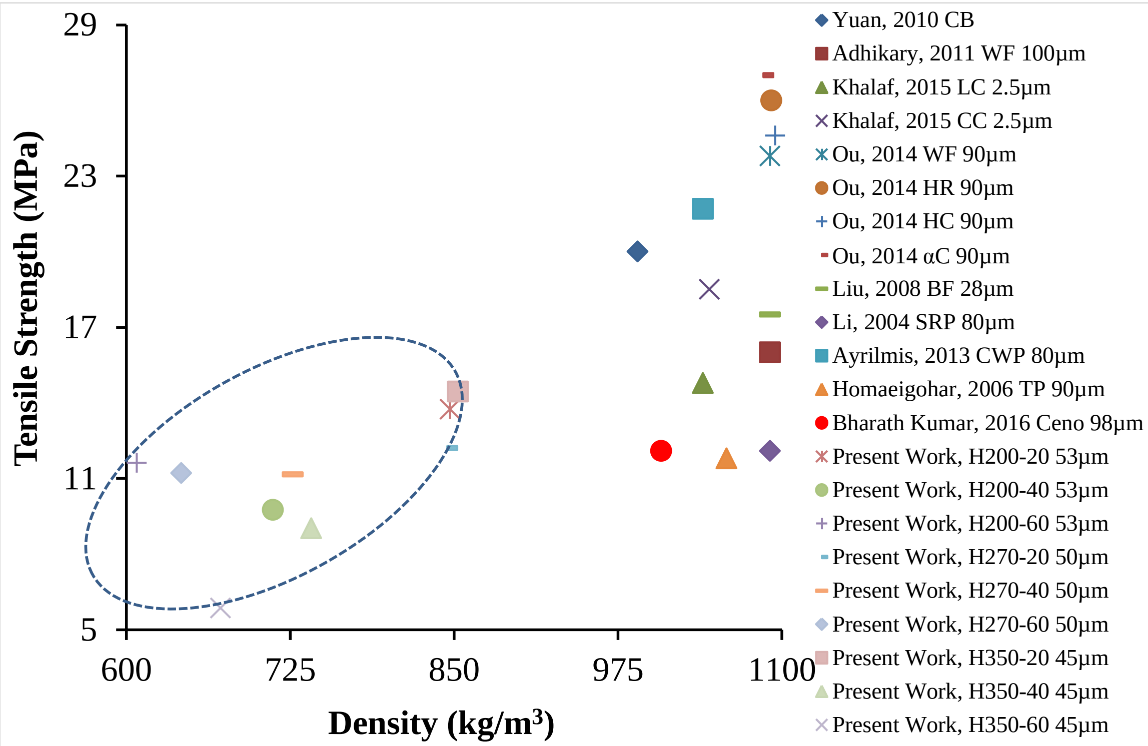
H350-60 outperformed wood powder and cenosphere filled HDPE composites for flexural modulus (Figure 3.20a). H200-20 exhibited superior flexural strength compared to wood powder, cenosphere, natural and hemp fiber HDPE composites with density reduction of almost 1.5 times for GMB/HDPE syntactic foams developed in the present study (Figure 3.20b).

Choice of appropriate constituent materials and concentrations, the tensile and flexural properties can be tailored over a wide range as seen from Figure 3.19 and Figure 3.20. It is desired to have higher mechanical properties for lower densities, where syntactic foams can provide advantage as their specific modulus and specific strength would be comparable to several composites having higher absolute properties.

Syntactic foams prepared by compression molding technique registered higher tensile and flexural modulus for H350-60 foam. GMB inclusion in HDPE matrix effectively reduced density and enhanced the specific modulus. Compared to other thermoplastic foams available in literature, developed GMB/HDPE foams exhibited better tensile and flexural behavior with substantial weight saving potential. In the sections to follow, GMB/HDPE syntactic foams are investigated for quasi-static compression, dynamic mechanical analysis and crystallinity influence on the selected property.

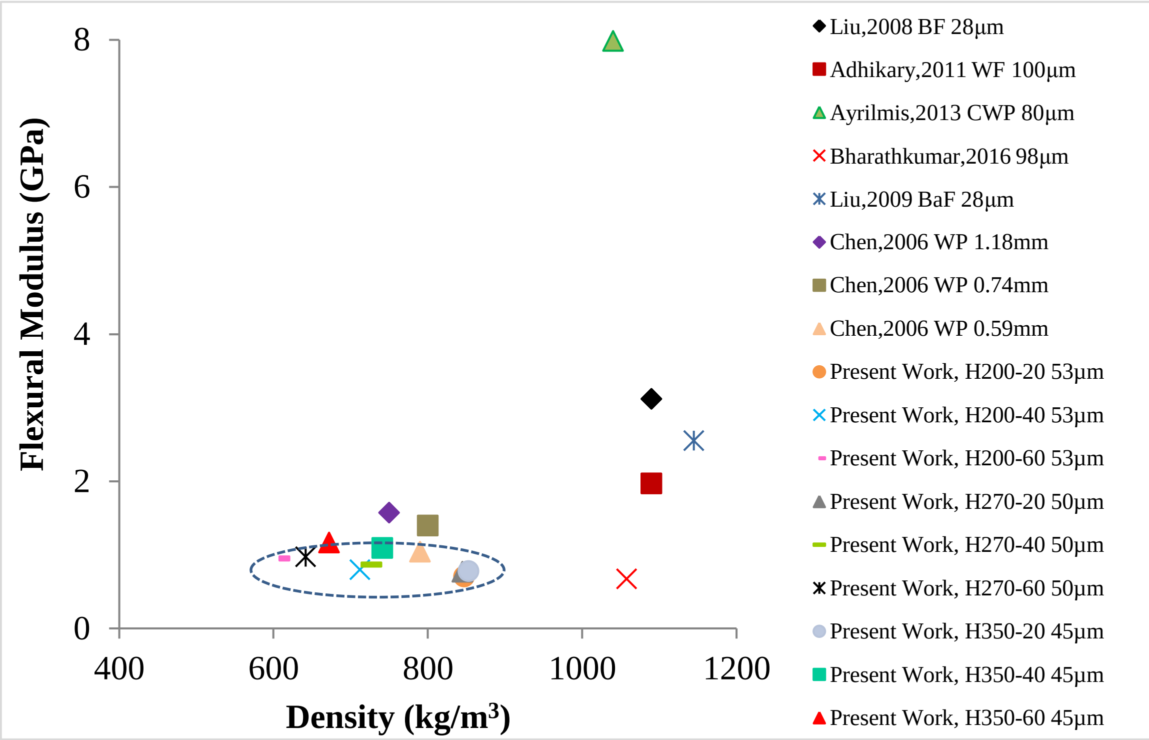


(a)

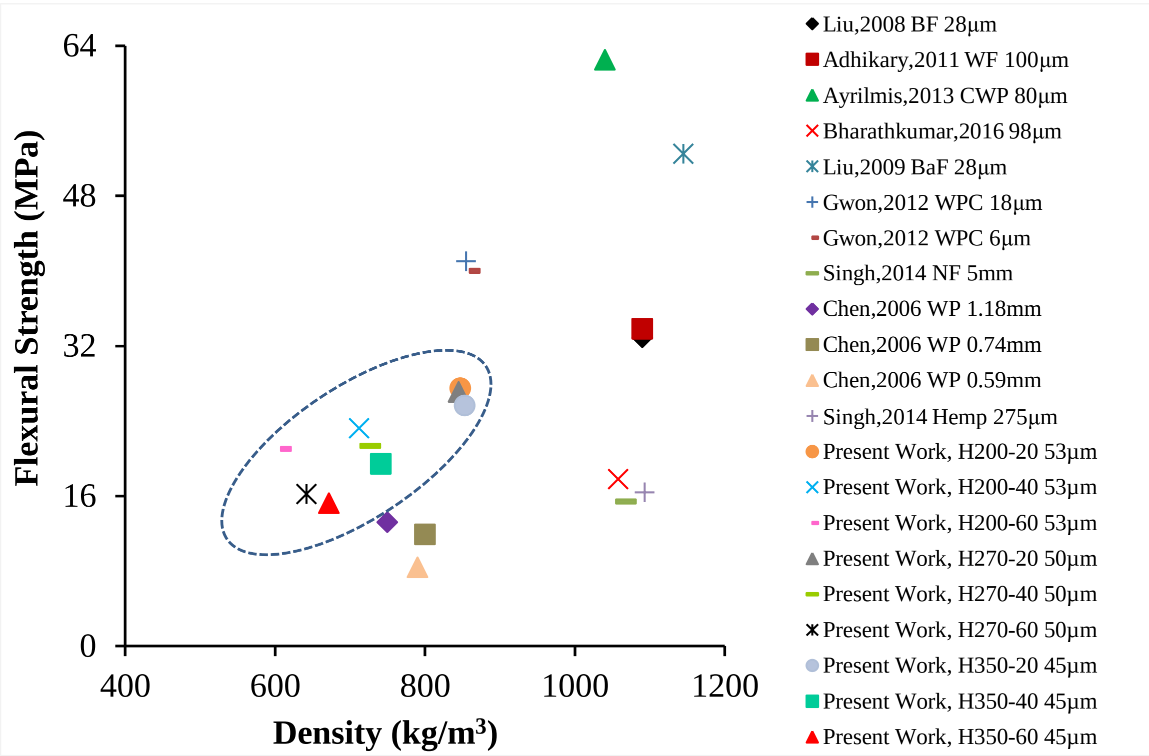


(b)

Figure 3.19 (a) Tensile modulus and (b) strength of HDPE composites plotted against density (Adhikary et al. 2011, Bharath Kumar et al. 2016, Homaeigohar et al. 2006, Khalaf 2015, Liu et al. 2008, Ou et al. 2014, Sim et al. 1997, Yuan et al. 2010).



(a)



(b)

Figure 3.20 (a) Flexural modulus and (b) strength of HDPE composites plotted against density from available studies (Adhikary et al. 2011, Ayrilmis 2013, Bharath Kumar et al. 2016, Chen et al. 2006, Gwon et al. 2012, Liu et al. 2008, Liu et al. 2009, Singh et al. 2014, Yuan et al. 2010).

3.8 Quasi-static compression

Figure 3.21- Figure 3.23 presents the quasi-static compressive stress strain plots for neat HDPE and their foams at different strain rates. The stress-strain profile of neat HDPE processed through compression molding as presented in this study is similar to the trend observed in injection molded specimens (Bharath Kumar et al. 2016).

HDPE syntactic foams exhibits different behavior as compared to thermoset foams. In vinyl ester and epoxy syntactic foams, matrix being brittle, stress drops significantly at the end of the initial linear elastic region, followed by a stress plateau (Gupta et al. 2010). Such stress drop is due to successive failure of brittle particles in the matrix owing to stress concentration in the localized region around broken particles (Kim et al. 2000, Wong and Bollampally 1999)

At room temperature above T_g, HDPE is significantly more compliant and such effects are mitigated. Strain rate sensitivity is clearly evident from Figure 3.21- Figure 3.23 for all the foams showing rise in modulus and strength with higher strain rates. Such behavior is very useful in designing materials for impact mitigation applications.

Three distinct regions can be observed from representative stress-strain plots as presented in Figure 3.24. These regions are (1) constant slope initial elastic region (2) a post-yield plastic deformation region with stress plateau and (3) higher and increasing slope plastic deformation region.

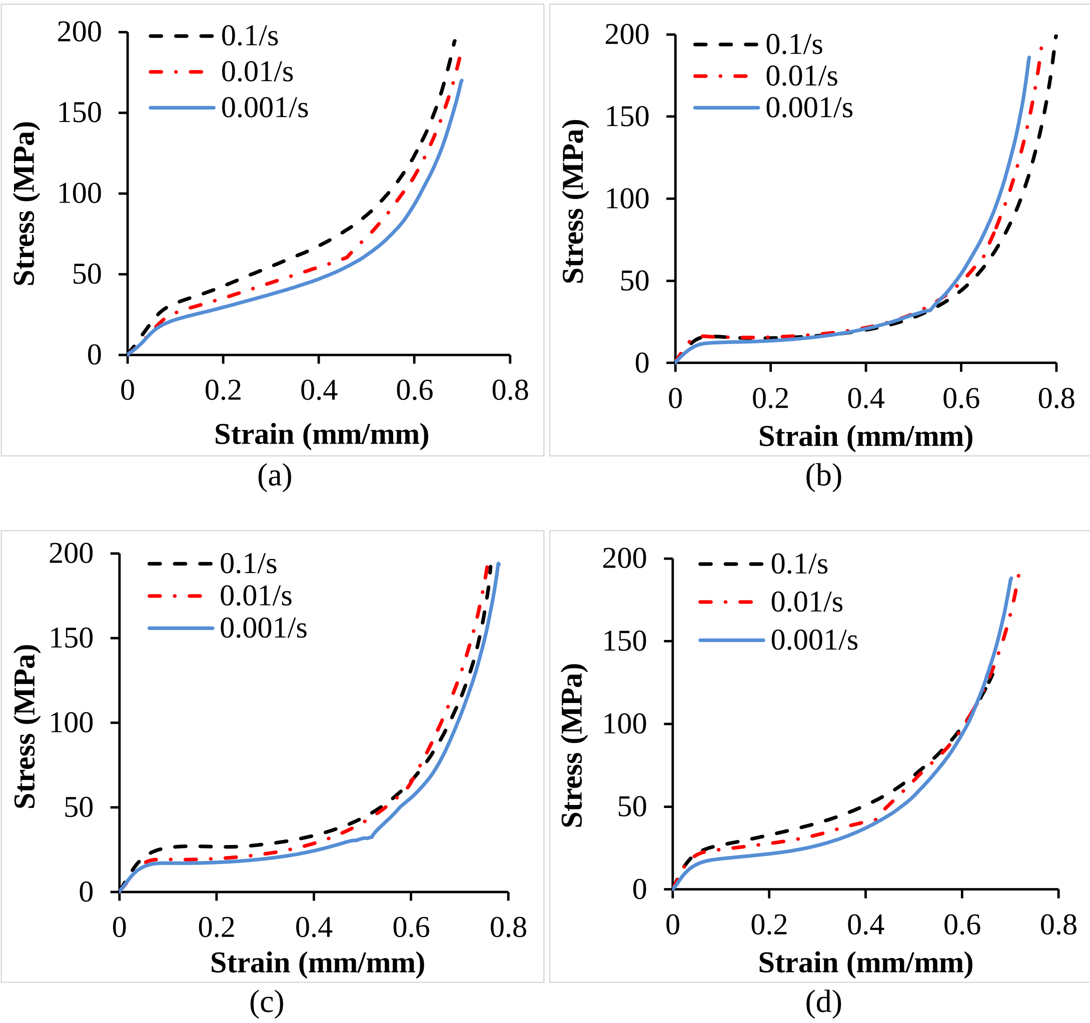


Figure 3.21 Stress–strain response of (a) neat HDPE (b) H200-20 (c) H200-40 and (d) H200-60 at different strain rates.

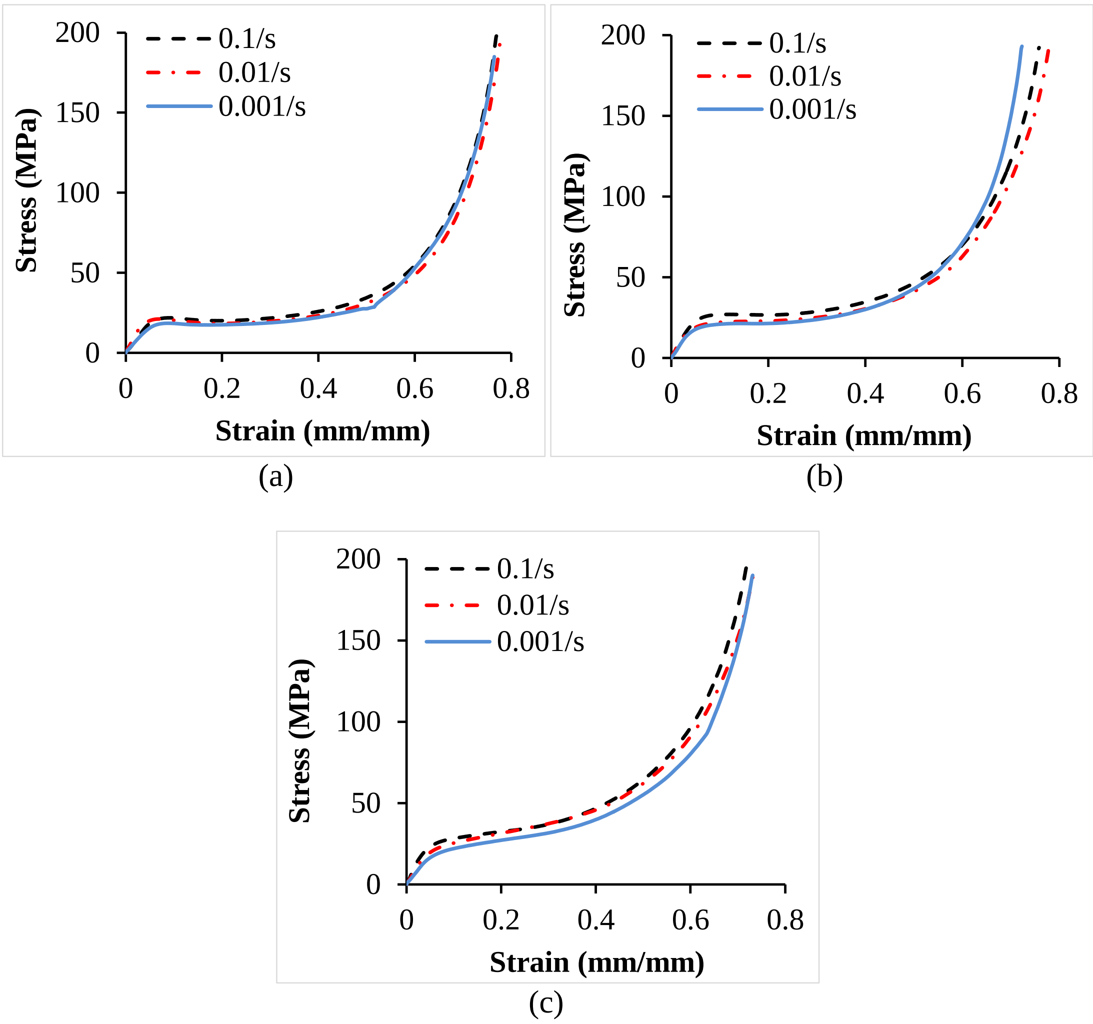


Figure 3.22 Stress–strain response of (a) H270-20 (b) H270-40 and (c) H270-60 at different strain rates.

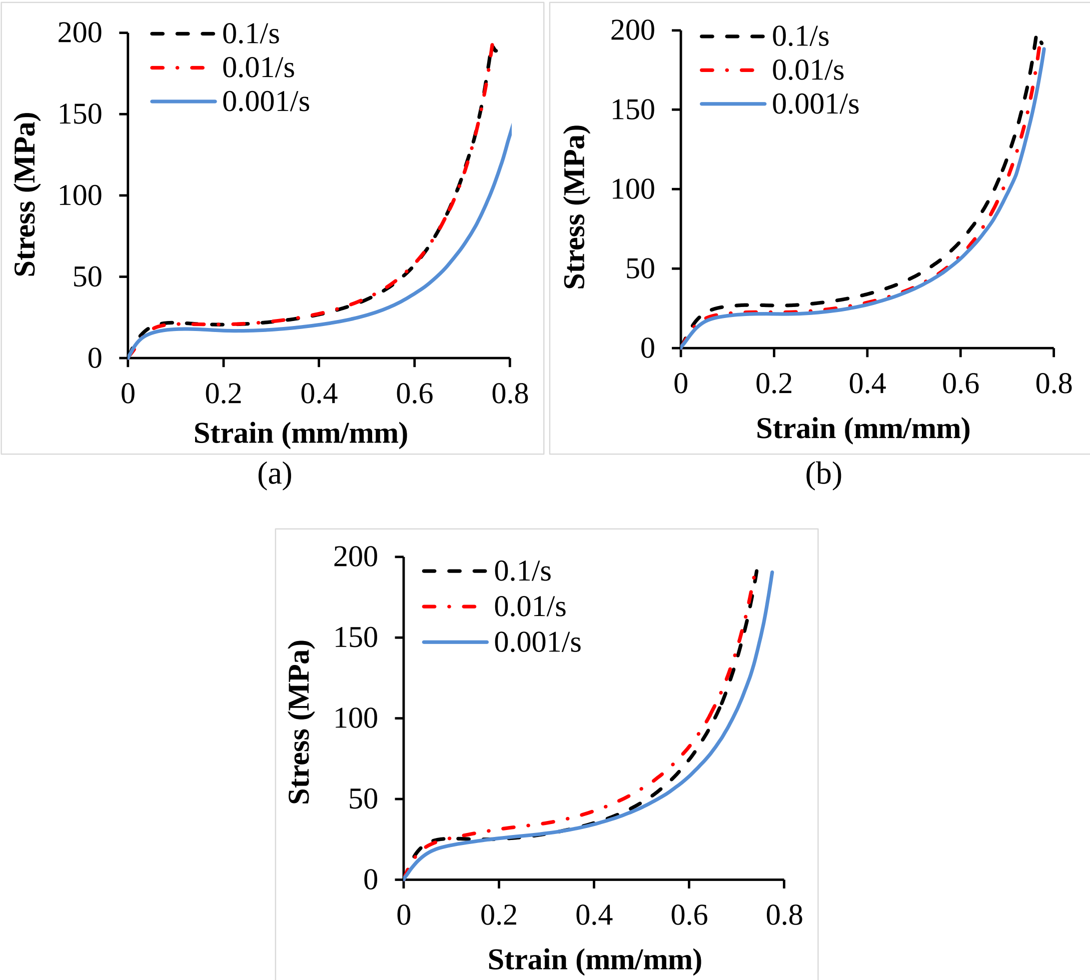


Figure 3.23 Stress–strain response of (a) H350-20 (b) H350-40 and (c) H350-60 at different strain rates.

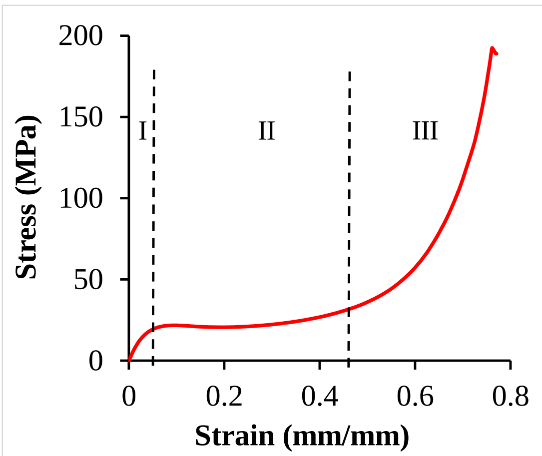


Figure 3.24 Schematic stress–strain response at $0.1s^{-1}$ in H350-60 showing three distinct regions (I - linear elastic, II - plateau, III - densification region) of deformation behaviour.

In GMB/HDPE foams the increasing slope plastic deformation zone is named as densification region and is observed after 0.5 mm/mm strain value. In this region some of the stress strain responses (Figure 3.21b, Figure 3.21d, Figure 3.22b and Figure 3.23c) scatter in the strength values with respect to the strain rate. This attributes to the change in geometry of the crushed microballoon and the fluctuation encountered due to the presence of more void spaces within the microballoon. Lowest filler content foams exhibits clearly distinguishable stress plateau irrespective of particle wall thickness which is a characteristic of foams and porous materials (Figure 3.21b, Figure 3.22a, Figure 3.23a). GMB reinforcement of 20 vol. % in HDPE might be effective in constraining the matrix deformation. These foams can be effectively used for energy absorbing applications. Neat HDPE and other syntactic foams continue to harden at all strains.

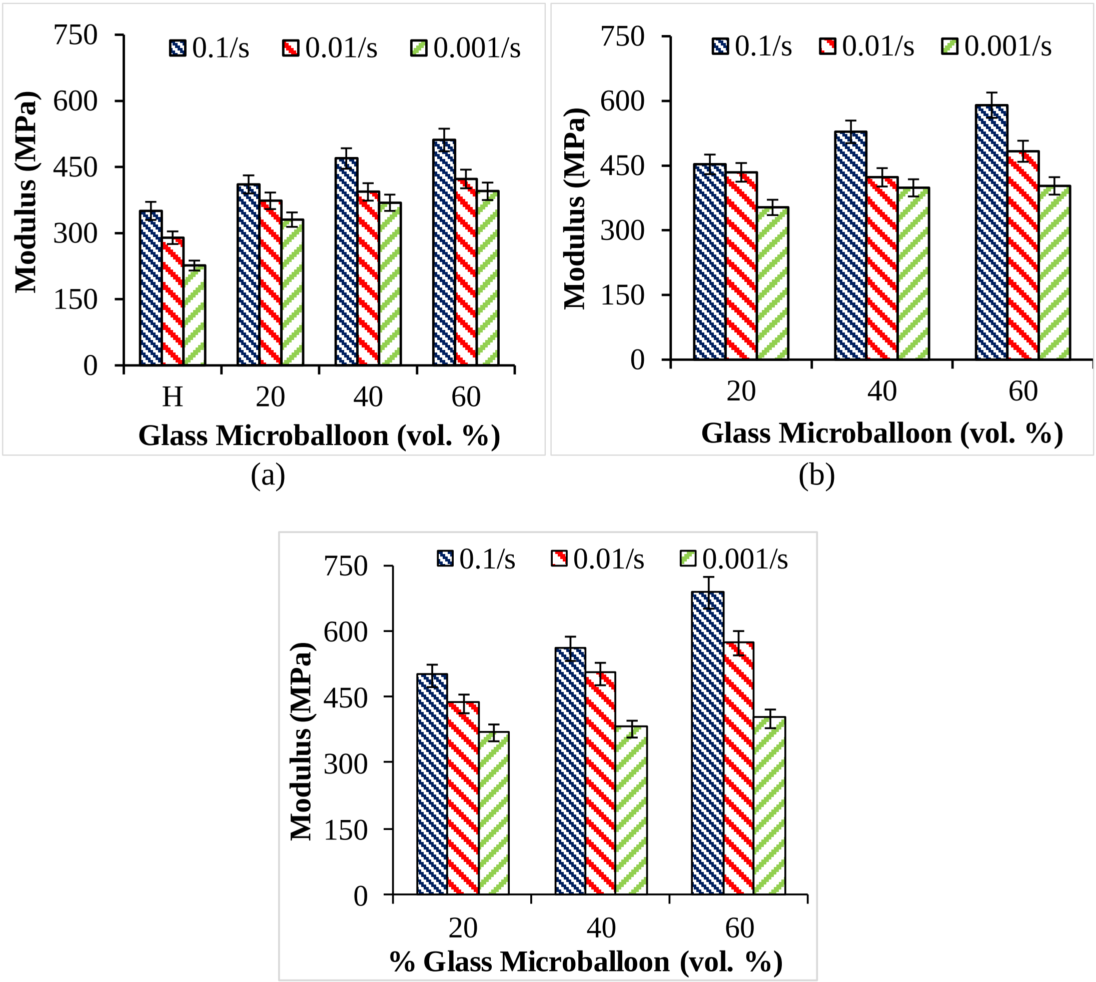
Table 3.7 presents measured mechanical properties of syntactic foams in quasi-static compressive mode. Mean elastic modulus and compressive yield strength are observed to increase with increasing strain rate for all the syntactic foams though for few standard deviation values are overlapping as seen from Figure 3.25 and Figure 3.26. H350-60 shows highest modulus and yield strength for all compressive strain rates among the foams investigated. GMB wall thickness has a higher influence as compared to filler volume fraction.

Thick walled GMB particles have more stress resistance and higher strain energy absorption resulting in higher modulus. Thicker walled particles at higher strain rates with increasing filler content increases modulus in the range of 27-68% in comparison to neat HDPE (Table 3.7).

Neat HDPE registered maximum yield strength of 34.92 MPa at highest strain rate as compared to all the syntactic foams developed in the present study. Nevertheless, specific properties need to be looked in to from weight saving perspective.

Table 3.7 Mechanical properties for HDPE and their foams in quasi-static compression mode.

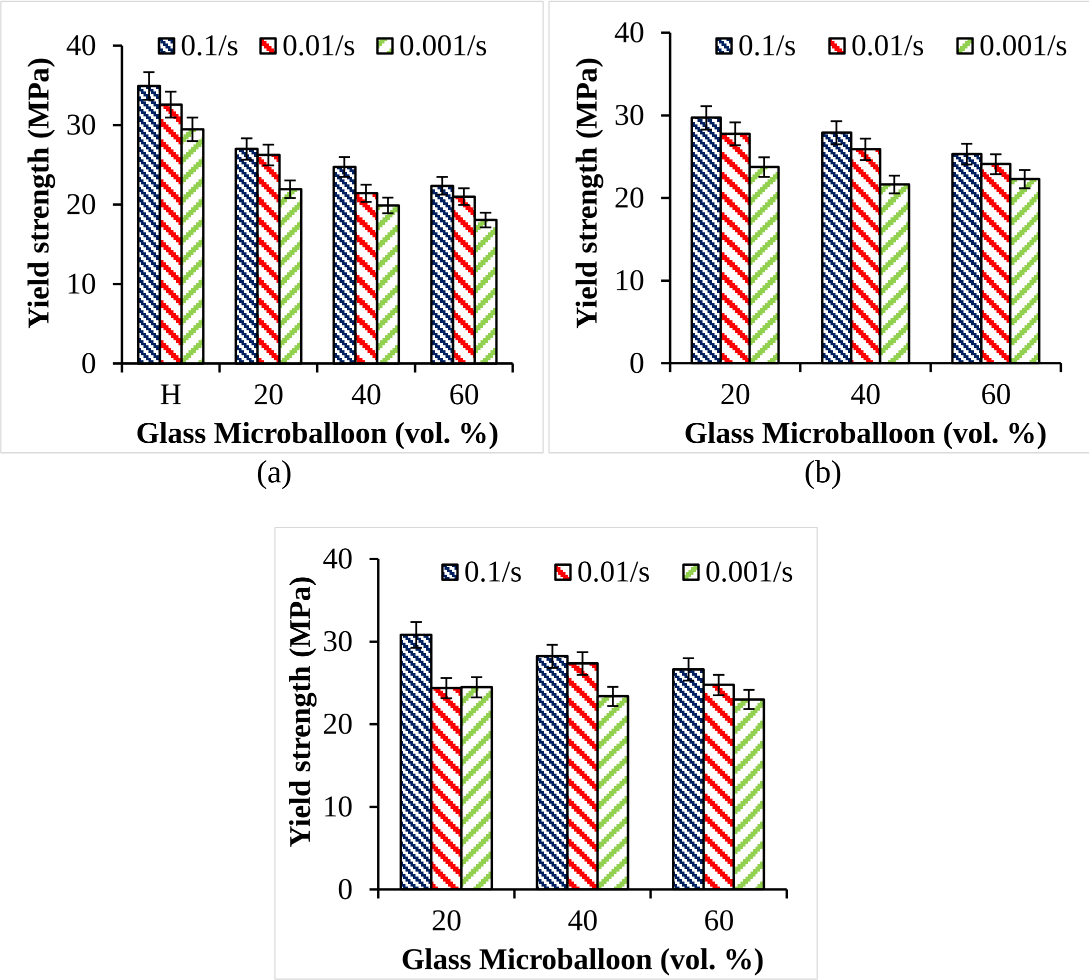
Material	Strain rate (s^{-1})	Modulus (MPa)	Yield strength (MPa)	Yield strain (%)	Energy absorbed to 40% strain (MJ/m^3)	Densification Stress (MPa)	Densification Strain (%)
H	0.001	226.31±11.31	29.47±1.47	2.25±0.11	14.71±0.74	-----	-----
	0.01	289.60±14.48	32.58±1.63	3.72±0.19	16.63±0.83	-----	-----
	0.1	350.52±20.47	34.92±1.75	4.19±0.21	17.99±0.90	-----	-----
H200-20	0.001	330.70±16.53	21.94±1.09	1.99±0.10	10.81±0.54	42.79±2.14	49.37±2.46
	0.01	373.30±18.66	26.23±1.31	2.45±0.12	13.29±0.67	48.19±2.41	41.45±2.07
	0.1	410.43±20.52	26.99±1.35	2.12±0.11	10.96±0.55	54.64±2.73	58.07±2.91
H200-40	0.001	368.99±18.45	19.89±0.99	1.70±0.09	8.79±0.44	41.78±2.08	55.32±2.76
	0.01	393.71±19.68	21.43±1.07	1.72±0.09	9.81±0.49	61.49±3.07	59.26±2.96
	0.1	469.50±23.47	24.73±1.24	2.62±0.13	11.06±0.55	63.70±3.18	59.45±2.97
H200-60	0.001	395.23±19.76	18.05±0.92	1.56±0.08	7.56±0.38	35.93±1.79	54.68±2.73
	0.01	423.21±21.15	21.00±1.05	2.23±0.11	10.08±0.50	55.85±2.79	59.27±2.96
	0.1	511.30±25.56	22.35±1.12	2.50±0.12	8.47±0.42	55.30±2.76	63.90±3.19
H270-20	0.001	353.10±17.65	23.74±1.19	1.89±0.09	11.55±0.58	61.06±3.05	54.03±2.70
	0.01	434.38±21.71	27.77±1.39	1.95±0.09	13.71±0.69	80.03±4.01	56.87±2.84
	0.1	453.20±22.66	29.71±1.48	2.58±0.13	15.11±0.76	82.46±4.12	56.44±2.82
H270-40	0.001	398.40±19.92	21.62±1.09	1.52±0.08	10.33±0.52	41.60±2.08	49.30±2.46
	0.01	423.12±21.15	25.88±1.29	3.13±0.16	10.31±0.52	46.40±2.32	53.24±2.66
	0.1	528.30±26.41	27.90±1.39	2.31±0.12	12.32±0.62	68.35±3.41	59.50±2.97
H270-60	0.001	403.00±20.15	22.29±1.11	2.11±0.11	8.83±0.44	32.65±1.63	56.44±2.82
	0.01	483.30±24.16	24.10±1.21	1.61±0.08	9.59±0.48	41.38±2.06	51.34±2.56
	0.1	590.23±29.51	25.30±1.27	2.66±0.13	10.17±0.51	62.34±3.11	62.26±3.11
H350-20	0.001	368.60±18.43	24.46±1.22	1.91±0.09	13.28±0.66	59.71±2.98	58.32±2.91
	0.01	435.28±21.76	27.36±1.36	2.29±0.11	14.20±0.71	75.58±3.77	57.99±2.90
	0.1	500.15±26.61	30.81±1.54	3.04±0.15	14.33±0.72	80.04±4.01	61.42±3.07
H350-40	0.001	410.06±19.01	23.37±1.17	2.16±0.11	10.18±0.51	48.83±2.44	56.87±2.84
	0.01	505.39±25.27	24.35±1.21	2.02±0.10	11.10±0.56	59.74±2.98	60.48±3.02
	0.1	562.03±27.10	28.22±1.41	2.46±0.12	12.44±0.62	66.08±3.31	59.64±2.98
H350-60	0.001	480.90±20.09	22.99±1.15	2.07±0.10	9.49±0.48	31.90±1.59	55.19±2.76
	0.01	573.25±28.66	24.75±1.24	1.45±0.07	9.54±0.48	27.35±1.36	47.69±2.38
	0.1	689.01±34.45	26.64±1.33	2.71±0.13	10.61±0.53	52.89±2.64	58.58±2.93



(c)

Figure 3.25 Experimentally measured modulus for (a) neat HDPE and H200 (b) H270 and (c) H350 at different compressive strain rates.

Yield strength is seen to be increasing with particle wall thickness and strain rate as evident from Figure 3.26. Increasing filler content decreases yield strength to the tune of 17-39, 24-36 and 12-36% respectively at 0.001, 0.01 and 0.1s^{-1} strain rate for H200, H270 and H350 as compared to neat matrix. Higher energy absorption capabilities are noted in thicker walled foams.



(a) (b)

(c)

Figure 3.26 Experimentally measured yield strength for (a) neat HDPE andH200 (b) H270 and (c) H350 at different compressive strain rates.

Table 3.8 presents specific compressive modulus and yield strengths for various material compositions. All syntactic foams registered superior performance compared to neat HDPE for specific modulus (0.39 -1.03 MPa/kg/m^3) at all strain rates (Figure 3.27). Higher filler loading resulted in higher specific strength values compared to HDPE matrix as seen from Figure 3.28. Reducing filler breakage further might lead to higher specific yield strengths even at lower filler contents. Highest specific modulus (1.03 MPa/kg/m^3) and yield strength (0.03964 MPa/kg/m^3) is observed for H350-60. These finding implies that, H350-60 foam is useful in reducing thermoplastic resin usage for a given applications with overall weight saving of 29.26% (Table 3.2).

Table 3.8 Specific compressive properties for HDPE and their foams.

Material	Strain rate (s^{-1})	Specific compressive Modulus (MPa/kg/m^3)	Specific compressive Yield strength (MPa/kg/m^3) $\times 10^{-3}$
H	0.001	0.238	31.02
	0.01	0.305	34.29
	0.1	0.431	36.75
H200-20	0.001	0.390	25.90
	0.01	0.441	30.97
	0.1	0.485	31.87
H200-40	0.001	0.518	27.94
	0.01	0.553	30.10
	0.1	0.659	34.73
H200-60	0.001	0.650	29.68
	0.01	0.696	34.54
	0.1	0.891	36.76
H270-20	0.001	0.420	28.09
	0.01	0.500	29.74
	0.1	0.540	34.72
H270-40	0.001	0.550	32.86
	0.01	0.600	35.60
	0.1	0.730	37.54
H270-60	0.001	0.630	35.16
	0.01	0.750	38.38
	0.1	0.920	39.41
H350-20	0.001	0.430	28.09
	0.01	0.510	32.86
	0.1	0.620	35.16
H350-40	0.001	0.510	28.55
	0.01	0.680	36.92
	0.1	0.730	36.83
H350-60	0.001	0.600	36.12
	0.01	0.850	38.08
	0.1	1.030	39.64

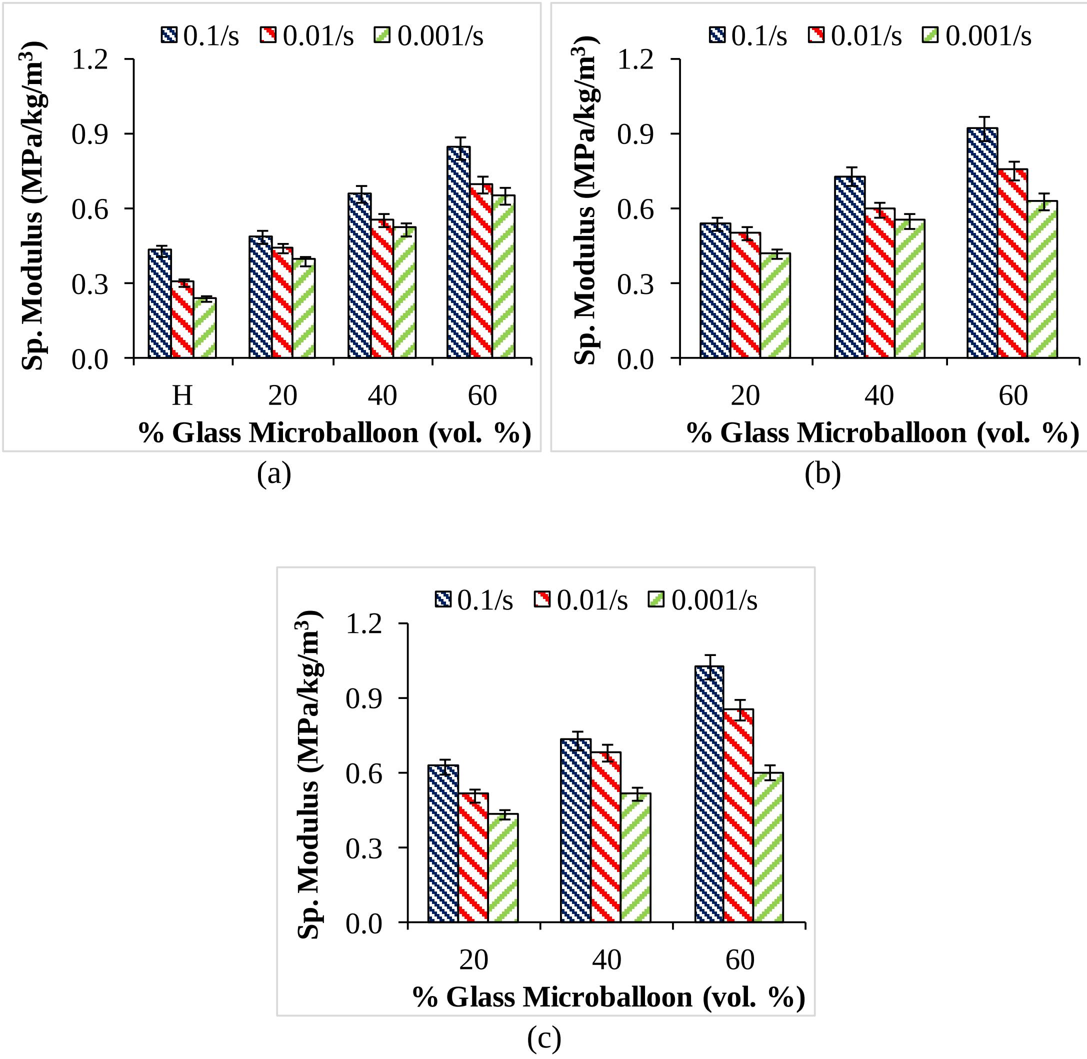


Figure 3.27 Experimentally measured specific modulus for (a) neat HDPE and H200 (b) H270 and (c) H350 at different compressive strain rates.

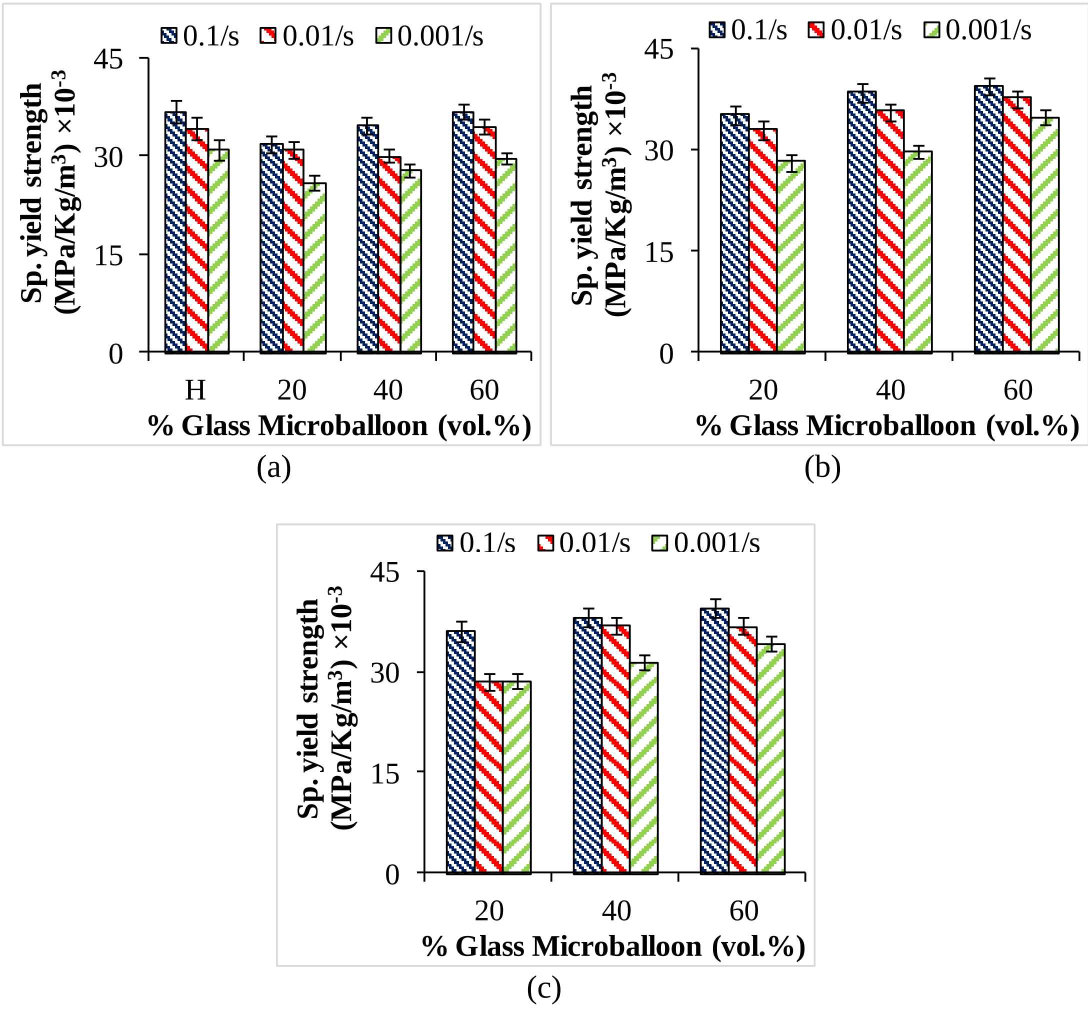
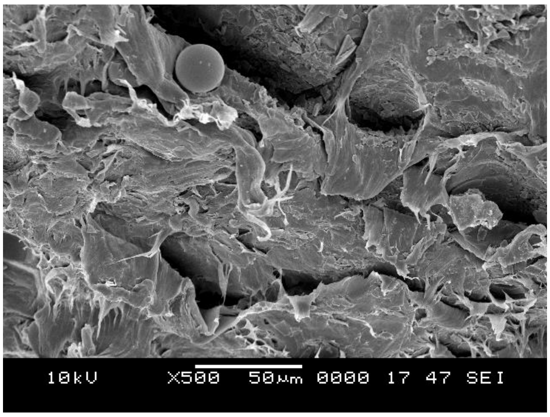
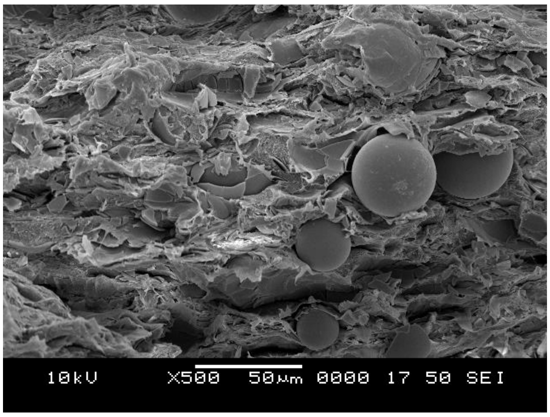


Figure 3.28 Experimentally measured specific yield strength for (a) neat HDPE and H200 (b) H270 and (c) H350 at different compressive strain rates.

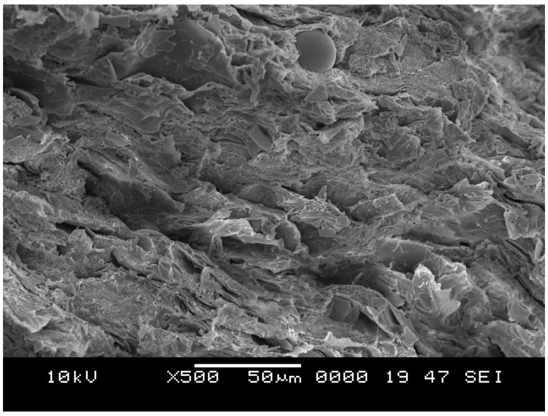
Table 3.7 presents measured densification strain and corresponding stresses for all the syntactic foams. The densification strain and their corresponding stress values increases as strain rate increases for all syntactic foams (Smith et al. 2012). Effect of particle wall thickness and volume fraction did not show any specific trend pertaining to densification values. Figure 3.29 presents SEM images of the compressed samples at lower and higher strain rates for all syntactic foams. Intact microballoons are observed post densification in all the samples (Figure 3.29). High strength bearing thicker walled particles (Figure 3.29g-Figure 3.29l) are survived more in number compared to thinners walled (Figure 3.29a-Figure 3.29f) ones. Figure 3.29a-Figure 3.29f exhibits extensive matrix deformation and debris as compared to Figure 3.29g-Figure 3.29l. Change in strain rate magnitude did not show any distinct change in failure features as observed from these micrographs. Nevertheless, these failure features might help in analysing failure patterns post high strain regime.



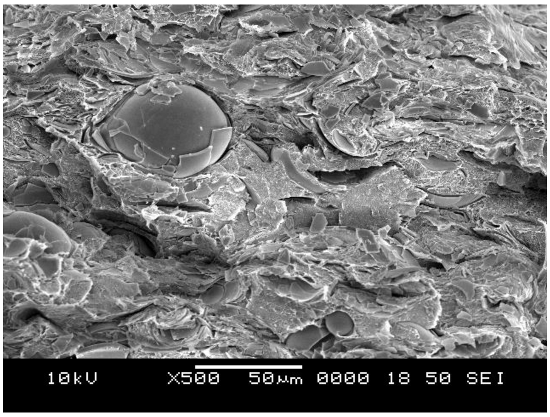
(a)



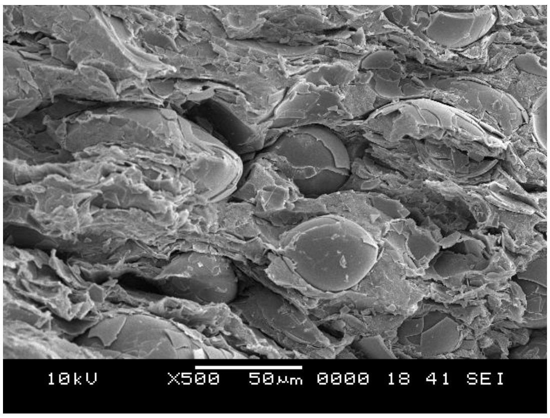
(b)



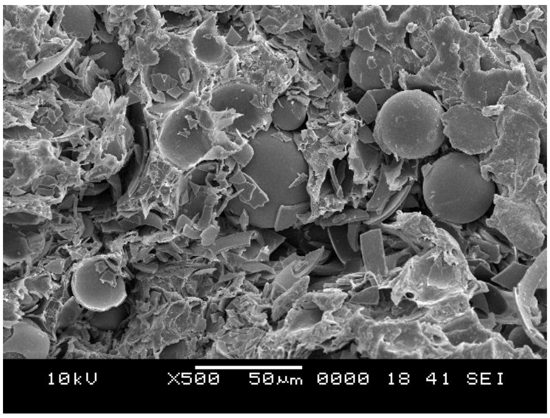
(c)



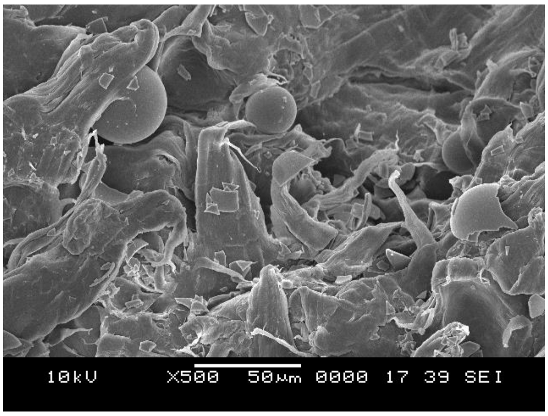
(d)



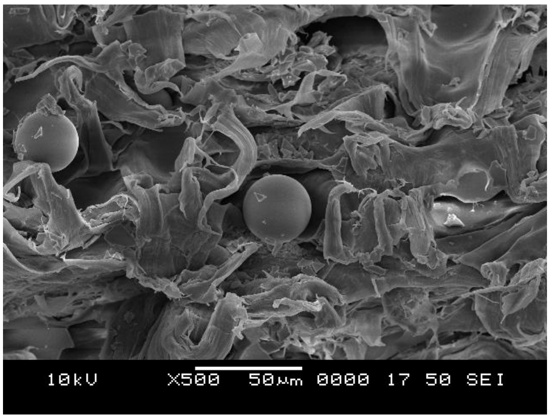
(e)



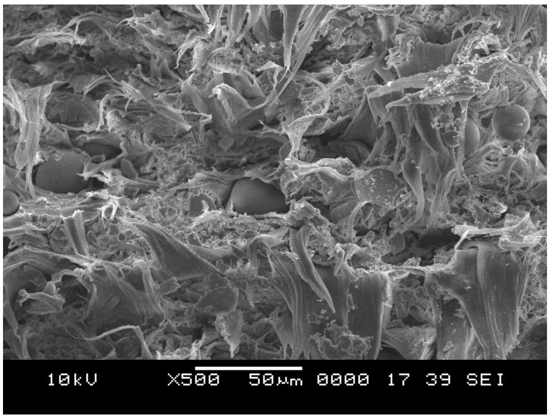
(f)



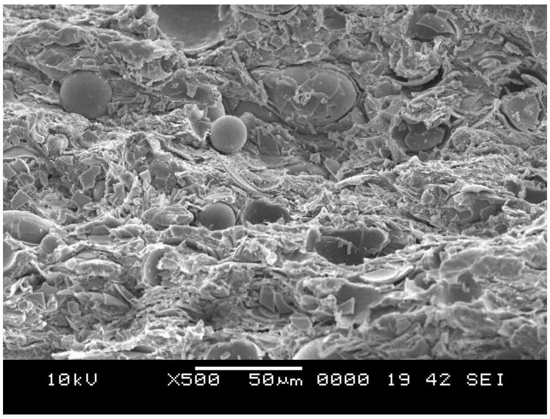
(g)



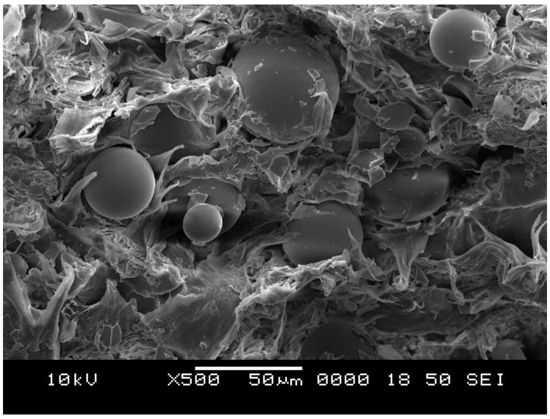
(h)



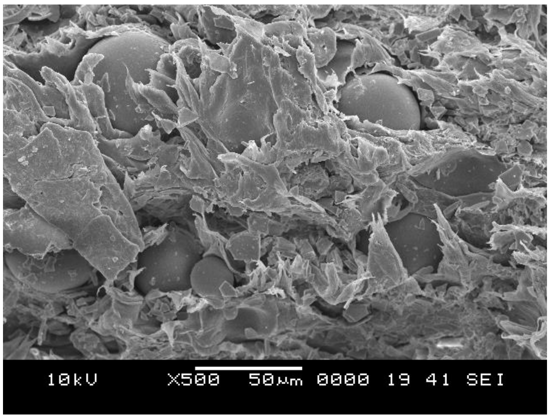
(i)



(j)



(k)



(l)

Figure 3.29 SEM image of compressed syntactic foam samples of (a) H200-20 specimen at $0.001s^{-1}$ (b) H200-20 specimen at $0.1s^{-1}$ (c) H200-40 specimen at $0.001s^{-1}$(d) H200-40 specimen at $0.1s^{-1}$ (e) H200-60 specimen at $0.001s^{-1}$ (f) H200-60 specimen at $0.1s^{-1}$ (g) H350-20 specimen at $0.001s^{-1}$ (h) H350-20 specimen at $0.1s^{-1}$ (i) H350-40 specimen at $0.001s^{-1}$ (j) H350-40 specimen at $0.1s^{-1}$ (k) H350-60 specimen at $0.001s^{-1}$and (l) H350-60 specimen at $0.1s^{-1}$. Survived GMB particles after densification are clearly evident from these micrographs.

3.8.1 Theoretical modelling for quasi-static behaviour

Elastic properties of syntactic foams in compressive mode can be estimated using several available theoretical models (Luong et al. 2013). Experimental results for compressive response are found to be in close agreement with the values predicted by these theoretical models developed for thermosetting syntactic foams (Aureli et al. 2010). Analysis of cenosphere filled thermoplastic foams is carried out using one of these models based on a differential scheme (Aureli et al. 2010, Porfiri and Gupta 2009). Porfiri-Gupta and Bardella-Genna models as discussed in Section 3.6 are used for predicting compressive modulus.

Matrix modulus is taken from the experimental result of compression test carried out for a strain rate of $0.1 s^{-1}$ and Poisson's ratio is assumed to be 0.425 (Bharath Kumar et al. 2016). GMB modulus and Poisson's ratio are taken as 60 GPa and 0.21 respectively (Tagliavia et al. 2010) as mentioned in Section 3.6. The parameter η is used from Table 2.1. Using differential scheme, compression modulus is estimated for all types of GMB/HDPE syntactic foams by varying Φ_f and η. Varying Φ_f and η, compression modulus is calculated for all types of GMB/HDPE syntactic foams at constant strain rate. Both the theoretical models are analyzed for strain rates of 0.001, 0.01 and 0.1 s^{-1}. It is observed that the compressive modulus increases with an increase of filler content and wall thickness. The comparison between PG and BG model values with experimental results for 0.1 s^{-1} strain rates is presented in Figure 3.30. Theoretical model takes into account particles survived (Table 3.2) for estimation of compressive modulus. Experimental results are found to be in good agreement with theoretical ones (less than 5%) for PG model as compared to BG predictions, though slight deviations are noted as seen from Figure 3.30. PG model is most feasible in predicting the compressive modulus for GMB/HDPE syntactic foams. Such theoretical predictions come handy to predict properties beforehand exhibiting behavioral trends.

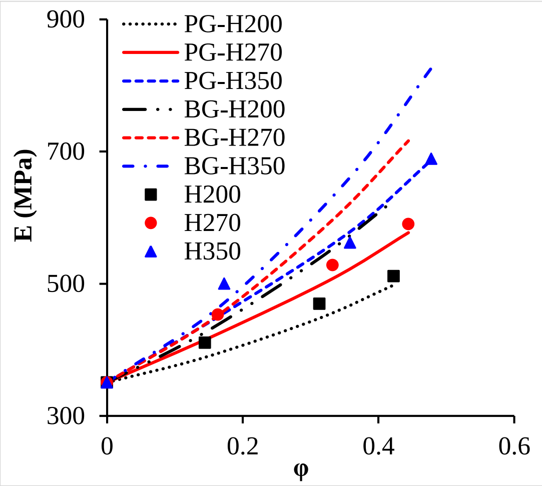
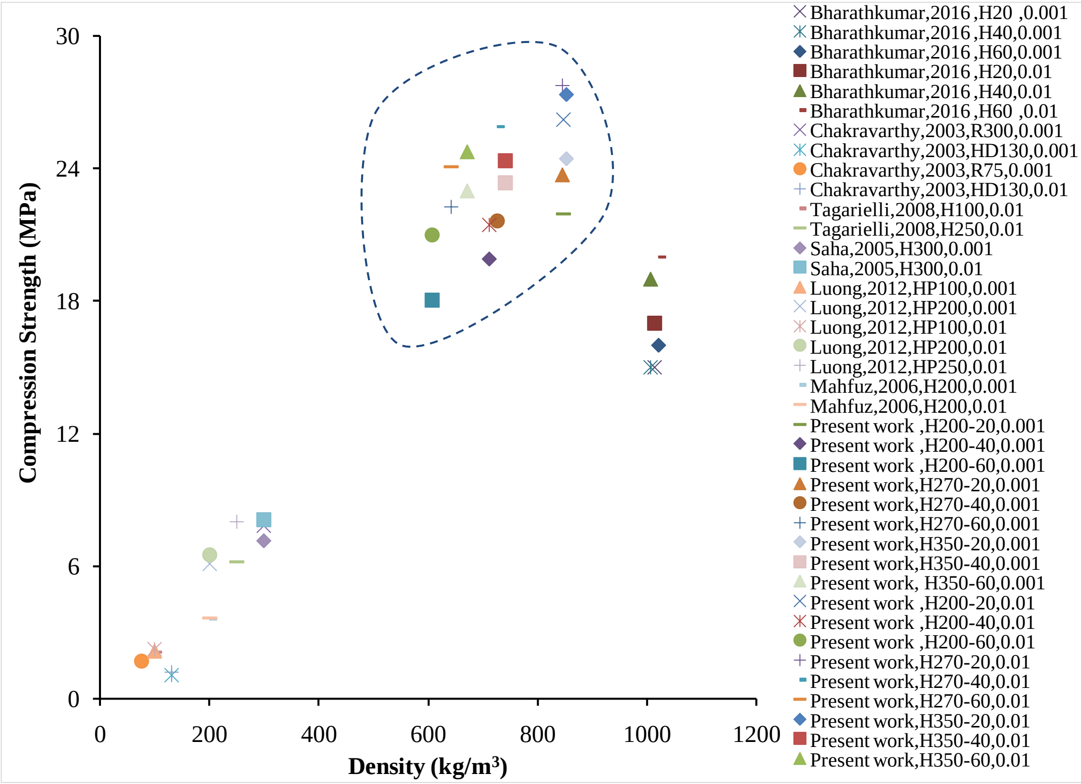


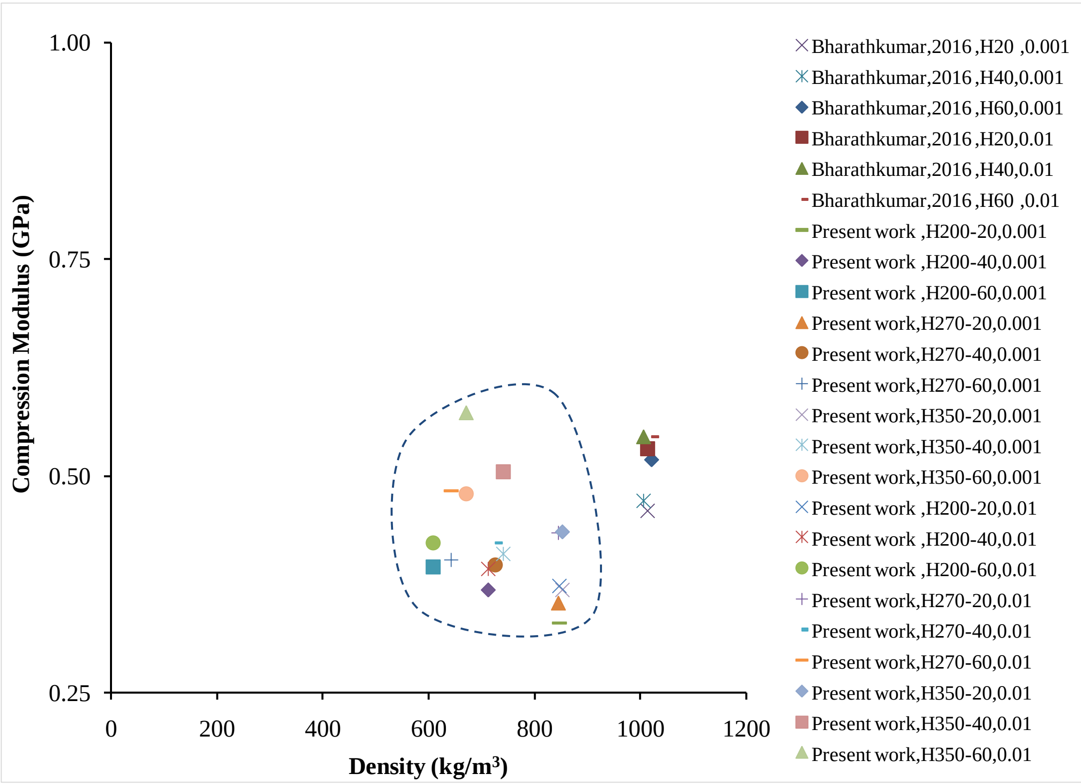
Figure 3.30 Comparison of experimental values with theoretical models for compressive modulus.

3.8.2 Property Map for quasi-static compressive property

Quasi-static compressive strength and modulus values are plotted with respect to density for thermoplastic foams containing different reinforcements tested at strain rates of 0.001 and 0.01 s^{-1} in Figure 3.31a (Bharath Kumar et al. 2016, Chakravarty et al. 2003, Luong et al. 2013, Mahfuz et al. 2006, Saha et al. 2005, Tagarielli et al. 2008) and Figure 3.31b (Bharath Kumar et al. 2016) respectively. The results extracted from the published literature are presented and compared with the present study. Present investigation shows that, GMB/HDPE foam is having lower density possessing high compressive strength compared to the published literature. H270-20 at 0.01 s^{-1} strain rate exhibits superior compressive strength. Density of GMB/HDPE foams is observed to be 1.75 times lower as compared with cenosphere/HDPE foams for 0.001 and 0.01 s^{-1} strain rate. H350-60 at 0.01 s^{-1} strain rate exhibits higher modulus compared to other published work (Bharath Kumar et al. 2016, Chakravarty et al. 2003, Luong et al. 2013, Mahfuz et al. 2006, Saha et al. 2005, Tagarielli et al. 2008). Choice of appropriate filler and the matrix tailored the compression properties of the foams over a wide range as seen from Figure 3.31. Such property maps come handy and useful for selection of particular foam for a given application.



(a)



(b)

Figure 3.31 (a) Compressive strength and (b) modulus of thermoplastic composites plotted against density from available studies.

3.9 Dynamic Mechanical Analysis

3.9.1 Temperature sweep

Figure 3.32 shows the representative set of storage modulus vs. temperature plots for the temperature range of 30-150°C. Neat HDPE results are plotted in each figure for comparison. The glass transition temperature of HDPE is approximately -110°C (Khanna et al. 1985). In the present study experiments are conducted entirely in rubbery region thus the variations of the dynamic properties with temperature does not show step changes or peaks which indicate phase transitions. Storage modulus of the syntactic foams is observed to be higher as compared to neat HDPE as seen from Figure 3.32 and Table 3.9. Increase in the filler content increases the storage modulus, though the difference between HYYY-40 and HYYY-60 is not significant particularly at higher temperatures. From Table 3.9, it can be observed that the standard deviations of these compositions overlap at the three selected reference temperatures.

Inclusion of GMB increases the stiffness of a material which resists the deformation by absorbing the energy resulting in higher storage modulus. Storage modulus is sensitive to the temperature. The extent of increase in storage modulus is relatively higher with increasing glass microballoon content at lower temperatures than at elevated temperatures. Thick walled GMB particle with highest GMB content registered higher storage modulus compared to thin walled GMB foams at lower temperature. This is due to higher energy absorption capabilities of thick walled microballoons. GMB content has more influence on storage modulus than wall thickness. H350-60 foam exhibits 64.64, 79.98 and 58.32% rise in storage modulus at three reference temperature (50, 80 and 120°C) as compared to neat HDPE. With increase in temperature, storage modulus decreases as matrix flows plastically beyond its softening temperature (124°C). Significantly higher fraction of broken particles at higher particle loading may be responsible for lack of stiffening effect. However, the use of higher particle volume fraction is still beneficial from the standpoint of reduced HDPE consumption. It is also observed that the syntactic foams are able to withstand approximately 5°C higher temperature before the storage modulus drops below the 20 MPa threshold.

Loss modulus results are graphed in Figure 3.33 and listed in Table 3.10. As with storage modulus, the loss modulus is higher at all temperatures for syntactic foams and increases with increasing particle content and wall thickness. Loss modulus is observed to be highest for H350-60 as compared to other GMB/HDPE foams (69.23%) and neat resin (80.45%). The peak observed in loss modulus is at around 50°C corresponding to the α-relaxation in HDPE (Khanna et al. 1985). The peak appears to occur at higher temperatures with increasing particle loading, which may indicate an increase in the crystallinity of the specimens due to the presence of the hollow particles. Thereby, crystallinity needs to be looked into. GMB content has more prominent effect on loss modulus than wall thickness.

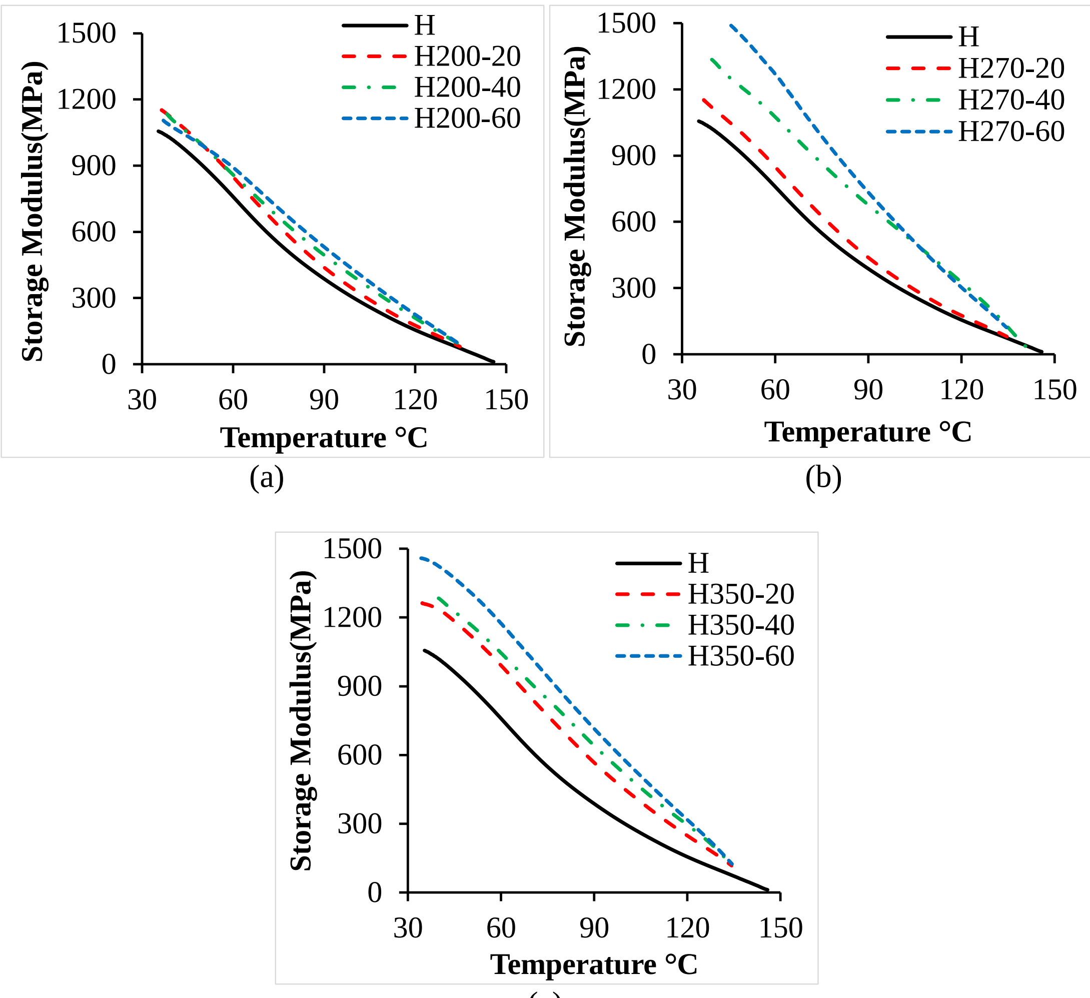


Figure 3.32 Storage modulus of (a) H200 (b) H270 and (c) H350 foams vs. temperature at 1 Hz.

Figure 3.34 and Table 3.11 presents Tanδ for chosen temperature range at 1 Hz. This property, also known as the damping parameter, loss factor or loss tangent, is the ratio of the loss and storage moduli and represents the relative magnitudes of the elastic and viscous behavior of the material.

Except H350-ZZ at higher temperature, all of the syntactic foams have lower damping parameter than the virgin HDPE at all temperatures. Damping parameter of HYYY-60 foams is comparable to HDPE at all the selected temperatures. Highest Tanδ is noted for H350-60 at 120°C i.e. below vicat softening point (124°C, Table 2.2). Tanδ is less sensitive to the hollow particle content than the storage and loss moduli.

Damping parameter is observed to be increasing with increasing GMB content and wall thickness. Thick wall GMB reinforced HDPE exhibited higher damping among the other foams (Table 3.11). GMB content is more influential than wall thickness variation on Tanδ.

The developed H350-60 syntactic foams synthesized by compression molding route is having higher storage and loss modulus coupled with higher damping. Such a foam when deployed for structural components results in 29.26 % weight saving and hence can be successfully deployed in weight sensitive applications.

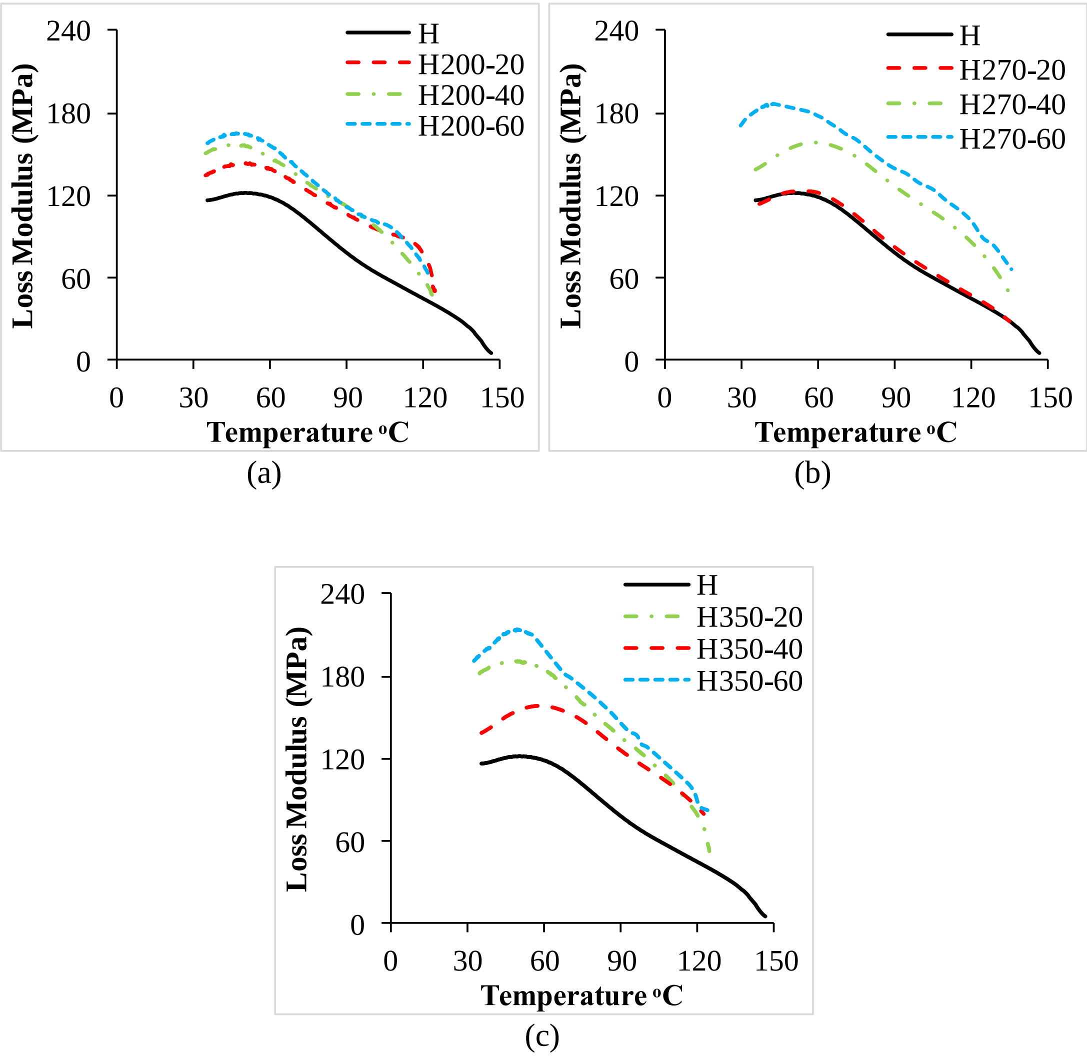
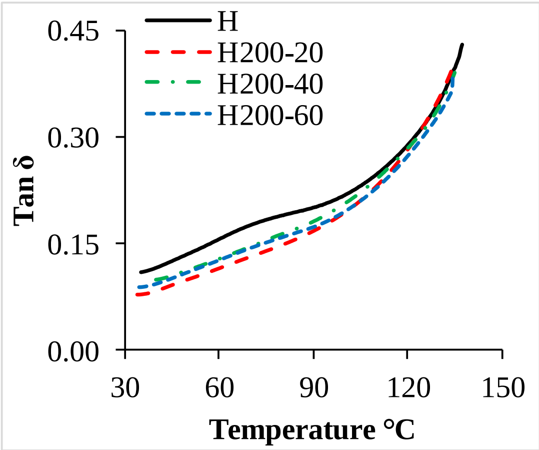
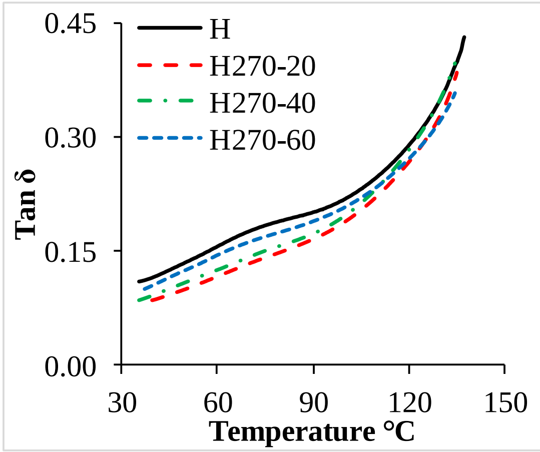


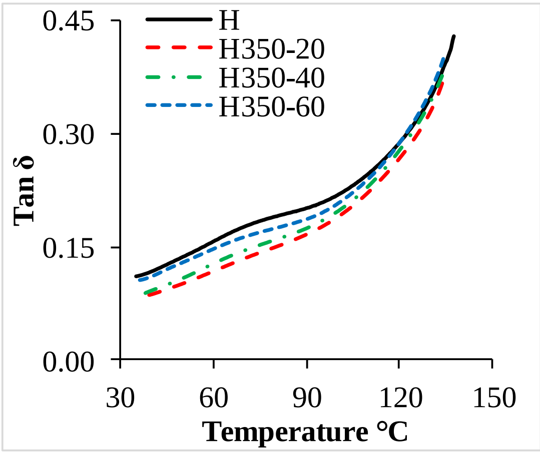
Figure 3.33 Loss modulus of (a) H200 (b) H270 and (c) H350 foams vs. temperature at 1 Hz.



(a)



(b)



(c)

Figure 3.34 Tanδ of (a) H200 (b) H270 and (c) H350 foams vs. temperature at 1 Hz.

Table 3.9 Comparison of storage modulus at three representative temperatures.

Syntactic foam type	E' at 50 °C (MPa)	E' at 80 °C (MPa)	E'at 120 °C (MPa)
H	899.31±17.98	500.51±10.01	220.02±4.40
H200-20	1000.08±18.60	580.09±11.60	260.15±5.60
H200-40	1080.28±19.98	618.37±12.40	260.80±5.20
H200-60	1080.28±22.05	620.34±12.37	293.25±5.86
H270-20	1100.03±19.96	580.15±11.60	280.05±5.60
H270-40	1197.04±23.98	880.51±17.61	320.46±6.40
H270-60	1350.04±27.01	880.23±17.60	340.52±6.81
H350-20	1180.72±23.61	750.06±15.00	280.72±5.61
H350-40	1203.49±23.96	800.50±16.01	330.18±6.61
H350-60	1480.63±29.61	900.83±18.01	348.34±6.96

Table 3.10 Comparison of loss modulus at three representative temperatures.

Syntactic foam type	E'' at 50 °C (MPa)	E'' at 80 °C (MPa)	E'' at 120 °C (MPa)
H	122.21±2.41	80.04±1.61	50.08±1.01
H200-20	128.84±2.80	115.75±2.31	60.14±1.60
H200-40	144.65±3.01	122.15±2.34	65.22±1.30
H200-60	150.51±3.36	122.23±2.44	68.59±1.37
H270-20	128.26±2.42	120.22±2.01	60.08±1.00
H270-40	160.99±3.27	135.71±2.71	70.19±1.40
H270-60	195.88±3.62	150.43±3.01	90.23±1.80
H350-20	148.09±3.20	140.25±2.80	85.66±1.71
H350-40	161.80±3.80	165.01±3.31	90.27±1.60
H350-60	218.04±4.41	165.82±3.30	90.84±1.30

Table 3.11 Comparison of damping parameter at three representative temperatures.

Syntactic foam type	tan δ at 50 °C ($\times 10^{-2}$)	tan δ at 80 °C ($\times 10^{-2}$)	tan δ at 120 °C ($\times 10^{-2}$)
H	13.59±0.001	18.51±0.003	28.12±0.005
H200-20	12.88±0.001	14.36±0.002	25.65±0.004
H200-40	13.39±0.002	15.21±0.003	26.12±0.005
H200-60	13.41±0.003	15.33±0.003	28.11±0.005
H270-20	12.85±0.002	14.68±0.003	26.62±0.005
H270-40	13.45±0.002	15.25±0.002	27.33±0.005
H270-60	14.51±0.003	16.49±0.003	28.63±0.006
H350-20	12.55±0.002	15.32±0.002	28.11±0.006
H350-40	13.45±0.004	15.51±0.001	28.65±0.006
H350-60	14.72±0.003	17.61±0.004	31.51±0.006

Mechanical property characterization of GMB/HDPE syntactic foam composites as dealt in the present work, gives a valuable insight for a materials designer to select most appropriate configuration. Increase in filler content decreases the density promising weight saving potential. GMB/HDPE foams achieved 36% weight saving in the virgin HDPE in addition to replacing the expensive matrix. These syntactic foams exhibit high stiffness to weight ratio. As seen from the preceding discussions, inclusion of GMBs in HDPE matrix changes material behavior from ductile to brittle mode owing to stiffer fillers. This material behavior is analyzed using the crystallinity quantification in the last segment of this work. Crystallinity measurement is carried out for the neat HDPE and their foams synthesized through compression molding route using WAXD and DSC analysis.

3.10 WAXD analysis

HDPE is processed most commonly by injection and compression molding processes. Thereby, polymer injection molded (PIM) HDPE samples are also considered (only for comparative analysis) with compression molded (CM) samples in WAXD analysis. Figure 3.35 shows WAXD pattern of pristine, injection and compression molded neat HDPE samples. Depending on the processing conditions and parameters, the crystal structure of HDPE is found to be monoclinic, orthorhombic and hexagonal (Gladyshevskii et al. 1961, Takahashi et al. 1988). Strong peaks arising at 21.7° and 24.3°, respectively correspond to the typical orthorhombic unit cell of (110) and (200) crystal planes (Lin et al. 2015, Xiang et al. 2017). These peaks show an interplanar distance of 0.41 and 0.37 nm, respectively. In pristine HDPE, these peaks are found to be broad and less intense as compared to the injection and compression molded samples.

Further, weak peaks occurring at 30.1° and 36.2°, respectively correspond to the (210) and (020) crystal planes with an interplanar distance of 0.27 and 0.25 nm. These peaks indicate that the HDPE samples have orthorhombic structure (Butler et al. 1995, Chouit et al. 2014). In addition, weak peaks are also observed at 39.7, 40.7, 41.6, 43.0, 46.9, 53.0 and 54.8° corresponding to the crystal plane of (011), (310), (111), (201), (221), (121) and (321). These values are in good agreement with previous reports published in Refs. (Fei et al. 2014, He et al. 2012). It is well known fact that the % crystallinity (X_c) and crystal size varies with processing conditions.

The physical properties are largely dependent on the HDPE crystallinity. It is observed that the peaks for injection and compression molded are sharp and intense compared to the pristine HDPE. X_c of pristine HDPE, injection and compression molded samples are found to be 52.4, 64.7 and 67.8% (Table 3.12). Compression molding being a slow cooling process, sufficient time for crystallization results in longer polymer chain (Balani et al. 2014). Rapid cooling cycles like in injection molding, polymers will have lower degree of crystallization as there is no sufficient time for crystallization. The crystallinity, crystallite size of HDPE might get affected by addition of glass microballoon.

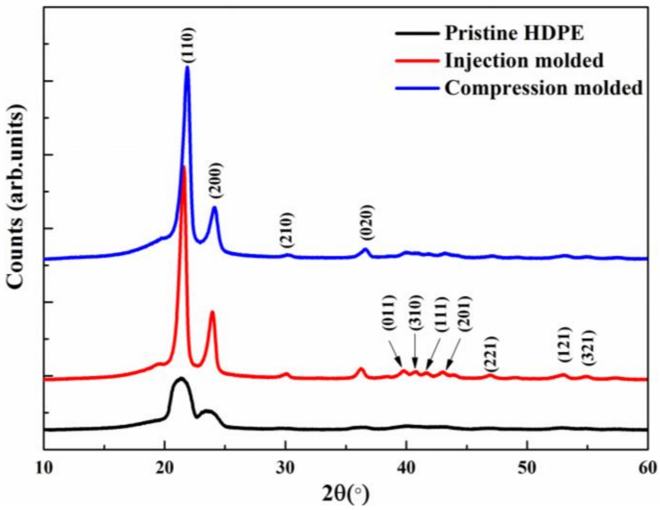
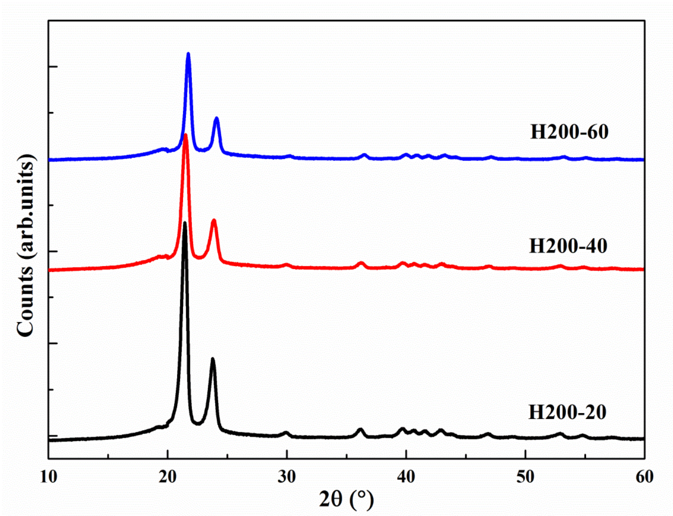


Figure 3.35 WAXD pattern of HDPE samples.

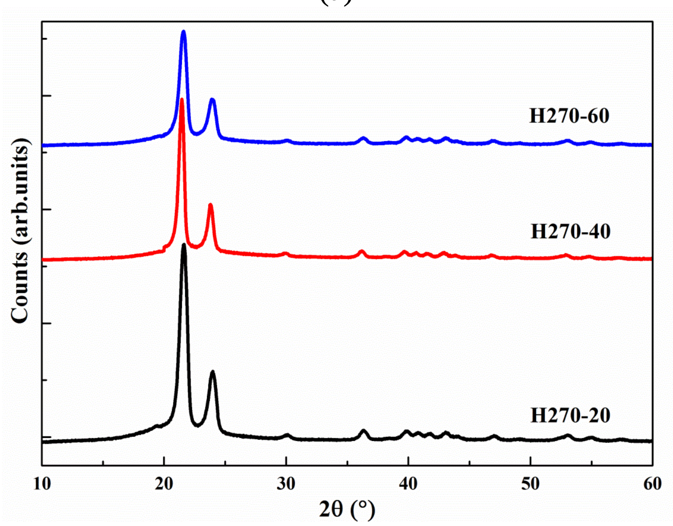
WAXD patterns of GMB/HDPE foam composite are almost similar to that of compression molded HDPE (Figure 3.36). However, the most important feature of these patterns is its decreased intensity of characteristic peaks accompanied by reduction in width with GMB addition. There is no considerable shift in peaks for foam samples as compared to CM HDPE. Interplanar distance is almost same indicating crystal structure is unaffected by filler addition. The crystallinity of GMB/HDPE foam composites are presented in Table 3.13. With increase in filler content, crystallinity of HDPE decreases. In addition, with an increase in wall thickness of filler, the crystallinity of HDPE decreased further. The decrease in crystallinity of HDPE suggests that the addition of glass microballoon hinders the HDPE chain mobility.

Table 3.12. Crystallinity and d-spacing of pristine HDPE samples

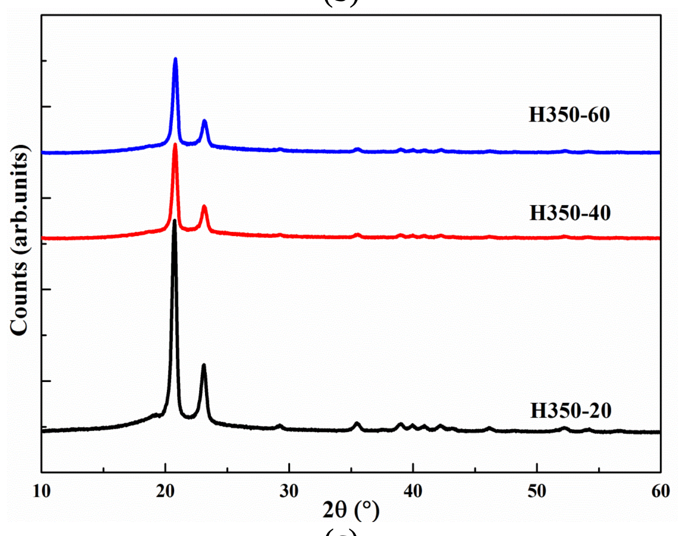
Sample type	WAXD results		DSC results	
	2Θ	% crystallinity (X_c)	Melting temperature (T_m)	% crystallinity (X_c)
As received HDPE	21.3	52.4	130.4	50.4
PIM HDPE	21.6	64.7	130.4	62.5
CM HDPE	21.9	67.8	130.5	67.1



(a)



(b)



(c)

Figure 3.36 WAXD pattern of (a) H200 (b) H270 and (c) H350 syntactic foams.

3.11 DSC analysis

DSC is carried out to study the variation in crystallinity of HDPE by PIM and CM process with respect to the as received HDPE. Figure 3.37 shows DSC curves of as received, PIM and CM HDPE samples for second heating cycle. There is no significant change in the melting point of CM sample compared to as received and PIM sample.

However, there is a considerable change observed in the crystallinity of PIM and CM sample compared to as received HDPE. Melting temperature for as received HDPE is noted to be 130.4 ºC which increased to 130.45ºC and 130.50ºC, respectively for PIM and CM samples. Similarly, the crystallinity of HDPE increased from 50.4 to 62.5% and 67.1% for PIM and CM samples respectively as observed from Table 3.12.

Change in melting temperature and crystallinity indicates the rearrangement of polymer chains. It is well known fact that the crystallinity of HDPE varies with processing condition such as temperature, cooling rate etc. Increase in crystallinity results in increase in stiffness in the polymer backbone (Bharath Kumar et al. 2016, Jayavardhan et al. 2017).

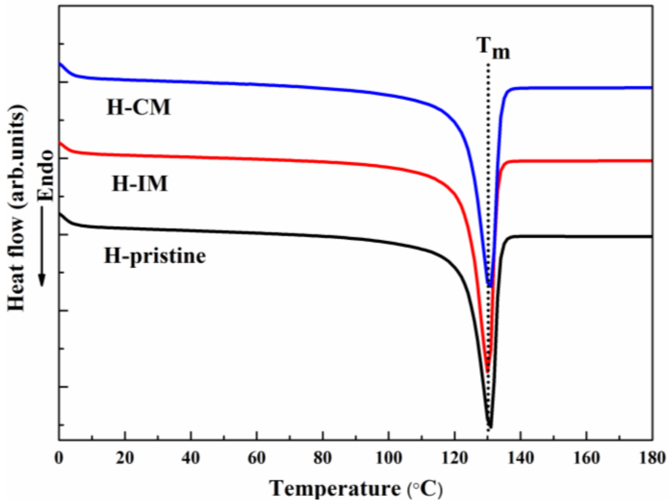


Figure 3.37 DSC traces of HDPE samples. Note : H denotes HDPE in the plot.

Figure 3.38 exhibits DSC traces of HDPE syntactic foams. Melting temperature of HDPE foams gets shifted to a higher temperature as compared to CM HDPE. In addition, the %X_c of HDPE decreased with GMB inclusion.

Crystallinity decreased further with increased density and volume fraction of the fillers. This may be attributed to the fact that, owing to GMB infusion in HDPE matrix, molecular structure of HDPE interrupts the nucleation and ordering of polymer chains during the cooling cycle of the process. Such hindering of HDPE chain mobility affects the crystallinity and HDPE crystal size.

Melting temperature, crystallinity and heat of fusion data of HDPE foams is presented in Table 3.13. X_c results obtained from DSC are in line with WAXD results for all the samples under investigation.

However, small deviations are inevitable in WAXD measurements due to unavoidable errors creeping in because of separation of amorphous and crystalline region form the diffraction. In the present work, both WAXD and DSC techniques are used for comparative analysis. Further, error in DSC may be due to the baseline correction carried out during heat of fusion determination (George et al. 2014, Khalifa et al. 2016).

Table 3.13. WAXD and DSC results of GMB/HDPE foams.

Sample type	WAXD results		DSC results	
	2Θ	% crystallinity (X_c)	Melting temperature (T_m)	% crystallinity (X_c)
H200-20	21.5	51.0	129.9	49.9
H200-40	21.5	40.1	130.9	41.1
H200-60	21.5	31.1	131.0	32.5
H270-20	21.6	48.1	129.9	47
H270-40	21.5	39.0	130.8	39.7
H270-60	21.6	27.8	131.7	30.1
H350-20	21.1	45.1	131.2	44.5
H350-40	21.0	39.0	131.6	38.2
H350-60	21.0	26.0	131.8	28.1

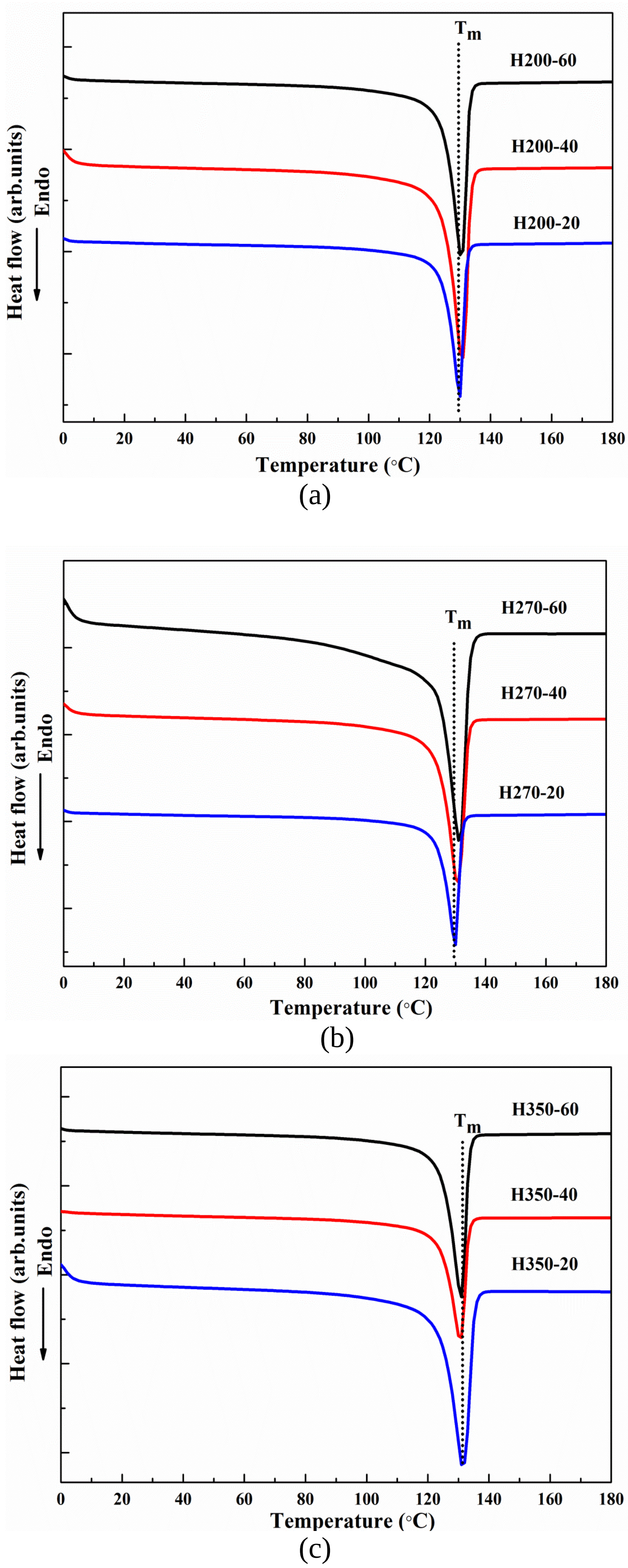


Figure 3.38 DSC traces of (a) H200 (b) H270 and (c) H350 syntactic foams.

Prevailing observation confirm that the filler additions has an influence over crystallinity along with processing route utilized to synthesize such foams.

Conclusive remarks of this study are presented hereafter.

4 CONCLUSIONS

Present work deals with developing lightweight syntactic foams using industrial scale compression molding route and analyzing effect of filler loading and wall thickness variation on physical and mechanical properties. Brabender blending and compression molding is used to synthesize HDPE syntactic foams containing 20, 40 and 60 volume % glass microballoons of different densities.

A comprehensive study is conducted to optimize the blending parameters of brabender followed by compression molding in developing lightweight GMB/HDPE syntactic foams. GMBs with three different densities (same outer diameter with varying wall thickness) are used in this study to reduce the density and HDPE consumption. Pilot study is carried out for optimizing brabender screw speed to minimize the hollow particle breakage during blending. Compression molding is a widely used method for manufacturing thermoplastic composites. However, this method has not been utilized in fabricating GMB/HDPE syntactic foams. Further, theoretical models (Porfiri-Gupta and Bardella-Genna) are used to predict elastic modulus of the developed syntactic foams and results are compared with the experimental data.

The effect of GMB content and wall thickness variations (varying density particles) on tensile and flexural behavior of GMB/HDPE syntactic foams is investigated first. Further, GMB/HDPE foams are investigated for compressive and DMA properties. Quasi-static compression tests are conducted for analyzing effect of strain rate, volume fraction and wall thickness variations. The effect of temperature (35-150°C) on the dynamic mechanical properties of GMB/HDPE syntactic foams is also studied. Finally, WAXD and DSC analysis is carried out to quantify crystallinity of HDPE and their foams.

The main conclusions can be summarized as:

Brabender process

- The most favorable screw rotation in brabender used in blending GMB and HDPE with minimal filler breakage is 10 rpm.
- Poor interfacial bonding between as received GMBs and HDPE is seen in microscopic observations. Chemical reactants might promote good interfacial bonding between the constituents. Nevertheless, they happen to leach out and make the exterior surface of hollow glass particles rough which might lead to compromised properties. Thereby constituent materials are used in as received condition for the present investigation.

Compression molding

- Adopted methodology for processing of GMB/HDPE syntactic foams using compression molding is successfully demonstrated showing uniform dispersion of glass microballoons in compliant HDPE matrix (Figure 3.4a).
- Pressure-temperature cycle as presented in Figure 2.5a shall help polymer industries to develop different thermoplastic based syntactic foams using available compression molding machine.

Density

- Measured density of all the syntactic foams is lower than neat HDPE resin signifying potential weight saving. Significant weight reduction of 10-36% is possible by reinforcing hollow GMB in HDPE matrix.
- Foam density reduces with increase in GMB content and increases with increase in particle density (wall thickness) as noted from Table 3.2. Theoretical density of syntactic foams is noted to be lower than their experimental values suggesting microballoon failure during blending.
- Fracture of hollow glass particles increases with volume fraction which is due to increased particle to particle interaction and shear forces during mixing in brabender.

- Although fractured particles do not provide the reduction in density as planned, they still help in replacing more expensive HDPE resin and make the component cheaper.

Tensile behavior

- Tensile modulus is found to be relatively insensitive to GMB wall thickness. Modulus increases with the increase in GMB content and wall thickness.
- H350-60 and H200-20 foams registered highest modulus of 603.95 MPa and UTS of 14.95 MPa respectively at 5 mm/min strain rate. These values are 80.44 and 97.75 % higher as compared to H200-20 and H350-60 respectively.
- Specific modulus is highest for H350-60 foam as compared to neat HDPE (199.27%) and other foams for 5 mm/min strain rate.
- Syntactic foams exhibit failure at lower strain as compared to neat HDPE. Higher filler content and wall thickness decreases the fracture strain; filler content effect being more prominent. The fracture strength of all the developed syntactic foams is 1.5-3 times lower than that of neat HDPE.
- Neat HDPE and syntactic foams exhibit failure closer to UTS. All the samples exhibited brittle mode of failure with no sign of necking. Increase in the filler content and particle wall thickness decreases UTS. Ultimate strength of Neat HDPE sample (22.19 MPa) is highest as compared to syntactic foams.
- Modulus and yield strength are observed to be strain rate sensitive showing increasing trend with strain rates. For same GMB volume fraction, the effect of wall thickness on foam modulus is greater at lower strain rates compared to higher ones.
- Fracture strength of all the syntactic foams is up to 3.1, 2.6 and 3.4 times lower than that of the neat HDPE at strain rates 1.6×10^{-5}, 1.6×10^{-4} and 1.6×10^{-3} s^{-1} respectively.
- Specific modulus of syntactic foams increased with GMB wall thickness at all strain rates. H350-60 registered maximum specific modulus at lowest strain rate. No clear trend is observed for specific strength.

- Two theoretical models are used for measuring the elastic modulus. Bardella-Genna model holds good agreement with the experimental results.

Flexural behavior

- Except HDPE samples, all syntactic foams are failed at midpoint. Extensive plastic deformation of HDPE is observed from the micrographs (Figure 3.17) at higher filler loadings in thicker walled particles.
- Flexural modulus and strength are found to increase and decrease respectively with increasing GMB content for syntactic foams. Highest modulus (1165.73 MPa) and strength (27.47 MPa) are recorded for H350-60 and H200-20 foams respectively.
- Specific modulus and strength of H350-60 and H200-60 are observed to be 147 and 8% higher compared to neat HDPE samples.
- Flexural properties are sensitive to volume fraction variations as compared to wall thickness variation.
- Flexural modulus of syntactic foams is predicted by the theoretical models. Bardella-Genna model shows 2-17% agreement with the experimental values and is better suited for predicting flexural modulus of GMB/HDPE foams.

Quasi-static compression testing

- Compressive modulus and yield strength are strain rate sensitive properties showing rise with increasing strain rates.
- Neat HDPE and other syntactic foams with higher filler loading continue to harden at all strains except H200 foams which exhibits clearly distinguishable stress plateau irrespective of particle wall thickness. These foams can be effectively used for energy absorbing applications.
- All syntactic foams registered superior performance compared to neat HDPE for specific modulus at all strain rates. H350-60 shows highest modulus and yield strength for all compressive strain rates among the foams investigated.
- GMB wall thickness has a higher influence as compared to volume fraction for the properties investigated in the present work.

- Theoretical approach by Porfiri-Gupta model is found to be in good agreement (less than 5%) with experimental results.
- Compressive strength of GMB/HDPE foams exhibited better results (except H200-60) compare to other polymeric foams in the literature. H350-60 exhibited better modulus as compared to other available thermoplastic foams.

Dynamic Mechanical Analysis

- Storage and loss modulus increases with GMB content and wall thickness.
- Neat HDPE registered lower storage and loss modulus as compared to syntactic foams.
- Damping factor (Tan δ) increases with filler content and wall thickness.
- Particle wall thickness variations are observed to be more prominent than volume fraction on Tanδ.
- H350-60 foam registered highest Tan δ, storage and loss modulus.

Crystallinity

- Neat HDPE sample exhibits highest crystallinity of 67.8% as compared to all other GMB/HDPE foams.
- Percentage of crystallinity is decreased with increase in filler content and particle wall thickness.
- Among foams, lowest and highest crystallinity values are shown by H350-60 (26%) and H200-20 (51%) respectively.
- Decrease in tensile and flexural strength might be attributed to lower crystallinity values in foams.

Present work successfully demonstrated feasibility of industrial scale compression molding for developing thermoplastic syntactic foam composites. Molded components using GMB and HDPE have weight saving potential of 36%. Additionally, hollow GMBs replace more expensive HDPE resin. Different shape and size components of glass microballoon/HDPE syntactic foams can be manufactured in large volume using compression molding technique leading to lower costs.

Compression molding results in better quality syntactic foams i.e. better strength and modulus compared to Injection molding route. Further, wall thickness has a strong influence on quasi-static and damping behavior of GMB/HDPE foams. In addition to filler volume fraction, wall thickness variation results in wider range of compressive and damping properties which can cater to different sectors based on the application. Present work provides guideline to polymer industries in developing GMB based polymeric foams without changing existing machine parameters and their setups.

The experimental results presented as part of this work can be used by industry professionals for development of syntactic foams for specific applications. Theoretical models can help researchers and industry professionals in predicting the properties of various compositions of syntactic foams and reduce experimentation. The data can be used in design and evaluation of consumer products for manufacture with this low cost lightweight material. Optimization data on industrial scale machine for syntactic foam manufacture can help other industries to adopt similar practices.

SCOPE OF FUTURE WORK

Present work demonstrates feasibility of industrial scale compression molding in developing thermoplastic syntactic foams. Though, the approach is successful, hollow GMBs are observed to break in such pressurized techniques. Filler breakage needs to be addressed and minimized further, by adopting CFD simulations to get the optimized temperature profile with compressive forces creeping in due to pressure-temperature cycle in compression molding. Theoretical models can be adopted for comparing the experimental data with considering the interaction between the hollow particles and HDPE matrix. Further, the performances of the developed composites are to be tested in real application.

REFERENCES

Adhikary, K. B., Park, C. B., Islam, M.R. and Rizvi, G. M. (2011). "Effects of Lubricant Content on Extrusion Processing and Mechanical Properties of Wood Flour-High-density Polyethylene Composites." *Journal of Thermoplastic Composite Materials*, 24(2), 155-171.

Agarwal, BD and Broutman, LJ. (1980). Analysis and performance of fiber composites: John Wiley, New York.

Arza, Seidel. (2012)." Fillers " Encyclopedia of Polymer Science and Technology Fourth edition. *John Wiley & Sons,* New York.

Arzamasov, B. (1989)." Materials Science." *Mir publishers*, Moscow.

ASTM D638-14, *Standard Test Method for Tensile Properties of Plastics*, ASTM International, PA, USA.

ASTM D790-10, *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*, ASTM International, PA, USA.

ASTM D792-13, *Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement*, ASTM International, PA, USA.

ASTM D3102-78, *Practice for Determination of Isostatic Collapse Strength of Hollow Glass Microspheres*, ASTM International, PA,USA.

ASTM D3878, *Standard Terminology for Composite Materials*, ASTM International, PA,USA.

Aureli, M., Porfiri, M. and Gupta, N. (2010). "Effect of polydispersivity and porosity on the elastic properties of hollow particle filled composites." *Mechanics of Materials,* 42(7), 726-739.

Ayrilmis, Nadir. (2013). "Combined effects of boron and compatibilizer on dimensional stability and mechanical properties of wood/HDPE composites." *Composites Part B: Engineering,* 44(1), 745-749.

Bachmatiuk, Alicja, Börrnert, Felix, Schäffel, Franziska, Zaka, Mujtaba, Martynkowa, Grazyna Simha, Placha, Daniela, Schönfelder, Ronny, Costa, Pedro M. F. J., Ioannides, Nicholas, Warner, Jamie H., Klingeler, Rüdiger, Büchner, Bernd and Rümmeli, Mark H. (2010). "The formation of stacked-cup carbon nanotubes using chemical vapor deposition from ethanol over silica." *Carbon,* 48(11), 3175-3181.

Balani, Kantesh, Verma, Vivek, Agarwal, Arvind and Narayan, Roger. (2014)." Physical, Thermal, and Mechanical Properties of Polymers."

Bardella, Lorenzo and Genna, Francesco. (2001). "On the elastic behavior of syntactic foams." *International Journal of Solids and Structures,* 38(40-41), 7235-7260.

Bardella, Lorenzo, Sfreddo, Alessandro, Ventura, Carlo, Porfiri, Maurizio and Gupta, Nikhil. (2012). "A critical evaluation of micromechanical models for syntactic foams." *Mechanics of Materials,* 50, 53-69.

Benchekchou, B, Coni, M, Howarth, HVC and White, RG. (1998). "Some aspects of vibration damping improvement in composite materials." *Composites Part B: Engineering,* 29(6), 809-817.

Bharath Kumar, B. R., Doddamani, Mrityunjay, Zeltmann, Steven E., Gupta, Nikhil, Ramesh, M. R. and Ramakrishna, Seeram. (2016). "Processing of cenosphere/HDPE syntactic foams using an industrial scale polymer injection molding machine." *Materials & Design,* 92, 414-423.

Bharath Kumar, B. R., Doddamani, Mrityunjay, Zeltmann, Steven E., Gupta, Nikhil, Uzma, Gurupadu, S. and Sailaja, R. R. N. (2016). "Effect of surface treatment and blending method on flexural properties of injection molded cenosphere/HDPE syntactic foams." *Journal of Materials science,* 51(8), 3793-3805.

Bharath Kumar, B. R., Singh, Ashish Kumar, Doddamani, Mrityunjay, Luong, Dung D. and Gupta, Nikhil. (2016). "Quasi-Static and High Strain Rate Compressive Response of Injection-Molded Cenosphere/HDPE Syntactic Foam." *JOM,* 68(7), 1861-1871.

Bharath Kumar, B. R., Zeltmann, Steven Eric, Doddamani, Mrityunjay, Gupta, Nikhil, Uzma, Gurupadu, S. and Sailaja, R. R. N. (2016). "Effect of cenosphere surface treatment and blending method on the tensile properties of thermoplastic matrix syntactic foams." *Journal of Applied Polymer Science,* 133(35).

Bunn, P and Mottram, JT. (1993). "Manufacture and compression properties of syntactic foams." *Composites,* 24(7), 565-571.

Burgiel, Jonathan, Beck, RW and Kirk, Diana R. (1994). "Cost evaluation of automated and manual post-consumer plastic bottle sorting systems."

Burgueño, Rigoberto, Quagliata, Mario J, Mohanty, Amar K, Mehta, Geeta, Drzal, Lawrence T and Misra, Manjusri. (2004). "Load-bearing natural fiber composite cellular beams and panels." *Composites Part A: Applied Science and Manufacturing,* 35(6), 645-656.

Butler, Michael F, Donald, Athene M, Bras, Wim, Mant, Geoffrey R, Derbyshire, Gareth E and Ryan, Anthony J. (1995). "A real-time simultaneous small-and wide-angle X-ray scattering study of in-situ deformation of isotropic polyethylene." *Macromolecules,* 28(19), 6383-6393.

Calahorra, A, Gara, O and Kenig, S. (1987). "Thin film Parylene coating of three-phase syntactic foams." *Journal of Cellular Plastics*, 23(4), 383-398.

Capela, Carlos, Ferreira, José A Martins and Costa, Jose Domingos M. (2010) "Viscoelastic properties assessment of syntactic foams by dynamic mechanical analysis." *Materials Science Forum*,Trans Tech Publ, 280-286.

Chakravarty, U., Mahfuz, H., Saha, M. and Jeelani, S. (2003). "Strain rate effects on sandwich core materials: An experimental and analytical investigation." *Acta Materialia*, 51(5), 1469-1479.

Chand, Navin, Sharma, Prabhat and Fahim, M. (2010). "Correlation of mechanical and tribological properties of organosilane modified cenosphere filled high density polyethylene." *Materials Science and Engineering: A,* 527(21–22), 5873-5878.

Chanda, Manas and Roy, Salil K. (2006)." Plastics technology handbook." *CRC press*.

Chawla, Krishan K. (2012)." Composite materials: science and engineering." *Springer Science & Business Media*.

Chen, H.C., Chen, T.Y. and Hsu, C.H. (2006). "Effects of Wood Particle Size and Mixing Ratios of HDPE on the Properties of the Composites." *Holz als Roh- und Werkstoff,* 64(3), 172-177.

Chouit, Fairouz, Guellati, Ounassa, Boukhezar, Skander, Harat, Aicha, Guerioune, Mohamed and Badi, Nacer. (2014). "Synthesis and characterization of HDPE/N-MWNT nanocomposite films." *Nanoscale research letters*, 9(1), 288.

Colloca, M., Gupta, N. and Porfiri, M. (2012). "Mechanical properties and failure mechanisms of closed-cell PVC foams." *International Journal of Crashworthiness,* Accepted, in press.

Das, Arijit and Satapathy, Bhabani K. (2011). "Structural, thermal, mechanical and dynamic mechanical properties of cenosphere filled polypropylene composites." *Materials & Design*, 32(3), 1477-1484.

Deepthi, M. V., Sharma, Madan, Sailaja, R. R. N., Anantha, P., Sampathkumaran, P. and Seetharamu, S. (2010). "Mechanical and thermal characteristics of high density polyethylene–fly ash Cenospheres composites." *Materials & Design,* 31(4), 2051-2060.

Deepthi, MV, Sailaja, RRN, Sampathkumaran, P, Seetharamu, S and Vynatheya, S. (2014). "High density polyethylene and silane treated silicon nitride nanocomposites using high-density polyethylene functionalized with maleate ester: mechanical, tribological and thermal properties." *Materials & Design (1980-2015),* 56, 685-695.

Dimchev, Momchil, Caeti, Ryan and Gupta, Nikhil. (2010). "Effect of carbon nanofibers on tensile and compressive characteristics of hollow particle filled composites." *Materials & Design,* 31(3), 1332-1337.

Divya, V. C., Ameen Khan, M., Nageshwar Rao, B. and Sailaja, R. R. N. (2015). "High density polyethylene/cenosphere composites reinforced with multi-walled carbon nanotubes: Mechanical, thermal and fire retardancy studies." *Materials & Design*, 65, 377-386.

Fei, Peng, Fei, Benhua, Yu, Yan, Xiong, Hanguo and Tan, Jun. (2014). "Thermal properties and crystallization behavior of bamboo fiber/high-density polyethylene composites: Nano-TiO_2 effects." *Journal of Applied Polymer Science,* 131(3).

Ferreira, JAM, Capela, C and Costa, JD. (2010). "A study of the mechanical behaviour on fibre reinforced hollow microspheres hybrid composites." *Composites Part A: Applied Science and Manufacturing,* 41(3), 345-352.

Ferreira, JAM, Capela, C and Costa, JD. (2011). "Dynamic mechanical analysis of hybrid fibre/glass microspheres composites." *Strain,* 47(3), 275-280.

Ferrigno, TH, Katz, HS and Milewski, JV. (1978). "Handbook of fillers and reinforcements for plastics." *H. S. Katz and J.V. Milewski eds, Van Nostrand Reinhold,* 11-58.

George, Gibin, Mahendran, Arunjunairaj and Anandhan, S. (2014). "Use of nano-ATH as a multi-functional additive for poly (ethylene-co-vinyl acetate-co-carbon monoxide)." *Polymer bulletin,* 71(8), 2081-2102.

Ghamsari, Ali Kadkhoda, Zegeye, Ephraim and Woldesenbet, Eyassu. (2015). "Viscoelastic properties of syntactic foam reinforced with short sisal fibers." *Journal of Composite Materials*, 49(1), 27-34.

Gladyshevskii, EI, Kripyakevich, PI, Teslyuk, M Yu, Zarechnyuk, OS t and Kuz'ma, Yu B. (1961). "Crystal structures of some intermetallic compounds." *Sov. Phys.-Crystallogr,* 6, 207-208.

Grosjean, François, Bouchonneau, Nadège, Choqueuse, Dominique and Sauvant-Moynot, Valérie. (2009). "Comprehensive analyses of syntactic foam behaviour in deepwater environment." *Journal of Materials science,* 44(6), 1462-1468.

Gupta, N., Woldesenbet, E. and Kishore. (2002). "Compressive fracture features of syntactic foams-microscopic examination." *Journal of Materials science,* 37(15), 3199-3209.

Gupta, Nikhil. (2007). "A functionally graded syntactic foam material for high energy absorption under compression." *Materials Letters,* 61(4-5), 979-982.

Gupta, Nikhil, Gupta, Sandeep Kumar and Mueller, Benjamin J. (2008). "Analysis of a functionally graded particulate composite under flexural loading conditions." *Materials Science and Engineering: A*, 485(1–2), 439-447.

Gupta, Nikhil, Karthikeyan, CS and Sankaran, S. (1999). "Correlation of processing methodology to the physical and mechanical properties of syntactic foams with and without fibers." *Materials Characterization,* 43(4), 271-277.

Gupta, Nikhil, Maharsia, Rahul and Jerro, H Dwayne. (2005). "Enhancement of energy absorption characteristics of hollow glass particle filled composites by rubber addition." *Materials Science and Engineering: A,* 395(1-2), 233-240.

Gupta, Nikhil and Nagorny, Ruslan. (2006). "Tensile properties of glass microballoon-epoxy resin syntactic foams." *Journal of Applied Polymer Science,* 102(2), 1254-1261.

Gupta, Nikhil, Pinisetty, Dinesh and Shunmugasamy, Vasanth Chakravarthy. (2013)." Reinforced Polymer Matrix Syntactic Foams : Effect of Nano and Micro-Scale Reinforcement." *Springer International Publishing*.

Gupta, Nikhil and Woldesenbet, E. (2002). "Effect of wall thickness of cenospheres on the compressive properties of syntactic foams." *Submitted for publication*.

Gupta, Nikhil, Ye, Raymond and Porfiri, Maurizio. (2010). "Comparison of tensile and compressive characteristics of vinyl ester/glass microballoon syntactic foams." *Composites Part B: Engineering,* 41(3), 236-245.

Gupta, Nikhil, Zeltmann, StevenE, Shunmugasamy, VasanthChakravarthy and Pinisetty, Dinesh. (2013). "Applications of Polymer Matrix Syntactic Foams." *JOM*, 1-10.

Guru, K, Mishra, SB and Shukla, KK. (2015). "Effect of temperature and functionalization on the interfacial properties of CNT reinforced nanocomposites." *Applied Surface Science,* 349, 59-65.

Gwon, Jae Gyoung, Lee, Sun Young, Kang, Himchan and Kim, Jung Hyeun. (2012). "Effects of sizes and contents of exothermic foaming agent on physical properties of injection foamed wood fiber/HDPE composites." *International Journal of Precision Engineering and Manufacturing,* 13(6), 1003-1007.

Harris, Bryan. (1986)." Engineering composite materials." *Institute of metals London*.

He, Qingliang, Yuan, Tingting, Zhu, Jiahua, Luo, Zhiping, Haldolaarachchige, Neel, Sun, Luyi, Khasanov, Airat, Li, Yutong, Young, David P and Wei, Suying. (2012). "Magnetic high density polyethylene nanocomposites reinforced with in-situ synthesized Fe@ FeO core-shell nanoparticles." *Polymer,* 53(16), 3642-3652.

Hobaica, EC and Cook, SD. (1968). "The characteristics of syntactic foams used for buoyancy." *Journal of Cellular Plastics,* 4(4), 143-148.

Homaeigohar, S. Sh, Sadi, A. Yari, Javadpour, J. and Khavandi, A. (2006). "The effect of reinforcement volume fraction and particle size on the mechanical properties of β-tricalcium phosphate–high density polyethylene composites." *Journal of the European Ceramic Society,* 26(3), 273-278.

Hu, Yan, Mei, Riguo, An, Zhenguo and Zhang, Jingjie. (2013). "Silicon rubber/hollow glass microsphere composites: Influence of broken hollow glass microsphere on mechanical and thermal insulation property." *Composites Science and Technology,* 79, 64-69.

Huang, J. S. and Gibson, L. J. (1993). "Elastic moduli of a composite of hollow spheres in a matrix." *Journal of the Mechanics and Physics of Solids,* 41(1), 55-75.

Huang, Ruoxuan and Li, Peifeng. (2015). "Elastic behaviour and failure mechanism in epoxy syntactic foams: The effect of glass microballoon volume fractions." *Composites Part B: Engineering,* 78, 401-408.

Jayavardhan, ML, Kumar, BR Bharath, Doddamani, Mrityunjay, Singh, Ashish K, Zeltmann, Steven E and Gupta, Nikhil. (2017). "Development of glass microballoon/HDPE syntactic foams by compression molding." *Composites Part B: Engineering,* 130, 119-131.

John, Bibin and Nair, CP Reghunadhan. (2014). "Syntactic foams." *Elsevier*, 511-554.

John, Bibin, Nair, CP Reghunadhan, Devi, K Ambika and Ninan, KN. (2007). "Effect of low-density filler on mechanical properties of syntactic foams of cyanate ester." *Journal of Materials science,* 42(14), 5398-5405.

John, Bibin, Nair, CP Reghunadhan and Ninan, KN. (2010). "Effect of nanoclay on the mechanical, dynamic mechanical and thermal properties of cyanate ester syntactic foams." *Materials Science and Engineering: A,* 527(21-22), 5435-5443.

Kang, DongHo, Hwang, Sung Wook, Jung, Bich Nam and Shim, Jin Kie. (2017). "Effect of hollow glass microsphere (HGM) on the dispersion state of single-walled carbon nanotube (SWNT)." *Composites Part B: Engineering,* 117, 35-42.

Karthikeyan, CS, Sankaran, S and Kumar, Jagdish. (2001). "Processing and compressive strengths of syntactic foams with and without fibrous reinforcements." *Journal of Applied Polymer Science,* 81(2), 405-411.

Khalaf, Moayad N. (2015). "Mechanical properties of filled high density polyethylene." *Journal of Saudi Chemical Society,* 19(1), 88-91.

Khalifa, Mohammed, Mahendran, Arunjunairaj and Anandhan, S. (2016). "Probing the synergism of halloysite nanotubes and electrospinning on crystallinity, polymorphism and piezoelectric performance of poly (vinylidene fluoride)." *RSC Advances,* 6(115), 114052-114060.

Khanna, Yash P, Turi, Edith A, Taylor, Thomas J, Vickroy, Virgil V and Abbott, Richard F. (1985). "Dynamic mechanical relaxations in polyethylene." *Macromolecules,* 18(6), 1302-1309.

Kim, Ho Sung and Khamis, Mohammad Azhar. (2001). "Fracture and impact behaviours of hollow micro-sphere/epoxy resin composites." *Composites Part A: Applied Science and Manufacturing,* 32(9), 1311-1317.

Kim, JI, Ryu, SH and Chang, YW. (2000). "Mechanical and dynamic mechanical properties of waste rubber powder/HDPE composite." *Journal of Applied Polymer Science,* 77(12), 2595-2602.

Kishore, Shankar, Ravi and Sankaran, S. (2005). "Gradient syntactic foams: Tensile strength, modulus and fractographic features." *Materials Science and Engineering: A,* 412(1-2), 153-158.

Kishore, Shankar, Ravi and Sankaran, S. (2005). "Short beam three point bend tests in syntactic foams. Part I: Microscopic characterization of the failure zones." *Journal of Applied Polymer Science,* 98(2), 673-679.

KSSPMA. (1992). A Guide to Plastics. Bangalore.

Kulkarni, MB and Mahanwar, PA. (2014). "Studies on the effect of maleic anhydride–grafted polypropylene with different MFI on mechanical, thermal and morphological properties of fly ash-filled PP composites." *Journal of Thermoplastic Composite Materials,* 27(12), 1679-1700.

Kumar, Nityanshu, Mireja, Shubham, Khandelwal, Vinay, Arun, Byravan and Manik, Gaurav. (2017). "Light-weight high-strength hollow glass microspheres and bamboo fiber based hybrid polypropylene composite: A strength analysis and morphological study." *Composites Part B: Engineering,* 109, 277-285.

Kutz, Myer. (2015)." Mechanical Engineers' Handbook, Volume 1: Materials and Engineering Mechanics." *John Wiley & Sons*.

Lee, Stuart M. (1992)." Handbook of composite reinforcements." *John Wiley & Sons*.

Lefebvre, X, Choqueuse, D and Chauchot, P. (2009). "Durability of syntactic foams for deep offshore insulation: modelling of water uptake under representative ageing conditions in order to predict the evolution of buoyancy and thermal conductivity." *Oil & Gas Science and Technology-Revue de l'IFP,* 64(2), 165-178.

Lin, Jia-Horng, Pan, Yi-Jun, Liu, Chi-Fan, Huang, Chien-Lin, Hsieh, Chien-Teng, Chen, Chih-Kuang, Lin, Zheng-Ian and Lou, Ching-Wen. (2015). "Preparation and compatibility evaluation of polypropylene/high density polyethylene polyblends." *Materials,* 8(12), 8850-8859.

Liu, H., Wu, Q., Han, G., Yao, F., Kojima, Y. and Suzuki, S. (2008). "Compatibilizing and toughening bamboo flour-filled HDPE composites: Mechanical properties and morphologies." *Composites Part A: Applied Science and Manufacturing,* 39(12), 1891-1900.

Liu, H., Wu, Q. and Zhang, Q. (2009). "Preparation and properties of banana fiber-reinforced composites based on high density polyethylene (HDPE)/Nylon-6 blends." *Bioresource Technology*, 100(23), 6088-6097.

Luong, Dung D, Pinisetty, Dinesh and Gupta, Nikhil. (2013). "Compressive properties of closed-cell polyvinyl chloride foams at low and high strain rates: Experimental investigation and critical review of state of the art." *Composites Part B: Engineering*, 44(1), 403-416.

Mae, Hiroyuki, Omiya, Masaki and Kishimoto, Kikuo. (2008). "Effects of strain rate and density on tensile behavior of polypropylene syntactic foam with polymer microballoons." *Materials Science and Engineering: A*, 477(1-2), 168-178.

Maharsia, Rahul, Gupta, Nikhil and Jerro, H. Dwayne. (2006). "Investigation of flexural strength properties of rubber and nanoclay reinforced hybrid syntactic foams." *Materials Science and Engineering: A,* 417(1–2), 249-258.

Maharsia, Rahul R. (2005). Development of high performance hybrid syntactic foams: structure and material property characterization. *Louisiana Tech*, Ruston, U.S.A.

Maharsia, Rahul R and Jerro, Harlan D. (2007). "Enhancing tensile strength and toughness in syntactic foams through nanoclay reinforcement." *Materials Science and Engineering: A*, 454, 416-422.

Mahfuz, Hassan, Thomas, Tonnia, Rangari, Vijay and Jeelani, Shaik. (2006). "On the dynamic response of sandwich composites and their core materials." *Composites Science and Technology*, 66(14), 2465-2472.

Manoj, MK, Galgali, RK, Nath, SK and Ray, S. (2008). "Synthesis, characterization and effect of microstructure on slurry erosion resistance of cast Fe-TiC composites." *Journal of Naval Architecture and Marine Engineering,* 5(1), 19-26.

Mueller, Dieter H and Krobjilowski, Andreas. (2003). "New discovery in the properties of composites reinforced with natural fibers." *Journal of Industrial Textiles,* 33(2), 111-130.

Nanavaty, K. (1997). "Recycling of Plastics: Indian Experience". *3rd International Plastics Exhibition and Conference on Environment/Recycling of Plastics*, New Delhi.

Ou, Rongxian, Xie, Yanjun, Wolcott, Michael P., Sui, Shujuan and Wang, Qingwen. (2014). "Morphology, mechanical properties, and dimensional stability of wood particle/high density polyethylene composites: Effect of removal of wood cell wall composition." *Materials & Design,* 58(0), 339-345.

Ozkutlu, Merve, Dilek, Cerag and Bayram, Goknur. (2018). "Effects of hollow glass microsphere density and surface modification on the mechanical and thermal properties of poly (methyl methacrylate) syntactic foams." *Composite Structures*.

Patankar, SN, Das, Anirban and Kranov, YA. (2009). "Interface engineering via compatibilization in HDPE composite reinforced with sodium borosilicate hollow glass microspheres." *Composites Part A: Applied Science and Manufacturing,* 40(6-7), 897-903.

Patnaik, Amar, Satapathy, Alok, Mahapatra, SS and Dash, RR. (2009). "A comparative study on different ceramic fillers affecting mechanical properties of glass—polyester composites." *Journal of Reinforced Plastics and Composites,* 28(11), 1305-1318.

Porfiri, Maurizio and Gupta, Nikhil. (2009). "Effect of volume fraction and wall thickness on the elastic properties of hollow particle filled composites." *Composites Part B: Engineering,* 40(2), 166-173.

Poveda, Ronald L., Achar, Sriniket and Gupta, Nikhil. (2014). "Viscoelastic properties of carbon nanofiber reinforced multiscale syntactic foam." *Composites Part B: Engineering,* 58(0), 208-216.

Poveda, RonaldL and Gupta, Nikhil. (2013). "Carbon-Nanofiber-Reinforced Syntactic Foams: Compressive Properties and Strain Rate Sensitivity." *JOM,* 1-12.

Reinhart, Theodore J. (1998). "Overview of composite materials." *Springer,* 21-33.

Ren, Sue, Li, Xiutao, Zhang, Xiuju, Xu, Xiqing, Dong, Xue, Liu, Jiachen, Du, Haiyan and Guo, Anran. (2017). "Mechanical properties and high-temperature resistance of the hollow glass microspheres/borosilicate glass composite with different particle size." *Journal of Alloys and Compounds,* 722, 321-329.

Rizzi, Egidio, Papa, Enrico and Corigliano, Alberto. (2000). "Mechanical behavior of a syntactic foam: experiments and modeling." *International Journal of Solids and Structures,* 37(40), 5773-5794.

Rugele, Kristine, Lehmhus, Dirk, Hussainova, Irina, Peculevica, Julite, Lisnanskis, Marks and Shishkin, Andrei. (2017). "Effect of Fly-Ash Cenospheres on Properties of Clay-Ceramic Syntactic Foams." *Materials,* 10(7), 828.

Sachinkumar, Narendranath, S and Chakradhar, D. (2018) "Study on microstructure and tensile properties of fly ash AMCs welded by FSW." *AIP Conference Proceedings,*AIP Publishing, 020118.

Saha, MC, Kabir, Md E and Jeelani, S. (2008). "Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles." *Materials Science and Engineering: A,* 479(1-2), 213-222.

Saha, MC, Mahfuz, H, Chakravarty, UK, Uddin, M, Kabir, Md E and Jeelani, S. (2005). "Effect of density, microstructure, and strain rate on compression behavior of polymeric foams." *Materials Science and Engineering: A,* 406(1-2), 328-336.

Sankaran, S, Sekhar, K Ravi, Raju, Govinda and Kumar, MN Jagdish. (2006). "Characterization of epoxy syntactic foams by dynamic mechanical analysis." *Journal of Materials science,* 41(13), 4041-4046.

Santhosh, Kumar S and Hiremath, Somashekhar S. (2014). "Microstructure and Mechanical Behavior of Nanoparticles Reinforced Metal Matrix Composites-A Review." *Applied Mechanics & Materials,* 939-944.

Satapathy, Alok, Jha, Alok Kumar, Mantry, Sisir, Singh, SK and Patnaik, Amar. (2010). "Processing and characterization of jute-epoxy composites reinforced with SiC derived from rice husk." *Journal of Reinforced Plastics and Composites,* 29(18), 2869-2878.

Scheetz, Barry E and Earle, Russell. (1998). "Utilization of fly ash." *Current Opinion in Solid State and Materials Science,* 3(5), 510-520.

Scott, Gerald. (2000). "Green polymers." *Polymer degradation and stability,* 68(1), 1-7.

Shah, Esha and Rajaram. (1997) "Plastic Recycling in Bangalore, India."Waste.

Shahapurkar, Kiran, Garcia, Carlos D, Doddamani, Mrityunjay, Kumar, GC Mohan and Prabhakar, Pavana. (2018). "Compressive behavior of cenosphere/epoxy syntactic foams in arctic conditions." *Composites Part B: Engineering,* 135, 253-262.

Shaikh, AA and Channiwala, SA. (2006). "Experimental and analytical investigation of jute polyester composite for long continuous fiber reinforcement." *Journal of Reinforced Plastics and Composites,* 25(8), 863-873.

Shekhar, B. (2012). "Roadmap to 13 Million Tons ". *Plastindia in-house journal,* 37, 6-11.

Shunmugasamy, Vasanth Chakravarthy, Gupta, Nikhil, Nguyen, Nguyen Q. and Coelho, Paulo G. (2010). "Strain rate dependence of damage evolution in syntactic foams." *Materials Science and Engineering: A,* 527(23), 6166-6177.

Shunmugasamy, VasanthChakravarthy, Pinisetty, Dinesh and Gupta, Nikhil. (2013). "Viscoelastic properties of hollow glass particle filled vinyl ester matrix syntactic foams: effect of temperature and loading frequency." *Journal of Materials science,* 48(4), 1685-1701.

Shunmugasamy, VasanthChakravarthy, Zeltmann, StevenE, Gupta, Nikhil and Strbik, OliverM, III. (2014). "Compressive Characterization of Single Porous SiC Hollow Particles." *JOM,* 66(6), 892-897.

Shutov, F. (1986). "Syntactic polymer foams." 63-123.

Sim, C. P., Cheang, P., Liang, M. H. and Khor, K. A. (1997). "Injection moulding of hydroxyapatite composites." *Journal of Materials Processing Technology,* 69(1), 75-78.

Singh, Akant Kumar and Siddhartha. (2015). "Leverage of cenosphere filler size on mechanical and dry sliding wear peculiarity of polyester composites." *Journal of Composite Materials,* 49(22), 2789-2802.

Singh, Sukhdeep, Deepak, Dharmpal, Aggarwal, Lakshya and Gupta, V. K. (2014). "Tensile and Flexural Behavior of Hemp Fiber Reinforced Virgin-recycled HDPE Matrix Composites." *Procedia Materials Science,* 6, 1696-1702.

Smith, Brooks H, Szyniszewski, Stefan, Hajjar, Jerome F, Schafer, Benjamin W and Arwade, Sanjay R. (2012). "Characterization of steel foams for structural components." *Metals,* 2(4), 399-410.

Srinivasan, N. K. and Ramakrishnan, S. S. (1983)." The science of engineering materials." *Oxford & IBH publishing*, New Delhi.

Swetha, C and Kumar, Ravi. (2011). "Quasi-static uni-axial compression behaviour of hollow glass microspheres/epoxy based syntactic foams." *Materials & Design,* 32(8-9), 4152-4163.

Tagarielli, VL, Deshpande, VS and Fleck, NA. (2008). "The high strain rate response of PVC foams and end-grain balsa wood." *Composites Part B: Engineering,* 39(1), 83-91.

Tagliavia, G, Porfiri, M and Gupta, N. (2009). "Vinyl ester—glass hollow particle composites: dynamic mechanical properties at high inclusion volume fraction." *Journal of Composite Materials,* 43(5), 561-582.

Tagliavia, G., Porfiri, M. and Gupta, N. (2010). "Analysis of flexural properties of hollow-particle filled composites." *Composites Part B: Engineering,* 41(1), 86-93.

Tagliavia, G., Porfiri, M. and Gupta, N. (2010). "Analysis of hollow inclusion-matrix debonding in particulate composites." *International Journal of Solids and Structures,* 47(16), 2164-2177.

Tagliavia, Gabriele, Porfiri, Maurizio and Gupta, Nikhil. (2012). "Influence of moisture absorption on flexural properties of syntactic foams." *Composites Part B: Engineering,* 43(2), 115-123.

Takahashi, Yasuhiro, Ishida, Takeshi and Furusaka, Michihiro. (1988). "Monoclinic-to-orthorhombic transformation in polyethylene." *Journal of Polymer Science Part B: Polymer Physics,* 26(11), 2267-2277.

Torquato, Salvatore. (2013)." Random heterogeneous materials: microstructure and macroscopic properties."   Vol. 16. *Springer Science & Business Media*.

Wang, Lijun, Zhang, Jing, Yang, Xu, Zhang, Chun, Gong, Wei and Yu, Jie. (2014). "Flexural properties of epoxy syntactic foams reinforced by fiberglass mesh and/or short glass fiber." *Materials & Design*, 55, 929-936.

Wong, CP and Bollampally, Raja S. (1999). "Thermal conductivity, elastic modulus, and coefficient of thermal expansion of polymer composites filled with ceramic particles for electronic packaging." *Journal of Applied Polymer Science,* 74(14), 3396-3403.

Wouterson, Erwin M, Boey, Freddy YC, Hu, Xiao and Wong, Shing-Chung. (2005). "Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures." *Composites Science and Technology*, 65(11-12), 1840-1850.

Xiang, Dong, Guo, Jiadong, Kumar, Amit, Chen, Biqiong and Harkin-Jones, Eileen. (2017). "Effect of processing conditions on the structure, electrical and mechanical properties of melt mixed high density polyethylene/multi-walled CNT composites in compression molding." *Materials Testing,* 59(2), 136-147.

Yuan, Qiang, Bateman, Stuart A and Wu, Dongyang. (2010). "Mechanical and conductive properties of carbon black-filled high-density polyethylene, low-density polyethylene, and linear low-density polyethylene." *Journal of Thermoplastic Composite Materials,* 23(4), 459-471.

Zeltmann, Steven Eric, Prakash, Keerthana A., Doddamani, Mrityunjay and Gupta, Nikhil. (2017). "Prediction of modulus at various strain rates from dynamic mechanical analysis data for polymer matrix composites." *Composites Part B: Engineering*, 120, 27-34.

Zhang, Qiang, Lin, Yingfei, Chi, Haitao, Chang, Jing and Wu, Gaohui. (2018). "Quasi-static and dynamic compression behavior of glass cenospheres/5A03 syntactic foam and its sandwich structure." *Composite Structures,* 183, 499-509.

Zhang, Xin, Wang, Pengfei, Zhou, Yihao, Li, Xiaotuo, Yang, En-Hua, Yu, TX and Yang, Jinglei. (2016). "The effect of strain rate and filler volume fraction on the mechanical properties of hollow glass microsphere modified polymer." *Composites Part B: Engineering*, 101, 53-63.

LIST OF PUBLICATIONS

INTERNATIONAL JOURNALS

1. M. L. Jayavardhan, B R Bharath Kumar, Mrityunjay Doddamani, Ashish Singh, Nikhil Gupta, Steven Zeltmann. (2017). "Development of glass microballoon/HDPE syntactic foams by compression molding." *Composite Part B*, 130, 119-131. **(Elsevier, 4.92)**
2. M. L. Jayavardhan and Mrityunjay Doddamani (2018). "Quasi-static Compressive Response of Compression molded Glass microballoon/HDPE syntactic foam." *Composite Part B*, 149, 165-177. **(Elsevier, 4.92)**

INTERNATIONAL CONFERENCES

1. Jayavardhana, M. L., Bharath Kumar, B. R., Doddamani, M., Zeltmann S. E., Gupta, N. (2016). "Tensile Behaviour of Compression Molded Glass Microballoon/HDPE Syntactic Foams." *American Society for Composites, 31st Technical Conference and ASTM Committee D30 Meeting*, September 19-22, Williamsburg Virginia, USA, Paper No.3716
2. Jayavardhana, M. L and Mrityunjay Doddamani (2017). "Mechanical behavior of compression molded glass microballoon/HDPE syntactic foams." *Proceedings of the 6th International Engineering Symposium*, March 1-3, Kumamoto University, Japan, Paper ID – IES2017-27.
3. Jayavardhana, M. L and Mrityunjay Doddamani (2017). "Thermoplastic Syntactic Foams Response under Varying Strain Rates." *2nd International Conference on Frontiers of Composite Materials*, November 15 -17, Melbourne, Australia.
4. Jayavardhana, M. L and Mrityunjay Doddamani (2017). "Quasi-static Compressive response of thermoplastic syntactic foam." *International Conference on Advances in Polymer Science and Technology*, November 23 - 25, Indian Institute of Technology, New Delhi, India.
5. Jayavardhana, M. L and Mrityunjay Doddamani (2017). "Compressive Response of Thermoplastic Syntactic foams." *International Conference on*

Advances in Materials and Processing: Challenges and Opportunities, November 29-December 02, Indian Institute of Technology, Roorkee, India.

6. Jayavardhana, M. L and Mrityunjay Doddamani (2017). "Flexural Response of Compression Molded Glass Microballoon/HDPE Syntactic Foam Composite." *International Conference on Composite Materials and Structures*, December 27-29, Indian Institute of Technology, Hyderabad, India.

RESEARCH OUTCOME IN PRINT MEDIA

Research outcome on Lightweight composite is reported by THREE leading National News Papers, The Hindu (28.08.2017), Deccan Herald (25.08.2017), Times of India (31.08.2017) and Bangalore Mirror (30.08.2017) in India.

THE HINDU

KARNATAKA

State, U.S. researchers develop cheaper plastics

Mohit M. Rao

BENGALURU,AUGUST 27, 2017 00:00 IST
UPDATED: AUGUST 27, 2017 03:38 IST

It will lead to more fuel-efficient cars, planes: researchers

Applying high-end technologies of the laboratory to the cruder machines used in industries, a team of researchers from the National Institute of Technology, Karnataka, and the New York University, U.S., have developed composite plastics that are up to 36% lighter than those being used.

The team focussed on incorporating hollow microspheres into high density polyethylene, the most commonly moulded plastic product.

Through a trial and error method spanning two years, researchers have managed to shed plastic use by 20%. They have replaced it with fly ash cenospheres and glass microballoons.

"The problem with composite materials is that it is done in controlled conditions in the laboratory which cannot be replicated in the industry. But with the technique we have developed, low-cost, light-weight composites can be produced at any industry using the normal compression moulding machines," said Mrityunjay Doddamani, lead researcher and an assistant professor in the Mechanical Engineering Department of the institute in Surathkal.

The research — done along with M.L. Jayavardhan from NITK; B.R. Bharath Kumar from the Jain College of Engineering and Technology at Hubbali; and Ashish K. Singh, Steven E. Zeltmann and Nikhil Gupta from NYU — was published in the journal, *Composites Part B* , recently. While hollow microspheres and composites are lighter and cheaper, the challenge facing the team was to ensure the microspheres remained intact despite the processes of industrial moulding.

By successfully imbibing hollow spheres into otherwise solid plastic base, Prof. Doddamani said the density of the material was brought down by nearly half. The end material was found to have a significantly greater ability to absorb energy.

The researchers believe that this could see the production of more light-weight material and the reduced use of plastics. In cars and planes, for instance, the reduction in weight significantly improves fuel efficiency.

Districts

Workshop on soft skills

UDUPI, DHNS: A UGC-sponsored university-level workshop on soft skills was held at Crossland College, Brahmavar for the students of rural development recently.

Dr Vincent Alva, principal, Milagres College, Kalyanpur, called upon the students to learn life skills from different experiences. Citing the example of the life of Dr APJ Abdul Kalam, he narrated how Dr Kalam took efforts to overcome the obstacles to become the people's president.

Prof Samuel K Samuel, principal, Crossland College, Brahmavar, in his presidential remarks, asked the students to develop their human relations skills and also to spend time in talking to others in order to create a more humane society.

Shammy Shiri of Manipal University and Rayan Mathias from Milagres college, Kalyanpur, were resource persons.

Experts impart skills to students

MANGALURU, DHNS: A team of doctors lead from KSHEMA, Nitte University, imparted cardiopulmonary resuscitation skills to interns, postgraduate students and staff of KVG Dental College and Hospital, Sullia.

Dr Moksha Nayak, principal, KVG Dental College and Hospital, inaugurated the workshop. A total of 117 participants were taught in cardiopulmonary resuscitation.

A first aid and resuscitation training workshop was conducted at Indian Strategies Petroleum Reserve Limited in SEZ by Dr Sripada G Mehandale, professor of Anaesthesiology, K S Hegde Medical Academy and Critical Care, coordinator, Resuscitation Training Cell, Nitte University recently.

Thirty factory workers participated in the workshop that was organised by Hindustan Institute of Safety and Multi Learning in association with Indian Red Cross Society DK district branch.

NITK-NY varsity team devises composites for automotive use

'Lightweight materials reduce weight of vehicles, increase mileage'

MANGALURU: A team of researchers from National Institute of Technology Karnataka (NITK), Surathkal, and New York University, the United States, has developed lightweight composite materials with an aim of using them in automotive components.

"Vehicle weight reduction is a top priority for many automobile companies. Lighter vehicles can provide good mileage. Even electric vehicles are benefitted by structural weight reduction because of increased driving range. The desire to use light weight materials has resulted in replacing metals with plastics in the interior of the vehicles. However, the next destination for weight reduction is to develop high performance composite materials that can provide improved performance at even lower weight," said Dr Mrityunjay Doddamani, lead researcher at NITK and an assistant professor in the Mechanical Engineering Department, who was part of the research.

"While many such efforts were made in the past, this particular project has involved an industry partner to use industrial scale manufacturing methods for producing composite specimens. There is a perception that composite materials cost more but our effort has specifically shown that low cost composites can be developed by innovative use of materials and processing methods," he said.

"The composites studied by this team incorporate hollow microspheres like fly ash cenospheres and glass microballoons in high density polyethylene, a plastic that is extensively used in molded products. Hollow microsphere fillers can reduce the weight of the component, make them cheaper and reduce the carbon footprints. However, manufacturing them at industrial scale was a major challenge," he added.

He said India houses many small-scale industries having basic manufacturing machines used for plastic molding.

The collaborator on this study Dr Nikhil Gupta, an associate professor at NYU, the USA and renowned scientist in the field of lightweight materials said "such efforts of materials development with industry participation can significantly reduce the entry barrier for new materials and with many small scale industries supplying part to major manufacturers, India is well poised to benefit from the new technologies."

The team from NIT-K and NYU recently published their findings in Composites Part B, a leading journal published by Elsevier. Study revealed weight reduction potential in plastics to the tune of 36% with better mechanical properties. Jayavardhan M L, a doctoral student at NIT-K is working on this project.

Prof S Narendranath, Head, Mechanical Engineering, applauded the joint work carried out between NIT-K and NYU and noted that "the research programme is focused on industrial relevance of basic research, which is the need of the day in India."

Director of NIT-K Prof K Uma Maheshwar Rao said, "this project is an excellent example where a cutting edge materials technology jointly developed between India and the USA will benefit many industries in India." The research team now plans to extend the work to cast prototype components with the help of industry and test them in actual applications.

DH News Service

'Rs 10 crore released to train sportspersons'

District In-charge Minister Pramod Madhwaraj inaugurates taluk-level Dasara sports meet in Udupi on Sunday. DH PHOTO

UDUPI, DHNS: The state government has released Rs 10 crore to provide training to select talented sportspersons in Karnataka, said Minister for Youth Empowerment and Sports Pramod Madhwaraj.

He was speaking after inaugurating Udupi taluk-level Dasara sports meet organised by district administration, ZP, Department of Youth Empowerment and Sports and Udupi Taluk Panchayat.

Madhwaraj, who is also District-In-charge Minister of Udupi, said that to give impetus to sports, the government will provide all required training and encouragement for them to excel under Sahasra Kreeda Prathiba Yojana. Under the scheme, 750 sports talents (below 19 years of age) and 250 sportspersons (above 19 years old) would be selected and imparted training. The department is presently accepting applications from sportspersons under the scheme.

He called upon the sportspersons to be consistent in their practice. If any sports talent puts in at least eight hours of hard work in a day, he/she can excel in the field of his/her choice. The sports personnel from Karnataka should get medals in the national and international sports meet, he added.

Aquatics: Vaishnav Hegde wins medals

MANGALURU, DHNS: Vaishnav Hegde from Puttur Aquatic club won two gold and two silver medals at the Senior State Aquatic Championship conducted by Dolphin Aquatics, at Ramakrishna Hegde Swimming pool, Mattikere, recently.

According to a press release, in 50 metres breast, Hegde won gold (29.60) and created a new meet record by breaking his own record of last year at 29.98. He also won gold in 50 metres freestyle (24.26). He won silver in 100 metres breast stroke and 50 metres butterfly stroke.

The Puttur Aquatic team stood overall fifth in the state by winning 30 points. Hegde is a student of BBM at St Philomina College, Puttur. He is being trained by coach Partha Varanashi, coach Vasanth kumar and coach Niroop G R at Balawana swimming Pool, Puttur.

DH News Service

Dakshina Kannada receives 439mm rainfall in 12 days

Dist, However, Short By 579mm To Jan-Aug Normal Rainfall

Stanly.pinto@timesgroup.com

TOI

WELCOME SHOWERS: Water levels in Nethravathi and Kumaradhara rivers have also been witnessing a steady rise for the past few days

Mangaluru: The month of August saw more rains than in the previous months, and provided much relief to the beleaguered district, which had fallen behind the average rainfall of last year, till mid-August.

The pounding the district received in the last fortnight has been last year's rainfall average of eight months—from January to August — being surpassed by 67mm, as on Tuesday. The fury of the rains could be gauged from the fact the district received 439mm rain in 12 days, from August 19 to August 30, as against 142 mm in the same period last year. But, it is still short by 579 mm compared to normal rainfall from January to the end of August, with just a day remaining in the month, as the district receives normal rainfall of 3,249 mm.

As far as the rainfall in the five taluks in the last 12 days of August is concerned, it rained 439 mm more than last year. The five taluks in the district last year, in the same period of last 12 days of August, received just 142 mm of rainfall. The taluks also received more rainfall in the last 12 days of August, with Belthangady taluk receiving 505mm rain, while last year it was 182 mm, followed by Sullia taluk at 478 mm, while last year it was 137 mm in the corresponding period. Puttur taluk received 422 mm rain in the same period, while it was 114 mm last year, and Mangaluru taluk received 401 mm, which was 147 mm last year in the corresponding period. Only Bantwal taluk received less than 400mm of rainfall, compared to last year's August statistics, at 394 mm. Last year, the taluk received 130 mm rain.

The five taluks of Dakshina Kannada district received an average 30 mm rainfall in the last 24 hours till Wednesday. Belthangady taluk received the highest rainfall at 38mm, followed by Sullia at 34 mm. Mangaluru taluk received 32 mm rain. The taluks of Bantwal and Puttur received 21 mm and 24 mm rain respectively. The five taluks of the district received 9.8 mm rain on this day last year.

The water level in the Nethravathi river at Bantwal and Uppinangady and Kumaradhara rivers at Uppinangady were well below the danger levels, and water levels in the latter two were at 21 metres, with the danger level being 28.5 metres. The cumulative rainfall from January to August was 2,670mm this year, while it was 2,583 mm last year. The district receives an average of 3,249 mm of rainfall by August end, in the first eight months of the year.

BJP angry over civic body's act to remove its pandal

TIMES NEWS NETWORK

Udupi: As per an order from Udupi municipal commissioner, Manjunathayya, officials of the city municipal council forcibly removed a pandal set by BJP members, who had organized an overnight protest in front of the Clock Tower on Wednesday.

The district BJP unit was protesting against the district administration starting sand mining in the district in 170 traditional sand mining blocks, instead of 45.

The BJP held a protest around 4 pm at the Clock Tower. After the protest meet, they organized a march to the DC's office to submit a memorandum. If the district administration do not accept their demand, they planned to stage an overnight protest. However, as soon as the protesters left the venue, CMC officials removed the pandal, stating that the pandal was set up without getting permission from the CMC.

The BJP members demanded that CMC commissioner Manjunathayya should apologise for removing the pandal without giving any intimation.

Mumbai rains: Several trains cancelled

TIMES NEWS NETWORK

Mangaluru: Due to dislocation of train services due to floods in Mumbai area, the railways has rescheduled or cancelled the services of several trains.

Trains Rescheduled

Mangaluru Junction – Mumbai CSMT Express (12134) scheduled to leave Mangaluru Junction at 4.45pm on Wednesday has been rescheduled to 2pm on Thursday due to late running of pairing train.

Ernakulam Junction – Lokmanya Tilak Terminus Express (12224) scheduled to leave Ernakulam Junction at 11.30pm on Wednesday, has been rescheduled to 8pm on Thursday.

Kochuveli – Lokmanya Tilak Terminus Express (22114) scheduled to leave Kochuveli at 12.35am on Thursday has been rescheduled to 11.45pm on Thursday.

Ernakulam Junction – Nizamuddin Mangala Express (12617) scheduled to leave Ernakulam Junction at 10.45am on Thursday has been rescheduled to 4pm on Thursday.

Trains Cancelled

Mumbai CSMT – Chennai Central Express (11041) scheduled to leave Mumbai CSMT on Wednesday has been cancelled.

Lokmanya Tilak Terminus – Coimbatore Epress (11013) scheduled to leave Lokmanya Tilak Terminus on Wednesday has been cancelled.

Mumbai CSMT – Nagercoil Express (16339) scheduled to leave Mumbai CSMT on Wednesday has been cancelled.

Mumbai CSMT – Kanniyakumari Express (16381) scheduled to leave Mumbai CSMT on Wednesday has been cancelled.

Chennai Central – Mumbai CSMT Express (11042) scheduled to leave Chennai Central at 11.55am on Thursday has been cancelled.

2 massage parlours raided, 7 arrested

TIMES NEWS NETWORK

Mangaluru: Mangaluru city police on Wednesday raided two massage parlours, which were allegedly being used for illegal activities. Police rescued 11 women and arrested seven persons.

Hanumantharaya, DCP (Law and Order), said that acting on a tip-off, police made two separate teams and raided two massage parlours in Kadri Shivabagh and KS Rao Road. During the raids they rescued five victims aged between 20 to 45 from Indian Sandal Ayurvedic Massage Parlour in Kadri Shivabagh. They have arrested four persons: Pradeep, parlour owner from Thokkottu and co-owner Reshma, resident of Hosabettu and customers Abhishek Mulihitlu and Chandrakanth Bokkapatna.

During the raid at Sanjeevini Ayurvedic Therapy Clinic, police rescued six victims aged between 28 to 31. They have arrested parlour owner Harish Shetty, Nagaraj from Surathkal and Ravi, resident of Manjeshwara.

The cases have been registered at respective jurisdictional police stations.

Manual scavenging should be wiped out: Bezwada

TIMES NEWS NETWORK

Bengaluru: The practice of manual scavenging should be wiped out from the country, Magsaysay award winner **Bezwada Wilson** said here on Wednesday.

Speaking to TOI on the sidelines of a seminar, Wilson said: "It's a shame that our country which is focusing on the Mars mission and satellites doesn't have resources to come up with proper machines or technology to clean drains and manholes without humans entering them."

Manual scavengers have long been denied justice and compensation since they are not vote banks. "The Centre is talking about Swachh Bharat Abhiyan, but eradication of manual scavenging is not on their priority list because Dalits, Adivasis and other weaker sections of society are not vote banks," said Wilson. He is the national convener of Safai Karamchari Andolan, an NGO working for the welfare of manual scavengers.

"What we need is 'smart sanitation'. Most cities in the country are yet to have a proper sewerage system. But the central government's priorities are bullet trains and to build smart cities," he pointed out. He said rehabilitation of scavengers remains a concern. "Civic bodies could recruit them for non-scavenging jobs in the corporation, so at least their next generation will not take up this dirty job."

Referring to the impact of the Magsaysay award on his work, Wilson said: "It has helped others to recognize our work. It's not about an individual but a collective struggle of several people, especially women. I am just part of this revolution."

EVENTS

Mangaluru City Corporation: Monthly meeting of council of City Corporation, Mayor Kavitha Sanil presides, Mangaluru meeting hall, MCC main office, Lalbagh, 10.30am

GAIL India Ltd: Meeting with land losers of gas pipeline project from Mangaluru and Bantwal taluk, Town Hall, 10.30am

Srinivas College of Hotel Management: Inter-collegiate flower rangoli competition as part of onam celebration, Pandeshwara, 10am-1pm

Samarpan Meditation: Samarpan meditation camp through video conferencing, residence of Manish Karia, flat #201, 2nd floor, Divya Enclave, in front of Canara College, Jail Road, Kodialbail, 5.30pm-7.30pm

Sri Kshetra Dharmasthala: Two-month religious discourse on Karnataka Bhagavatha by local scholars, Pravachana Mantap, in front of Sri Manjunateshwara Temple, Dharmasthala, 6.30pm-8pm

A soldier who became a priest at Durga Devi temple

TIMES NEWS NETWORK

TOI

DEDICATED: Ramamurthy Rao, who served in the Army between 1962 and 1982, is busy in temple service

Udupi: Here is the life story of a retired Indian Army soldier, who served as a driver carrying soldiers and army chiefs, and even carried ammunition into the battlefield. He is now serving as a priest. Padubidri-based retired warrior Ramamurthy Rao, a resident of Kunjur Durganagar in Elluru village, is now finding happiness by serving devotees in the temple.

The 71-year-old soldier lives alone and is a disciplinarian. He is restrained, self-confident and impartial, which has given him the courage to live alone. Though the temple job is not permanent, whenever he is called, he is ready to serve God. He visits the Durga Devi temple every week, and when the temple priest approaches him for help, he does not deny it.

"Military discipline is still there in my life. I joined the army in 1966 and retired in 1982. I was then a driver with the BMTC for about 22 years. From the past 4 years, I am working at the temple, and even organize private poojas there. I have received six medals for good work, which includes a medal for service in Nagaland, after completing the army's primary-level training. I also received a medal called the 'Pashchima Star,' for continuous service without a bad remark. I was appreciated for my contribution in the India Pakistan war in 1971. After I retired from the army, I settled in Bengaluru with my family. My wife Rukmini was a teacher and died a few years back because of a heart attack.

"I lost my father when I was ten, and I had to discontinue my studies, as I had to take care of the family. I then worked in a hotel in Hyderabad. When a retired British army man used to speak about the military, it inspired me a lot. I tried to join the army and got selected for the Madras Engineer Group (MEG) at Secundarabad. I realized that we are the real strength of the fighting force. We needed physical efficiency to construct bridges for the army to enter dangerous areas, once they finished the mission, we destroyed the bridge. Our primary job in the field is to make the army move by breaking hurdles. Language is not a barrier to me. I know all the South Indian languages, but don't know English. Now in my retired life, keeping aside politics, I am thankful to Prime Minister Narendra Modi for introducing OROP for military men, which help us to get a good pension amount. I also thank former Prime Minister Atal Bihari Vajpayee, who revised our pay scale as per the 7th Pay Commission. Now, every ten years, the commission decides the increment for us.

Athletic meet in Mudabidri

Mangaluru: A three-day state junior and senior athletic championship will be held at Swarajya Maidan in Mudbidri from September 4. Jointly organized by the Karnataka Athletics Association and Alva's Education Foundation, the event will see the participation of teams from all the districts. TNN

NITK study reveals lighter fuel efficient cars possible

Kevin.mendonsa
@timesgroup.com

Mangaluru: Is it possible to get lighter cars that give better mileage? Yes, say faculty of National Institute of Technology - Karnataka (NITK), Surathkal, whose recent study reveals weight reduction potential in plastics to the tune of 36% with better mechanical properties.

A team of researchers from NITK and New York University, USA, have collaborated to develop lightweight composites with the aim of using them in automotive components.

While many such efforts have been made in the past, this particular project has involved an industry-partner to use the industrial scale manufacturing methods for producing composite specimens, says Mrityunjay Doddamani, lead researcher at NIT-K and assistant professor at the department of mechanical engineering.

There is a perception that composite materials cost more but our effort has specifically shown that the low cost composites can be developed by innovative use of materials and processing methods, Mrityunjay says.

The composites studied by his team incorporate hollow microspheres like fly-ash cenospheres and glass microballoons in high density polyethylene, a plastic that is extensively used in moulded products. Hollow microsphere fillers can reduce the weight of the component, make them cheaper and reduce their carbon footprint. However, manufacturing them at industrial scale is a major challenge.

India houses many small-scale industries having basic manufacturing machines used for plastic moulding. Nikhil Gupta, associate professor at NYU, USA and renowned scientist in the field of lightweight materials, said, "Such efforts of materials development with industry participation can significantly reduce the entry barrier for new materials. With many small scale industries supplying parts to major manufacturers, India is well poised to benefit from the new technologies".

This team from NIT-K and NYU recently published their findings in Composites Part B, a leading journal published by Elsevier. Jayavardhan M L, a doctoral student at NIT-K, is working on this project.

K Uma Maheshwar Rao, director, NIT-K, said "This project is an excellent example where a cutting edge materials technology jointly developed by India and the USA will benefit many industries in India."

S Narendranath, HoD, mechanical engineering, noted that the research programme is focused on industrial relevance of basic research, which is need of the hour in India".

The research team now plans to extend their work to cast prototype components with the help of industry and test them in actual applications.

Udupi man set to walk 850km

Udupi: Jayaprakash Shetty from Kadekar village in Udupi is all set to walk from Sabaramati Ashram in Gujarat to Seva Grama in Vardha district of Maharashtra to make people develop patriotism.

Speaking to reporters in Udupi, Shetty said he would cover the 850km distance in 30 days. He said members of few like-minded organizations will join him in his epic walk.

This is not the first time he is walking for a social cause. Earlier, he accompanied late actor Sunil Dutt in his 2,000 km 'Walk for Peace' from Mumbai to Amritsar in 1998. He was also part of a walk from Kasaragod to Mumbai in March 2017. Shetty wants to cover 30-40km everyday by holding a national flag.

"I had borrowed Rs 2.5lakh from friends during my previous walks but this time I have decided to bring down the cost by staying at hostels and religious centres," Shetty said. TNN

MANGALURU: LIGHTWEIGHT MATERIAL WILL ADD A ZING TO VEHICLES

Bangalore Mirror Bureau | Updated: Aug 30, 2017, 04.00 AM IST


Jayavardhana ML, Nikhil Gupta and Mrityunjay Doddamani

Team of experts from NIT-K Surathkal and NYU have developed composite material for use in automotive components

A team of researchers from the National Institute of Technology-Karnataka (NITK), Surathkal, and New York University has collaborated to develop lightweight composite material with the aim of using them in automotive components. An industry partner has been involved to use industrial-scale manufacturing methods to make the composites.

Dr Mrityunjay Doddamani, lead researcher at NIT-K and an assistant professor in the Mechanical Engineering Department, said, "There is a perception that composite material are costly, but our effort has shown that low-cost composites can be developed by the innovative use of materials and processing methods."

Reducing the weight of vehicles is a top priority for many automobile companies as lighter vehicles can provide more mileage.

The composites studied by this team incorporate hollow microspheres like fly-ash cenospheres and glass micro-balloons in high-density polyethylene, a plastic that is extensively used in molded products. Hollow microsphere fillers can reduce the weight of the component, make them cheaper and reduce their carbon footprint.

However, manufacturing them on an industrial scale was a major challenge. The collaborator on this study, Dr Nikhil Gupta, an associate professor at NYU, USA, said, "Such efforts of material development with industry participation can reduce the entry barrier for new material and with many small-scale industries supplying parts to major manufacturers, India, is well-poised to benefit from the new technologies."

This team from NIT-K and NYU recently published their findings in Composites Part B, a leading journal published by Elsevier. The study reveals weight reduction potential in plastics to the tune of 36 per cent with better mechanical properties. Jayavardhan ML, a doctoral student at NIT-K, is working on this project.

The research team plans to extend the work to cast prototype components and test them in actual applications.

BIO-DATA

1. **Name** : M. L. Jayavardhana
2. **Father's Name** : B. K. Lingappa
3. **Date of Birth** : 18th March 1988
4. **Nationality** : Indian
5. **Marital Status** : Single
6. **Address** : Department of Mechanical Engineering
   National Institute of Technology Karnataka
   Surathkal, PO Srinivasnagar 575 025
   Karnataka, India.
7. **Mobile Number** : +91 9901724992
8. **E-mail id.** :*gautham879@gmail.com*
9. **Educational Qualification** :

Qualification	University/Board	Year of Passing
Ph.D. (Mechanical Engineering)	National Institute of Technology Karnataka	Pursuing
M.Tech. (Mechanical Engineering)	Visvesvaraya Technological University, Belgaum	2012
B.E. (Mechanical Engineering)	Visvesvaraya Technological University, Belgaum	2009