# PREPARATION AND CHARACTERIZATION OF POLYPROPYLENE BIO-FILLER COMPOSITE

A Major Project Report submitted in partial fulfilment for the award of the degree

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In

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# CERTIFICATE

This is to certify that the M.Tech major project entitled **“Preparation and Characterization of Polypropylene Bio-Filler Composite”** has been submitted by **Rajkumar Singh Rawat**, for the award of the degree of —Master of Technology in Polymer Technology is a record of bonafide work carried out by him. Rajkumar Singh Rawat has worked under our guidance and supervision and has fulfilled the requirements for the submission of the dissertation. The project work has been carried out during the session 2011-2012.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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# CONTENTS

## TABLE OF FIGURES

# LIST OF TABLES

# LIST OF GRAPHS

| | |
|---|---|
| **Graph 16:** flexural strength of (PP+10%normal $CaCO_3$) | **98** |
| **Graph 17:** flexural strength of (PP+10%modified egg shell) | **99** |
| **Graph 18:** flexural strength of (PP+10%un modified egg shell) | **100** |
| **Graph 19:** flexural strength of (PP+20%normal $CacO_3$) | **101** |
| **Graph 20:** flexural strength of (PP+20%modified egg shell) | **102** |
| **Graph 21:** flexural strength of (PP+20%un modified egg shell) | **103** |
| **Graph 22:** flexural strength of (PP+30% normal$CaCO_3$) | **104** |
| **Graph 23:** flexural strength of (PP+30% modified egg shell) | **105** |
| **Graph 24:** flexural strength of (PP+30%un modified egg shell) | **106** |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| **ES** | Egg shell |
| **ASTM** | American society of testing and materials |
| **PP** | Polypropylene |
| **HPP** | Homopolymer polypropylene |
| **RCP** | Random copolymer |
| **ICP** | Impact copolymer |
| **ABS** | Acrylonitrile butadiene styrene |
| **PVC** | Polyvinyl chloride |
| **UMES** | Unmodified egg shell |
| **MES** | Modified egg shell |
| **FH** | Maximum force (tensile or compression) |
| **RH** | Tensile or compression force |
| **AH** | Overall extension at maximum force |
| **dLH** | Elongation at maximum force |
| **RB** | Stress at break |
| **AB** | Overall extension at sample break |
| **dLB** | Elongation at sample break |
| **AO** | Antioxidant |
| **RIM** | Reaction injection moulding |
| **UTM** | Universal testing machine |

# ABSTRACT

Polypropylene is one of the most important polymers being used today. The applications of polypropylene range from household appliances to packaging and the greatest use of it is in automobiles. To enhance its properties, fillers are added to it such as talc, calcium carbonate, etc. An attempt has been made in this regard to replace commercial calcium carbonate filler by egg shells. Egg shells constitute about 95 percent of calcium carbonate and its disposal constitutes a serious environmental hazard. Varying compositions of polypropylene (PP) composites were prepared and the results were compared with commercial calcium carbonate reinforced PP. The results indicated a substantial improvement in the Young's modulus (E) with the increment of egg shell content, moreover impact strength was also found to increase. A further improvement in the properties was observed by surface modification of egg shells with isophthalic acid. Scanning electron microscopy images revealed an improvement in the interfacial bonding the surface modified egg shell powder as compared to the unmodified egg shell powder and calcium carbonate. The results indicate the potential of egg shells to be used as filler for polypropylene replacing the commercial calcium carbonate.

# AIM AND OBJECTIVE

In common industrial usage in the preparation of Polypropylene composite, $CaCO_3$ is employed as filler. $CaCO_3$ is obtained from rock and mineral deposits. It is known that the commonly available egg-shell has up to 93-96% $CaCO_3$, 5% polysaccharides and other materials. Egg-shells are environmental hazard as it is a household and industrial waste. The objective of this study was to prepare and characterize eggshell based composites and later compare with composites prepared using $CaCO_3$. For this purpose, egg-shell based and $CaCO_3$ composites with Polypropylene were prepared and tested for various properties. Morphological (dispersion and adhesion using SEM), thermal (crystallinity and melting temperature) and mechanical (impact, flexural strength and tensile strength) properties were determined. The results showed that Eggshell based composites had better adhesion with polymer matrix as well as better mechanical properties as compared with $CaCO_3$ properties.

# CHAPTER-1

# INTRODUCTION

## 1.1 Introduction

Polypropylene is a class of materials called Polyolefin's. Composites based on this resin are relatively new by the standards of those early materials of construction. Recent efforts to use these types of materials combine inherent cost-effectiveness with a wide spectrum of end-use applications as film, fiber, and moldings. Polypropylene was discovered in 1950's by Guilio Natta.**[1]** In1953 Ziegler, a German scientist, discovered that polyethylene could be prepared with a mixture of metal salts and transition metal salts (Busico and Cipullo (2001)). Guilio Natta succeeded in preparing polypropylene using the Ziegler catalyst and was able to obtain and characterize isotactic polypropylene by fractionation (Salamone (1996)). In 1957 polypropylene was taken into commercial production (Karger-Kocsis (1995) **[2,3],** and henceforth isotactic polypropylene (PP) became one of the fastest growing commodity thermoplastic throughout the world with different grades depending on their specific uses.

Three geometric forms of the polymer chain can be obtained (Figure 1). Natta classified them as:

I. Isotactic

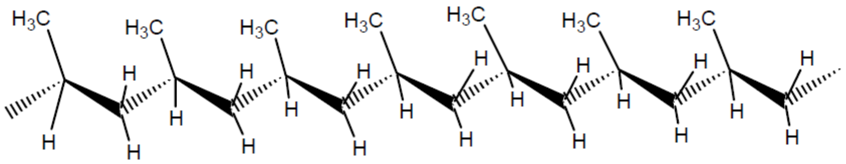
   All methyl groups aligned on one side of the chain

II. Syndiotactic

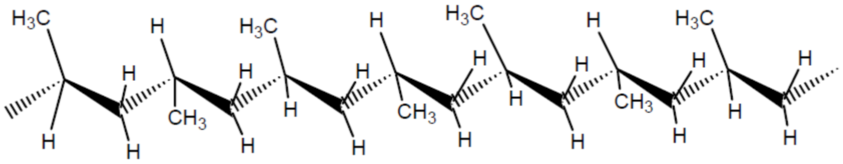
   Methyl groups alternating

III. Atactic

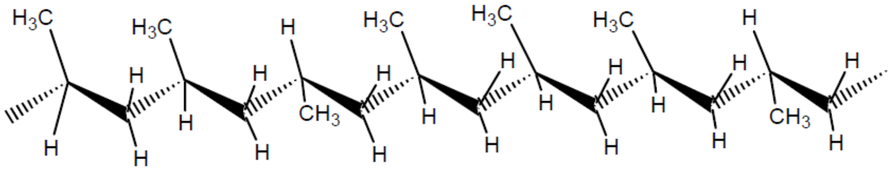
   Methyl groups randomly positioned



(a) Isotactic



(b) Syndiotactic



(c) Atactic

**Figure 1: Polypropylene structures (a) Isotactic, (b) Syndiotactic, (c) Atactic**

Both isotactic and syndiotactic forms will crystallize when there are cooled from molten states. Commercial injection molding and extrusion grade polypropylene (PP) are generally 94 to 97% isotactic. Fabricated parts are typically 60% crystalline, with a range of polyhedral spherulite forms and sizes, depending on the particular mode of crystallization from the melt. Atactic polypropylene, though is not suited to structural plastic uses, have been developed as modifiers in hot melt adhesives, roofing compounds, and communications cable- filler gels.The significant growth of PP use is attributed to a combination of many factors besides a good balance in physical and chemical properties. Because of appropriate melt rheology and thermal behaviour, PP-based materials are widely process able on a variety of different equipment ranging from injection moulding, calendaring and air-quenched blow film equipment. Additionally Polypropylene has the lowest density among commodity plastics at approximately 0.90 g/cm$^3$. Finally, because many major companies are designing their products, polypropylene stands out as the main product with the widest design flexibility and simplicity of recycling. It's excellent thermal stability, low density (assisting in separating from other materials), chemical and environmental inertness, and even its caloric content in the case of incineration all add to its attractiveness as the material of construction. Additionally, in the next 10 years, significant amounts of polypropylene from recycled sources will be available. The quality of this recycled material varies widely in cleanliness but is thought to be suitable for a variety of applications, including automotive.

## 1.2 Types of Polypropylene

Polypropylene containing only propylene monomer in the semicrystalline solid form is referred to as homopolymer polypropylene (HPP).

Polypropylene containing ethylene as a comonomer in the PP chains at levels in about the 1–8% range is referred to as random copolymer (RCP). HPP containing an ethylene content of 45–65% is referred to as an impact copolymer (ICP).

### 1.2.1 Homopolymer

Homopolymer polypropylene (HPP) is a two-phase system because it contains both crystalline and noncrystalline regions. The noncrystalline, or amorphous, regions are comprised of both isotactic PP and atactic PP. The isotactic PP in the amorphous regions is crystallizable, and it will crystallize slowly over time up to the limit that entanglement will allow. The crystallizability of the chains is one factor that determines how thick the crystallites will be and the thickness of the crystallites determines how much heat energy is required to melt them (the melting temperature). A typical HPP has an array of crystallites from thick ones to very thin ones, and these manifest themselves as an array of melting points.

### 1.2.2 Random Copolymer

Random copolymers are ethylene/propylene copolymers that are made in a single reactor by copolymerizing propylene and small amounts of ethylene (usually 7% and lower). The copolymerized ethylene changes the properties of the polymer chains significantly and results in thermoplastic products that are sold into markets in which slightly better impact properties, improved clarity, decreased haze, decreased melting point, or enhanced flexibility are required. The ethylene monomer in the PP chain manifests itself as a defect in the chain regularity, thus inhibiting the chain's crystallizability. As the ethylene content increases, the crystallite thickness gradually decreases, and this manifests itself in a lower melting point.

### 1.2.3 Impact Copolymers

Impact copolymers are physical mixtures of Homopolymer and Random Copolymer, with the overall mixture having ethylene contents on the order of 6–15% wt%. These are sold into markets where enhanced impact resistance is needed at low temperatures, especially freezer temperature and below.

The Random Copolymer part of the mixture is designed to have ethylene contents on the order of 40–65% ethylene and is termed the rubber phase.

The rubber phase can be mechanically blended into the Impact Copolymer by mixing rubber and Homopolymer in an extruder or it can be polymerized in situ in a two-reactor system.

The Homopolymer is made in the first reactor and the Homopolymer with active catalyst still in it is conveyed into a second reactor where a mixture of ethylene and propylene monomer is polymerized in the voids and interstices of the Homopolymer polymer powder particle. The amount of rubber phase that is blended into the Homopolymer by mechanical or reactor methods is determined by the level of impact resistance needed. The impact resistance of the ICP product is determined not only by its rubber content but also by the size, shape, and distribution of the rubber particles throughout the ICP product. Reactor products usually give better impact resistance at a given rubber level for this reason. As the rubber content of the ICP product is increased, so is the impact resistance, but this is at the expense of the stiffness (flexural modulus) of the product. Consequently, polymer scientists often describe a product as having a certain impact–stiffness balance. The stiffness of the ICP product is dictated by the stiffness of the Homopolymer phase and the volume of rubber at a given rubber size distribution in the product. The impact resistance is dictated by the amount and distribution of the rubber phase in the ICP product.

## 1.3 Competition with other Polymers

Polymer selection for any specific design is often governed by a complex set of characteristics. The most common design parameters are cost, temperature performance, toughness–stiffness balance, chemical resistance, electrical properties, optical properties, long-term dimensional stability, or environmental resistance. Competitive penetration of polypropylene into other applications has primarily taken place in polyethylene, polystyrene, polyvinyl chloride (PVC), thermoplastic polyester, nylon-6 or -6/6, and phenolic or reinforced reaction injection moulded (RIM) urethane.

## 1.4 Fillers

Fillers play a crucial role in the manufacture of plastics. Alone many plastics are virtually useless, but they are converted into highly useful products by combining them with fillers. For example, phenolic and amine resins are almost always used in combination with substances like wood flour, pure cellulose, powdered mica, and asbestos. Glass fiber is used as filler for fiber-reinforced composites with epoxy, polypropylene or polyester resins. Enhancement of properties like tensile strength, stiffness, tear resistance, and abrasion resistance are called reinforcement, and the fillers which produce the strengthening effect are known as reinforcing fillers. Other fillers may not appreciably increase strength, but they may improve other properties of the polymer, thus, making it easier to mold, which reduces cost.

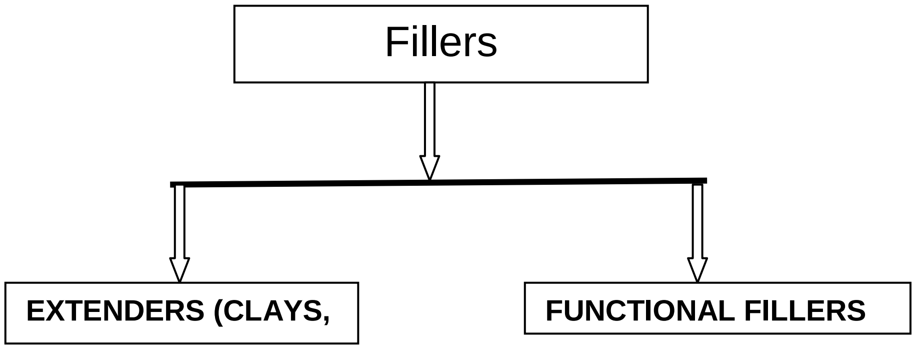
The addition of fillers also requires a balance of formulation for optimum processing properties. Therefore, before making a final decision on a filled compound, it is critical to establish the following:

- Optimum loading level for property and benefit.
- Optimum formulation for processing and production output.
- Economics of filled formulation.

## 1.5 Classification of filler

Fillers have been classified in many different ways, ranging from their shapes to specific characteristics. Broadly, fillers can be classified into two categories, which are as follows:

### Classification based on performance



### 1.5.1. Extenders

The extender fillers primarily occupy space and are mainly used to lower the formulation cost. Properties of extender fillers:

In general, ideal extender filler should

- Be spherical to permit retention of anisotropic properties.
- Have an appropriate particle size distribution for particle packing.
- cause no chemical reactivity with the polymer or the additives
- Have low specific gravity.
- Have desirable refractive index and colour.
- Be low in cost.

### 1.5.2 Functional fillers

Functional fillers on the other hand have a definite and required function in the formulation apart from lowering the formulation cost.

However, some of the extender fillers when reduced to a finer particle size and/or surface treated would perform as functional filler. Fillers that are functional in one polymer may be merely extenders in another polymer. Such factors seriously complicate the task of establishing sharp boundary lines between extenders and functional fillers in terms of their generic composition; however, on the performance basis they can be separated as shown in the fig 2

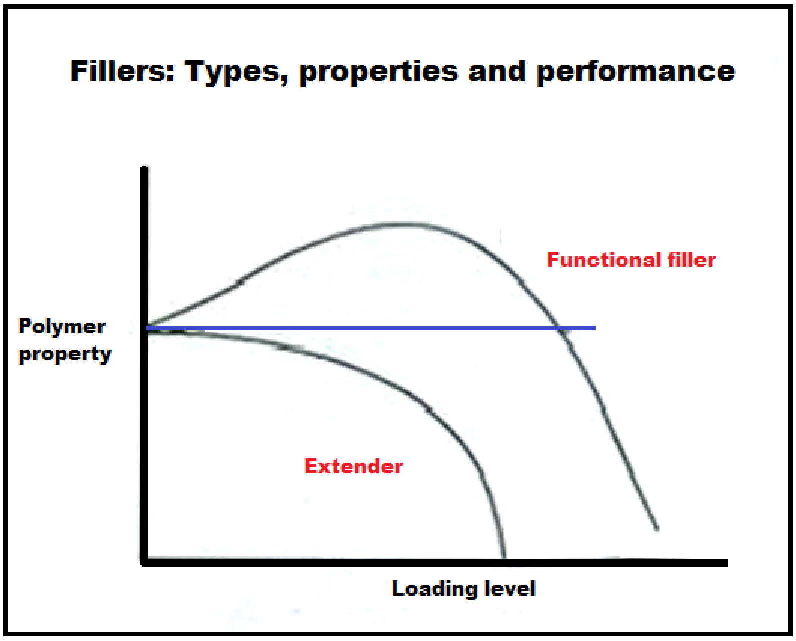


**Figure 2**: **Characteristics of functional and extender fillers.**

## 1.6 Classification based on type

### 1.6.1 Particulate fillers

Particulate fillers are divided into two types,[ inert fillers and reinforcing fillers]. The term inert filler is something of a misnomer as many properties may be affected by incorporation of such filler. For normal uses, such fillers should be quite insoluble in any liquids that the polymer compound is liable to come into contact. Each type of filler may differ in the following ways:

- Average particle size and size distribution.
- Particle shape and porosity.
- Chemical nature of the surface.
- Impurities such as grit and metal ions.

The common observation is that the finer the particle sizes the higher the values of the tensile strength, modulus and hardness. Coarser particles will tend to give less strong compounds than the virgin material (i.e. material without the filler), but if the particle size is fine there is an enhancement of the mechanical properties and the phenomenon is called as reinforcement.

Impurities in the fillers can have serious effects on the polymer compound. Coarse particles lead to points of weakness in soft polymers and will therefore fail under stresses below that which might be expected. In general, the phenomenon of reinforcement appears to depend on three factors:

- An extensity -factor the total amount of surface area of filler per unit volume in contact with the polymer.
- An intensity factor – the specific activity of the filler – polymer interface causing chemical and/or physical bonding.
- Geometrical factors such as structure and porosity of the particles.

### 1.6.2 Particles as Reinforcements

Non-bio based particles which are used for reinforcing polymer composites are minerals, ceramics, metals or amorphous materials such as carbon black. A filler should have a low aspect ratio and can be added to a polymer matrix for a variety of functions. The addition of fillers can affect physical, mechanical, thermal or electrical properties and cost. The most commonly used general purpose fillers are clays, silicates, talc’s, carbonates, asbestos fines and paper. It is possible fillers can also act as pigments, e.g., carbon black, chalk and titanium dioxide or act as a lubricant, e.g. graphite and molybdenum disulfide. By using magnetic materials as fillers magnetic properties can be obtained. Metallic fillers are used to increase specific gravity or impart higher thermal and electrical conductivity. The particles can be used to increase the modulus of the matrix, to decrease the permeability of the matrix and to decrease the ductility of the matrix. Particles are specially used to decrease the cost of composites. The word filler is generally associated with a low cost material that is added to the formulation primarily to decrease cost. However some fillers can contribute to the improvement of certain properties, those are known as functional fillers. Very popular filler used as a reinforcement particle is carbon black when used in natural rubber/caoutchouc. Making particle reinforced composites is much easier and less costly than making fiber reinforced thermoplastic composites. With polymeric matrices, the particles are more easily added to the polymer melt in an extruder or injection moulding apparatus during polymer processing. Inorganic (non-bio based) fillers do not have a hydrocarbon basis in their chemical structure. Inorganic substances used as fillers are minerals, ceramics and metals. Some examples for inorganic filler are silica ($SiO_2$), titania, alumina, calcium carbonate ($CaCO_3$), aluminium hydroxide, strontium carbonate ($SrCO_3$), clay, talk and mica. Bio based particles used as fillers can be any kind of plant material or by-product during the processing of plant materials that has a shape which is particle-like. Most plant materials are milled to flour like particles and used as filler in composites.

### 1.6.3 Fibrous fillers

Fibrous fillers have been long used in plastic materials. Fibrous fillers are often embedded in the laminar form. The fibers have higher modulus than the resins in which they are embedded so that when the composite of resin plus the fiber is strained in the plane of the fibrous layer the bulk of the stress is taken up by the fiber. As a result of this, both the strength and the modulus are enhanced when compared to the unfilled resin. Fibre-reinforced composites are materials in which a fibre made of one material is embedded in another material. Any material which can reinforce the properties of the composite can be used as a fibre. Depending on the application of the composite there are different treatments of the reinforcements. Biological and chemical composition as well as particle size (nanocomposites) and formation are important parameter of the fibre which can have a significant effect on the composite. Fibre-reinforced composites can take diverse forms such as continuous bundles of fibres, woven fabrics and chopped fibres. Fibre reinforced materials can be continuous aligned or discontinuous, randomly orientated or aligned due to use of short fibers. In comparison to metals, polymers generally possess about 100 times lower module and about 5 time's lower strengths. The use of particles or fibres as reinforcements can improve the stiffness and strength of the composites and thus expand the application of plastics. Some examples of non-bio based fibers used primarily for reinforcement are glass fibres, carbon fibres and oriented polymeric fibres (McCrum, Buckley et al. 1990). Successful reinforced polymers are fiber-reinforced plastic (epoxy resin in which are embedded continuous Kevlar and carbon reinforcing fibres), carbon-fibre reinforced polymer (nylon), FiberglasTM, and reinforced material at several different levels (carbon black with polymer, rigid cords) (McCrum, Buckley et al. 1990). Natural Fibers are grouped into three types: seed hair (e.g. cotton), bast fibers (e.g. ramie, jute, flax), and leaf fibers (e.g. sisal, abaca), depending upon the source (Saheb, Jog 1999).

### 1.6.4 Rubbery fillers

Rubbery fillers are often incorporated into rigid thermoplastics to improve their toughness. The increase in toughness of the material leads to significant increase in the fracture resistance of the material

### 1.6.5 Biofillers

A bio-composite is a material formed by a matrix (resin) and a reinforcement of natural fibres (usually derived from plants or cellulose) or particles ($CaCO_3$, Talc etc). With wide-ranging uses from environment-friendly biodegradable composites to biomedical composites for drug/gene delivery, tissue engineering applications and cosmetic orthodontics. Those markets are significantly rising, mainly because of the increase in oil price, and recycling and environment necessities.

### 1.6.6 Egg-shell as a Biofiller

Eggshell is a biomaterial containing 95% by weight of CC and 5% by weight of organic materials. Waste eggshell (ES) is often turned into a low protein supplement for animal feed making it a marginally profitable venture with supply exceeding demand. In addition the ES is an abundant by-product of poultry industry. These characteristics qualify ES as excellent candidates for bulk quantity, inexpensive, low-load bearing composite applications such as the automotive industry, trucks, homes, offices, and factories.

## 1.7 Polymeric Composites

Composite materials can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. These heterogeneous systems obtained by artificial combination of different materials in order to get better mechanical properties that the individual components by themselves cannot attain. Concerning the mechanical properties of final composite product, polymers usually mixed with materials that have high strength/stiffness properties. Thus, the definition can be narrowed to systems that contain reinforcing material and a matrix that surrounds and supports the reinforcing material. Hence, it would be concluded that composites generally have a discontinuous phase, which can be fibers or particles, stiffer and stronger than the continuous matrix phase and physical or mechanical properties of composites are generally derived from that phase.

Composite systems can be classified in many ways, such as, by categorizing according to the geometry or according to the matrix material. Fibrous, laminated, and particulate fillers are the classes of geometrical categorization. Particulate fillers which cover a wide range of different materials are often spherical, or at least have dimensions of similar order in all directions (isometric). The particle characteristics can be classified as spheres, cubes, blocks, rods, flakes, and any other shapes of roughly equal axes. Common fillers used in polymeric composites are glass (spheres), $CaCO_3$ (cube and block), kaolin, mica, talc (flakes), and wood flour (flakes) **[4].** Generally, particulate fillers improve some of the properties while degrading others, such as improving the strength and stiffness but reducing the impact strength.

These composites are considered as particulate composites. Besides some filler can only be used for extending rather than reinforcing, as these filler particles are employed for the main purpose of cost reduction and these composites are generally referred as filled systems.

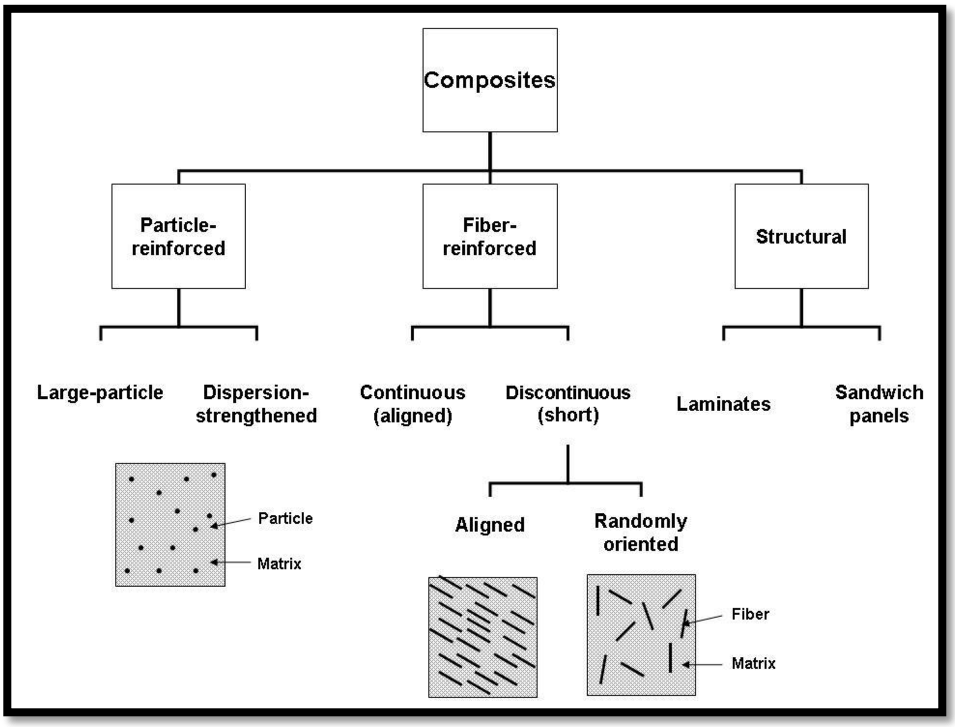


**Figure 3: Classification scheme for the types of composites (Callister 1996).**

### 1.7.1 Biocomposite

In order to call a composite “bio based” or “bio composite” the following definitions need to be considered:

According to the ASTM standards, bio based materials are materials that contain “carbon based compound(s) in which the carbon comes from contemporary (non-fossil) biological sources” (ASTM International 2008). Compared the ASTM definition of bio based materials with their definition of bio based products, a “product generated by blending or assembling bio based materials, either exclusively or in combination with non-bio based materials, in which the bio based material is present as a quantifiable portion of the total product mass of the product"(ASTM International 2008), the bio composite from polypropylene and egg-shell can be considered as bio based product, thus a bio composite. Bio composites are characterised by the fact that the petrochemical resin is replaced by a vegetable or animal resin, and/or the bolsters (fibreglass, carbon fibre or talc) are replaced by natural fibre (wood fibres, hemp, flax, sisal, jute). In biomaterials, it is important that each constituent of the composite be biocompatible. Moreover, the interface between constituents should not be degraded by the body environment. Normally, Bio-composite material can be classify in to three groups

- Particulate Composites
- Fibrous Composites
- Porous Materials

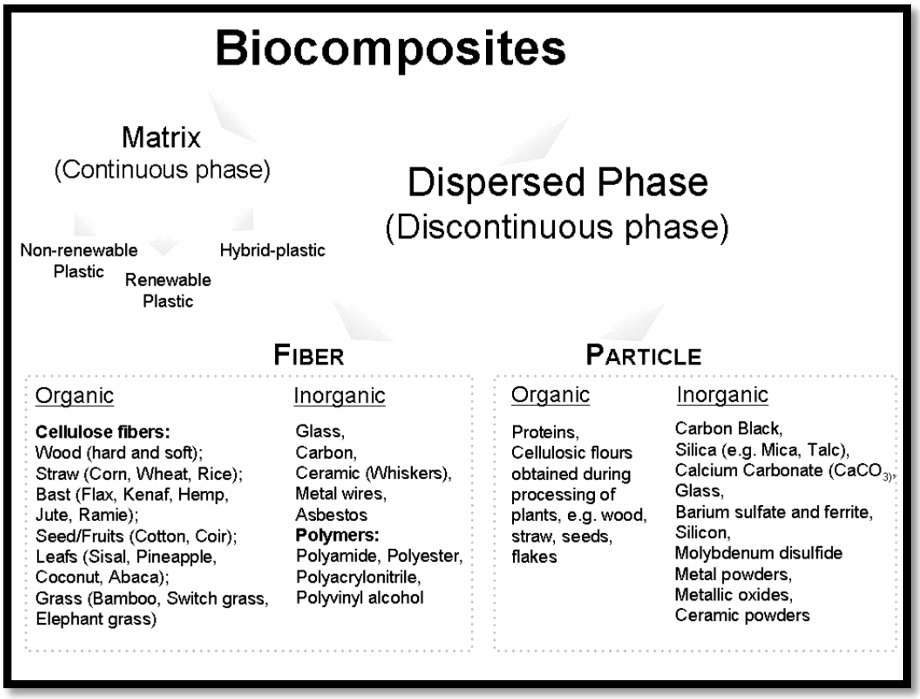


**Figure 4: Overview about possible bio composite components.**

## 1.8 Polypropylene Eggshell Bio composite

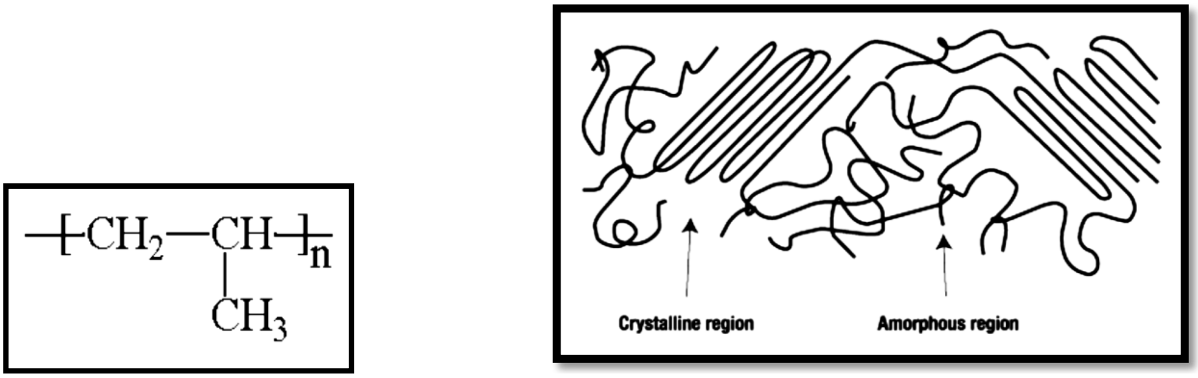
Polypropylene (PP) composites have been used in large quantities in numerous fields of applications for many years (Pukanzsky, 1995). The success of PP composites lies in its extremely advantageous price/volume/performance relations, with the result that PP composites successfully penetrate fields traditionally occupied by other engineering plastic material such as ABS and nylon.

Considerable efforts have been made to extend the application of PP composites to fields where engineering thermoplastic have been used up to now. Today, particulate filled PP composites such as talc-filled PP is still widely used. Particularly in the automotive industry for the production of bumpers, heater housings, door pockets and trimmings, timing belt covers cladding. Other common fillers include $CaCO_3$ kaolin, mica and carbon black, while glass fibre is still one of the most commonly used fibrous reinforcements in PP. In this study Eggshell has been used as reinforcement in a Polypropylene matrix.

### 1.8.1 The matrix: polypropylene

In fiber or particle reinforced composites the matrix is the material in which the dispersed phase (fiber or particle) is embedded. There are common polymer matrices used in composites, they can be classified in thermoplastics, thermo sets or elastomers. Thermoplastics can be melted during processing, which is convenient when recycling. Thermosets are processed by transforming a viscous liquid into a rigid polymer upon polymerization; they cannot be melted after the polymerization. Polyethylene (PE) and polypropylene (PP) belong to a group of polymers known as polyolefins, the synthetic polymer with the largest volume of applications. Polypropylene because of its high-volume, low-cost has been produced in large quantities and widely used in fabrication of automotive parts since 1959. Polypropylene is a obtained by polymerization of propene. The most common polymerization method for manufacturing polypropylene is the Ziegler-Natta system introduced in the early 1950s', metallocene catalysts were introduced in the late 1980s' and today they contribute to a minor fraction of the total polypropylene manufacturing. Polypropylene belongs to the thermoplastics and has a semi-crystalline crystalline (isotactic or syndiotactic) or amorphous (atactic) morphology.

The melting temperature of polypropylene is at 165 °C (100 % isotactic) and the glass transition temperature at -10 °C to 0 °C **[5].** At temperatures below -20 °C (Tg) polypropylene is brittle. A classification scheme for the characteristics of the polymer molecules is shown in Figure 5



(a) (b)

**Figure 5: (a) Structure of polypropylene and (b) Crystalline and amorphous regions after polymerization (Rosner 2001)**

Density of semi-crystalline polypropylene is between 0.9 – 0.91 $g/cm^3$ (homopolymer). The elastic modulus for polypropylene is between 1.05 – 2.10 GPa (homopolymer). Total burning of polypropylene without additives produces $CO_2$ and water. The calorific value of polypropylene is 43.5 MJ/kg which shows a high amount of energy. The energy consumption for producing of the feedstock (pellets) is about 80 MJ/kg. Polypropylene has good mechanical properties, low density, durability, resistance to X-rays, low water permeability, relatively good impact resistance (when modified with copolymers) and good temperature resistance up to 135 °C. It also has good properties in terms of electrical isolation. These properties, the low cost and easy processing allows a large variety of uses: various household items, plastic packaging, automobile parts, batteries, (garden) furniture, syringes, bottles and appliances.

### 1.8.2 The Filler Eggshell

Chicken eggshell is classified as a natural biomaterial. It is a waste material from food and hatchery industry. Nowadays, the eggshell waste is discarded by buried in a landfill. Actually, the discarded eggshell comprises a valuable calcium carbonate ($CaCO_3$) as high as 94 wt% from eggshell; calcium carbonate can be obtained by chemical or physical treatment. Calcium carbonate is popularly used as filler for polypropylene (PP). It will be greatly beneficial if the eggshell can be employed, without any treatment, as filler for PP.

The utilization of eggshell has long been investigated due to the high content of calcium, magnesium, and phosphorus. The egg shell carbonate can be employed as a fertilizer, soil conditioner or an additive for animal feed **[6]** It can also be used as a sources of Ca for human nutrition **[7]** Due to the intrinsic pore structure of the egg shell, it was proposed as a low cost adsorbent as alternative to expensive activated carbon. Several studies proved the effectiveness of egg shell for the sorption of heavy metals such as Cr, Cd, Cu **[8]** and the removal of dye effluent**[9]** Chicken egg shell has been applied as a bio filler for polymer composites**[10]** and the possibility of the use of powdered egg shells as a bone substitute has also been investigated **[11].**

# CHAPTER-2

# LITERATURE REVIEW

**Toro et al. [12]** in their paper have described a process in which Different proportions of chicken eggshell as bio-filler for polypropylene (PP) composite were compared with different particle sizes and proportions of commercial talc and calcium carbonate fillers by tensile test. It has been shown that the Young's modulus (E) improves considerably with the increment of egg-shell content. It is thus seen that this bio-filler is better than all types of carbonate fillers with different particle sizes used in the study.

The lower E values of the samples with ES is not considered a deterrent, as up to 75% of the sample can be replaced with egg-shell content with satisfactory results. Scanning electron microscopy showed an improved interfacial bonding on the tensile fractured surface. The improvement in the mechanical properties was shown to be a result of better ES/matrix interface related to the geometric ratio of the ES particles similar to talc particles.

**Pakdeechote et al. [13]** in their paper describe the beneficial properties of Chicken eggshell as a natural biomaterial, and how the eggshell, generally considered as a waste, comprises a valuable calcium carbonate ($CaCO_3$) as high as 94 wt%. The $CaCO_3$ obtained by physical and chemical process is popularly used as filler for high density polyethylene (HDPE), but they propose a way that can incorporate it without any additional process, and makes use of recent studies extrapolating this to polypropylene (PP) composites.

The results showed improvement of Young’s modulus of PP composites with increasing ESP content. Thus, in this paper, the utilization of eggshell powder as alternative filler for HDPE was attempted. The mechanical properties of the filled HDPE were then compared to those of HDPE filled with traditional filler, calcium carbonate and analysed.

**Shuhadah et al. [14]** in their work have studied the effects of chemical modification on the mechanical properties, morphology and water absorption of low density polyethylene/egg shell powder composites.

An Instron machine and scanning electron microscopy (SEM) was used to characterize the mechanical and morphological properties of low density polyethylene/egg shell powder composites with and without modifications (NaOH-isophthalic acid). The composites were prepared by using a Z-blade mixer at 180°C and at a rotor speed of 50 rpm for 6 min. It is shown that the interfacial adhesion has enhanced the tensile strength and water absorption resistance of the LDPE/modified egg shell powder composites (LDPE/ESPI), as compared to LDPE/unmodified egg shell powder composites (LDPE/ESP). Both the introduction of interfacial adhesion to composites and better interaction adhesion between LDPE and egg shell powder are responsible for the improvement of the mechanical properties of the LDPE/ESPI, as evidenced by SEM on the tensile fracture surface of the composites.

**Hussein et al. [15]** in their work have investigated the water absorption and mechanical properties of (high-density polyethylene /egg shell) composites as a function of egg shell powder weight content in two different grain sizes (75,125 micro metres) were investigated. Polymer composite were fabricated by mixing (HDPE) with (5, 10, 15, 20, 25) wt.% of egg shell powder to obtain desirable properties. The parameters such as tensile strength, tensile modulus, elongation at break and impact test were carried out on the prepared samples. It is shown that that the addition of egg shell powder to the polymer leads to decrease the tensile strength, modulus of elasticity, shore-D hardness on other hand it increases the % elongation at break, and for the impact strength. Water absorption of the composites behaviours as function of days has also been studied, and it is seen that it increases by increasing exposure time for the same filler content, while the absorbed amount of water increases, by increasing the wt.% of egg shell constant exposure time.

**Kim et al. [16]** in their research have studied the thermal properties of bio-flour-filled, polypropylene (PP) bio-composites with different pozzolan contents. With increasing pozzolan content, the thermal stability, 5% mass loss temperature and derivative thermogravimetric curve (DTGmax) temperatures of the bio-composites slightly increased. It is shown that the coefficient of thermal expansion (CTE) and thermal expansion of the bio-composites decreased as the pozzolan content increased.

The glass transition temperature (*T*g), melting temperature (*T*m) and percentage of crystallinity (*X*c) of the bio-composites were not significantly changed. The thermal stability, thermal expansion and *X*c of the maleic anhydride-grafted PP (MAPP)-treated bio-composites were much higher than those of non-treated bio-composites at 1% pozzolan content due to enhanced interfacial adhesion. X-ray diffraction (XRD) analysis confirmed the crystallinity of pozzolan-added bio-composites. From these results, they have concluded that the addition of pozzolan in the bio-composites was an effective method for enhancing the thermal stability and thermal expansion.

**Li HY et al. [17]** in their research try to find a suitable use for Waste shellfish shell stacking with a significant odor and toxicity which are hazardous to human. Granule of shellfish shell (SS) was prepared from waste shellfish shell by removing cuticle, crushing, grinding and shearing emulsification and was introduced as a filler to reinforce polypropylene (PP). The mechanical behavior of PP/SS composite is seen to display a higher yield strain, yield strength, tensile strength and elongation at break than traditional commercial calcium carbonate (CC) filled PP. Yield strength of PP/SS composite with 2% SS is improved by

1.1% due to the formation of β-crystalline PP phase. Thus it is seen that using waste SS for producing bio-filler for filling PP is an effective and prospective measure to deal with waste SS.

**Luan et al [18]** in their paper used former exploratory research to utilize seaweed (SW) fibre as a novel biofiller for the production of polypropylene (PP) biocomposites. Maleic anhydride-grafted polypropylene (MAPP) and a CNT master batch (CESA) were applied as compatibilizers. Mechanical proper- ties, crystallization behaviour, dynamic mechanical performance as well as interfacial morphology were characterized. They have successfully incorporated SW fiber in the PP matrix in terms of mechanical reinforcement. Accelerated crystallization process of PP matrix was observed during the experimentation. DMA results also indicated the favourable adhesion between SW fiber and PP matrix, which could be confirmed by SEM characterization. The effect and efficiency of MAPP and CESA as compatibilizers were evaluated in the course of the study. Moreover, potential flame retardancy of SW fibers for PP matrix was observed.

**Yoo et al. [19]** in their work highlight eggshell usage because of its reclamation potential. This study presents an economical treatment process to recover useful bio products from eggshell waste and their utilization in commercial products. It was seen that the dissolved air floatation (DAF) separation unit, which successfully recovered 96% of eggshell membrane and 99% of eggshell calcium carbonate (ECC) particles from eggshell waste within 2 h of operation. The recovered ECC particles were utilized as coating pigments for ink-jet printing paper and their impact on the ink density and paper gloss were investigated.

The addition of the ECC particles as coating pigments enhances the optical density of cyan, magenta and yellow inks while decreasing the black ink density and the gloss of the coated paper.

Sivarao et al. **[20]** in their research have focused on utilising eggshell as a natural composite improving the mechanical properties of polyethylene (PE) used in manufacturing goods by industries in Malaysia. The PE's virgin mechanical properties were modified by reinforcing eggshell, and then tensile, creep and flexural tests were carried out to characterize the developed composites. The eggshells were then tried to improve bonding capability. They were then particulate into polyethylene matrix according to certain weight ratios. From the experimental results, it was learnt that the ES filler has improved mechanical properties of virgin PE as far as 5% to 9%.

**Lin et al [21]** in their work have formulated a novel eggshell/β-PP bio-composite and evaluated it. First the waste chicken eggshell (ES) was modified by a stingy amount of pimelic acid (PA) through solution method, and then compounded with PP through melt blending method. The crystalline form, mechanical properties, and morphology of the ES/β-PP composites were studied. The results showed that ES modified by PA was a β nucleating agent with high efficiency and selectivity, resulting in the maximum $K_\beta$ value of 0.99 in PP composites.

PA modification promoted the dispersion and interfacial bonding of ES in PP. Although the addition of PA-modified ES slightly decreased tensile properties and flexural properties of PP, it increased the impact strength of PP by 228% than that of pure PP. Taking all factors into consideration, the optimal mass ratio of PP/ES/PA composites for reaching optimum mechanical properties should be 100/5/0.000471. Thus, it is seen that the application of modified ES to prepare ES/β-PP bio-composites represents a promising way to mitigate environmental pollution and to reduce the cost of polyolefin products.

**Thomas et al. [22]** has worked to obtain the melt viscosity and melt elasticity data over a wide range of temperatures and shear rates on a series of four polypropylenes of different molecular weight but approximately the same molecular weight distribution. The superposition technique was employed in this work to shift flow curves for all four materials at three temperatures each along the shear rate axis to generate a master flow curve at a given temperature and molecular weight. For polypropylenes of this type, and molecular weight distribution shift, factors which can be used to extend the useful range of experimentally obtained flow data were determined. The dependency of apparent viscosity on weight average molecular weight at shear stresses as high as 106 dynes/cm2 is analysed. The dependency of melt elasticity on molecular weight and temperature has also been discussed.

**Flood et al. [23]** has studied three polypropylene polymer samples possessing three different molecular weight distributions. The three resins have been used to produce uniaxially oriented stretched tapes, which were evaluated for physical properties and morphological characteristics. In addition, five different drawing temperatures were used to investigate the effect of temperature on the physical properties and molecular morphology of the tape. It has been shown that as the MWD became broader, the tape modulus and tenacity increased slightly and the percent elongation and shrinkage decreased slightly.

These effects were attributed to decreases in molecular mobility and increases in the number of tie molecules present in broad MWD resins. Morphological studies determined that the crystalline orientation was not affected by MWD. However, the amorphous orientation, at higher draw temperatures, demonstrated a small increase as the MWD became broader. It was also seen that the MWD did not have a large effect on the percent crystallinity but the long period spacing (LPS) did exhibit a small decrease as the MWD broadened.

**Kord et al. [24]** has examined the effect of reinforcing filler loading on the mechanical properties of wood plastic composite. Wood floor sample has been compounded with polypropylene and coupling agent in internal mixer, after which the sample was fabricated by injection moulding. The reinforcing filer loading concentration was varied by weight of composite and coupling agent for all reinforcing sample was kept at a constant. The mechanical properties such as tensile strength, flexural strength, tensile modulus, and flexural modulus, elongation at brake and impact strength were evaluated. It has been shown that the reinforcing filler loading had significant effect ($p<0.05$) on the mechanical property of wood plastic composite. The increasing reinforcing filler loading reduced the flexural strength tensile strength and elongation at break and impact strength on wood plastic composite. In contrast, the tensile modulus and flexural modulus improved with increasing the reinforcing filler loading.

**Sanmuang et al. [25]** has studied the effect of heating times on the content of $CaCO_3$. For this they have thermally treated the eggshell at 700°C for 1-3 hrs and at 800°C for 1- 4 hrs. After the treatment, thermally treated eggshell was characterized via X-ray diffraction spectrometer, particle size analyzer and thermo gravimetric analyzer. From the XRD patterns, it revealed that calcium carbonate was obtained when chicken eggshell was treated at 700°C. The content of calcium carbonate, however, decreased with increasing heating times and temperature. After the eggshell was heated at 800°C, calcium hydroxide was mainly obtained and eventually when the treatment time was 4 hrs, instead of calcium carbonate, calcium hydroxide and calcium oxide were obtained. The size of the treated eggshell was about 0.06 – 878.7 µm depending on the treatment times and temperatures. The size distribution of 800°C-treated eggshell was narrower than that of the 700°C-treated eggshell.

# CHAPTER-3

# EXPERIMENTAL

## 3. Experimental

During the course of this project various experimental methods/techniques were used for the preparation and characterization of the polypropylene-biofiller composites. All the testing / analysis were carried out as per the ASTM or available international standards.

## 3.1 Raw material

### 3.1.1 Polypropylene

Indian Oil homopolymer Polypropylene grade 1110MG was used for preparation of composites. This grade is used for applications like rigid packaging, house hold article, furniture, automobile etc because of its high flow ability, rigidity and good gloss.

**Table 1**: **Grade details of PP.1110 MG**

| **Property** | **Value** |
|---|---|
| **MFI** | 11 |
| **Melting Point (°C)** | 164 |
| **Tensile strength (Mpa)** | 35.4 |
| **Flexural modulus (Mpa)** | 1300 |
| **Izod impact strength (J/m)** | 21.5 |

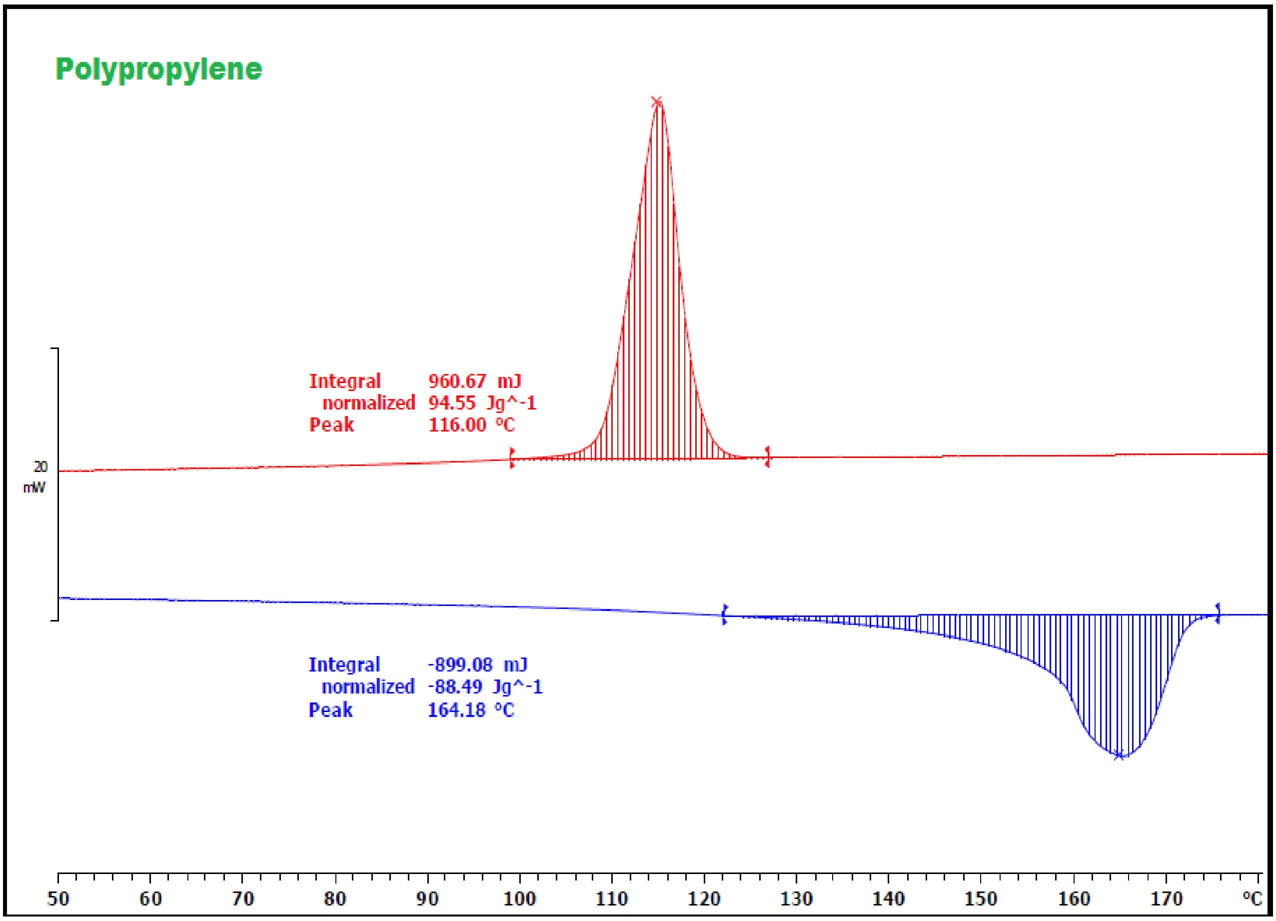


**Figure 6: Showing melting and crystallization temperature of PP**

### 3.1.2 Calcium carbonate

For the present study, $CaCO_3$ was purchased from M/s. Saurashtra solid Industries Pvt. Ltd having particle size 3.2 microns. Detailed specifications of the calcium carbonate used are given in the table 2 below.

**Table 2: Specifications and particle size distribution of $CaCO_3$**

| **Physical Specifications** | |
|---|---|
| Specific gravity | 2.6-2.9 |
| Particle Size | 6-8 µm |
| Bulk density | 0.50-0.55 gm/ml |
| Whiteness | 95 min. |

Calcium carbonate initially had particle size of 6-8 microns which was further micronized to 3.2 microns by ball mill grinding. Particle size distribution of the calcium carbonate given in figure 7

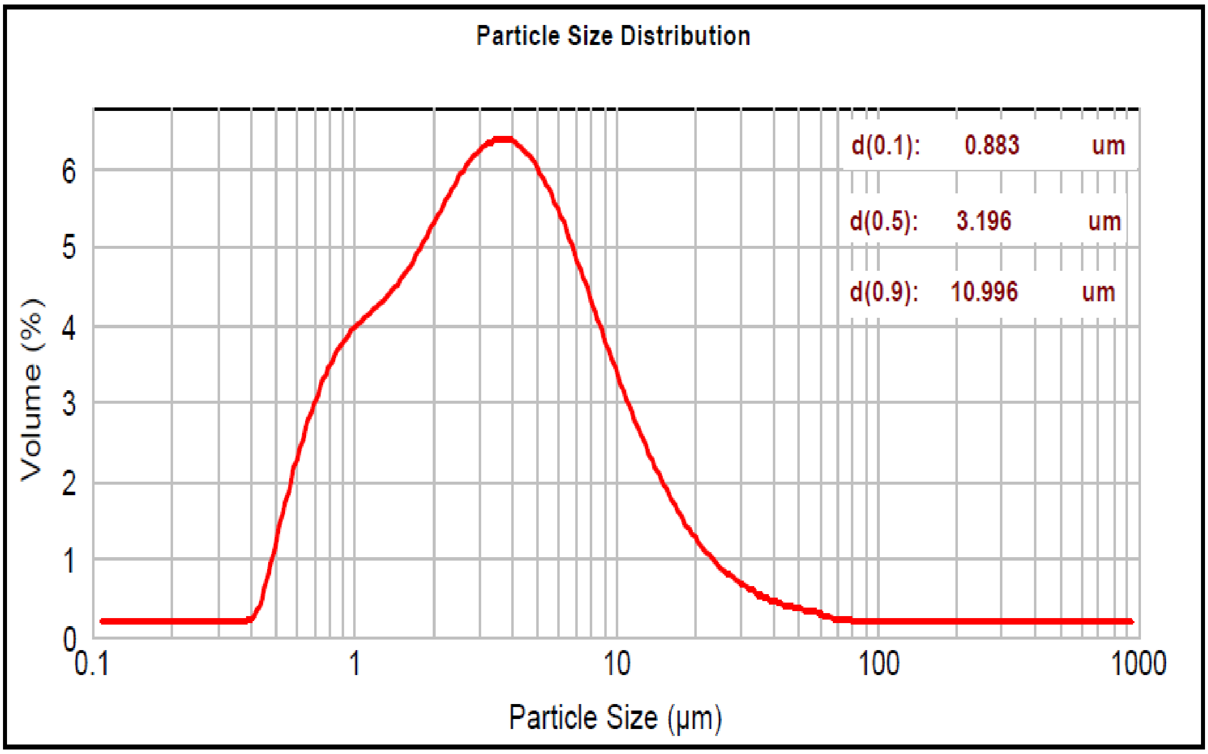


**Figure 7: Particle size distribution of the calcium carbonate**

### 3.1.3 Eggshell

Eggshells were collected locally. Prior to use the eggshell were washed with water to remove dirt and protein membrane attached to inside of eggshell. After through washing eggshells were put in an oven at 90°C for 6 to 7 hours. After drying the eggshell were grinded to fine powder by grinder whose particle size was measured to 20 microns. Particle size of the eggshell was further reduced to 2.4 microns.

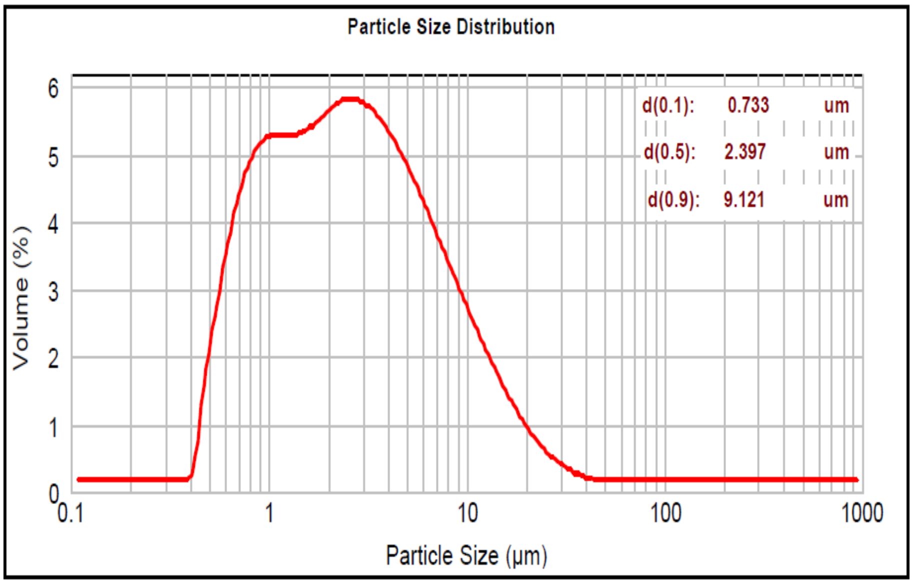


**Figure 8: showing particle size distribution of eggshell**

**Figure 9: showing** (a) **dried eggshells** (b) **powdered eggshells**

## 3.2 Elemental analysis by XRF

X ray fluorescence technique was used for quantitative elemental analysis of calcium carbonate and eggshell used for the study. Results show that eggshell used for the study had more calcium content than calcium carbonate. Calcium carbonate had higher percentage of magnesium, silica and iron as compared to eggshell. Phosphorous, aluminium, sulphur etc were also present in traces in both samples.

**Table 3: Showing XRF elemental analysis of $CaCO_3$ and egg shell**

| ***S.No.*** | ***Description (%)*** | ***$CaCo_3$*** | ***Eggshell*** |
|---|---|---|---|
| *1* | *Ca* | *94.4* | *99.7* |
| *2* | *Mg* | *2.1* | *.1* |
| *3* | *Al* | *0.02* | *.01* |
| *4* | *Si* | *1.7* | *.01* |
| *5* | *P* | *0.4* | - |
| *6* | *S* | *0.3* | *.1* |
| *7* | *K* | *0.3* | *.03* |
| *8* | *Mn* | *0.3* | - |
| *9* | *Fe* | *3.8* | - |

### 3.3 Thermogravimetric analysis (TGA) of $CaCO_3$ and eggshell

Thermal stability of the both type of fillers (calcium carbonate and eggshell) used for preparation of composites was determined as a function of temperature using TGA.

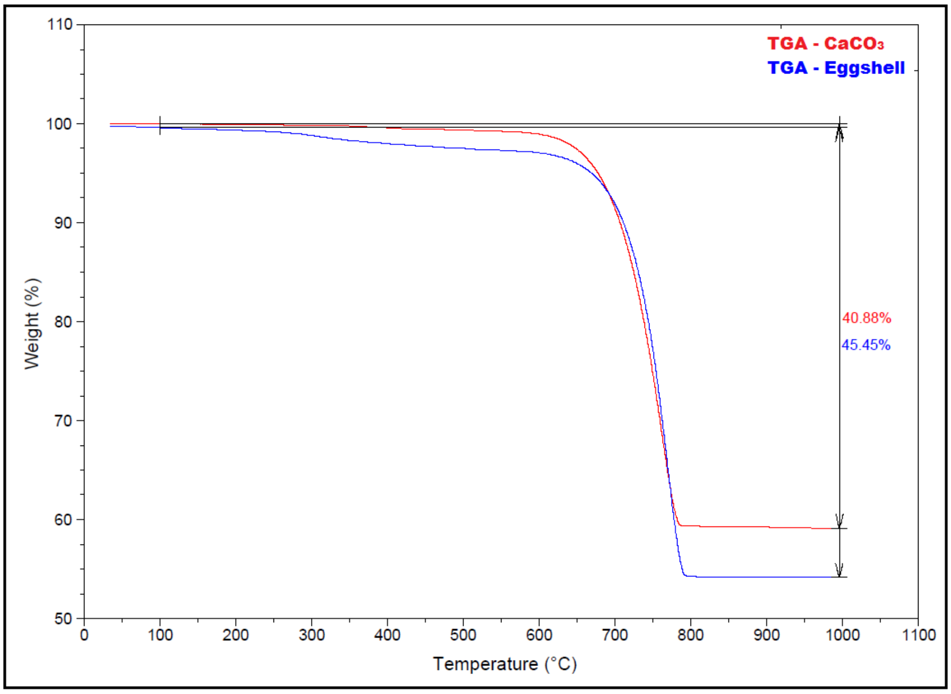


**Figure 10: showing TGA curve of $CaCO_3$ and eggshell**

About 10 mg sample was taken for analysis. Weighing pan of the Instrument was tarred before taking measurements. Instrument was equilibrated at 30 $^0$C before sample was heated up to 1000 $^0$C @ 10 $^0$C. No significant weight loss up to 500 $^0$C was observed for $CaC0_3$ which means that it is thermally stable and can be extruded without effecting its properties up to temperature of 500 $^0$C. Drop in the weight % above 250 $^0$C was observed for eggshell. Significant loss in the weight for both samples was observed above 600 $^0$C. From figure above it was observed that %age loss in weight in eggshell (45%) was more than in calcium carbonate (40%).

## 3.4 Estimation of $CaCO_3$ in Egg-Shell powder

Washed, dried and grinded eggshell powder was used for estimation of calcium carbonate content. Two different techniques/methods were used for determination of calcium carbonate content present in eggshells. Two techniques used were

1. **Microwave ashing**
2. **Titration**

### 3.4.1 Estimation of calcium carbonate in eggshell by Microwave ashing

A clean and dry crucible was taken. The empty crucible weight and sample weight were taken upto four decimal place. To determine the moisture content entrapped inside, sample was placed in already heated microwave ashing unit at 110 $^0$C for 1 hour. After 1 hour, crucible was taken out from oven and placed immediately inside desicator from preventing absorbing moisture. Crucible was allowed to cool for few hours. After cooling, crucible containing sample was weighted. Loss in weight was calculated which will give indication of moisture lost. Crucible containing sample was again placed in heated microwave oven at 550 $^0$C for 1 hour to determine the organic mass in sample. After completion of 1 hr, sample was cooled once again and weight was taken. Accounted loss in weight was reported as loss of organic mass present in sample. To calculate the $Co_2$, same sample was put inside preheated microwave oven at 900 $^0$C for one hour. Loss in weight was recorded after heating and cooling of sample in crucible. This loss in weight will indication about amount of $Co_2$ lost due to ashing of sample at high temperature. Percentage of calcium carbonate was found to be around **95.4%** in eggshell used in the study.

### 3.4.2 Estimation of calcium carbonate in eggshell by Titration

Titration test volumetric analysis is done using a characteristic reaction of carbonate compounds. Though Calcium carbonate is insoluble in pure water, yet it will readily dissolve in acid according to the following reaction.

$$\boldsymbol{HCl(aq) + CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l) + 2Cl^-(aq)}$$

This reaction cannot be used directly to titrate the $CaCO_3$ because it is very slow when the reaction is close to end point, so excess of acid is used to dissolve all of the $CaCO_3$ and then titrating the remaining $H_3O^+$ with NaOH solution to determine the amount of acid which has not reacted with the $CaCO_3$. The difference between amounts of acid (HCl) initially added and the amount left over after the reaction is equal to the amount used by $CaCO_3$. The reaction is used to determine the left over acid.

$$\boldsymbol{HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + Na + Cl^-(aq)}$$

Three samples of eggshell of different weights were taken in a conical flask. The normality of NaOH was determined by titrating it against Potassium hydrogenthalate. The normality of HCl was found by titrating it against NaOH

**Table 4: Showing titration results of ESP-$CaCO_3$ with NaOH and HCL.**

| **Sample** | **1** | **2** | **3** |
|---|---|---|---|
| **Sample Wt.** | 0.5247 | 0.4196 | 0.2284 |
| **Normality of NaOH** | 0.075 | 0.075 | 0.075 |
| **Normality of HCl** | 0.972 | 0.972 | 0.972 |
| **Volume of NaOH** | 1.7 | 24.2 | 73.6 |
| **Mole of NaOH** | 0.1275 | 1.815 | 5.52 |
| **Volume of HCl remains** | 0.13 | 1.87 | 5.68 |
| **Volume of HCl for $CaCO_3$** | 9.87 | 8.13 | 4.32 |
| **No. of mol. HCl used** | 9.87 | 8.13 | 4.32 |
| **No. of mol. $CaCO_3$ dissolved** | 4.93 | 4.07 | 2.16 |
| **Mass of $CaCO_3$ dissolved** | 0.493 | 0.407 | 0.216 |
| **% $CaCO_3$** | 94.0 | 97.0 | 94.6 |

Using titration method average percentage of calcium carbonate was obtained around **95.2%.**

## 3.5. Particle size reduction and determination of particle size

Previous studies have shown that the particle and their surface area of particulate fillers are the relevant factors which affect the mechanical properties when used as filler in the preparation of composite materials. In this study calcium carbonate was used as particulate filler which has a particle size between 6-8 µm. previously it was shown that a smaller grain size of the filler could produce a maximum interface area. When the filler particles are small and homogeneously distributed in the polymer matrix, ultimately gives a more rigid structure **[5].** Therefore, for a better appreciation of results the particle size of normal $CaCO_3$ (6-8 µm) and egg shell powder was reduced to a common particle size distribution between 2-3 µm. Planetary Ball Mill PM-400 (Restsch) figure 11 (b) was used to reduce the particle size, and particle size analyzer figure 11 (a) used for determining the particle size of egg shell and normal $CaCo_3$, grinding process, Firstly about 90 gm of ESP was taken in the ball mill vessel and then about 200 ml of Isopropanol was added to the ball mill for about 40 minutes at a speed of 300 rpm

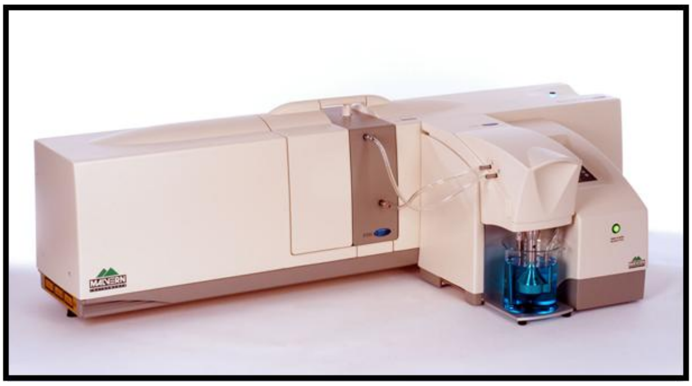


**Figure 11: (a): particle size analyzer**

**Figure 11: (b) Ball mill grinding**

## 3.6 Treatment of the Egg shell powder

The egg shell powder with an average particle size of 2-3 μm was treated with a solution of 10% NaOH. The powder was mixed with the solution and stirred for 30 minutes then kept at room temperature until two layers are formed. The upper layer was decanted and the deproteinised layer of precipitate was washed 10 to 12 times with distilled water. The washed precipitate was dried in the oven at 80°C until a constant weight was observed. The powder was then stirred in a mixture of 6% of isophthalic acid in ethanol for an hour, whereupon the treated powder was dried in the oven at 80°C until the constant weight found **(26).**

## 3.7 Extrusion and injection moulding of polypropylene with fillers

### 3.7.1 Twin screw extruder

Before compounding the fillers (calcium carbonate and eggshell) with polypropylene on twin screw extruder, antioxidants along with acid scavenger were mixed as part of composition. Concentration of the antioxidants was as per the ration of polymer in the composition. Four different formulations of filler (5%, 10%, 20% and 30%) with PP were prepared keeping the dosage of antioxidants and acid scavengers constant. Whole mixture was well shaken before feeding into the twin screw extruder at specified barrel and die temperature conditions. Granules thus produced were kept in an oven for 2 hrs at 80 °C to remove moisture.

**Table 5**: **Different recipe for the compounding of PP with CaCO3, Unmodified-ESP and Modified-ESP at different compositions**

| Composition (%) | PP (gm) | Calcium Carbonate | | | A.O-1 (ppm) | A.O-2 (ppm) | Acid scavenger (ppm) |
|---|---|---|---|---|---|---|---|
| | | Normal (gm) | Unmodified-ESP (gm) | Modified-ESP (gm) | | | |
| 5 | 1140 | 60 | 60 | 60 | 350 | 700 | 400 |
| 10 | 1080 | 120 | 120 | 120 | 350 | 700 | 400 |
| 20 | 960 | 240 | 240 | 240 | 350 | 700 | 400 |
| 30 | 840 | 360 | 360 | 360 | 350 | 700 | 400 |

Twin screw extruder used for extrusion was of M/s. Labtech Engineering company Ltd (Thailand) having counter rotating screws of L/D ratio 44 and screw diameter 26mm. Temperature range of the machine was from 50 to 450 $^0$C. It had four different feeding ports for liquid and solid raw material. Capacity of the machine had a capacity upto 100kg/hr ouput. It had 9 different barrel zones for precise temperature control. The extruder was accompanied with the assembly of water bath and the pelletlizer as shown in fig12 below

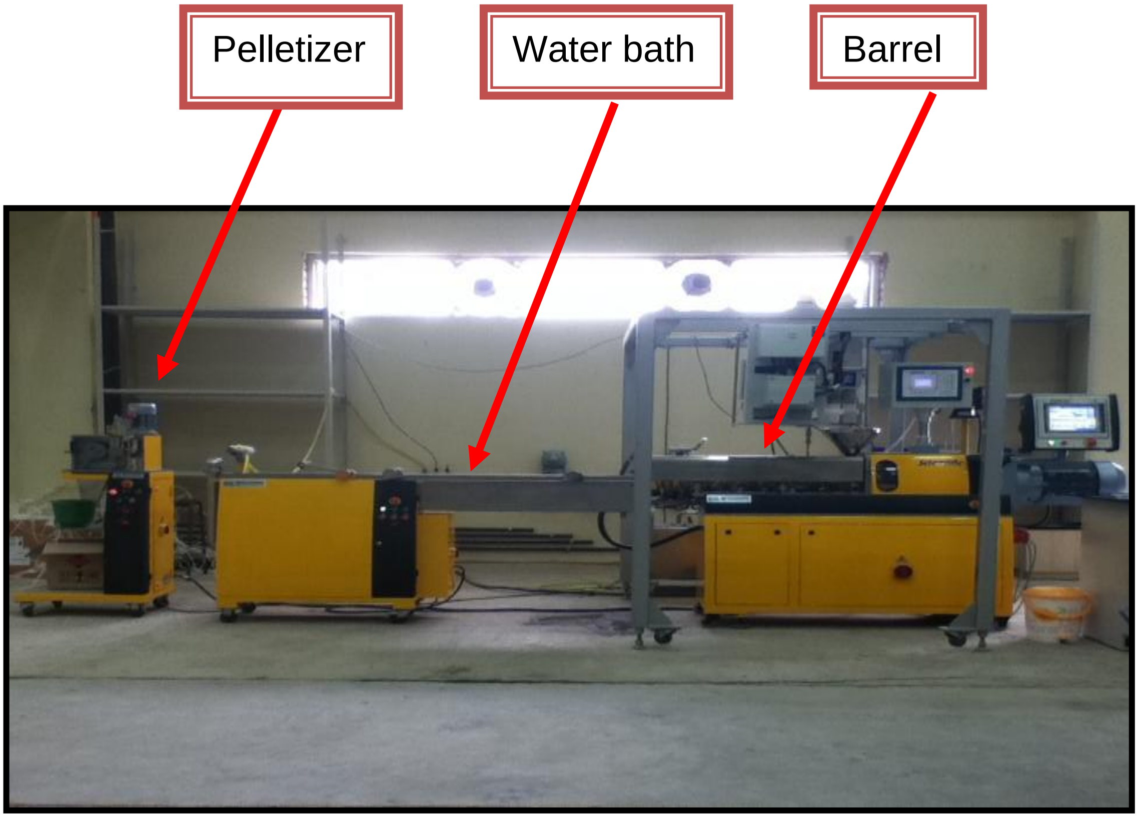


**Figure 12**: **Twin Screw Extruder**

Compounding was done at 230 $^{0}$C. The process conditions for the twin screw extruder are given below in the table 6

**Table 6: Temperature profile of the twin extruder**

| **Zones** | **Z-1** | **Z-2** | **Z-3** | **Z-4** | **Z-5** | **Z-6** | **Z-7** | **Z-8** | **Z-9** | **DIE** |
|---|---|---|---|---|---|---|---|---|---|---|
| **Actual Temperature in the Barrel (°C)** | 120 | 140 | 150 | 170 | 190 | 210 | 220 | 230 | 230 | 230 |
| **Screw rpm** | 200 | | | | | | | | | |

### 3.7.2 Injection Moulding

It is a shape-forming process in which molten plastic is injected into a stainless steel moulds (shaped like the end product) and squeezed under high pressure. Injection moulding is employed mainly in the production of solid objects. Material is fed into a heated barrel, mixed, and forced into a mould cavity where it cools and hardens to the configuration of the mould cavity.

The specimens for the tests (Tensile, Flexural and Impact) were prepared by Injection Moulding on **L&T Aswa 60/320 -310** having L/D ratio 20 and capacity 60 tonne. The processing conditions utilized for the Polypropylene samples are tabulated below in the table 7

**Figure 13: Injection moulding machine used for this work**

**Table 7**: **Processing Condition for Injection moulding of specimens for mechanical testing of PP-Biofiller composites**

| Sample Condition | Polypropylene-Biofiller Composite | | |
|---|---|---|---|
| **Cycle Time (Sec)** | 45 | | |
| **Cooling Time (Sec)** | 20 | | |
| **Injection Pressure (bar)** | 100 | | |
| **Injection Speed (mm/s)** | 35 | | |
| **Holding Time (Sec)** | 15 | | |
| **Holding Pressure (bar)** | 90 | | |
| **Dosing (mm)** | **Tensile** | **Flexural** | **Impact** |
| | 45 | 35 | 35 |
| **Mould temperature (°C)** | 60 | | |

**Table 8 showing temperature profile in Injection molding machine**

| Zones | Feed | Z-1 | Z-2 | Z-3 | Nozzle |
|---|---|---|---|---|---|
| **Set Temperature (°C)** | 94 | 200 | 220 | 230 | 230 |

## 3.8 Equipments used for preparation and characterization of composites

### 3.8.1 MFI (Melt Flow Index)

The Melt Flow Index (MFI) or Melt Flow Rate (MFR) test measures the rate of extrusion of a thermoplastic material through an orifice/die of specified length and diameter under prescribed conditions of temperature, load and piston position in the barrel as the timed measurement is being made.

This test is primarily used as a means of measuring the uniformity of flow rate of material. The reported MFI values help to distinguish between the different grades of polymer. A high molecular weight material is more resistant to flow than a low molecular weight material. The flow rate is an empirically defined parameter critically influenced by the physical properties and molecular structure of the polymer and the condition of measurement.

Melt flow index of the PP-biofiller composites was carried out as per the ASTM 1238 on CEAST Melt Flow Index machine at a 2.16 kg load at 230°C. In the Melt Flow Index machine the granules were preheated at 230°C for 240 seconds without any load.

Then the samples were flowed through a die of 2.09mm diameter and 8mm length under the pressure of two loads at 230°C and the extrudate were cut at a predetermined length (10mm). The extrudate was then weighed and the MFI was calculated.

$$\boldsymbol{MFI = \frac{t_{ref \times m}}{t}}$$

Where,

T = test temperature (°C)

tref = reference time (10 min), (sec)

m = average mass of cut-offs (gm)

t = time-interval for cut-offs (sec)

### 3.8.2 Tensile testing: (ASTM D 638)

Tensile tests measure the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point.

Tensile Test is the measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking.

The ductility of a sample is determined by conducting a tensile strength test on a Universal Testing Machine (UTM). The preferred specimen is prepared either by Injection or Compression Moulding. During the stretching process, the machine measures the load (F), or the force applied to the sample, and the displacement of the sample (s); along with the original cross sectional area of the sample (Ao) and the original length (Lo), an engineering Stress-Strain Curve can be generated.

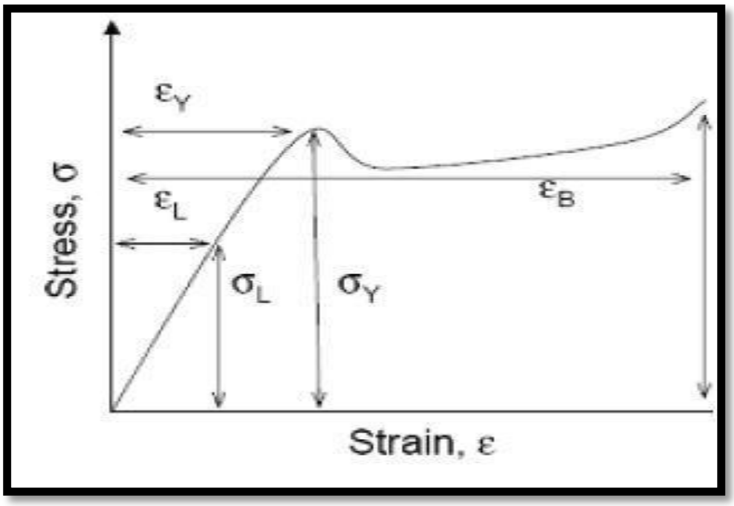
When the graph is analyzed, it is found that the strain hardening of the material increases up to a certain maximum point, after which the strain begins to deform the material, softening it until it breaks. Graphically, it is the highest point on the engineering stress-strain curve. Tensile Test Values:

(i) **Young's Modulus**: This is the slope of the linear portion of the stress-strain curve; it is usually specific to each material - a constant, known value.

(ii) **Yield Strength**: This is the value of stress at the yield point, which is calculated by plotting Young's Modulus at a specified percent of offset (usually offset = 0.2%).

(iii) **Ultimate Tensile Strength**: This is the highest value of stress on the stress-strain curve.

(iv) **Percent Elongation**: This is the change in gauge length divided by the original gauge length.



Where, $\frac{d\sigma}{d\varepsilon} = \frac{\sigma_L}{\varepsilon_L} = E$ (Young's Modulus)

$\sigma_y$= yield stress,

$\varepsilon_y$= elongation at yield,

$\sigma_s$= ultimate tensile strength,

$\varepsilon_l$= elongation at break.

### 3.8.3 Flexural strength test (ASTM D 790)

The flexural strength of a material is defined as its ability to resist bending forces applied perpendicular to its longitudinal axis. The stresses induced by the flexural load are a combination of compressive and tensile stresses. The test beam is under compressive stress at the concave surface and tensile stress at the convex surface.

For materials that deform significantly but do not break, the load at yield, typically measured at 5% deformation/strain of the outer surface, is reported as the flexural strength or flexural yield strength.

The test is done on an UTM, which operates at a constant rate of crosshead motion over the entire range and error in load measuring system should not exceed 1% of the maximum load expected. The strain rate is 0.01in/in/min. The method followed is a three-point loading system utilizing central loading on a simple supported beam. A bar of rectangular cross-section rests on two supports and is loaded by means of a loading nose midway between the supports. This method is useful for Quality Control and specification properties. Flexural test result is a plot of load versus displacement or stress versus strain. From this data, a number of properties can be calculated such as flexural modulus and yield strength. The Flexural Modulus is a measure of the stiffness during the first or initial part of the bending process. It is represented by the slope of the initial straight-line portion of the stress-strain curve and is calculated by dividing the change in stress by the corresponding change in strain.

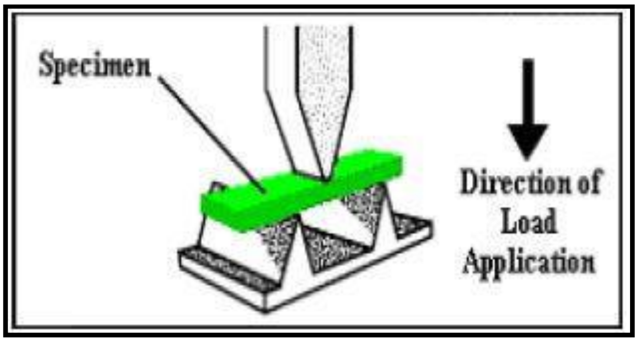


**Figure 14: Three Point Loading System for Flexural Testing**

**Figure 15**: **UTM Testing machine used for determine the tensile or flexural strength**

### 3.8.4 Izod impact strength (ASTM D 256)

Izod impact strength testing is an ASTM standard method of determining impact strength. A notched sample is generally used to determine impact strength. Izod Impact testing of plastics is ASTM D256. The results are expressed in energy lost per unit of thickness (such as ft-lb/in or J/cm) at the notch. The dimensions of a standard specimen for ASTM D256 are 63.5 x 12 x 2.5 mm. The most common specimen thickness is 2.5 mm, but the width can vary between 3.0 and 12 mm.

Impact tests are used in studying the toughness of material. A material's toughness is a factor of its ability to absorb energy during plastic deformation. Brittle materials have low toughness as a result of the small amount of plastic deformation that they can endure. The impact value of a material can also change with temperature. Generally, at lower temperatures, the impact strength of a material is decreased. The size of the specimen may also affect the value of the Izod impact test because it may allow a different number of imperfections in the material, which can act as stress risers and lower the impact strength.

**Figure 16**: **impact testing machine**

Izod impact test of notched specimen was measured on CEAST impact tester. A notch of 2.54 mm depth with $45^0$ was made on the impact specimen prior testing. The specimen dimensions were 4×10 mm. The impact strength was expressed in terms of J/m

### 3.8.5: Differential Scanning Calorimetric

Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the heat flow rate difference into the sample and a reference is measured as a function of temperature, while the sample is subjected to a controlled temperature program **[27].** The reference is an inert material such as alumina, or just an empty aluminium pan. The temperature of both the sample and reference are increased at a constant rate. The basic principle involved is that when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature.

Whether more or less heat must flow to the sample, it depends on whether the process is exothermic or endothermic.

Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes:

$$\left(\frac{d_q}{dt}\right) = \frac{dH}{dt}$$

In an endothermic process, mostly in the cases of phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence $\Delta \frac{dH}{dT}$ is positive. In an exothermic process, such as crystallization and oxidation reactions, and in some cases of cross-linking processes and decomposition reactions, the opposite is true and $\Delta \frac{dH}{dT}$ is negative.A flow of the Nitrogen gas is maintained on the samples to create a reproducible and dry atmosphere. The Nitrogen atmosphere also eliminates air oxidation of the samples at high temperatures. The samples are sealed into a small aluminium pan. The reference is usually an empty aluminium pan.

**Degree of crystallinity:**

Degree of crystallinity is the content of the crystalline phase in the polymer that melts in the temperature range evaluated. If the enthalpy of the fusion of a fully crystalline polymer is known the degree of crystallinity of an unknown polymer sample can be determined as follows

$$\%\text{Crystallinity} = \frac{\Delta H_s}{\Delta H_r} \times 100$$

Where Hs is the heat of fusion of the sample and Hr is the heat of fusion of the 100% cryatalline polymer, heat of fusion for 100% crystalline isotactic polypropylene is 209 J/gm

Studies were carried out on the Mettler Toledo 821E to get the heat flow pattern of the sample. The equipment was calibrated with Indium sample whose melting point is 156.6 deg C. About 10 mg of the sample was taken in the aluminium pan (40µl) and kept at 25˚C for 1 minute and then heated in an inert atmosphere from 25 ˚C to 210 ˚C at 20˚C /min. The whole process was carried out under the environment of Nitrogen gas in order to prevent any chance of thermal degradation. The samples are heated beyond the melting point @ 10°C/min and kept at that temperature for 5 minutes to remove its thermal history and then cooled down to the room temperature and kept at that temperature for 2 minutes. The cooled sample was again heated (second heating) @ 10°C/min to study the effect of crystallization and finally get the melting point (Tm) and Enthalpy of heating (ΔH j/g).

### 3.8.6 X-ray diffraction (XRD)

X-ray diffraction1 has played a central role in identifying and characterizing solids since the early part of this century. The nature of bonding and the working criteria for distinguishing between short-range and long-range order of crystalline arrangements from the amorphous substances are largely derived from X-ray diffraction and thus it remains as a useful tool to obtain structural information. X-ray diffraction pattern of amorphous polymer will not show any sharp and highly intensed peaks whereas crystalline polymer shows the sharp peaks.

The physical structure of the samples were evaluated by X-ray diffraction (XRD) using a Bruker AXS D8 Advance diffractometer with a scanning rate of 5 ◦C per min with Cu K_ radiation source (λ= 1.54060 A˚) operating at 40 kV and 30 mA. The patterns were obtained over the angular range 5–70◦.

### 3.8.7 IR Spectroscopy

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis. One of the important advantages of infrared spectroscopy over the other usual methods of structural analysis (X-ray diffraction, electron spin resonance, etc.) is that it provides information about the structure of a molecule quickly, without tiresome evaluation methods. This method can solve many problems in organic chemistry (polymeric materials) and coordination chemistry, and also advantageously complements the results obtained by other methods This method can solve many problems in organic chemistry (polymeric materials) and coordination chemistry, and also advantageously complements the results obtained by other methods. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region giving rise to close-packed absorption bands called an IR absorption spectrum, over a wide wavelength range. Various bands will be present in the IR spectrum, which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus an IR spectrum of a chemical substance is a fingerprint for its identification. IR spectrum of polymer composite shows the presence of (depending upon the polymer chain) at various frequencies.

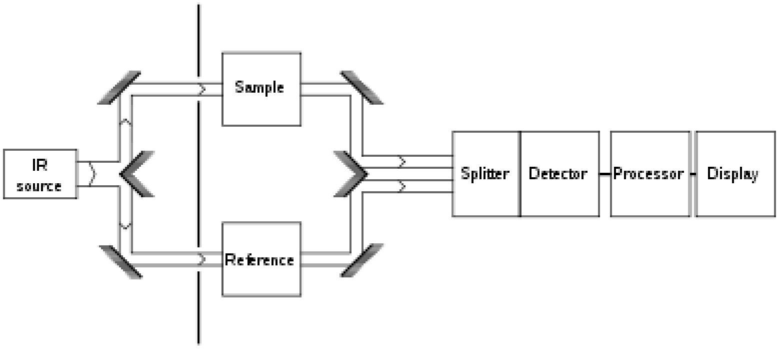


**Figure 17: Diagram for the Principle of IR Spectroscopy**

### 3.8.8 Scanning Electron Microscopy

SEM analysis of polypropylene bio filler composite and the fracture surfaces of bio filler composites were carried out using a HITACHI (S-3700N) scanning electron microscope. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signal at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2- dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semiquantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD)

.**Principle:**

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

**Instrumentation:**

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
- Power Supply
- Vacuum System
- Cooling system
- Vibration-free floor
- Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

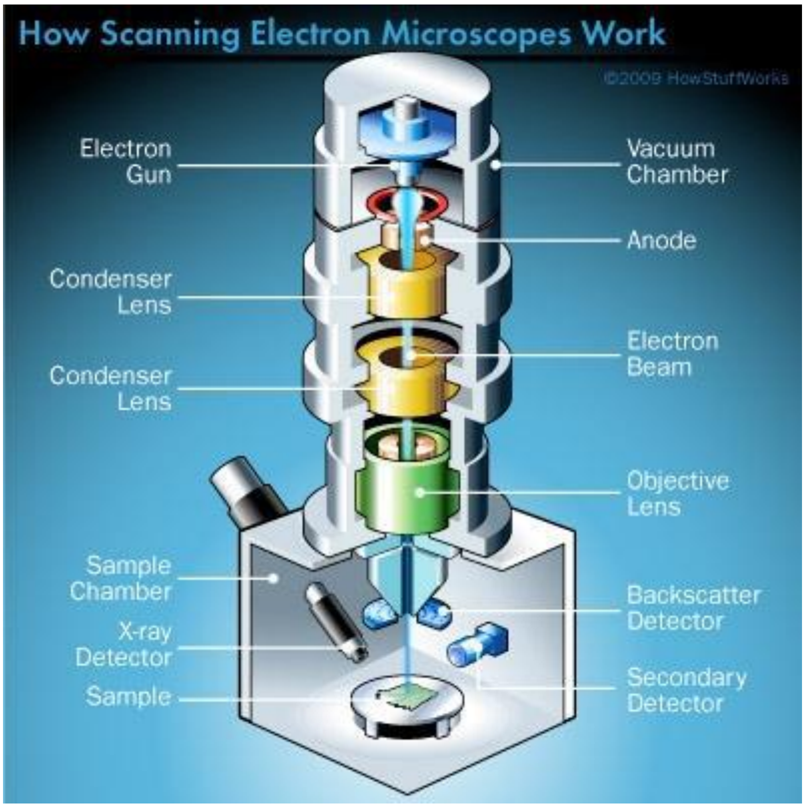


**Figure 18**: **Schematic diagram of the working of a scanning electron microscope**

# CHAPTER-4

# RESULTS AND DISCUSSION

## 4.1 Analytical measurement

### 4.1.1. IR spectroscopy

IR spectroscopy which is an common technique used for determination of the functional groups of organic and inorganic compounds was used primarily to find out the changes occurred in eggshell after its chemical treatment. Powder samples of the isophthalic acid, calcium carbonate, unmodified and modified eggshell were used for IR analysis. Figure – shows the IR spectra of the samples. Peak at 1434, 1432 and 1442 corresponds to carbonate group as observed in the samples. Peak at 1689.46 and 1280.61 in modified eggshell indicates the change occurred due to the treatment of eggshells with isophthalic acid since similar peaks were observed in isophthalic acid.

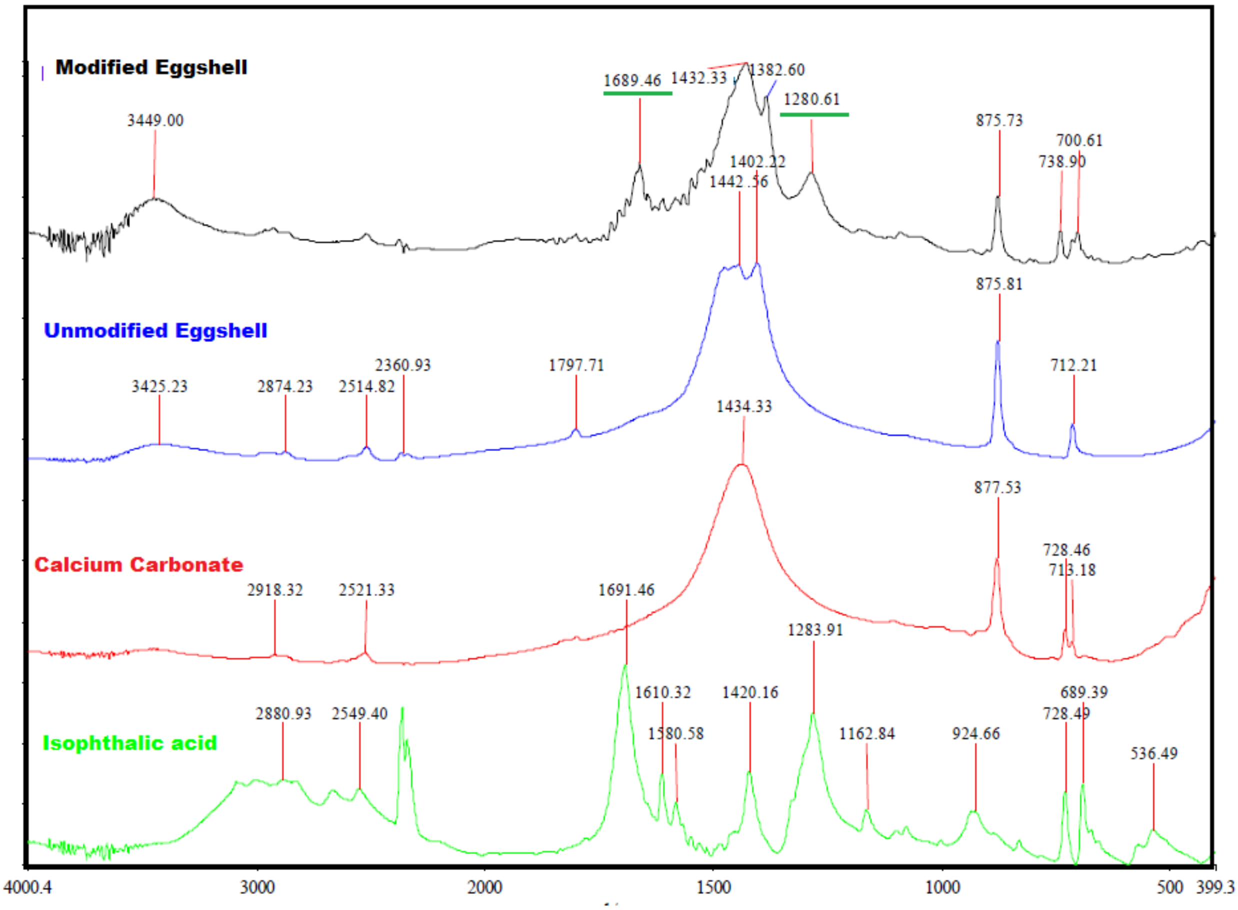


**Figure 19: Showing IR spectra of Isophtalic acid, calcium carbonate, unmodified and modified eggshell**

### 4.1.2 XRD

Powder samples were taken for the analysis. Majority of the peaks observed in calcium carbonate had match with unmodified and modified eggshell. XRD spectra's show the presence of dolomite and calcite in the calcium carbonate whereas only calcite peaks were observed in eggshell samples. Presence of acid peaks in the modified eggshell is due to the treatment of eggshell with the isophthalic acid which was not observed in unmodified eggshell sample. Acid peaks confirm that surface of the eggshell has been modified and new identity was present due to the chemical reaction which would have been taken place while treating eggshell with isophthalic acid.

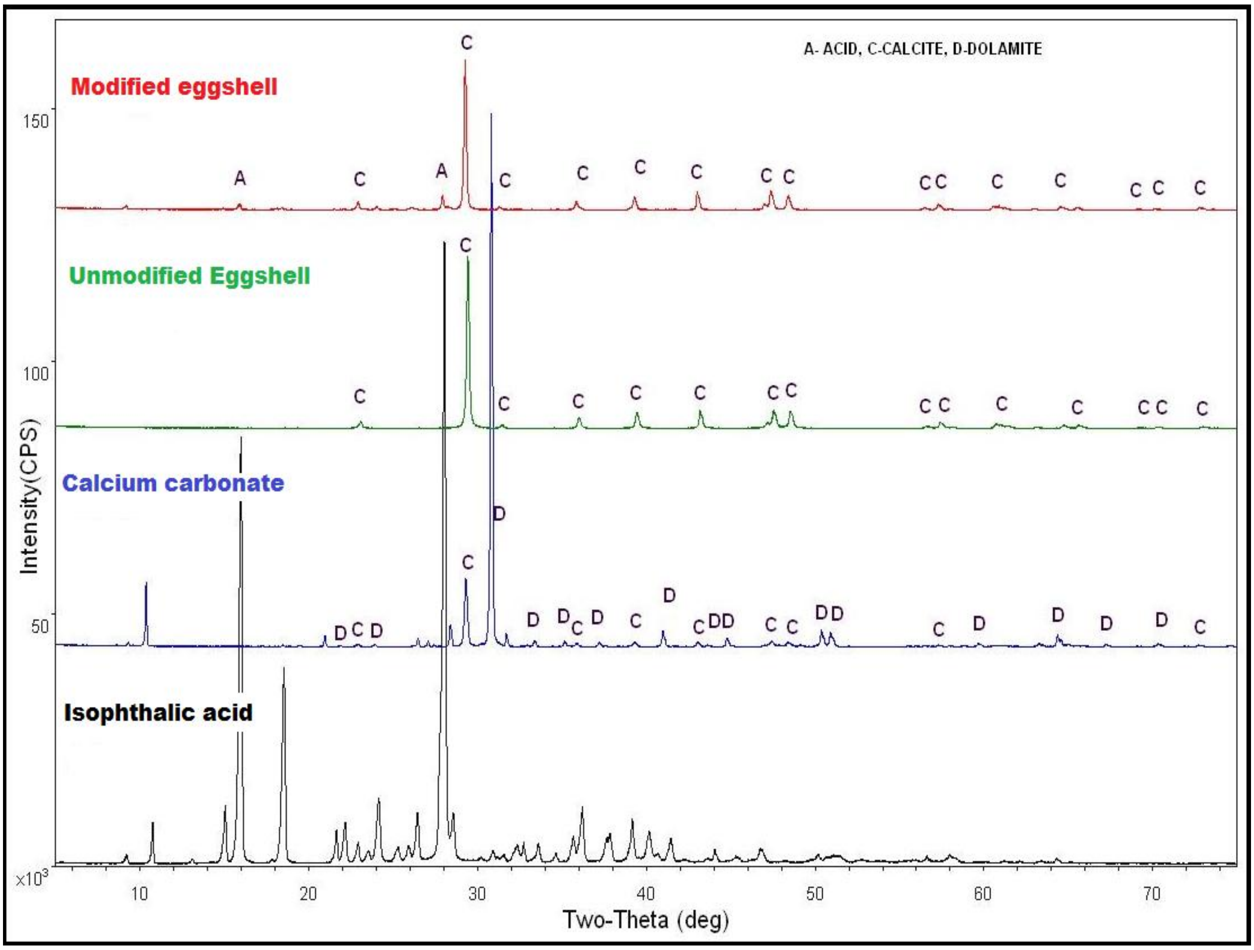


**Figure 20: showing XRD spectra of Isophtalic acid, calcium carbonate, unmodified and modified eggshell**

## 4.2 Mechanical Properties

### 4.2.1 Tensile strength

Figure 21 shows the tensile strength of PP composites as a function of filler content. It can be seen that compared to pure PP, the tensile strength has been found to decrease in case of all three PP composites i.e. PP-CaCO3, PP-UMES and PP-MES. Tensile strength of PP-CaCO3 though decreased with filler loading but still remained on higher side as compared to PP-UMES composites. This can be due to better adhesion and disperability of calcium carbonate with polymer matrix as compared to UMES with PP. Lower tensile strength of PP-UMES composite can also be due to agglomeration of UMES particles in PP matrix. Results show that, tensile strength of PP-MES composite was higher than PP-UMES composite. Higher tensile strength of the PP-MES composite means better interfacial bonding between eggshell and PP due to chemical treatment with Isophthalic acid. Strong adhesion between MES and PP resulted into composite having higher stiffness and rigidity due to which its tensile strength was increased. Strong adhesion between filler and matrix interface can cause better stress transfer from the matrix to the filler leads to a higher tensile strength.

**Table.9: Tensile strength of three different PP-composites based on normal *CaCO3*, Unmodified ESP and Modified ESP**.

| **Composition (%)** | **PP (Mpa)** | **PP+CaCO$_3$ (Mpa)** | **PP+UMES (Mpa)** | **PP+MES (Mpa)** |
|---|---|---|---|---|
| 0 | 35.4 | 0 | 0 | 0 |
| 5 | 0 | 33.0 | 31.4 | 32.1 |
| 10 | 0 | 31.7 | 30.8 | 31.4 |
| 20 | 0 | 30.0 | 29.7 | 31.3 |
| 30 | 0 | 29.8 | 28.0 | 30.1 |

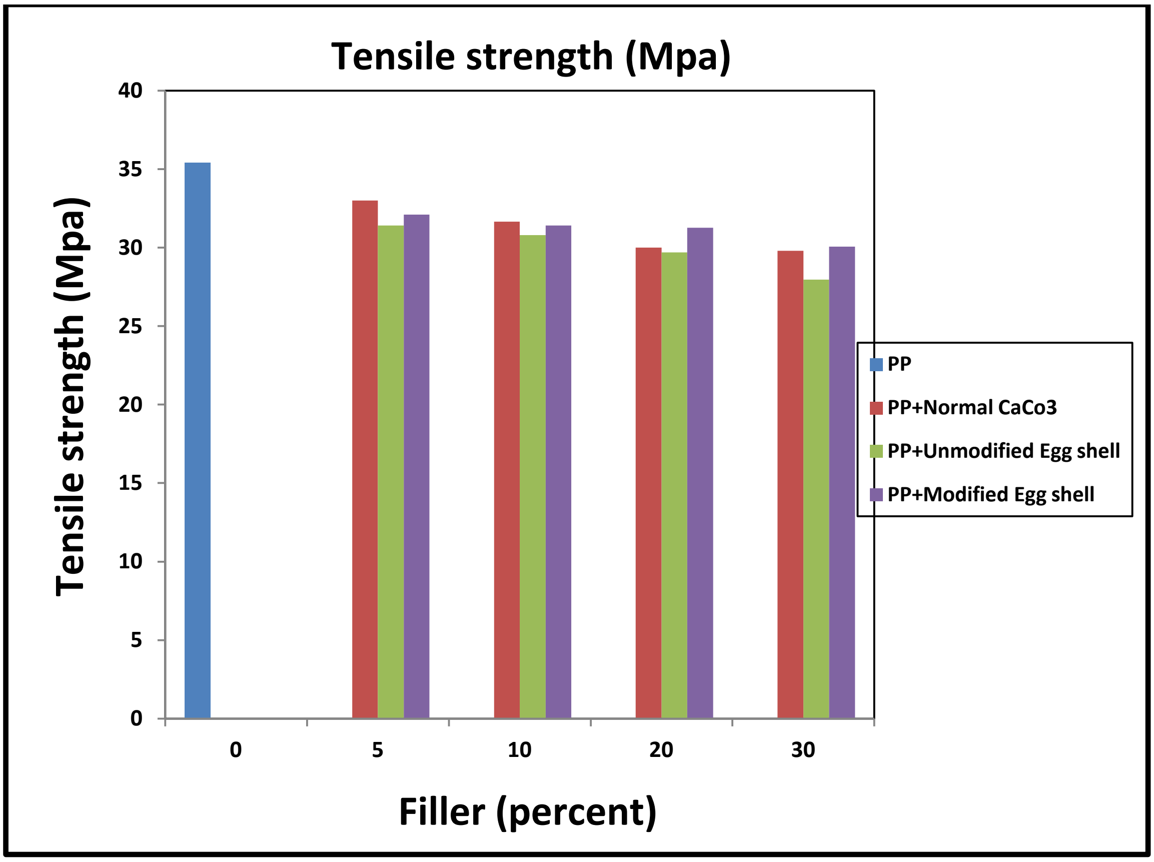


**Figure 21: Showing effect of filler loading on the tensile strength of CaCO3-filled PP composites, Unmodified ESP-filled PP composites and Modified ESP-filled PP composites**.

Isophthalic acid which was used for chemical treatment of eggshell has hydrophilic and hydrophobic side. Hydrophilic side of Isopthalic acid is compatible with the filler whereas its hydrophobic side is compatible with the polymer. Hydrophilic side reacted with the surface of the inorganic filler to form bonds which ultimately makes polymer more stiff resulting into higher tensile strength. There would be simply adhesion of the polymer to the filler through weak bonding, i.e., van der Waals or induction interactions if such type of chemical modifications in not employed while using biofillers like eggshell.

### 4.2.2 Tensile Modulus

The tensile modulus can be calculated from the slope of linear region for stress – strain curve using tensile test. Presence of the fillers reduces the ductility of the composites and increases their stiffness. It was found that the compared to pure PP, the tensile modulus of all the three composites i.e. PP-CaCO3, PP-UMES and PP-MES has increased considerably. Further in all the three types of composites, tensile modulus has been found to increase with increase in the filler loading. However, the increase in tensile modulus is less significant in case of PP-UMES compared to both PP-CaCO3 and PP-MES composites. Maximum increase has been observed in case of PP-MES, particularly at filler loading of 20% and 30%.

Modulus of PP-$CaCO_3$ composites was higher than PP-UMEG composites. Due to chemical treatment, filler bonding with the polymer matrix increases which actually restrain the mobility of the chains, thereby increasing the modulus. This was found to be true for PP-MES composites whose modulus was found to be higher than PP-UMES composites. Higher modulus means that composite will be able to withstand higher load.

**Table 10: showing effect of filler loading on the tensile modulus of $CaCo_3$, UMES and MES filled PP composites**

| Composition (%) | PP (Mpa) | PP+$CaCO_3$ (Mpa) | PP+UMES (Mpa) | PP+MES (Mpa) |
|---|---|---|---|---|
| 0 | 427 | 0 | 0 | 0 |
| 5 | 0 | 435 | 430 | 431 |
| 10 | 0 | 453.7 | 435.5 | 450.4 |
| 20 | 0 | 468.3 | 445.2 | 526.8 |
| 30 | 0 | 531.6 | 507.2 | 557.2 |

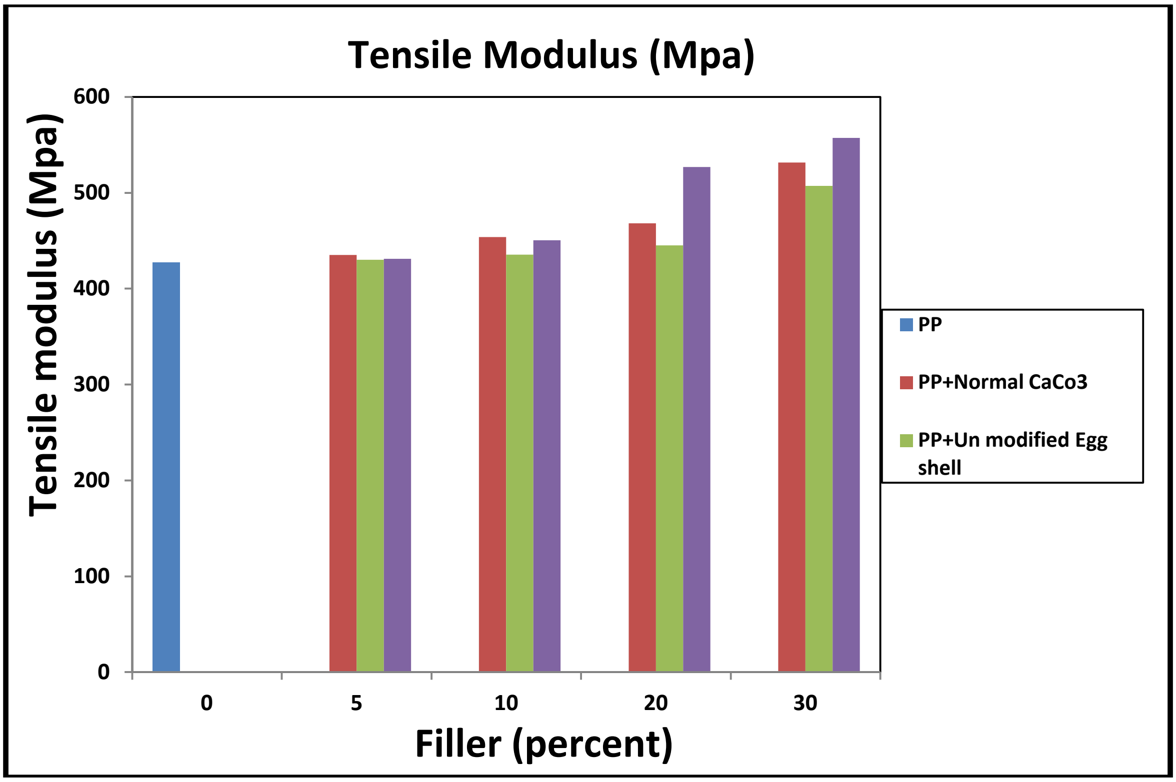


**Figure 22: showing effect of filler loading on the tensile modulus of $CaCo_3$, UMES and MES filled PP composites.**

### 4.2.3 Tensile Elongation at break

Table 11 and figure 23 shows the effect of filler loading on percentage elongation of the composites. It was observed that compared to pure PP, the percentage elongation at break has been found to decrease in all the three types of composites. It can be seen that elongation decreased with increase in filler loading. Increase in filler loading resulted into higher stiffness and hardening of composite. This reduces composite resilience and toughness, and ultimately led to lower elongation. Lower elongation with increase in filler loading means incapability of the filer to support the stress transfer from polymer system to matrix. Percent elongation of PP-UMES composite was found to be higher than PP-$CaCO_3$ composites. Since there was poor interfacial interaction of UMES with PP, composite thus formed were having lower stiffness and hardness as compared to $CaCo_3$ composites. However in case of PP-MES composite, percentage elongation was found to be lower than PP-UMES and PP-CaCO3 composites indicating much better adhesion of eggshell after chemical treatment with polymer. This has increased its matrix rigidity and decreased the elongation.

**Table 11: Showing effect of filler loading on the elongation of $CaCO_3$, UMES and MES filled PP composites**

| Composition (%) | PP (%) | PP+$CaCO_3$ (%) | PP+UMES (%) | PP+MES (%) |
|---|---|---|---|---|
| 0 | 20.3 | 0 | 0 | 0 |
| 5 | 0 | 17.7 | 20 | 18.6 |
| 10 | 0 | 16.2 | 19 | 16.6 |
| 20 | 0 | 13.7 | 14.3 | 12.1 |
| 30 | 0 | 11 | 10.3 | 9.8 |

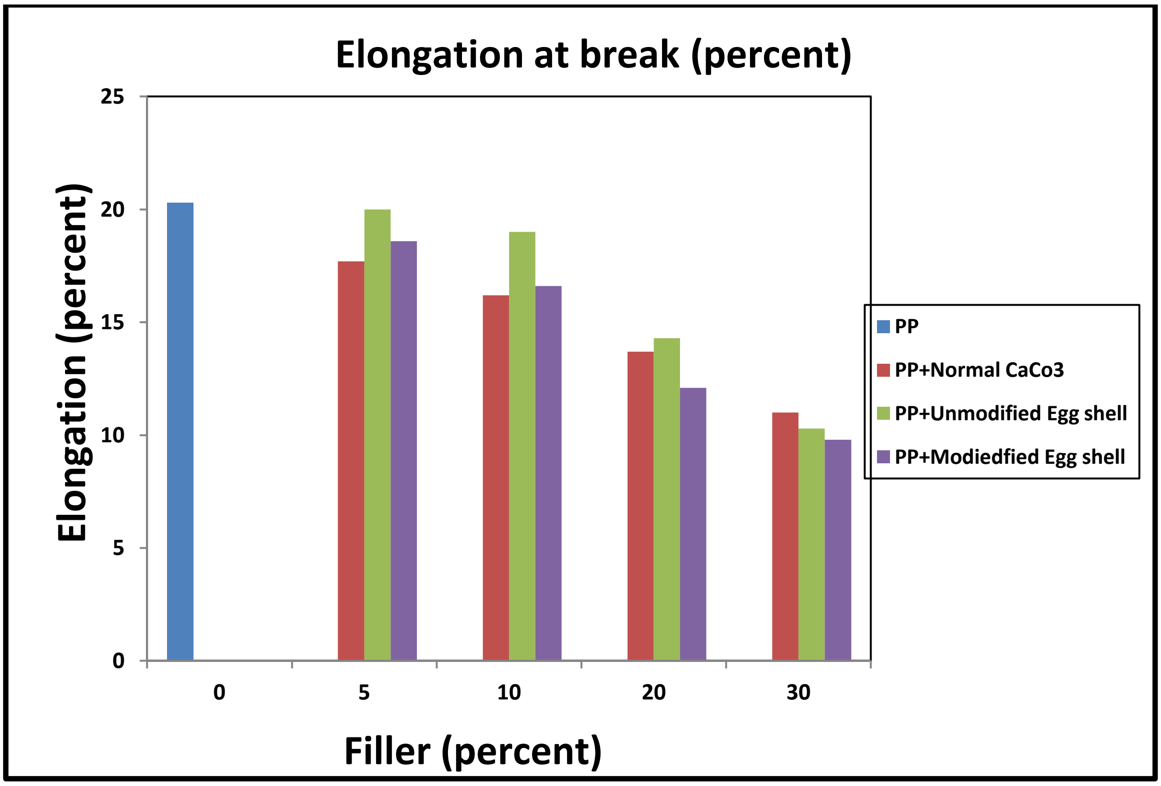


**Figure 23: Showing effect of filler loading on elongation of $CaCo_3$, UMES and MES filled PP composites**

### 4.2.4 Izod Impact Strength

Table 12 and figure 24 shows that impact strength increased in all types of composites with increase in filler loading though the increase is more significant in case of PP-CaCO3 and PP-MES composites. It was found that Impact strength of PP-CaCO3 composite was higher than PP-UMES composite which means $CaCO_3$ had better adhesion with PP as discussed earlier. From the results it can be said that MES composites exhibit synergistic improvement in impact strength as compared to UMES composites, synergy can be explained by the fine dispersion and better interfacial bonding of chemically treated eggshell with PP after chemical treatment. Around 46% higher impact strength was achieved in MES composites at 30% loading as compared to UMES composites.

**Table 12: Effect of filler loading on the Izod impact strength of $CaCO_3$, UMES and MES filled PP composites**

| Composition (%) | PP (Mpa) | PP+$CaCO_3$ (Mpa) | PP+UMES (Mpa) | PP+MES (Mpa) |
|---|---|---|---|---|
| 0 | 21.5 | 0 | 0 | 0 |
| 5 | 0 | 23.4 | 21.6 | 22.5 |
| 10 | 0 | 24.1 | 21.5 | 23.8 |
| 20 | 0 | 28.0 | 21.0 | 27.3 |
| 30 | 0 | 33.5 | 22.3 | 32.6 |

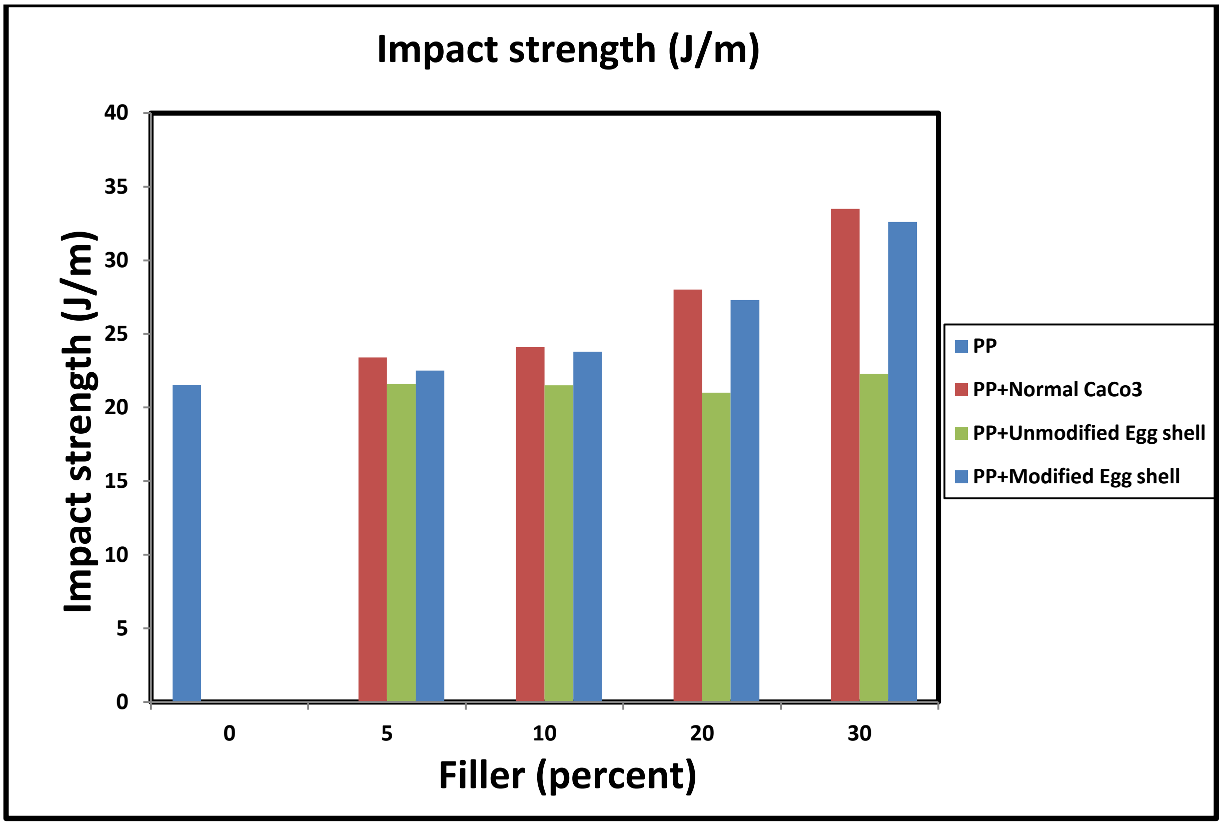


**Figure 24: Showing effect of filler loading on the Izod impact strength of $CaCO_3$, UMES and MES filled PP composites**

### 4.2.5 Flexural modulus

Table 13 and figure 25 show the effect of filler type and loading on flexural modulus of composites. Flexural modulus indicates the resistance of the material towards bending and should increase with the addition of filler in polymer matrix. It was observed that compared to pure PP, the flexural modulus was found to increase in all the three types of composites i.e. PP-CaCO3, PP-UMES and PP-MES. Further, the flexural modulus has been found to increase with increase with filler loading. Flexural modulus increased with addition of filler. Flexural modulus of unmodified eggshell composite was found to be lower than modified eggshell PP composites. On application of load, MES composite showed better resistance than UMES composite due to better bonding of polymer with filler which has ultimately increased its stiffness. This increase in stiffness of MES composites led to higher flexural modulus than UMES composites. Approximately 10% higher flexural modulus was achieved in MES composites as compared to UMES composites at 30% filler loading.

**Table 13: Flexural modulus values of $CaCO_3$, UMES and MES filled PP composites**

| Composition (%) | PP (Mpa) | PP+$CaCO_3$ (Mpa) | PP+UMES (Mpa) | PP+MES (Mpa) |
|---|---|---|---|---|
| 0 | 1300 | 0 | 0 | 0 |
| 5 | 0 | 1357.4 | 1320.4 | 1340.6 |
| 10 | 0 | 1467.6 | 1355.1 | 1426.3 |
| 20 | 0 | 1784.9 | 1426.7 | 1801.0 |
| 30 | 0 | 1924.0 | 1816.4 | 2016.0 |

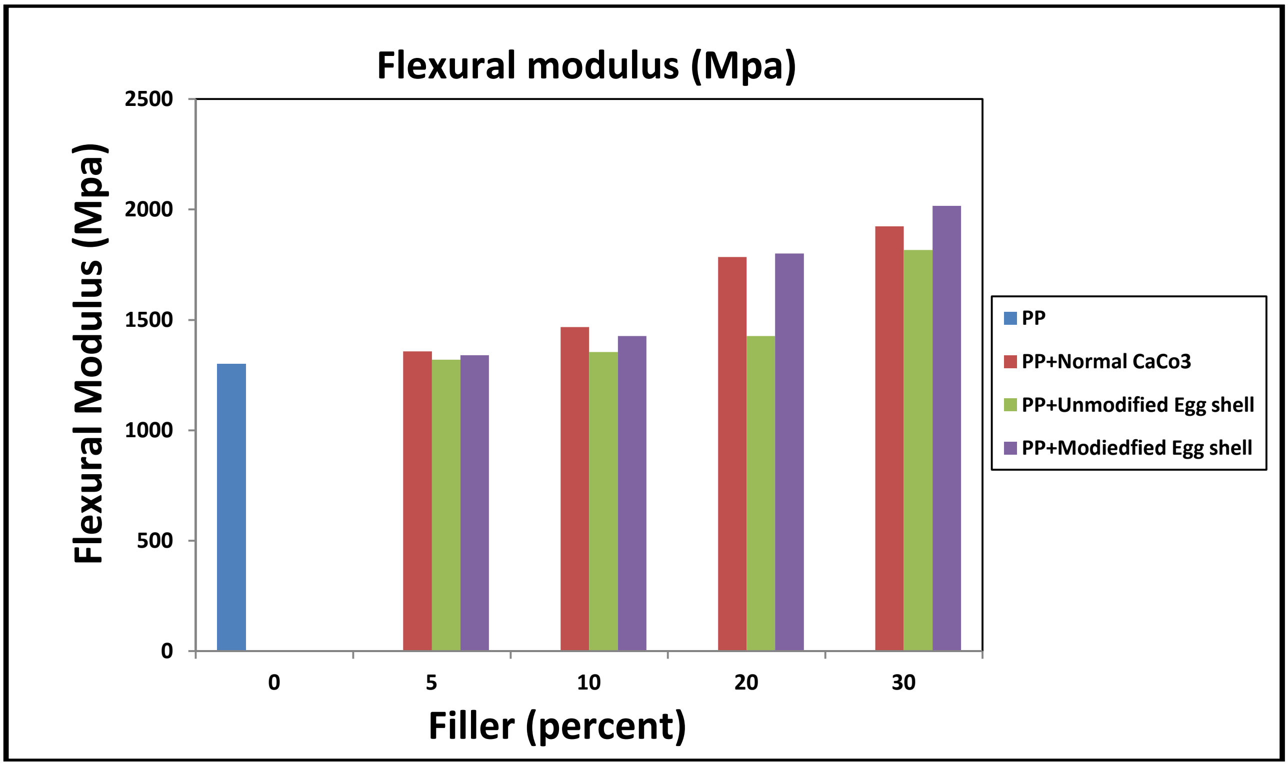


**Figure 25: Showing effect of filler loading on the flexural modulus of $CaCO_3$, UMES and MES filled PP composites**

# 4.3 Thermal characterization

## 4.3.1 Differential Scanning Calorimetry (DSC)

To find out the effect of bio filler on the melting characteristics of the composite, thermal characterization of the biofiller PP composite was done on DSC. The polymer was heated above its melting temperature to remove the thermal history. Cooling and 2nd heating was done at 10 $^0$C.

**Table 14: Showing the melting temperature, heat of fusion and crystallinity of the unmodified and modified eggshell PP composites**

| Sample Name | Melting Temperature (˚C) | Heat of Fusion, ΔH (J/gm) | Percent Crystallinity (%) |
|---|---|---|---|
| PP (Neat) | 164.2 | 88.5 | 42.7 |
| 5%PP+Unmodified-ESP | 162.8 | 87.6 | 42.3 |
| 10%PP+Unmodified-ESP | 162.5 | 82.9 | 40.0 |
| 20%PP+Unmodified-ESP | 163.1 | 72.8 | 35.2 |
| 30%PP+Unmodified-ESP | 163.3 | 63.3 | 30.5 |
| 5%PP+Modified-ESP | 163.8 | 86.1 | 41.5 |
| 10%PP+Modified-ESP | 163.5 | 84.5 | 40.8 |
| 20%PP+Modified-ESP | 164.0 | 72.7 | 35.1 |
| 30%PP+Modified-ESP | 164.1 | 63.9 | 30.8 |

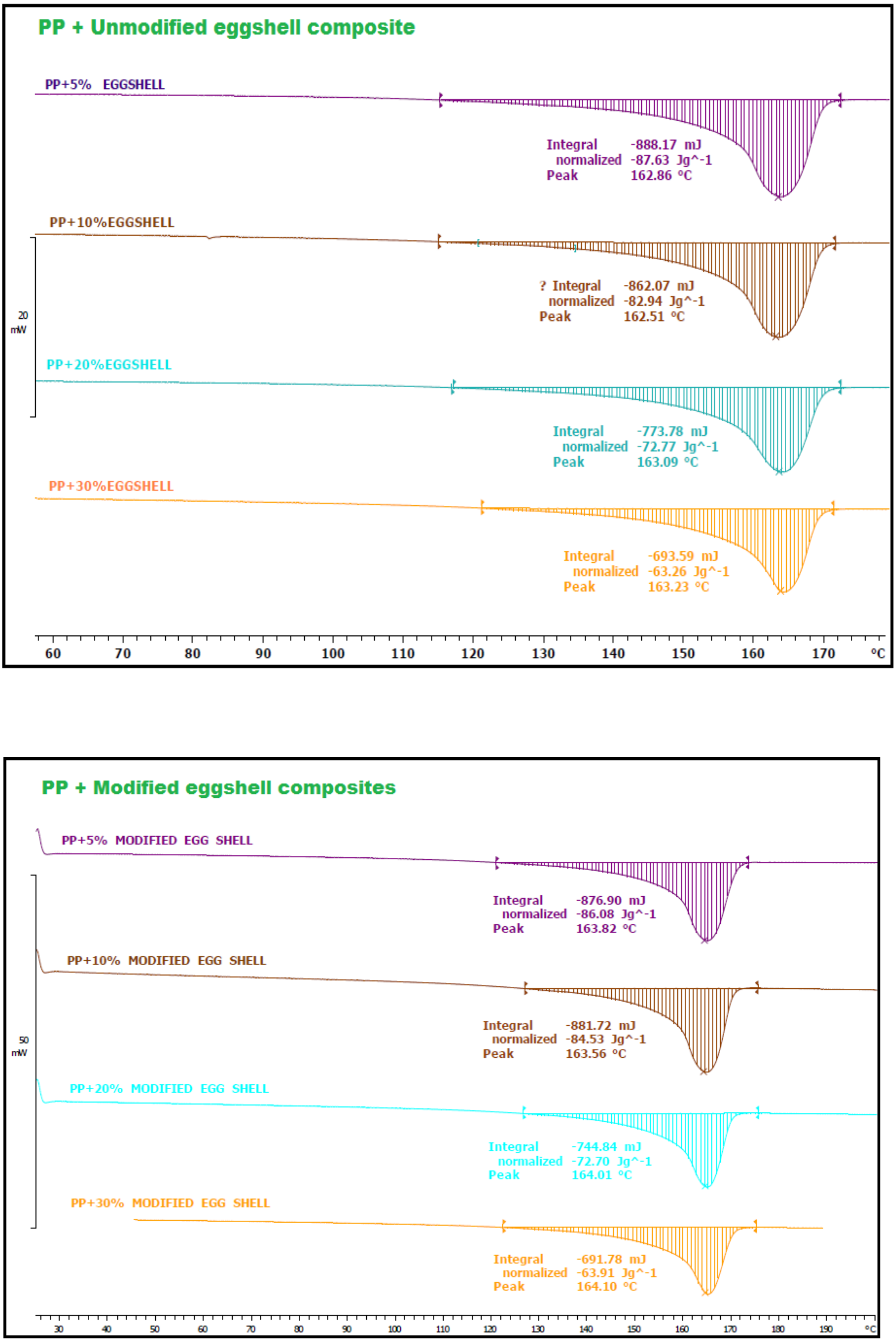


**Figure 26: DSC thermo gram of modified-ESP biofiller composites at 5%, 10%, and 20% and30%.**

From the table 14 it can be seen that with the addition of the filler the crystallinity of the composites decreased. With the increase in the filler loading the amount of the polypropylene in the composite decreases which means percentage of the polymer which is responsible for heat of fusion decreases thus overall decreasing overall crystallinity of the composite. No effect on the melting temperature was observed in all the composites. No significant difference in the crystallinity of the unmodified and modified polypropylene composites was observed. Decreasing trend in the crystallinity with the filler loading was almost similar in both types of unmodified and modified composites.

## 4.4 Morphology characterization

### 4.4.1 Scanning Electron Microscopy (SEM)

Figure below shows the tensile fracture micrographs of composite containing 5% and 30% filler. Figure 27(b) shows the composite containing 5% UMES which has a rough surface with agglomerated eggshell particles. Agglomerated eggshell particles indicate the poor dispersion of filler in the polymer matrix than composite containing CaCo3 and MES which ultimately resulted into poor mechanical properties.

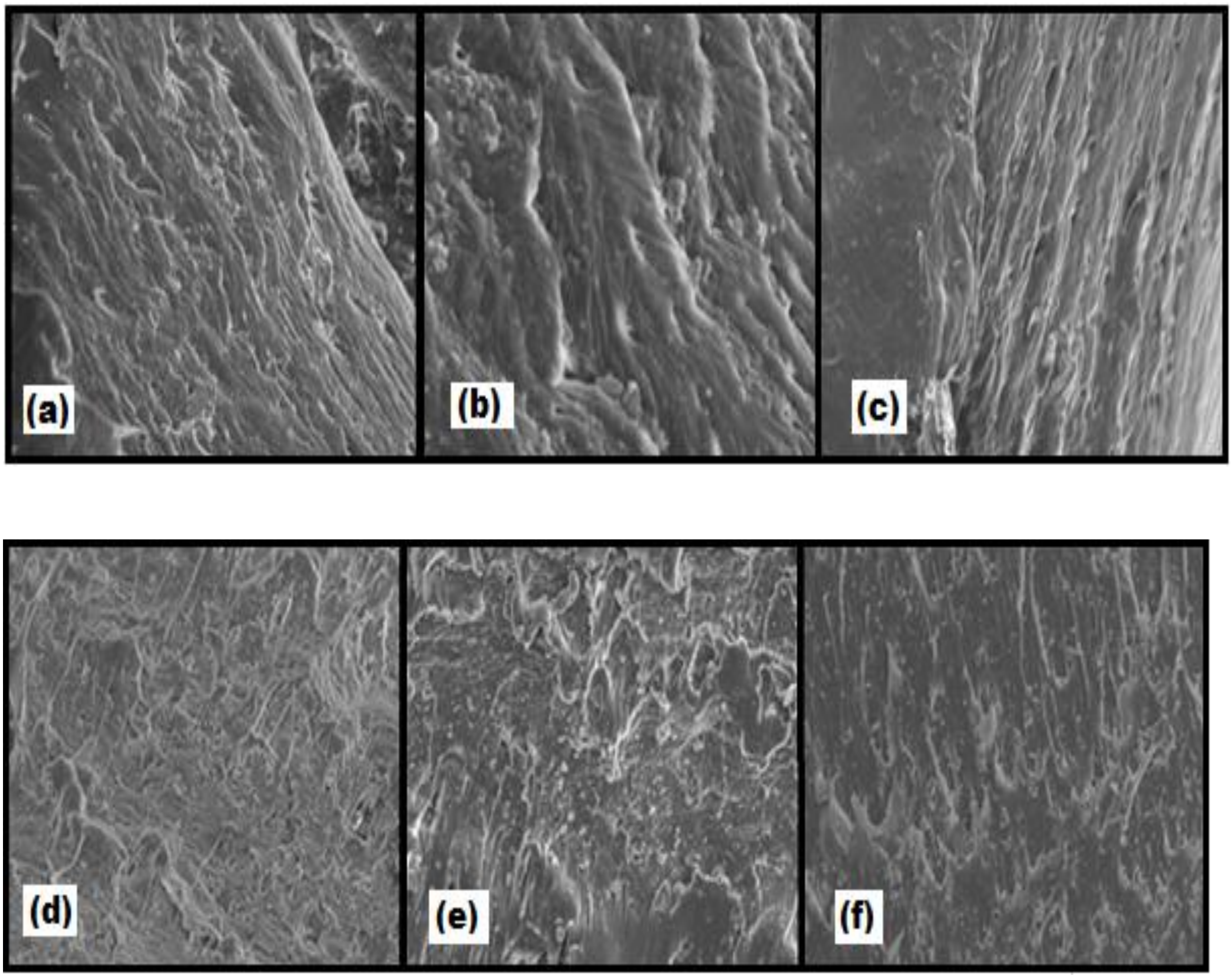


**Figure 27 showing micrographs of composite containing 5% filler (a) CaCo3; (b) UMES; (c) MES; composite containing 30% filler (d) CaCo3; (e) UMES; (f) MES**

Figure 27(e) indicate the fracture surface of composite containing 30% UMES. Many voids and plastic deformation was observed. These voids are due to the detachment of filler from the matrix surface. From figure 27(f), it was observed that surface of composite containing 30% MES was lesser deformed than the UMES and $CaCO_3$ composite. Lower voids and plastic deformation confirms the better disperse ability and adhesion of MES with polymer matrix due to which the mechanical properties of modified eggshell were better than UMES and $CaCO_3$ composites.

Non homogeneous dispersion and poor adhesion of UMES with polymer matrix resulted in the formation of microfiller (agglomeration). Due to the chemical treatment of eggshell with isophthalic acid the bonding of eggshell with polymer matrix increased therefore less pull out of filler from matrix was observed as compared to the UMES and $CaCO_3$ composite.

# CHAPTER-5

# SUMMARY AND CONCLUSION

The addition of filler resulted in improvement of the some mechanical properties of composites. Properties like tensile modulus, flexural modulus and impact strength increased with the filler loading while the tensile strength in all the types of the composites decreased. Composites prepared from chemically treatment eggshell showed better mechanical properties as compared to unmodified eggshell composites. Increase of about 3-18% in tensile modulus, 4%-44% in impact strength and 1.5%-26% in flexural modulus at different filler loading was observed in modified eggshell composite as compared to unmodified eggshell composites. Tensile and flexural modulus MES composites were observed higher as compared to conventionally used $CaCO_3$ by 5%. Better mechanical properties and economical aspect of eggshell can be exploited for its use in the industry as a better replacement of $CaCO_3$ at particular loading.

# APPENDIX

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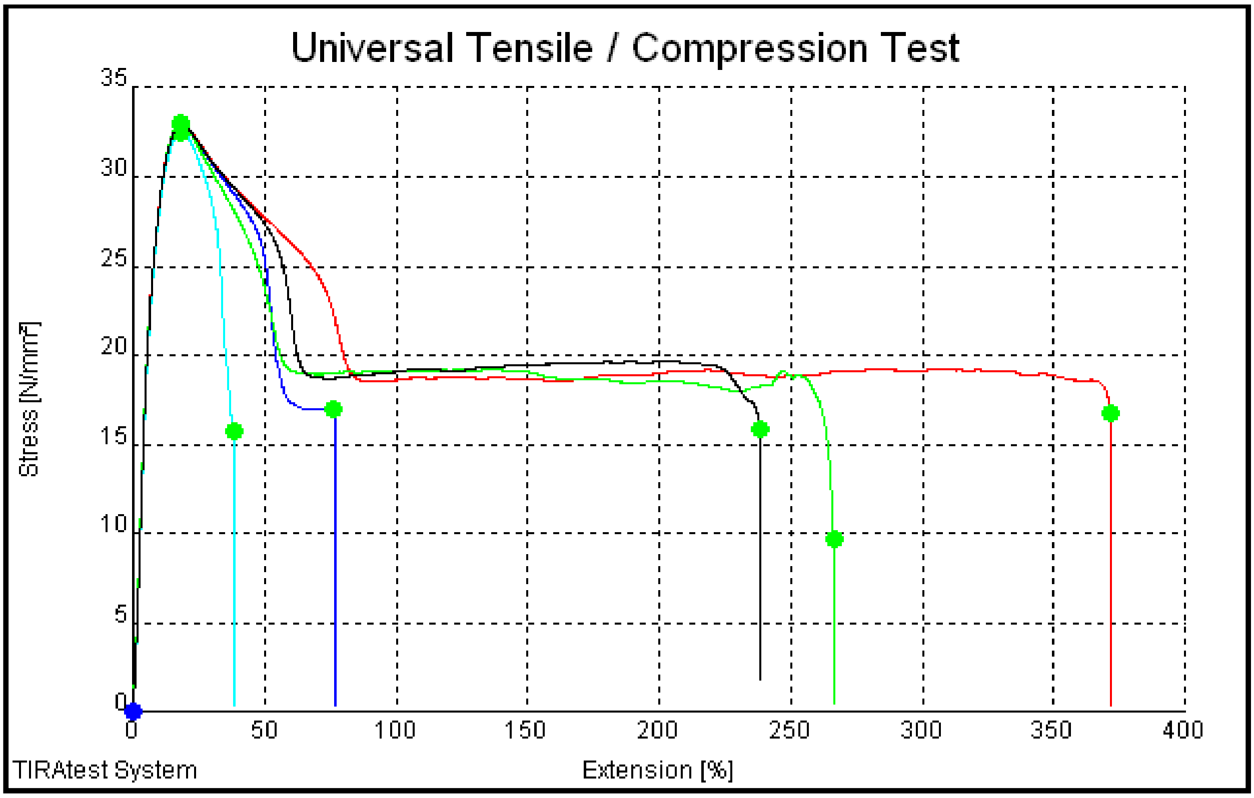
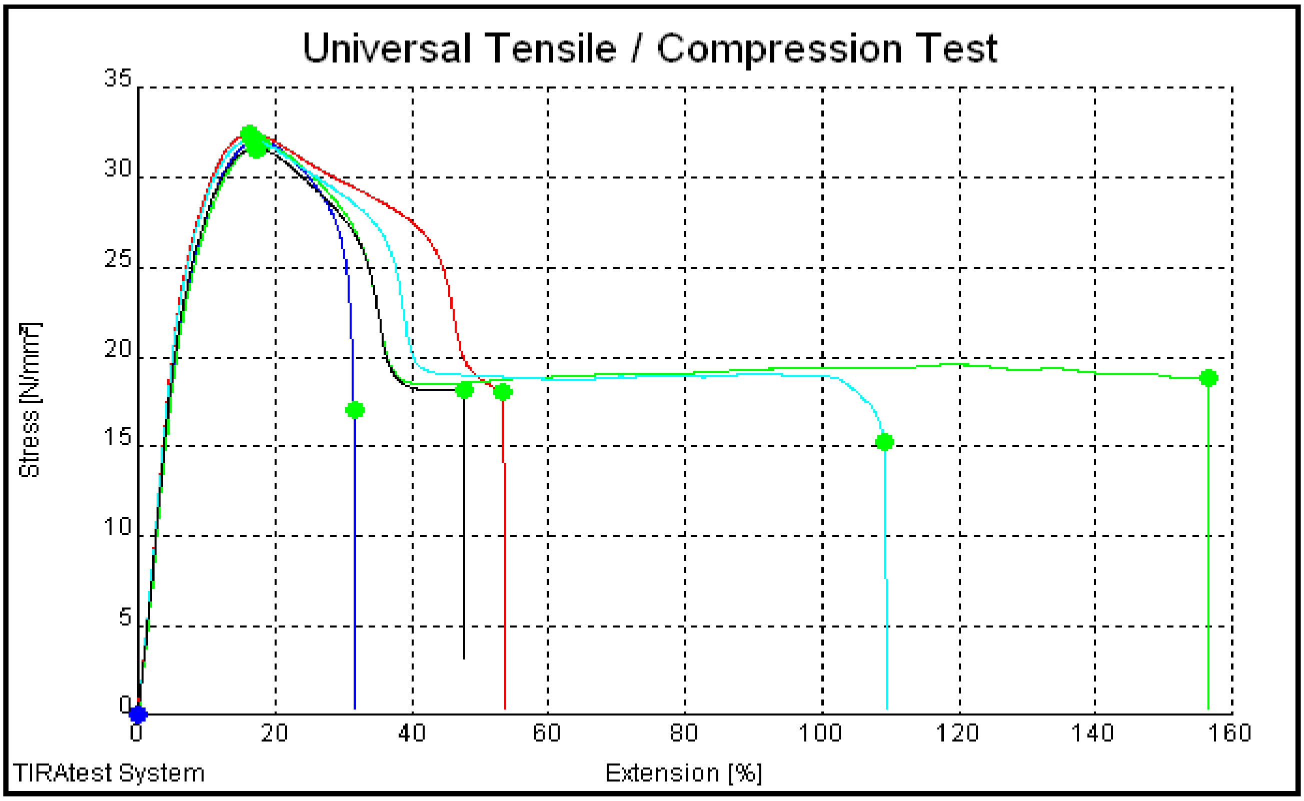
## 1.1: TENSILE STRENGTH GRAPH

**Graph 1: Tensile strength of (PP + 5%normal $CaCO_3$)**



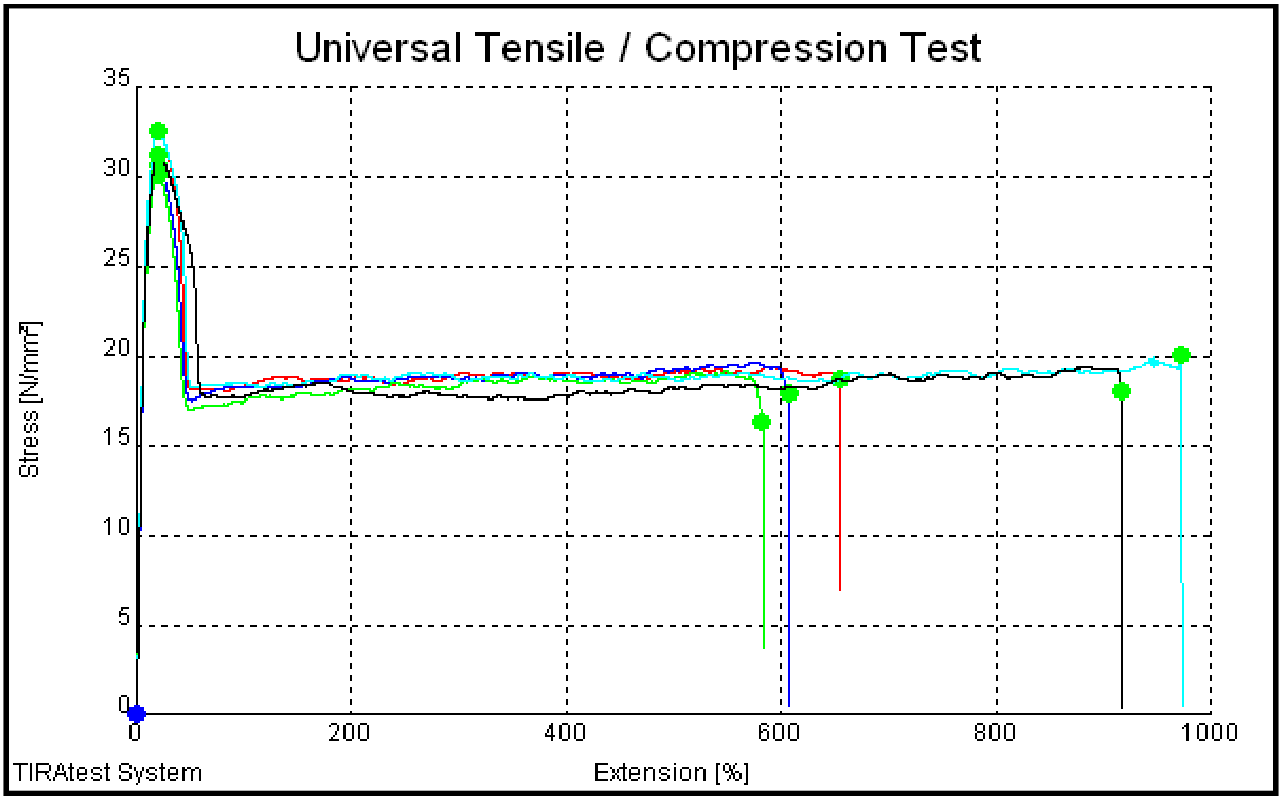
| FH[N] | RH[$N/mm^2$] | AH[%] | dLH[mm] | FB[N] | RB[$N/mm^2$] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1385.95 | 32.93 | 18.19 | 9.09 | 701.42 | 16.67 | 371.82 | 185.91 |
| 1384.34 | 32.89 | 18.27 | 9.14 | 714.18 | 16.97 | 76.40 | 38.20 |
| 1383.89 | 32.88 | 18.24 | 9.12 | 406.28 | 9.65 | 266.44 | 133.22 |
| 1361.82 | 32.46 | 18.27 | 9.14 | 656.63 | 15.65 | 38.47 | 19.24 |
| 1380.07 | 32.87 | 18.29 | 9.14 | 663.20 | 15.79 | 238.35 | 119.18 |

**Graph 2: Tensile strength of (PP +5% modify egg shell)**



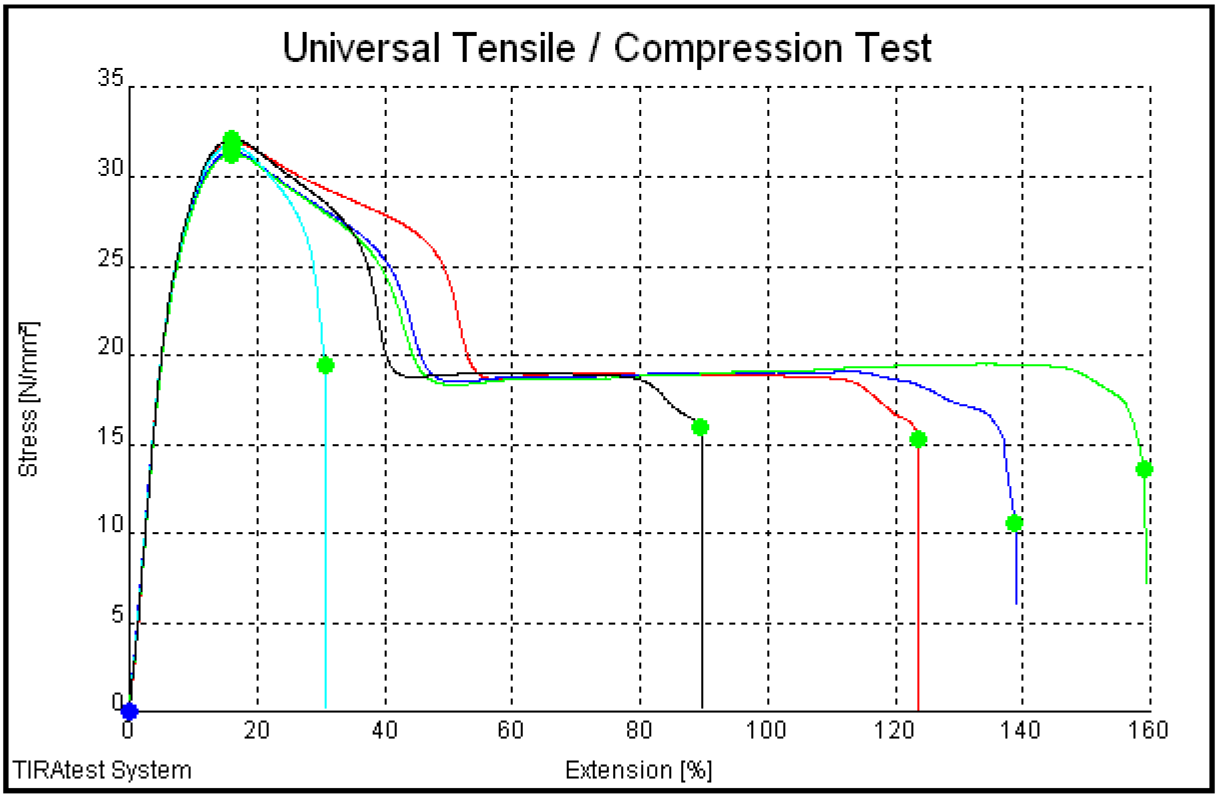
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1352.70 | 32.41 | 16.41 | 8.21 | 752.73 | 18.04 | 53.41 | 26.71 |
| 1332.42 | 32.00 | 17.72 | 8.86 | 708.19 | 17.01 | 31.62 | 15.81 |
| 1322.33 | 31.79 | 18.16 | 9.08 | 780.31 | 18.76 | 156.42 | 78.21 |
| 1332.36 | 32.05 | 16.49 | 8.25 | 632.21 | 15.21 | 109.19 | 54.60 |
| 1314.00 | 31.59 | 17.11 | 8.55 | 751.54 | 18.07 | 47.54 | 23.77 |

**Graph 3: Tensile strength of (PP +5% unmodified egg shell**



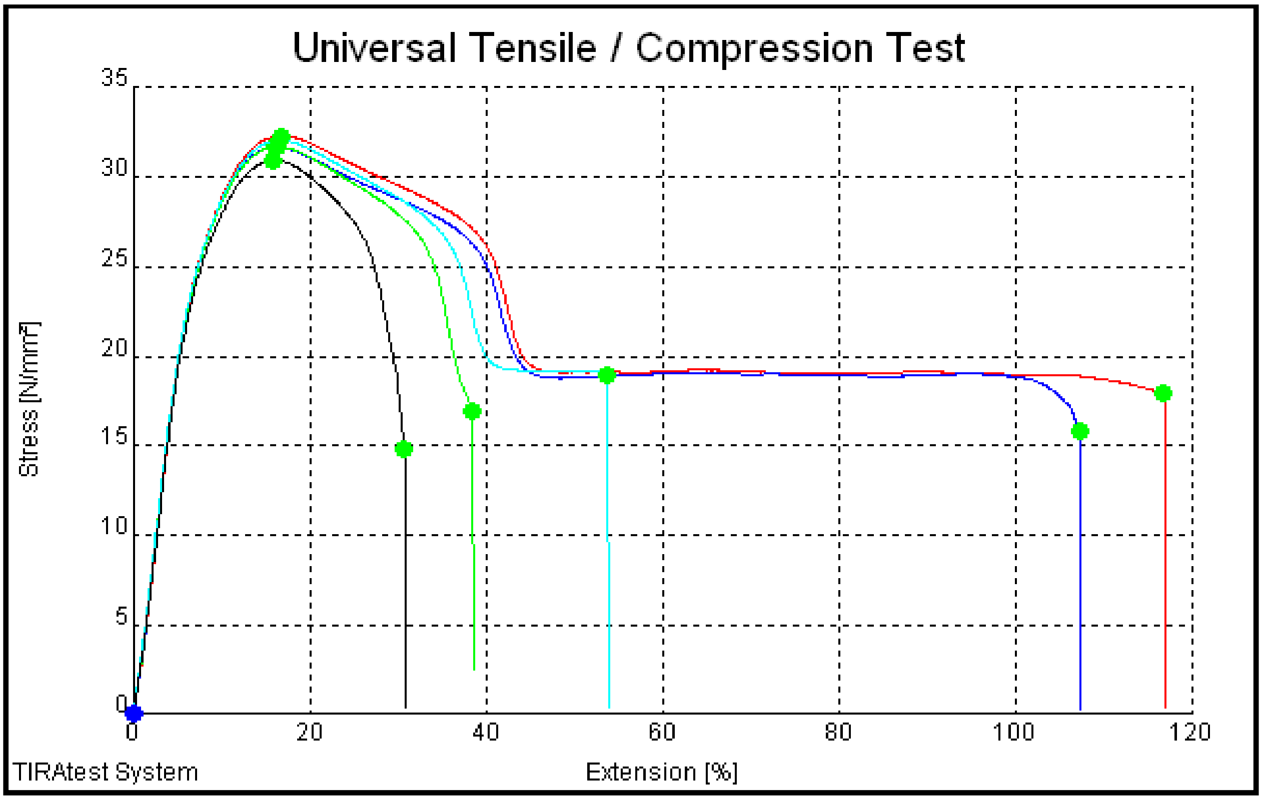
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1357.97 | 32.52 | 20.57 | 10.29 | 777.99 | 18.63 | 654.01 | 327.00 |
| 1278.32 | 30.59 | 19.94 | 9.97 | 750.00 | 17.94 | 606.71 | 303.35 |
| 1253.59 | 30.13 | 19.17 | 9.59 | 676.98 | 16.27 | 582.78 | 291.39 |
| 1351.94 | 32.50 | 19.99 | 10.00 | 831.48 | 19.99 | 973.22 | 486.61 |
| 1314.54 | 31.23 | 20.42 | 10.21 | 755.89 | 17.96 | 917.39 | 458.70 |

**Graph 4: tensile strength of (PP + 10% normal $CaCO_3$)**



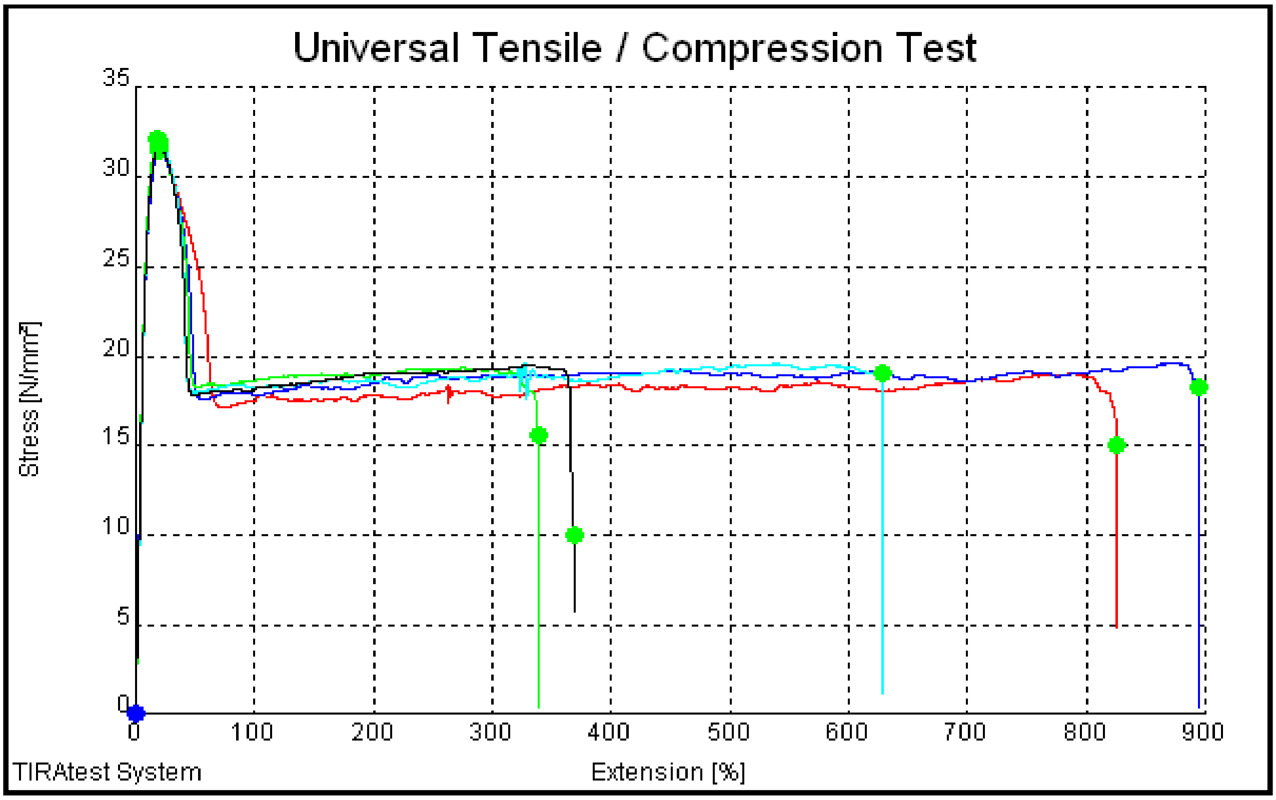
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1337.88 | 31.89 | 16.39 | 8.19 | 639.42 | 15.24 | 123.59 | 61.79 |
| 1316.40 | 31.37 | 15.94 | 7.97 | 444.12 | 10.58 | 138.77 | 69.39 |
| 1311.67 | 31.24 | 16.02 | 8.01 | 571.44 | 13.61 | 159.12 | 79.56 |
| 1331.67 | 31.74 | 15.94 | 7.97 | 816.25 | 19.45 | 30.67 | 15.34 |
| 1341.11 | 32.06 | 15.97 | 7.99 | 666.68 | 15.94 | 89.54 | 44.77 |

**Graph 5: tensile strength of (PP +10% modify egg shell)**



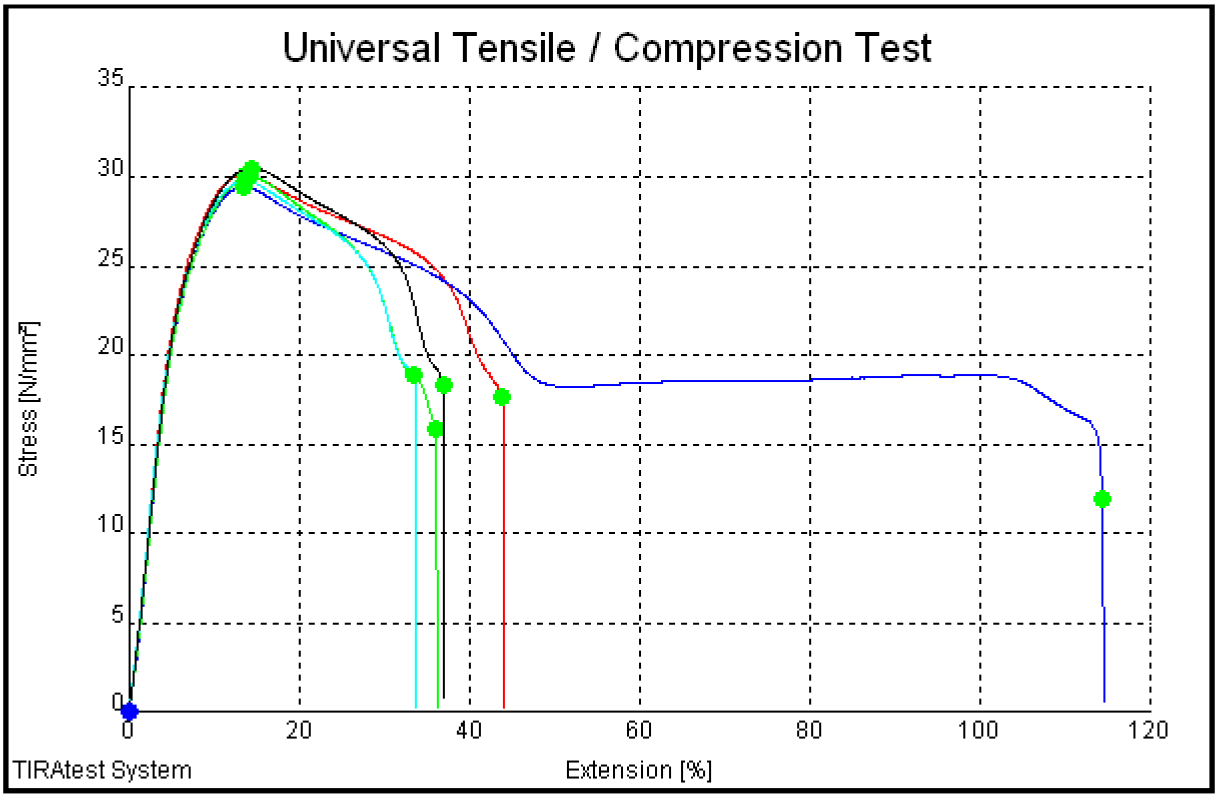
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1341.73 | 32.25 | 16.59 | 8.30 | 745.58 | 17.92 | 116.76 | 58.38 |
| 1315.46 | 31.62 | 15.99 | 8.00 | 656.63 | 15.78 | 107.20 | 53.60 |
| 1316.62 | 31.65 | 16.26 | 8.13 | 701.37 | 16.86 | 38.39 | 19.20 |
| 1335.13 | 31.99 | 16.43 | 8.21 | 790.41 | 18.94 | 53.62 | 26.81 |
| 1289.22 | 30.89 | 15.77 | 7.89 | 614.89 | 14.73 | 30.67 | 15.34 |

**Graph 6: tensile strength of (PP +10% unmodified egg shell)**



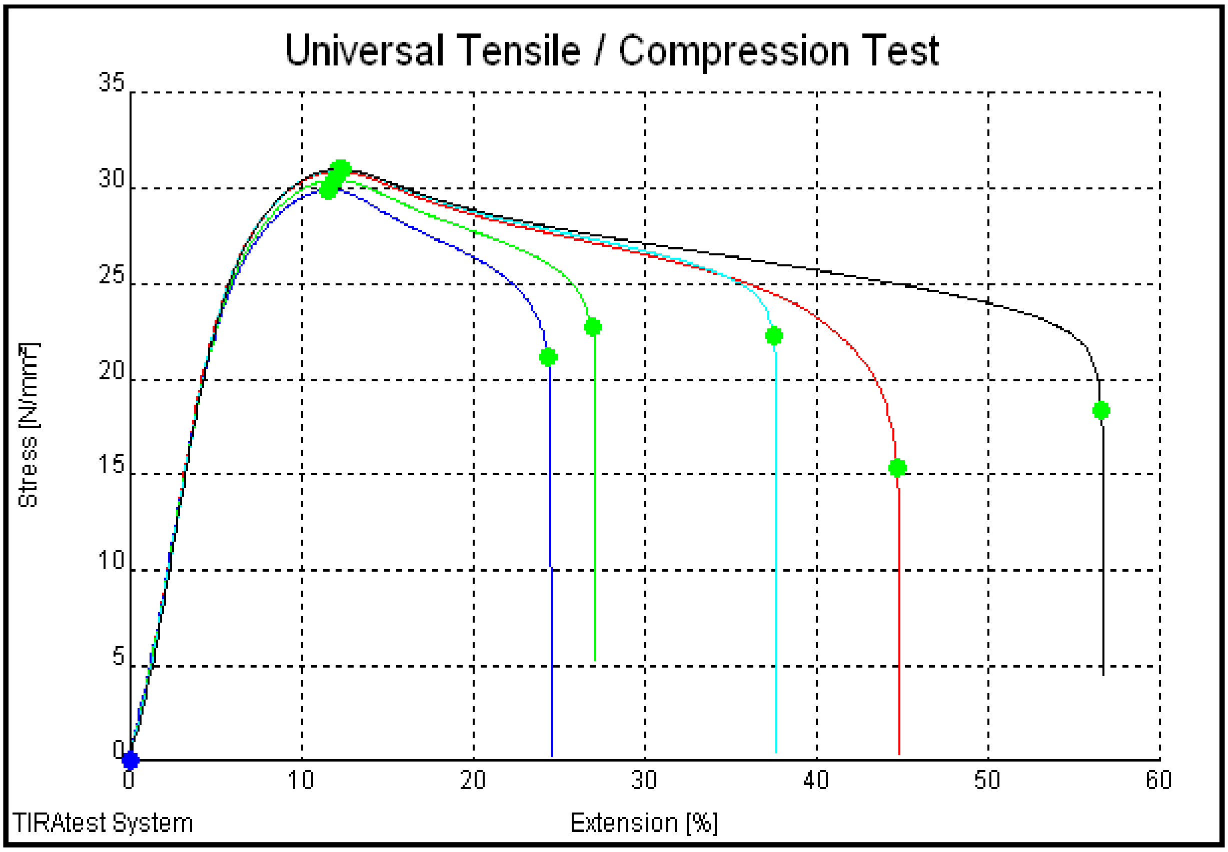
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1327.62 | 31.67 | 19.47 | 9.74 | 629.26 | 15.01 | 825.64 | 412.82 |
| 1308.80 | 31.44 | 19.52 | 9.76 | 756.90 | 18.18 | 894.06 | 447.03 |
| 1335.69 | 32.08 | 18.36 | 9.18 | 646.32 | 15.52 | 338.46 | 169.23 |
| 1334.01 | 31.94 | 20.23 | 10.12 | 795.81 | 19.06 | 628.72 | 314.38 |
| 1326.30 | 31.76 | 19.52 | 9.76 | 417.69 | 10.00 | 368.36 | 184.18 |

**Graph 7: tensile strength of (PP + 20% normal $CaCO_3$)**



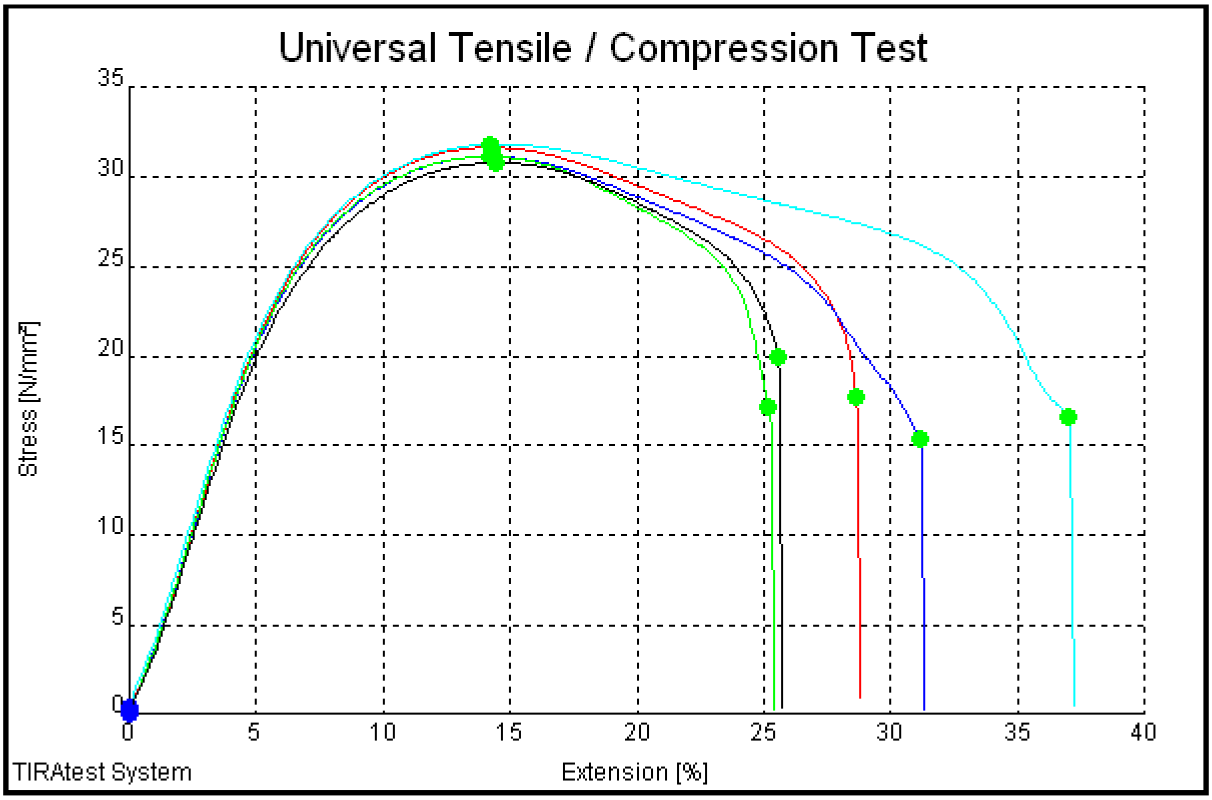
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1259.96 | 30.10 | 13.60 | 6.80 | 736.01 | 17.58 | 43.80 | 21.90 |
| 1229.96 | 29.38 | 13.34 | 6.67 | 496.25 | 11.85 | 114.34 | 57.17 |
| 1256.08 | 29.94 | 14.19 | 7.09 | 663.18 | 15.81 | 36.02 | 18.01 |
| 1248.49 | 29.73 | 13.67 | 6.84 | 789.44 | 18.80 | 33.44 | 16.72 |
| 1278.70 | 30.45 | 14.35 | 7.18 | 766.87 | 18.26 | 36.89 | 18.44 |

**Graph 8: tensile strength of (PP+ 20% modified egg shell)**



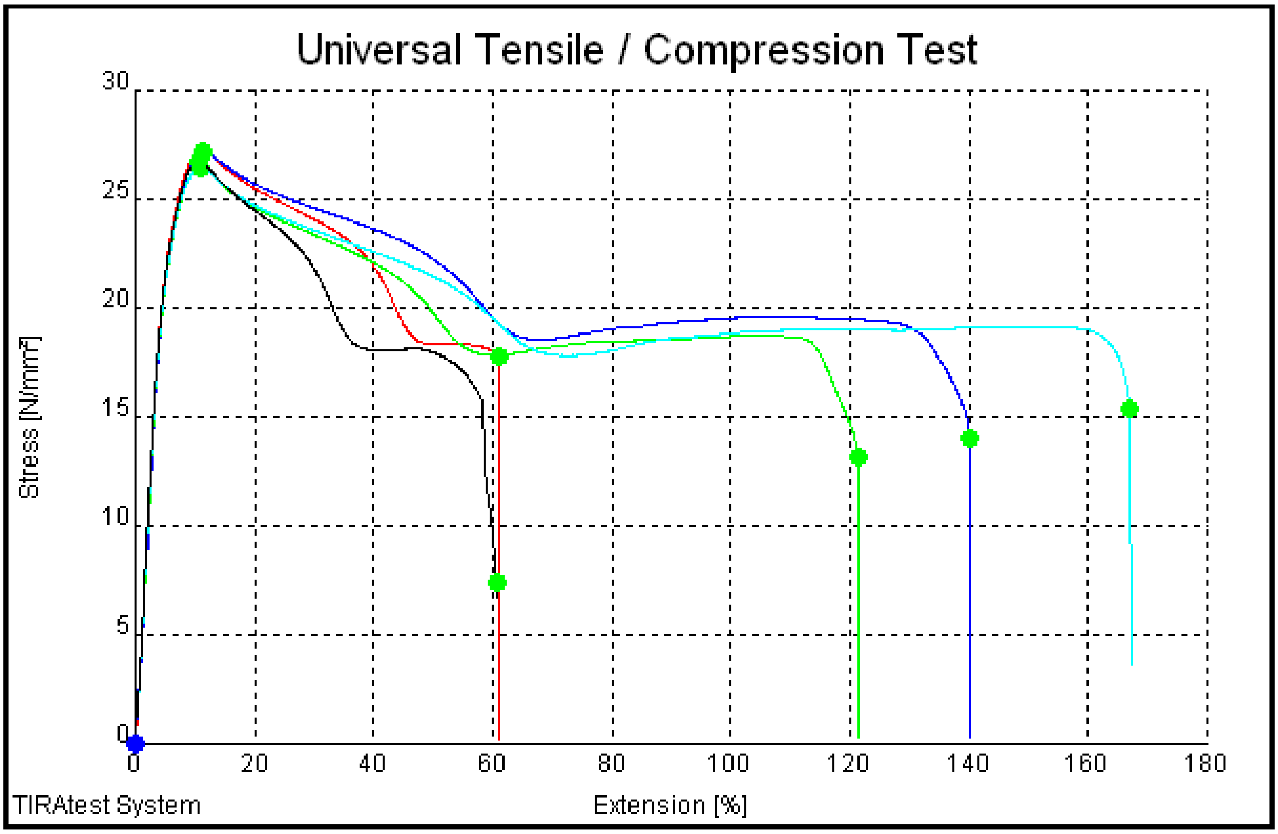
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1283.33 | 30.85 | 11.97 | 5.99 | 638.44 | 15.35 | 44.68 | 22.34 |
| 1250.69 | 29.90 | 11.50 | 5.75 | 885.68 | 21.17 | 24.40 | 12.20 |
| 1270.78 | 30.40 | 11.84 | 5.92 | 949.79 | 22.72 | 26.91 | 13.45 |
| 1293.89 | 30.96 | 12.09 | 6.05 | 928.20 | 22.21 | 37.49 | 18.75 |
| 1294.07 | 30.96 | 12.32 | 6.16 | 766.65 | 18.34 | 56.59 | 28.30 |

**Graph 9: tensile strength of (PP+ 20% unmodified egg shell)**



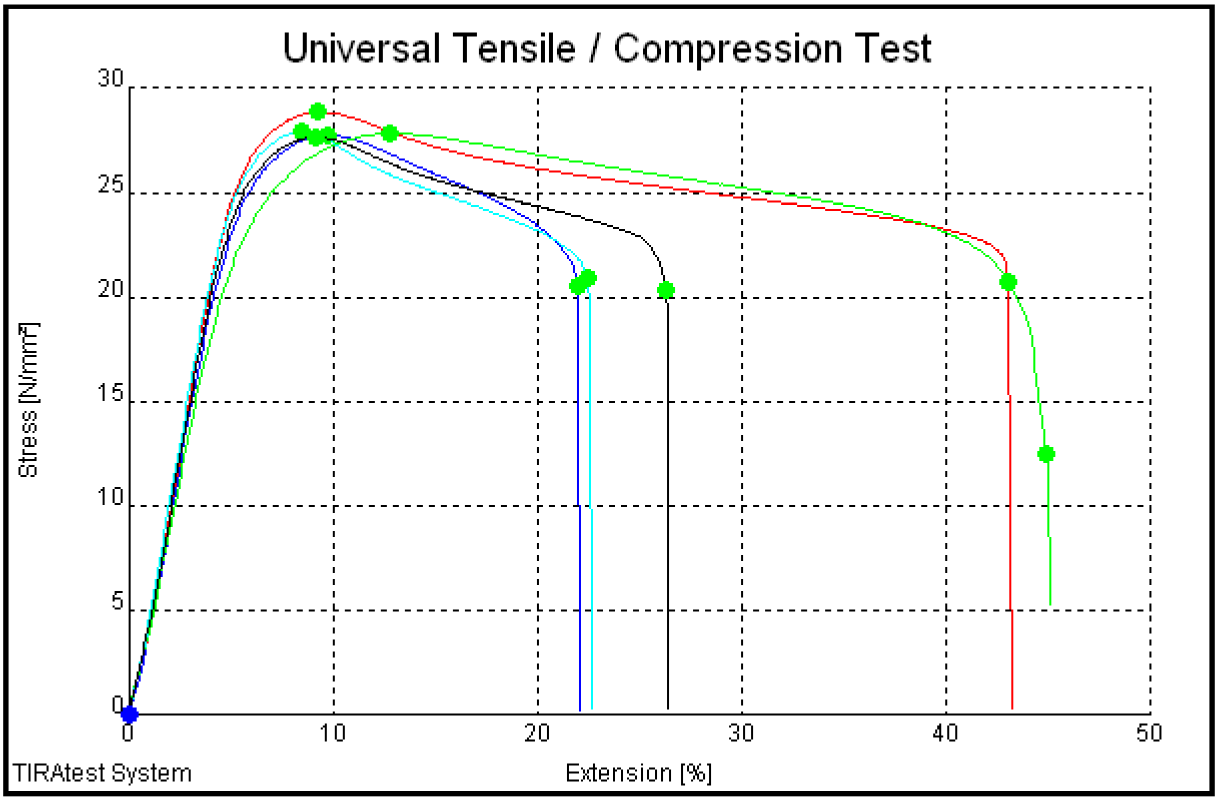
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1325.70 | 31.62 | 14.31 | 7.16 | 739.42 | 17.64 | 28.64 | 14.32 |
| 1305.19 | 31.11 | 14.23 | 7.11 | 641.20 | 15.28 | 31.19 | 15.60 |
| 1305.01 | 31.10 | 14.32 | 7.16 | 717.39 | 17.10 | 25.19 | 12.60 |
| 1324.87 | 31.80 | 14.22 | 7.11 | 690.65 | 16.58 | 37.03 | 18.53 |
| 1290.71 | 30.76 | 14.42 | 7.21 | 835.70 | 19.92 | 25.55 | 12.78 |

**Graph 10: tensile strength (PP+normal$CaCO_3$)**



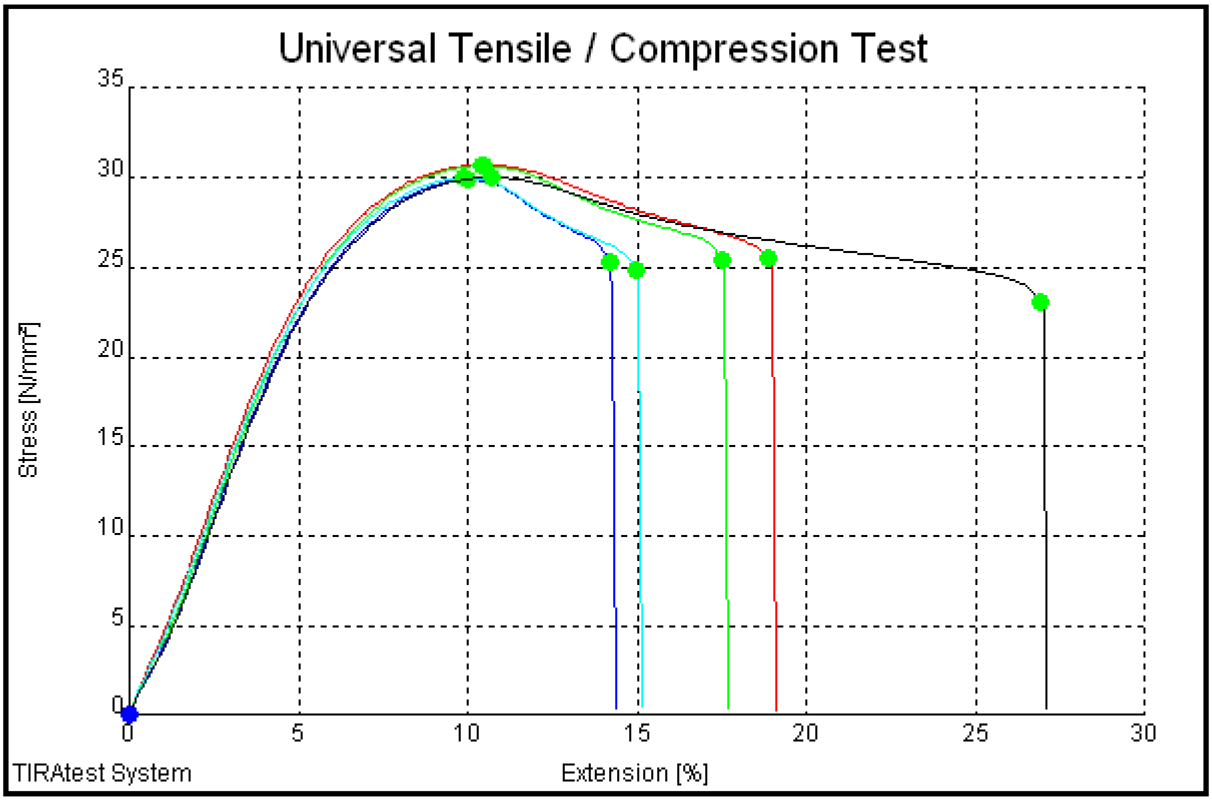
| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1142.78 | 27.22 | 11.19 | 5.59 | 748.63 | 17.83 | 60.92 | 30.46 |
| 1141.70 | 27.09 | 11.32 | 5.66 | 591.91 | 14.04 | 139.99 | 69.99 |
| 1110.35 | 26.44 | 10.80 | 5.40 | 552.93 | 13.17 | 121.24 | 60.62 |
| 1111.31 | 26.47 | 10.94 | 5.47 | 645.75 | 15.38 | 167.00 | 83.50 |
| 1122.74 | 26.74 | 10.62 | 5.31 | 311.54 | 7.42 | 60.62 | 30.31 |

**Graph 11: tensile strength of (PP+ 30% modify egg shell)**



| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1219.00 | 28.81 | 9.17 | 4.59 | 875.77 | 20.70 | 43.07 | 21.54 |
| 1171.41 | 27.70 | 9.69 | 4.85 | 865.48 | 20.47 | 21.92 | 10.96 |
| 1175.94 | 27.79 | 12.74 | 6.37 | 527.00 | 12.45 | 44.91 | 22.45 |
| 1181.55 | 27.90 | 8.44 | 4.22 | 884.82 | 20.89 | 22.44 | 11.22 |
| 1168.88 | 27.60 | 9.09 | 4.55 | 862.27 | 20.36 | 26.23 | 13.11 |

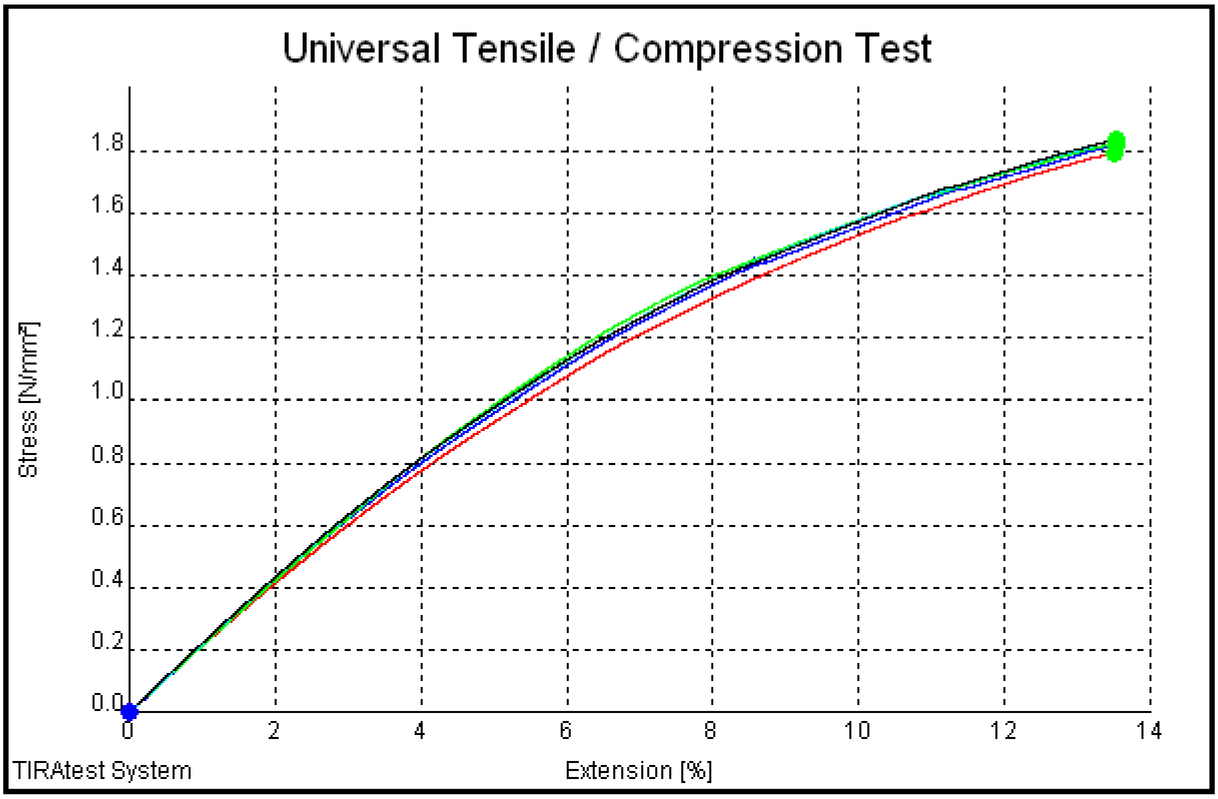
**Graph 12: tensile strength of (PP+30% unmodified egg shell)**



| FH[N] | RH[N/mm²] | AH[%] | dLH[mm] | FB[N] | RB[N/mm²] | AB[%] | dLB[mm] |
|---|---|---|---|---|---|---|---|
| 1286.71 | 30.67 | 10.49 | 5.24 | 1069.31 | 25.49 | 18.89 | 9.44 |
| 1252.28 | 29.82 | 9.97 | 4.99 | 1060.71 | 25.26 | 14.20 | 7.10 |
| 1285.27 | 30.61 | 10.42 | 5.21 | 1064.28 | 25.35 | 17.52 | 8.76 |
| 1257.50 | 29.92 | 9.85 | 4.93 | 1044.59 | 24.86 | 14.95 | 7.48 |
| 1258.17 | 29.96 | 10.72 | 5.36 | 967.78 | 23.05 | 26.92 | 13.46 |

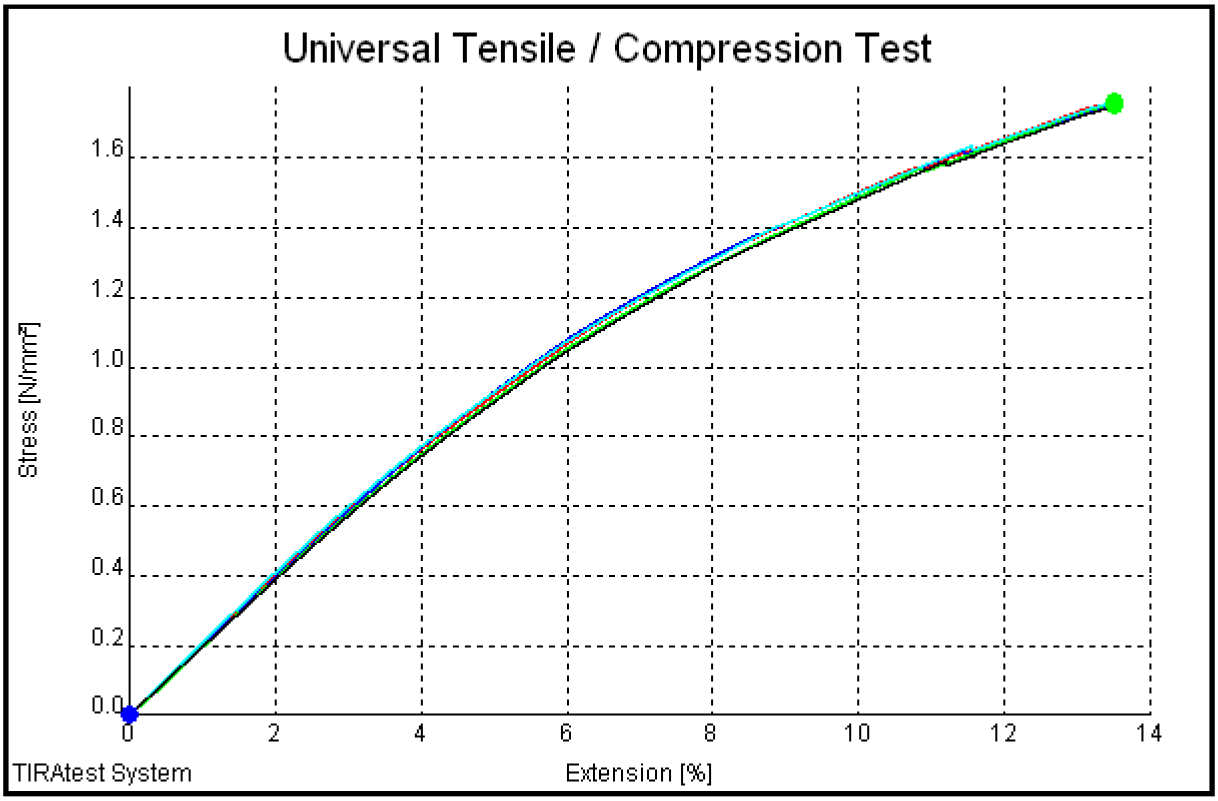
## 1.2: FLEXURAL STRENGTH GRAPH

**Graph 13: flexural strength of (PP+ 5% normal $CaCO_3$)**



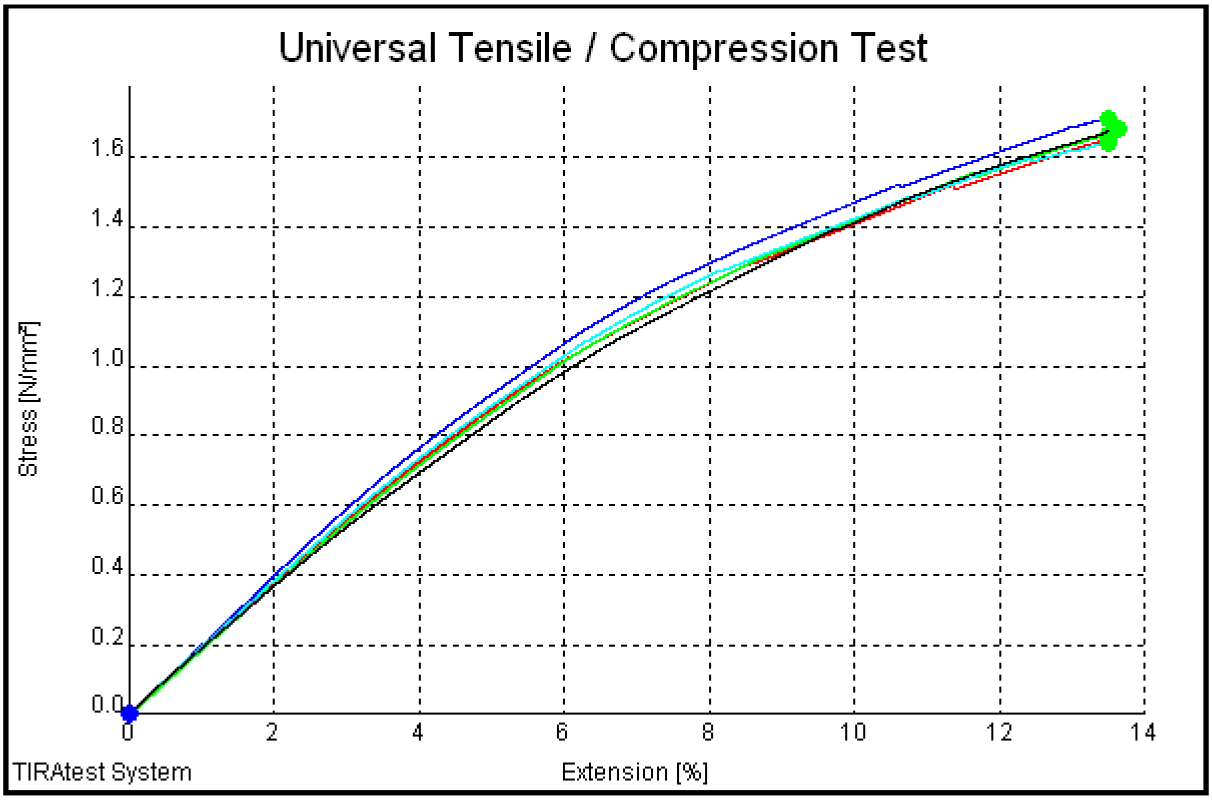
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 73.19 | 6.50 | 3.20 | 12.77 |
| 74.21 | 6.50 | 3.20 | 12.77 |
| 75.00 | 6.50 | 3.22 | 12.78 |
| 74.96 | 6.50 | 3.20 | 12.78 |
| 74.94 | 6.50 | 3.20 | 12.77 |

**Graph 14: flexural strength of (PP+ 5% modified egg shell)**



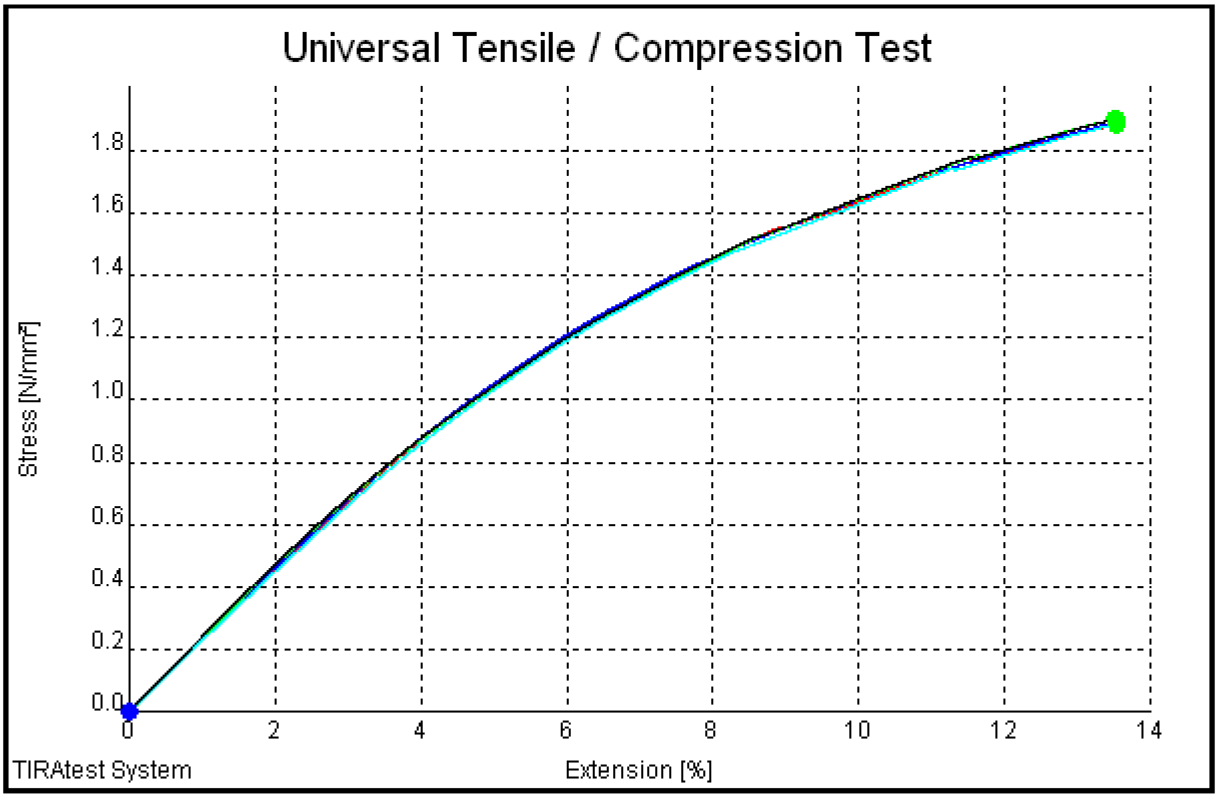
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 71.44 | 6.50 | 3.20 | 12.77 |
| 72.00 | 6.50 | 3.21 | 12.78 |
| 71.95 | 6.50 | 3.21 | 12.77 |
| 72.10 | 6.50 | 3.21 | 12.77 |
| 71.62 | 6.50 | 3.21 | 12.76 |

**Graph 15: flexural strength of (PP+ 5% unmodified egg shell)**



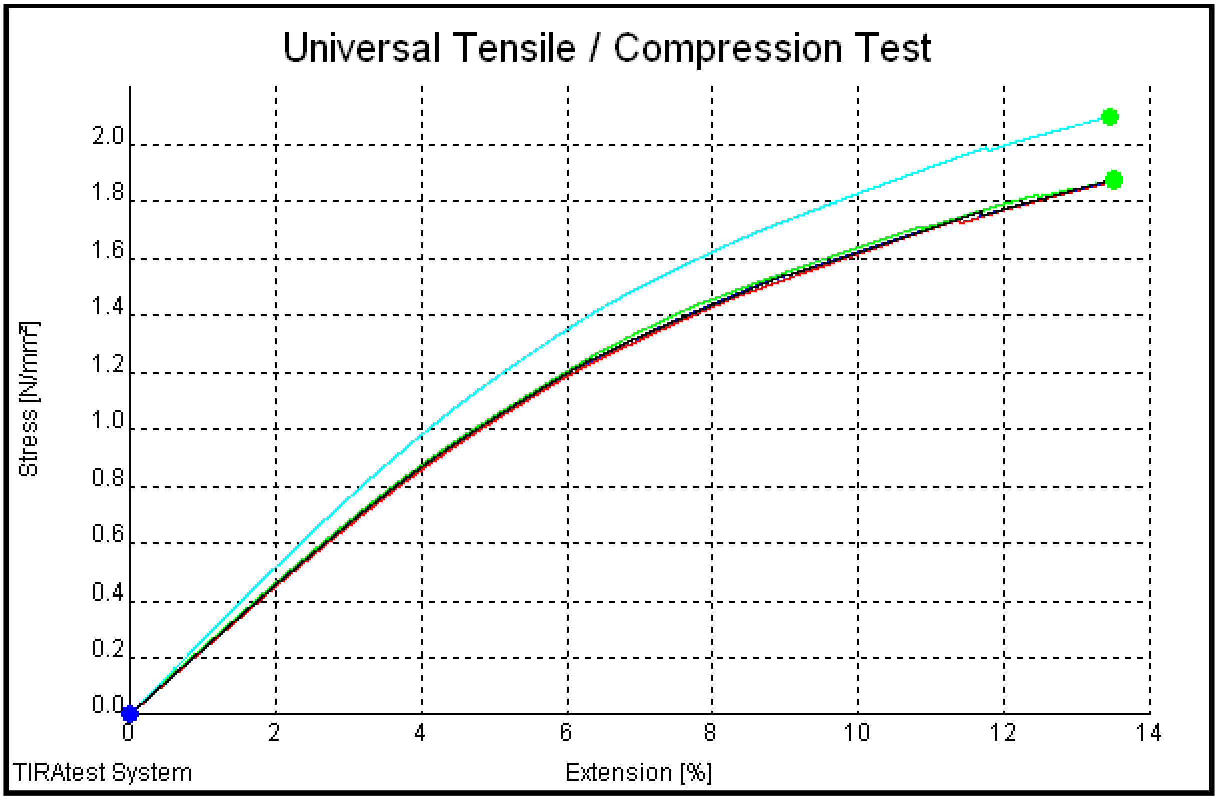
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 67.74 | 6.50 | 3.21 | 12.79 |
| 70.14 | 6.50 | 3.21 | 12.78 |
| 68.29 | 6.50 | 3.21 | 12.78 |
| 67.24 | 6.50 | 3.21 | 12.76 |
| 68.72 | 6.50 | 3.20 | 12.77 |

**Graph 16: flexural strength of (PP+ 10% normal $CaCO_3$)**



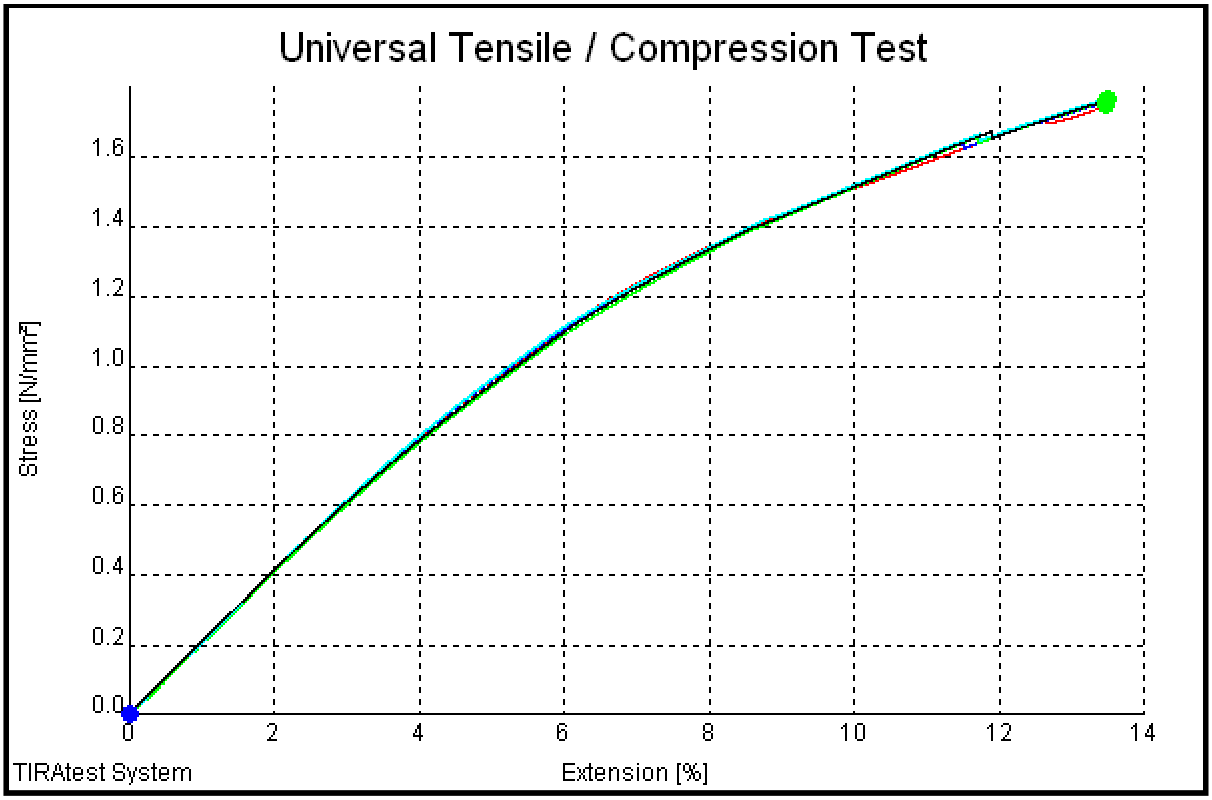
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 77.25 | 6.50 | 3.22 | 12.77 |
| 77.36 | 6.50 | 3.21 | 12.77 |
| 77.57 | 6.50 | 3.20 | 12.78 |
| 77.24 | 6.50 | 3.21 | 12.78 |
| 77.87 | 6.50 | 3.21 | 12.78 |

**Graph 17: flexural strength of (PP+ 10% modified egg shell)**



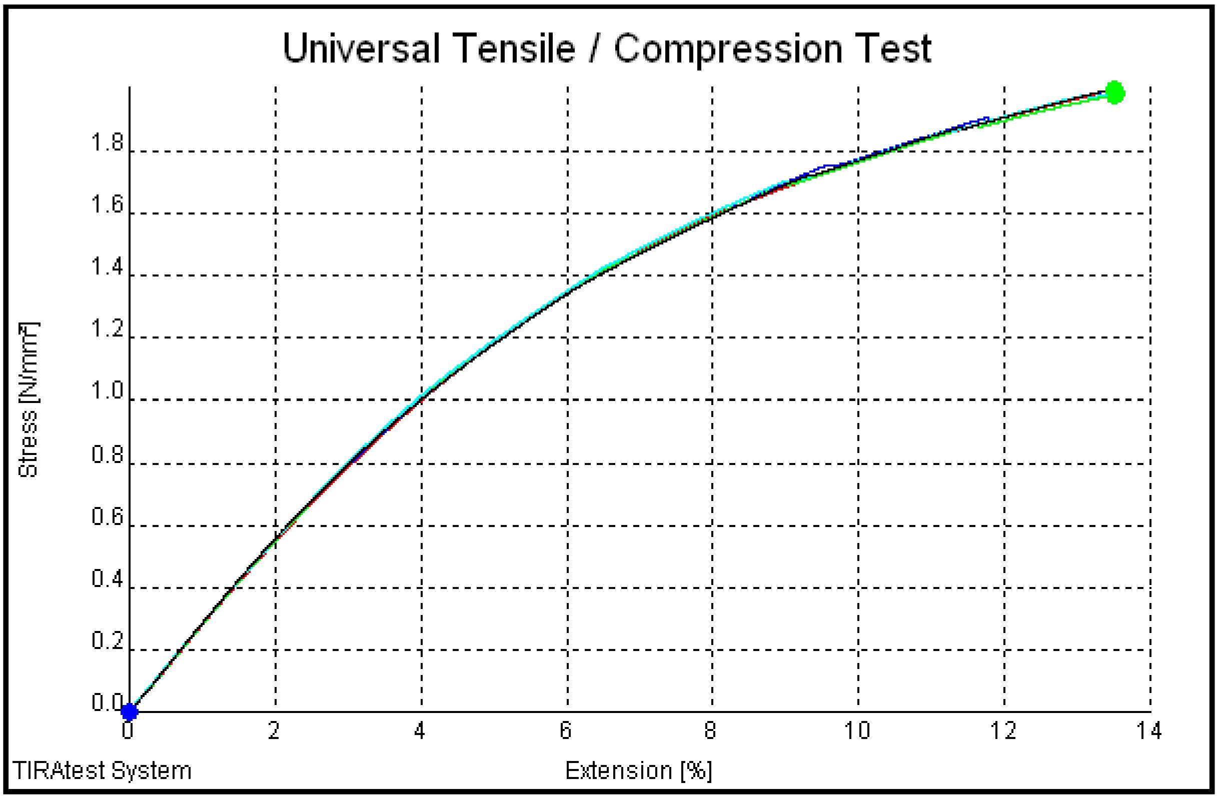
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 76.61 | 6.50 | 3.21 | 12.76 |
| 76.85 | 6.50 | 3.21 | 12.78 |
| 76.64 | 6.50 | 3.21 | 12.76 |
| 90.35 | 6.50 | 3.36 | 12.84 |
| 76.88 | 6.50 | 3.21 | 12.78 |

**Graph 18: flexural strength of (PP+ 10% unmodified egg shell)**



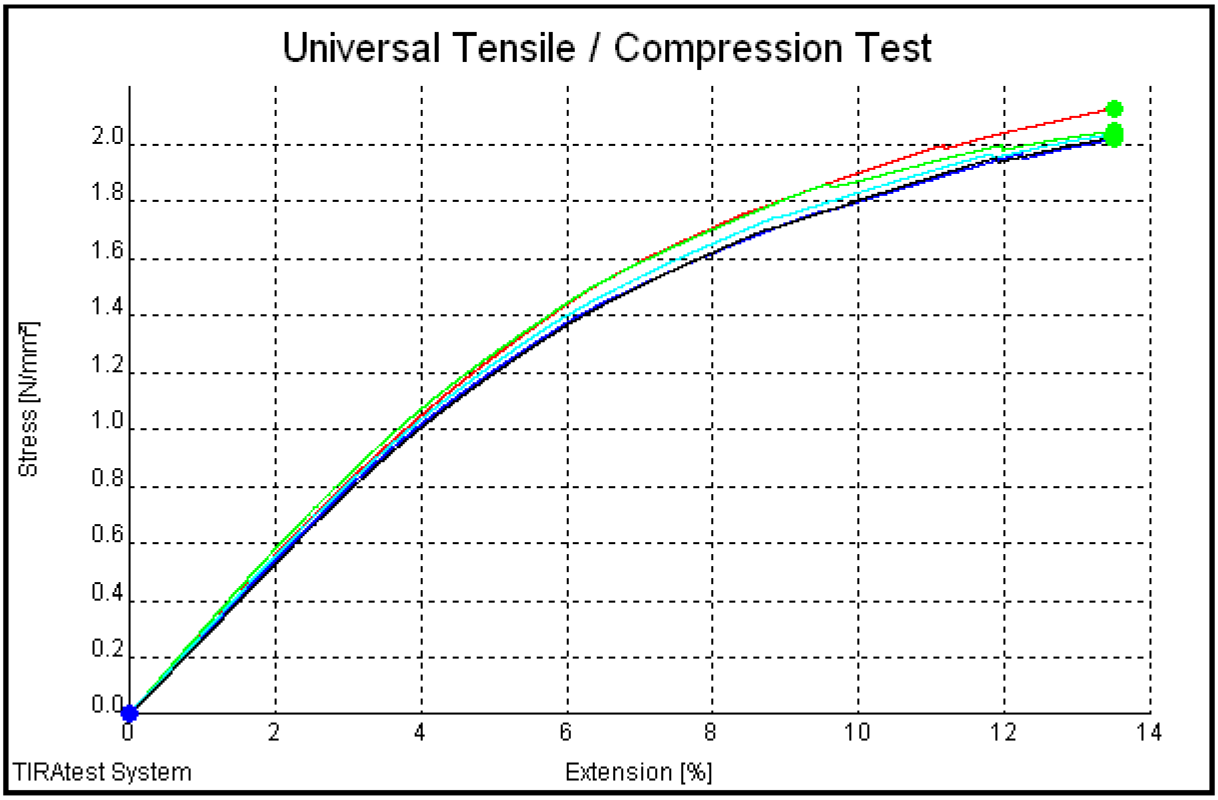
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 71.60 | 6.50 | 3.21 | 12.78 |
| 71.97 | 6.50 | 3.21 | 12.77 |
| 71.81 | 6.50 | 3.20 | 12.76 |
| 72.15 | 6.50 | 3.20 | 12.76 |
| 71.88 | 6.50 | 3.20 | 12.76 |

**Graph 19: flexural strength of (PP+ 20% normal $CaCO_3$)**



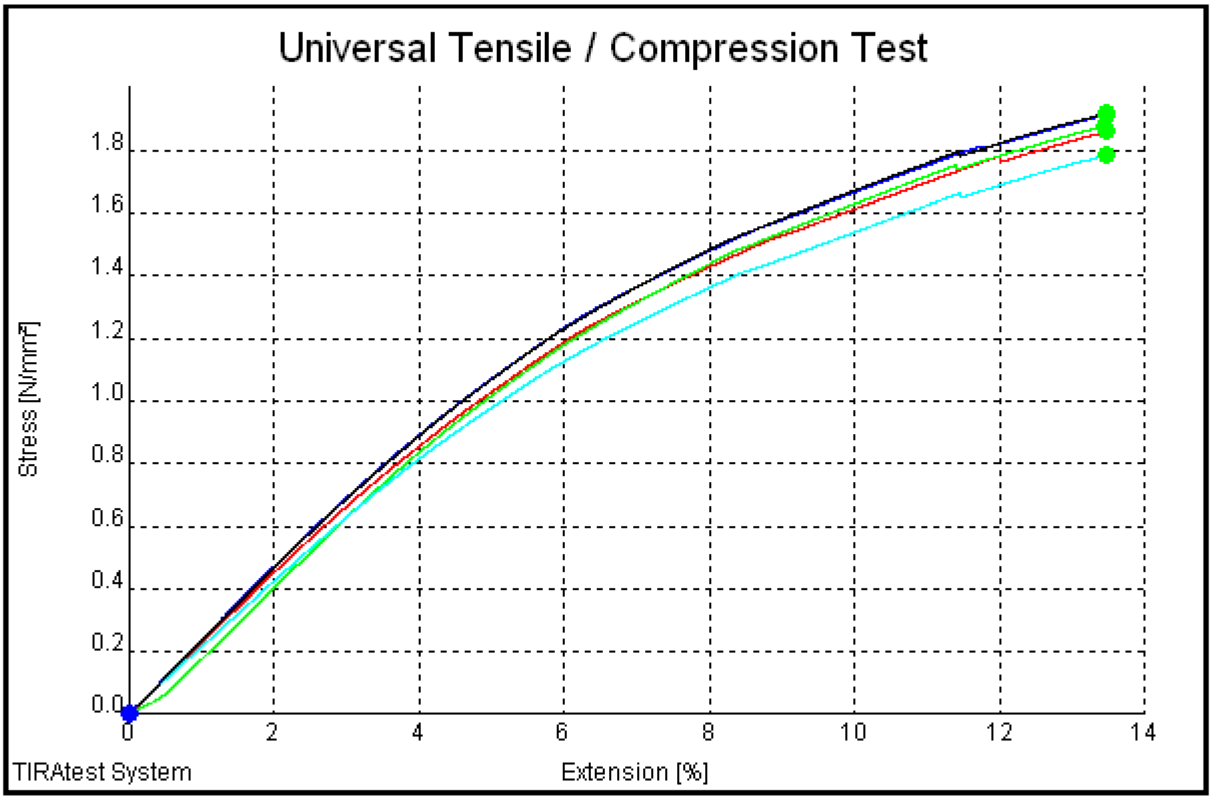
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 81.48 | 6.50 | 3.20 | 12.78 |
| 81.61 | 6.50 | 3.20 | 12.78 |
| 81.10 | 6.50 | 3.21 | 12.78 |
| 81.59 | 6.50 | 3.22 | 12.78 |
| 82.14 | 6.50 | 3.22 | 12.79 |

**Graph 20: flexural strength of (PP+ 20% modified egg shell)**



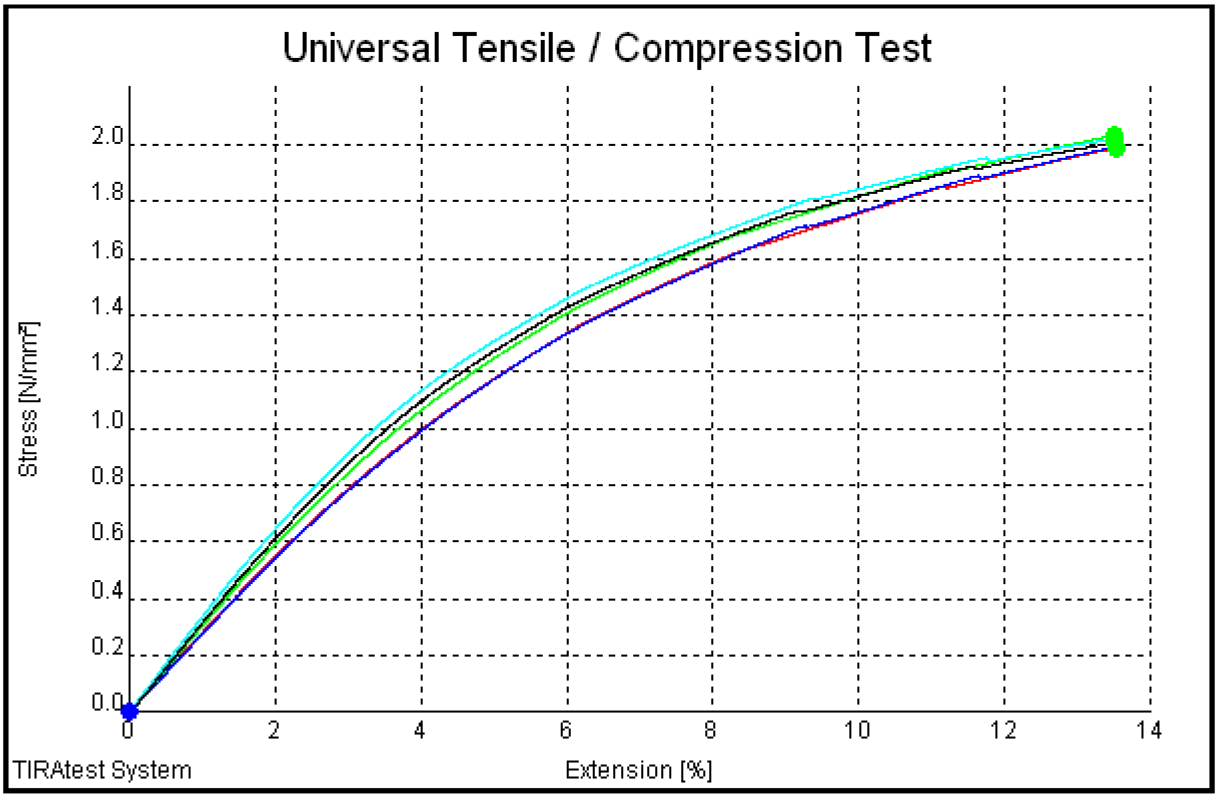
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 87.18 | 6.50 | 3.21 | 12.78 |
| 82.57 | 6.50 | 3.20 | 12.79 |
| 84.04 | 6.50 | 3.21 | 12.79 |
| 83.55 | 6.50 | 3.21 | 12.79 |
| 83.06 | 6.50 | 3.21 | 12.79 |

**Graph 21: flexural strength of (PP+ 20% unmodified egg shell)**



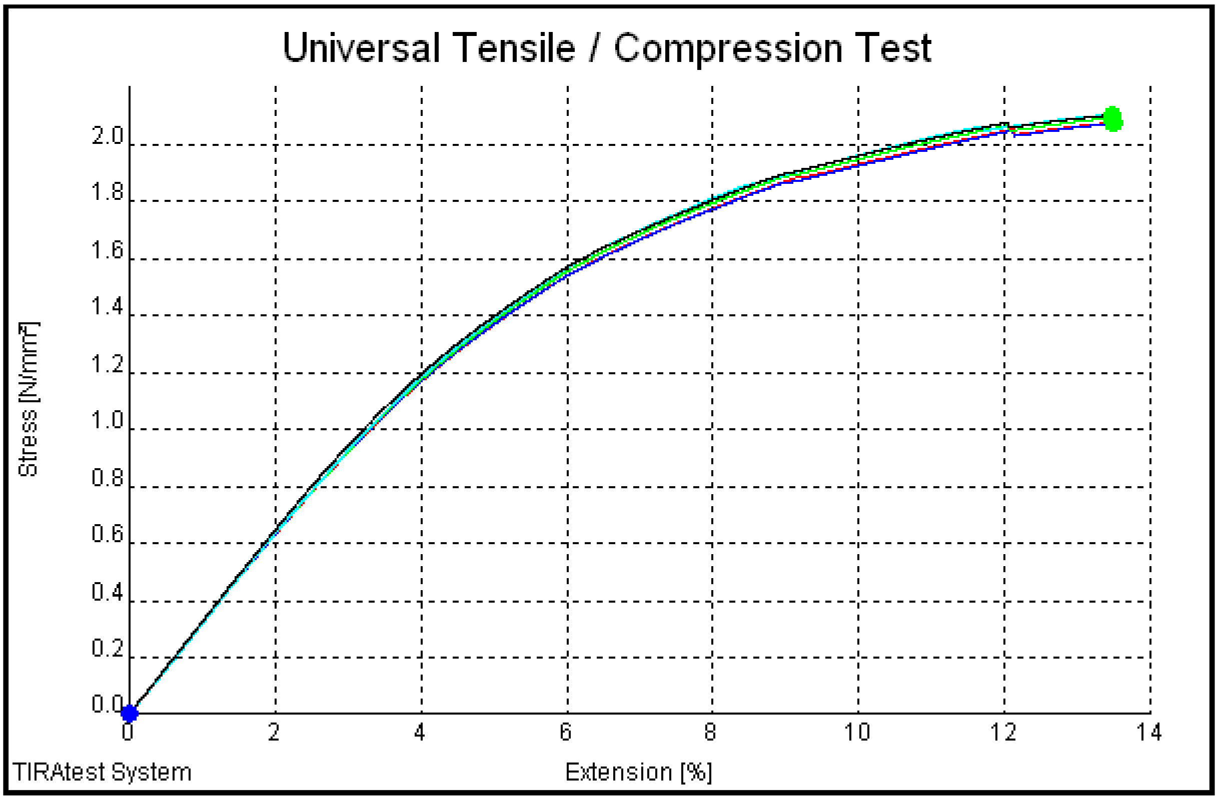
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 75.83 | 6.50 | 3.20 | 12.76 |
| 78.02 | 6.50 | 3.20 | 12.76 |
| 76.80 | 6.50 | 3.21 | 12.77 |
| 73.09 | 6.50 | 3.21 | 12.78 |
| 78.27 | 6.50 | 3.20 | 12.77 |

Graph 22: flexural strength of (PP+ 30% normal $CaCO_3$)



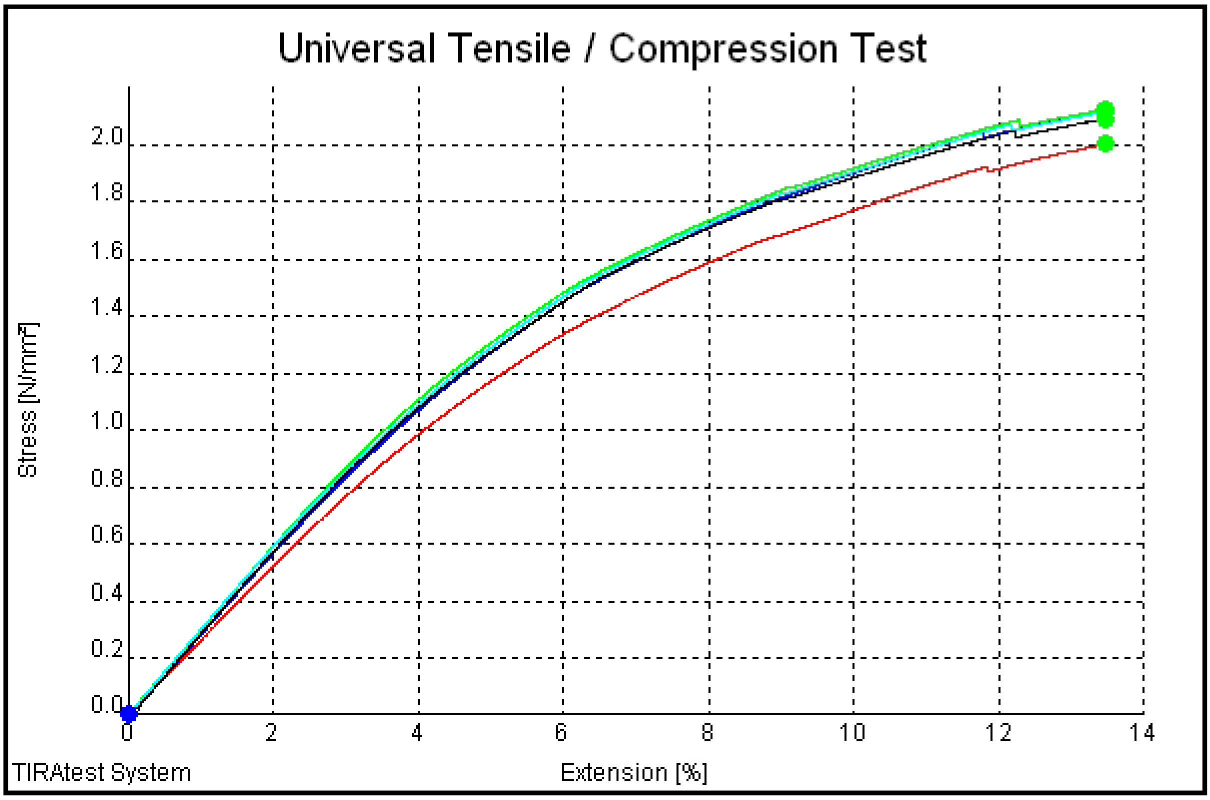
| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 81.73 | 6.50 | 3.22 | 12.79 |
| 81.40 | 6.50 | 3.20 | 12.79 |
| 83.29 | 6.50 | 3.21 | 12.79 |
| 82.54 | 6.50 | 3.20 | 12.78 |
| 82.28 | 6.50 | 3.21 | 12.79 |

**Graph 23: flexural strength of (PP+ 30% modified egg shell)**



| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 85.18 | 6.50 | 3.21 | 12.79 |
| 85.05 | 6.50 | 3.21 | 12.79 |
| 85.89 | 6.50 | 3.21 | 12.79 |
| 86.35 | 6.50 | 3.21 | 12.79 |
| 86.30 | 6.50 | 3.21 | 12.79 |

**Graph 24: flexural strength of (PP+ 30% unmodified egg shell)**



| FH[N] | dLH[mm] | a[mm] | b[mm] |
|---|---|---|---|
| 82.08 | 6.50 | 3.21 | 12.78 |
| 86.59 | 6.50 | 3.20 | 12.78 |
| 87.05 | 6.50 | 3.21 | 12.78 |
| 86.74 | 6.50 | 3.21 | 12.78 |
| 85.70 | 6.50 | 3.21 | 12.78 |

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