Study on Hybrid Composites Reinforced with Nano-material, Natural Fibres and Bio-material

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DOCTOR OF PHILOSOPHY
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By
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DECLARATION

I hereby declare that the thesis work entitled "Study on Hybrid Composites reinforced with Nano-material, Natural Fibres and Bio-material" is an original work carried out by me under the supervision of Dr. Ranganath M. Singari, Professor, Department of Mechanical Engineering, Delhi Technological University, Delhi and Dr. R.S.Mishra, Professor, Department of Mechanical Engineering, Delhi Technological University, Delhi. This thesis has been prepared in conformity with the rules and regulations of the Delhi Technological University, Delhi. The research work presented and reported in this thesis has not been submitted either in part or full to any other university or institute for the award of any other degree or diploma.

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CERTIFICATE

This is to certify that the thesis entitled **"Study on Hybrid Composites Reinforced with Nano-material, Natural Fibres and Bio-material"** submitted by Mr. Gurdevinder Singh Bajwa to the Delhi Technological University, Delhi for the award of the degree of Doctor of Philosophy in Mechanical Engineering is a bona fide record of original experimental work carried out by him under our supervision in accordance with rules and regulations of the university. The results presented in this thesis have not been submitted either in part or full to any other university or institute for the award of any degree or diploma.

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List of Abbreviations

Symbols	Description
PE	Polyethylene
PP	Polypropylene
HDPE	High Density Polyethylene
ST	Starch
TL	Talc
PVC	Poly Vinyl Chloride
CAGR	Compound Annual Growth Rate
PP-g-MA	Maleic Anhydride grafted Polypropylene
CNT	Carbon Nano Tube
UV	Ultra Violet
FTIR	Fourier Transmission Infrared Spectroscopy
ATR	Attenuated Total Reflection
ASTM	American standards of Testing Methods
DSC	Differential Scanning Calorimetry
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
UTM	Universal Testing Machine
MFI	Melt Flow Index
CRE	Constant Rate Extension
HDT	Heat Deflection Temperature
VST	Vicat Softening Temperature

Abstract

In this thesis the Hybrid Composites reinforced with nano-material, natural fibres and bio-material are prepared as an alternate to the synthetic fibres, to provide sustainable and environmental friendly material which is better alternate to the existing composites. The Mechanical and Thermal properties are studied and results are consistent with the existing trends of the field. This study would help researchers to find new application of this environmental friendly material in various fields. The contents of the thesis are as follows:

Chapter 1: This chapter illustrates the advantages of natural fibres filled composites over the synthetic fibres from various features. Types of fibres, their extraction and various treatment processes to enhance the reinforcement. The advantages of hybrid composites with nano-materials.

Chapter 2: This chapter is on literature review of composites with various polymers as matrix and various filler as reinforcements. It reviewed various chemical treatment methods and grafting methods for better mixing and homogeneous material. The various methods and parameters for preparing hybrid composites are discussed. Advantages, limitations are compared for various processing methods. It also includes analysis of research gap, objective of research work.

Chapter 3: This chapter discussed the various characterization techniques, including standards, details of equipments and conditions for studying the prepared Hybrid Composites for various Mechanical and Thermal properties.

Chapter 4: This chapter deals with synthesis of the Hybrid Composites with details of the various constituents and details about the composition with varying percentage to prepare the samples of the specimens. It also includes the details of extrusion and injection moulding process and their parameters.

Chapter 5: This chapter deals with the finding of results and discussions of the reinforced constituents to get the maximum values of Mechanical, Physical and Thermal properties of the prepared hybrid composites.

Chapter 6: It summarizes present research investigation for the successfully prepared hybrid composites having comparable properties to synthetic composites, while having advantages such as the reduction of plastic waste and energy savings advantages of natural

fibres and bio-material. It also includes the future scope for further research in this field for new application of these composites.

Chapter 1

Introduction:

Polymers are organic compounds usually containing oxygen, carbon, hydrogen, nitrogen, and sometimes other elements. 'Poly' means many, and 'mer' means a unit. The basic structural units of polymers are referred as monomers. By virtue of their thermal characteristics polymers are divided into two categories, thermoplastic or thermosetting. Thermoplastics are organic polymers and long chain macromolecules that undergo a transition from a solid to the molten state upon heating, and then back to a solid state upon cooling. This heating and cooling cycle can be repeated with minimal changes in the properties of the material. Therefore, thermoplastics can be moulded, extruded, or blown into different shapes, number of times and can be easily reused. Thermoplastics are widely used in industry as it offer advantages in weight, cost, moisture and chemical resistance, toughness, abrasive resistance, strength, appearance, formability and machinability. Thermoplastics mostly chosen due to better mould ability into various shapes and it can be re-melted and reprocessed into new a shape which is not possible for thermosets.

Polyolefins belong to a family of thermoplastics derived from ethylene and propylene monomers. Polyethylene (PE) and Polypropylene (PP) in particular, have been used extensively for various industrial applications. Both are photopolymer, produced by addition polymerization, and can be linear or branched.

The ability to adopt structure of different extents of branching endows polyolefins with a spectrum of performance and properties. PE/PP can be further "functionalized" by copolymerizing it with other monomers to form copolymers to enhance its functionality, such as increased toughness, improved adhesiveness, etc.

Polymers can be classified on the source of availability, like natural polymer they obtained naturally from plants, animals e.g. proteins, starch, cellulose and rubber. Semi synthetic polymer, they are derived from naturally occurring polymers and undergo further chemical modification e.g. cellulose nitrate, cellulose acetate etc. Synthetic polymer these are man-made polymer e.g. Polyethylene, Polypropylene, PVC, Nylon etc. The global plastic market size valued at USD 579.7 billion in 2020 and is expected to grow at CAGR of 3.2% from 2020-2027. Increasing plastic consumption in the construction, automotive and electrical &electronics industry is projected to drive the market for plastic over the forecast period. Regulations to decrease gross vehicle weight to improve fuel efficiency and eventually leads to reduced carbon emissions have promoted the use of plastic as a substitute to metals, including aluminium and steel for manufacturing of automotive components. Stringent regulations regarding depletion and recyclability of conventional materials such as metal and wood are anticipated to drive the demand for plastics from various sectors. Polypropylene accounted for 26% share of the global consumption of plastic, and it is expected to grow at CAGR of 12% by 2023 as reflected in Figure no. 1.1.
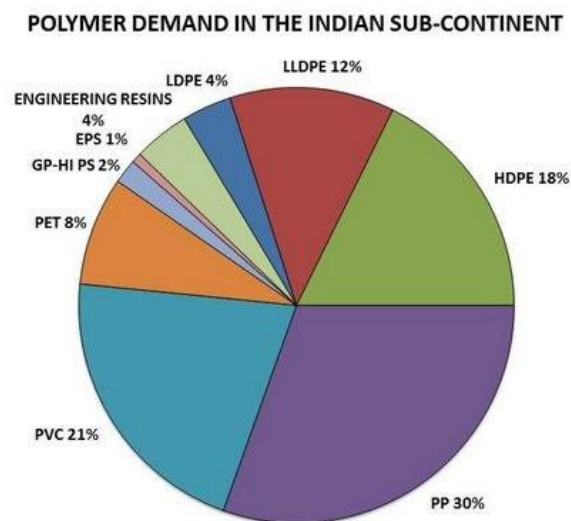
Figure no. 1.1: The polymer demand in the Indian sub-continent.

Polypropylene is one of the important thermoplastic polymers as it is light weight, excellent mechanical properties, good heat and chemical resistance. It is easily process able and economical, and have good impact resistance. Due to these better properties polypropylene is fastest growing thermoplastic in commodity and engineering applications. Polypropylene has a great potential for composite material, as it can be processed by conventional methods such as injection moulding, extrusion etc.

Polypropylene has excellent crystallization behaviour due to its regular chain structure. The most important industrial polypropylene is isotactic one. Isotactic polypropylene has been studied extensively for its polymorphic characteristics and crystallization behaviour since 1960 [NattaG.et al., 1960] and the results of these studies are reported in many publications [Binsbergen F. et al., 1968; Grozdanov A. et al., 1998; Zhou J.J et al., 2005], its crystalline structure influences the overall properties.

Polypropylene is a non-biodegradable thermoplastic. Due to the increased environment concern a new class of biodegradable polymer appeared produced from bio-material [Stevens E.S., 2002]. The biodegradables opened the way for new opportunities of waste management as these materials are designed to degrade itself, under environmental conditions.

Polypropylene has some disadvantageous like low toughness, low service temperature, low process ability due to high melt viscosity. These drawbacks can be overcome by combining other fillers to polypropylene to form composites.

1.1. Composites:

Composites materials are defined as the material consists of two or more phases/materials which when combined on macroscopic level gives a new material with enhanced

properties. Composites consist of two phases, matrix and reinforcements. Matrix is generally polymer which bonds, holds and protect the reinforcement. Reinforcement can be nano material or natural fibres which provides strength and toughness to the composite. On the basis of matrix materials composites can be classified as polymer matrix composite, metal matrix composite or ceramic matrix composite. The matrix of traditional polymer matrix composite consists of thermoplastic or thermoset polymers.

Thermoplastic composites are very much in use due to cost effective, improved mechanical properties and environmentally friendly. $CaCO_3$ as filler in thermoplastic reduces the production cost of moulded products. High filler content further can adversely affect the process ability, ductility and strength of composites. To enhance the durability and appearance of composites, additives such as elastomers, coupling agents, surface agents, ultra violet stabilizers and antioxidants may be added in the polymer composites.

Nano-materials are considered as potential filler materials for the nano composites based on synthetic or bio-based polymers [Njuguna J.et al., 2008]. In natural fibres composite, one or more materials obtained from natural resources are used. The ultimate property of natural fibres composite depends upon two factors, dispersion and adhesion of reinforcement within the matrix materials [Aftab A. et al., 2016].

The effects of additives on the crystallization of isotactic polypropylene have been well observed. The mineral filler like talc, $CaCO_3$, mica, pigments, dyes and carbon black etc. Many results are also reported on fibre reinforced composites [Kocsis J.K., 1995] which gives enhancement in material properties and cost saving possibilities.

Talc, mica and kaolin are used to enhance the stiffness and strength of filled polymers. The properties of polymer composites are determined by component properties (matrix and filler). In addition to the matrix /filler properties, the mechanical characteristics of these

materials are significantly influenced by inter facial interaction which depends on the size of the interface and strength of the interaction [Demjen Z.et al., 1998].

Fibrous filler can usually improve the tensile strength and plate like filler increases rigidity. Talc and kaolin are plate like filler. Filler with high specific surface area will contribute to more surface contact between the filler and matrix, herby increasing the mechanical properties of the composites.

Polypropylene is non- polar in nature, so it is chemically inert and does not interact with inorganic fillers, which results in poor filler dispersion and interfacial adhesion between polymers and filler. This problem can be overcome by compatibilization or oxidising the polymer. Polymer oxidation leads to the formation of polar groups in polymer and enhances the ability to mix with natural fibres having polar nature.

Maleic Anhydride grafted polypropylene mostly used as an adhesion modifier for polypropylene composite application. It changes the crystallization kinetics without changing spherulitic morphology of the polymer [Bogoeva G.et al., 2000]. Nucleating agents increase the crystallization temperature of the polymer, and reduces the crystallization time which gives shorter time cycle for injection moulding cycle [Sterzynski T. and Oysaed H., 2004; Dou Q., 2013].

Advantageous of filler in polymer

Reduction in composite cost, improve mechanical properties and improve physical properties. The driving force of the intercalation of polymer into clay galleries originates from the maleic anhydride group and oxygen groups of the silicate through hydrogen bonding. It was observed that low molecular weight of the maleated PP and high maleic

anhydride ratio of the maleated PP leads to better dispersion of the clay [Ray S.S. and Okamoto M., 2003; Hasegawa N. et al., 1998].

In addition to compatibilizer that improves mechanical and thermal properties of the composites, nowadays nano particles have received attention as filler for polymer composites to further increase the properties like mechanical and thermal. The addition of Nano –clay particles and compatibilizer in the composite produced from bamboo fibres and polyethylene polymer were studied by [Han G.et al., 2008] and concluded that the addition of 1% Nano clay increases the flexural elasticity modulus, dynamic elasticity modulus and thermal stability.

1.2.Nano Composites:

Nano originates from Greek word, and nano meter is one billionth (10^{-9}) of a meter. Various forms of nano materials are nano tubes (100nm), nano particle (50nm) and nano platelets (1nm). Different features of nano particles are their size, aspect ratio, specific surface area, volume, fraction used, compatibility with matrix and dispersion in the matrix composite, determine the performance of nano composite. Nano fillers are used to improve mechanical properties such as stiffness, strength of polymer composite. Nano composite have advantageous of light weight and surface finish over the conventional glass fibre composite. Nano particles into polymer enhance the mechanical stability and process ability. Nano fillers such as talc are effective at lower concentration. An improvement in modulus, dimensional and thermal stability achieved when nano fillers are less than 5% [Kotal M. and Bhowmick A.K., 2015].

Nano material is extensively used in polymer to enhance their properties as shown by number of review articles. Nano dimensions particles effects the transition zone between the macro-level and molecular level resulted in large modification in the properties of

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polymer nano composite materials [Paul D.R. and Robeson L.M., 2008; Alexandre M. and Dubois P., 2000; Ferreira J.A.M. et al., 2011].

The driving force for the increasing research work in the field of polymer Nano composites was the report from the Toyota research group in the 1990 of a Nylon-6/montmorillonite nano composites [Okada A. et al., 1990] for which very small amount of silicate loading resulted in large improvements of thermal and mechanical properties.

The improvement in different properties of Nano composites are related to the modifications of structure and dynamics of the polymer at and near the particle surface. Nano material increases the surface area to a great extent; this fraction of polymer contributes, significantly to the improvement of properties of the whole nano composite. In this respect, polymers nano composites are somehow similar to semi crystalline polymers where the crystals can be considered as nano fillers [Kawasumi M. et al., 1997].

In nanotechnology, polymer nano composites are defined as solids consisting of a mixture of two or more phase separated fillers, where one or more constituents phase is in Nano scale in a plyometric matrix. Materials can be referred to as nano scaled when their size, at least one of the dimensions lie in the range of 1nm to 100nm. [I.S.O. part4, 2011] it is a new class of multi-phase materials having dispersion of ultra-fine phase.

There are number of nanoparticle that has been used in Nano composite. These particles are divided in fibres (1D), platelets (2D) or particles (0D) depending upon the number of dimensions they display in nano scale [I.S.O. part2, 2015]. Performance of nano composite depends on various features of nanoparticle such as the size, specific surface area, aspect ratio, compatibility and dispersion in polymeric matrix.

The nanoparticle dispersion can be characterized by different states at nano, micro and macroscopic scales. For example, nano clay based composites can show three different types of morphology; immiscible, intercalated or exfoliated (miscible) composites. Good exfoliation of nano particles is the desired aim of the formation process. Exfoliation is the process of separation of platelets from one another in a homogenised way in the polymer matrix [Paul D.R. and Robeson L.M., 2008].

The stresses imposed during melt mixing break up aggregates of platelets and shear the stack into smaller one. By providing sufficient time in the mixing device all the platelets will be dispersed uniformly in the polymer matrix. The type of the extruder and the screw configuration are important to achieve good dispersion, more residence time in the extruder gives better dispersion. [Dennis H.R. et al., 2001].

Nano composites are prepared by adding sufficient nanoparticles to polymer matrix to improve its performance due to the nature and properties of the nano scaled particles. This produces high performance composites when good dispersion of the particles is achieved then the properties of the nano scale particles are better than those of the polymer matrix [Kamigaito O., 1991].

Nanoparticles are used in polymer matrix to enhance mechanical properties like strength and stiffness by reinforcement mechanism. It is proved that properly dispersed and aligned clay particles are very effective to improve stiffness of polymer matrix [Fornes T. and Paul D., 2003].The modifications of mechanical properties of the polymer matrix with clay seems to be a proper way due to their ability to act as a nucleating agent, clay particles may induces changes in crystallinity of the polymer matrix like PA6 or polypropylene [Hunter D.L.et al., 2007; Hotta S. and Paul D., 2004].

Talc qualifies as good reinforcement filler alternate to clay because it is layered mineral with a high aspect ratio (particle diameter/thickness ratio is 20:1), this is due to its plate type structure having micron sized dimensions on length and width with nano metric thickness. The effects of talc on polymer have been well studied. It was demonstrated that talc improves mechanical properties and macromolecules orientation of polypropylene [Castillo L.et al., 2013]. As filler talc may be used from 20 to 40 % by weight. And when it is used below 3 % by weight it is considered as nucleating agent and also helps in shortening the process time. Talc has unique reinforcing features as softness, lubricity, good wetting and dispersion in polymer.

The talc tends to agglomerate at higher filler contents so more amount of talc decreases the strength and toughness of nano composite. For uniform distribution of nano fillers we used melt intercalation method, as it is the most preferable due to its technical viability, versatility, economical and good compatibility with the polymer processing techniques. Well dispersed and exfoliated nano composite have excellent thermo mechanical, dimension stability, barrier properties, flame retardency, and heat distortion temperature, chemical resistance, low specific gravity etc.

Thermal properties can be improved by applying fire retardants during processing process or at the stage of finishing or by using non-flammable binders, resins or polymers and the addition of nanoparticles to the composite [Vaisanen T. et al., 2017].

Carbon Nanotube is stronger than steel, lighter than aluminium and highly conductive than copper. CNT are the long cylinders of covalently bonded carbon atoms, carbon nano tubes have excellent intrinsic properties, their production process are efficient and availability at low costs. Graphene is the most emerging advanced multifunctional nanomaterial. It can be prepared by chemical vapour deposition.

[Jordan J. et al., 2005] concluded in their review about nano composites that the elastic modulus in nano composites seems not to be dependent on interaction between the filler and the polymer, whereas the addition of nanoparticles with poor interaction with the matrix results in decrease of yield stress, yield strain and ultimate stress compared to the neat matrix.

Amount of nano particle limited to low level as high levels of nano particles results in retardation of the crystallization rate. High level of nano particles results in diffusion constraints which result in retardation of the crystallization [Li L. et al., 2007; Wu D. et al., 2005; Kim B.et al., 2004].

Incorporation of nano particles into polymer significantly affects the properties of the polymer matrix. Nano composite exhibit improved thermal, mechanical and fire retardancy properties, more dent and scratch- resistant, more recyclable. The properties of polymer composite depend upon the type of nano particle, their size, concentration and shape. The main problem with polymer nano composite is the agglomeration of nano particles due to their specific area and volume. To overcome this problem modification of the surface of nano particles is required. The modification improves the interfacial interactions between the nano particles and polymer matrix. The surface modification of reinforcement is done by grafting polymeric molecules, through covalent bonding to the hydroxyl groups. Grafting method is desirable due to the availability of numerous grafting monomers and the choice of grafting conditions [Kango S. et al., 2013].

The nanometre size produces huge and vast specific surface area, and also has tendency to improve properties of the materials into which they are incorporated. Nano fillers are incorporated in polymer from 1% to 10 % (in mass) [Marquis D.M. et al., 2011]. Nanoparticles produce high surface area which is homogeneous with fewer defects and

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with improved properties. Polymer /layered nano composite (talc) can be classified in three categories – Intercalated, Flocculated, Exfoliated [Ray S.S. and Okamoto M., 2003; Wypych F.et al., 2005].

1.3.Composites with Natural Fibres:

Natural fibres reinforced thermoplastics are also entering the global market of composite materials. Natural fibre composites consist of bio degradable or easily recyclable polymer and different natural fibres reinforcement. [Zini E. and Scandola M., 2011; Bogoeva G. et al., 2007].

Natural plant fibres, such as flax, hemp, kenaf, are renewable in nature, alternative to traditional glass fibre reinforcement, due to increased concern about environment and energy saving attitude. The lower density of natural fibres as compared to higher density of glass fibres helps in to produce lightweight structures especially in automobile sector which is a desired point for automobile sector. Further natural fibres have high specific modulus as compared to glass fibres.

In composite material polypropylene takes an important role since its recyclability represents an advantage from energy saving point of view. It has been demonstrated that the PP/natural fibre composite have the potential to replace PP/glass fibre composite [Joshi S.V. et al., 2004; Barkola N.M. et al., 2010; Shubhra Q.T.H. et al., 2013; Shah D., 2013; Koronis G.A. et al., 2013; Faruk et al., 2012; Mohanty A.K. et al., 2000].

The future research on natural fibres reinforced polypropylene composites mainly focused on a cost effective modification of natural fibres. The report related to the comparison of life cycle assessment of natural fibre composite with glass fibre reinforced composite, have found that natural fibre composites are superior in the specific automobile applications

due to their low density and easily recyclability [Ku H. et al., 2011; Shazad A., 2012; SanzMirabal A. et al., 2013]. Non-renewable energy requirement for production of glass fibre and flax fibre were studied in details and results shows that glass fibre production requires 5-6 times more non-renewable energy than natural fibre production [Diener J. et al., 1999].

The main components of plant fibre: Cellulose: is a linear homopolymer consisting of D-glucopyranose units linked together by glycosidic bonds. The large amount of hydroxyl groups in cellulose induces hydrophilic properties in natural fibres. Hemicellulose: are heterogeneous group of polysaccharides consisting of 5- and 6- rings polysaccharides. Lignin: is a phenolic compound and acts as binder. It contains hydroxyl, methoxyl and carbonyl groups. It is hydrophobic and amorphous. Chemical composition of natural fibres is shown in Table 1.1.

Table 1.1. The compositions of various fibres [Hulle A. et al., 2015].

Fibre	Cellulose	Hemi-Cellulose	Lignin	Wax
Sisal	66-78	10-14	10-14	02
Hemp	70-74	17.9-22.4	3.7-5.7	0.8
Flax	71-74	18.6-20.6	2.2-4.2	1.7
Jute	61-71.5	13.6-20.4	12-13	0.5
Agave	68-80	15-17	5-17	0.3

1.3.1. Types of Natural Fibres:

Various types of fibres based upon their origin i.e. bast, stalk, leaf and seed

Bast fibre: Bast fibres are collected from the inner bark or bast surrounding the stem of the plant i.e.

Flax, hemp, jute, kenaf, ramie,

Stalk Fibre: stalk fibre are rice, corn, wheat,

Leaf Fibre: are like pineapple leaf, sisal, agave Americana, abaca

Seed Fibre: are like coir, oil palm, kapok, cotton

Factors on which quality of fibre depends are type of plant, part of plant, local climate process, type of fibre extraction, supply & storage conditions and age of fibres [Dittenber D.B. et al., 2012].

1.3.2. Properties of Fibres:

Tenacity- it is the ability of the fibre to possess adequate strength. It also represents the materials resistance to the propagation of crack. Some fibres lose their tenacity when wet.

Flexibility- is the ability of the fibres to bend easily without breaking.

Colour- of fibre varies from pure white to deep grey, tan and black.

Natural fibre exhibit superior mechanical properties, such as stiffness, tensile and compressive strength compared with synthetic fibres like glass fibres. These natural fibres offers some more added advantageous are biodegradability, easy availability from nature, low cost, produces less CO_2 emission due to low energy consumption during their processing, non-abrasive to the equipment, less health hazard, renewability and recyclability. An environmental impact of natural fibre production produces less emission when compared to glass fibre production. For natural fibre production various emissions like carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen dioxide, and particulate

matter are much lower as compare to glass fibre production [Corbiere N.T. et al., 2001]. Polypropylene production requires about 20 times more energy (MJ/Kg) than natural fibres production and emissions to environment are also on higher side. Hence substitution of base polymer by high fraction of natural fibres will improve the environmental performance of the natural fibre reinforced composites [Joshi S.V. et al., 2004]. Hence natural fibres improve the green credential of the final composite.

1.3.3. Fibres Extraction by Retting Process:

Retting is the main and maximum used techniques which involves with extraction of fibres by natural microbial process. This process takes about three weeks in natural form without using the help of synthetic fibres. Retting process must be observed carefully as over retting decreases the quality of fibre and under retting process extraction of fibre is difficult due to presence of gummy matter such as pectin. Agave fibre have average diameter 3.1 micron and it is very small as compared to fibres like flax, sisal and Alfa. The colour of Agave Americana fibre ranges from milky white to golden yellow.

Fibres extracted from plants vary in lengths. For better processing fibres must be short as the longer fibres faces difficulty in homogeneous mixing and have higher chances to block or plug the dosing equipment. Short fibres are generally defined as fibres having length less than 1 cm. Very short fibres are about 1 mm size .Fibres are processed using melt mixing methods such as high speed mixers, single or twin screw extruders to disperse the fibre within the polymer matrix. According to the fibre reinforcement theory, the longer fibres have better strength of the composite, while shorter fibres have better dispersion during processing. During processing, morphology of fibres changes due to decreased fibre diameter, length in injection moulding [Bourmand A. and Baley C., 2010]. After mixing the final product is known as compound. To get desired mechanical properties after

processing adhesion between the fibre and matrix, and well distribution and dispersion are the top priority.

1.3.4. Different types of Chemical Treatments for fibres:

To have good adhesion with polymer fibres are pre-treated to removes certain amounts of lignin, wax and oils from the external surface of fibres. Treatment of fibre can be done by physical or chemical methods. In physical method, surface properties of the fibre changes, without changing chemical composition or structure of fibre. Physical methods consists of, sputtering, steam explosion, calendaring, stretching, plasma, UV, gamma rays etc. Chemical methods consist of alkali treatment, etherification, esterification, splenisation, mercerization, graft copolymerization, cynate treatment etc. Chemical modification improves the adhesion properties through generation of reactive functional groups on fibres [George J. et al., 2001].

Alkali Treatment: Crushed fibres washed with plenty of water and kept in 1.6mol/l sodium hydroxide aqueous solution for 48 hours. After 48 hours fibres removed from NaOH solution and then treated with acetic acid to neutralise effect of remaining hydroxide. After this these fibres left for air drying for 24 hours. In this process lignin waxes and resin removed from fibres external surface [Le Troedec M. et al., 2008; Le Troedec M. et al., 2011; Ku H.et al., 2011]. Alkali treatment of natural fibres increases the surface roughness which results to form new hydrogen bonds between the cellulose, further this treatment may increase the amount of cellulose exposed on the fibre surface [Essabir H. et al., 2016].

Ether Treatment: Solution of fibres (5g) and NaOH (20ml) in isopropanol mixed with 3 ml of Dodecanebromide. This mixture was stirred at 23°C for 12 hours. Fibres were recovered by filtration and then washed with isopropanol and ethyl ether and kept for drying, 12 hours at 50°C.

Ester Treatment: Fibres (2g) were added to CH_2Cl_2 (40ml) under stirring condition. Palmitic acid N-succinimidyl ester (0.30gm) then added as solid and mixture was stirred for 5 hours .Fibres were recovered by filtration , washed thoroughly with CH_2Cl_2 and then dried up under reduced pressure [Arrakhiz F.Z. et al., 2012].

Silane Treatment: After detergent washing, fibres were treated with 5%NaOH solution for 0.5hr then soaked in 2.5% aminopropyltriethoxysilane coupling agent for 0.5 hr. by maintaining the pH value between 3.5 and 4.0, washed with distilled water and dried overnight at $60^{\circ}C$.

Potassium permagnate treatment: After washing fibres with 2%NaOH solution for 1 hr., then treated with 0.2% potassium permagnate solution (in 2% acetone) for 10-30 min. Then the fibres were placed into thermostatic water bath at 50 $^{\circ}C$ for 2 hrs. Washing is done with distilled water and air dried for 24 hrs. [Li X. et al., 2009].

Fibre surface modification help to reduce the hydroxyl groups in the cell wall of cellulose, thus decreasing the ability to absorb the moisture absorption of composites.

Natural fibre filled polymer composite are cheaper and biodegradable, despite these advantageous natural fibre has low compatibility with polypropylene. To overcome this disadvantage and to improve the surface characteristics of the composite, the application of compatabilizer is suggested, Compatibilizer is a compound used as coupling agent to improve compatibility between polymer matrix and natural fibre. Oxidized polypropylene or maleic anhydride grafted polypropylene can be used as compatibilizer.

1.4. Compatibilization:

It is a chemical coupling method, and performed after alkali treatment in this process fibre is treated with a coupling agent who has a polar head and a non- polar hydrocarbon head

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which forms chemical bond between fibre and matrix .It improves the interfacial bonding .Maleic Anhydride is the most common coupling agent.

Maleic Anhydride modified the polymer matrix by providing the polar interaction to the hydroxyl groups of the cellulose and hence increased the composite strength and modulus.

Environmental issues increased the demand for environmental friendly products which are reinforced with biomaterials. Consumer industry looking for these new materials as their disposal is friendly to the atmosphere and saves lot of energy. At the end of their life cycle they can be disposed of without harming the environment. Natural fibres reinforcement is also preferred due to low energy consumption during their growth and processing. High cellulose content makes them easily biodegradable and recyclable [Wambua P. et al., 2003]. Composites derived from natural fibres are more ecological and less health hazardous for worker employed in producing it, when compared with composites of synthetic fibres [Jawaid M.et al., 2011].

Natural fibres reinforced polymer composites performance is influenced by various factors such as physical and chemical composition of fibres and fibres interaction with the polymer matrix [Kalia S. et al., 2009]. The development of natural fibre reinforced composite depends upon surface adhesion of fibres, thermal stability of fibres and good dispersion of the fibres within the composite [Saheb D.N. and Jog J.P., 1999]. Chemical modification or pre-treatment of the fibres is done to achieve the above said points. The manufacturing and processing of composite at high temperature can lead to degradation of natural fibre which results in unfavourable properties [Majeed K. et al., 2013].

Natural fibres polymer composite have advantageous of less toxicity, reduced effluent emission, improved safety during processing, less abrasive to machine tools causing less

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wear and tear, less energy consumption and lot of disposal options at end of life cycle [Patel M. et al., 2005].

Due to all these factors future of natural fibres composite is very promising from industrial point of view. Further work should focus on achieving equivalent or superior mechanical and thermal properties. Other factor which gives rise in demand for natural fibre polymeric composites are as follows:

- Rise in environmental awareness

- Political incentives

- Decreasing crude oil resources

- Low cost and easy availability   [Vaisanen T. et al., 2017]

Challenges with Natural Fibres Polymer Composite:

- Hydrophilic nature of natural fibre adversely affects the water absorption behaviour of composite

- Limited thermal stability results in polymer materials with low melting point

- Agglomeration of fibres which leads to decrease the mechanical performance

- Adhesion between the polymer and fibre

- Increased fibre content results in high viscosity of composite which decelerates the processing speed and makes difficult to produce uniform products.

- Moisture content of the fibre has a critical effect on the quality of final product as evaporation of water gives to bubbles formation and increases the porosity of the composite.

- Quality of fibre is not consistent for physical properties

- Properties of fibre can vary from season to season or on region of cultivation

- Storage problem cannot be stored for longer time as they have low microbial resistance[Vaisanen T. et al., 2017]

Natural fibres as fillers have some limitations as mentioned above which makes them unsuitable for advanced applications, which leads to more studies in combining the natural fibres with other fillers to overcome these limitations. Natural fibres are susceptible to degradation depending on individual constituents i.e. lignin is mainly responsible for UV and fire degradation, hemicellulose is responsible for biological degradation, thermal degradation and moisture absorption [Azwa Z.et al., 2013; Marques A.R.et al., 2014].

Natural fibres have degradation tendency due to biological, chemical, mechanical, thermal, photochemical and aqueous depending on the surroundings and environment to which they are exposed during their service [Azwa Z.et al., 2013; Marques A.R. et al., 2014]. Biological degradation is affected by the matrix and interfacial treatment and loss of interfacial strength is the indication for biological degradation [Terzi E.et al., 2018].

The above mentioned drawbacks of natural fibres can be overcome by combining various processes of chemical modification of fibres, efficient processing techniques and matrix modification by blending as elaborated by Figure no. 1.2.
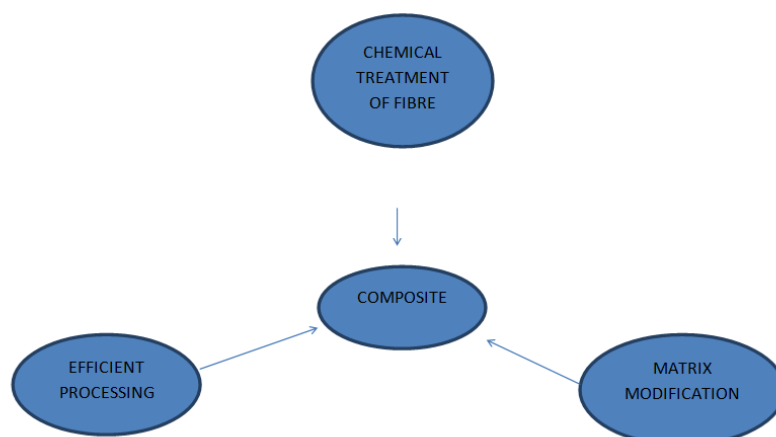
Figure 1.2: Elaborating various steps to get quality hybrid composite

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To get the hybrid composite of desired properties. Plant based materials are beneficial from various points as they processes various qualities like sustainable, environmental friendly, economically which leads to reduction in carbon dioxide emissions, reduced vehicle weight as they are lighter, lower manufacturing costs, reduced pressure on natural fossil resources, keeping waste out of landfill (easy degradation) and creation of new market and revenue streams for farming sector [John N. and Thomas S., 2008; Ford Company Report, 2015].

[Wortzel K. et al., 1999] Studied the cumulative energy use and emission for glass fibre reinforced composite and natural fibre reinforced composite and concluded, that natural fibre composites uses 45% less energy as compared to glass fibre composite and emissions like carbon dioxide, methane, sulphur dioxide, carbon monoxide are also on lower side.

[Corbiere N. T. et al., 2001] concluded that glass fibre production requires 5 times more non-renewable energy than natural fibres production. They also showed that pollutant emissions from glass fibre production are much higher than from natural fibre production. Natural fibre reinforced composite are 20 to 30% lighter than glass fibre reinforced composite which leads to more use in automobile which leads to higher efficiency and reduces emissions subsequently.

[Torres J.P. et al., 2017] observed that length of fibre affect the stability of the composite as the long fibres composites have less scatter on mechanical properties than short fibres composite. Fibres have much higher strength than that of the matrix.

[Arrakhiz F.Z. et al., 2013] observed that addition of any fibre gives higher young's modulus of the composite when compared to neat polypropylene. A linear increase in young's modulus observed with increased fibre content. This is due to high fibres tensile modulus compared to neat polypropylene.

1.5. HYBRID COMPOSITES

In hybrid composites we reinforced polymer matrix with natural fibre and nano material for getting enhanced mechanical and thermal properties. Hybrid is defined as a material that includes two moieties blended well on the molecular level.

A combination of two or more reinforcements results in Hybrid composites. Hybrid composites have combined properties of all the individual reinforcements in an enhanced way. The properties of hybrid composite are a weighed sum of the individual fillers and also governed by fibre to matrix bonding.

Hybrid polymer composite material offers the opportunity to obtain the desired characteristics in a controlled way by the choice of suitable fibres or fillers and polymer matrix. Hybrid composite are popular due to their capability of providing freedom of tailoring composites as per requirement and achieving properties that cannot be attained by composites having only one type of reinforcement [Kumar R. et al., 2015]. Another target of the composite hybridization is to reduce the price of the composite. Hybridisation gives products with a suitable balance of properties. Degree of crystalline generally increased in the presence of two types of fibres as they caused a reduction of melting temperature due to heterogeneous nucleation promoted by these fibres [Perez C.J.et al., 2007].

Over the time there has been an ever increasing trend to incorporate two or more fillers into a polymer matrix and number of published works based on hybrid composite also steadily increase since 2013. Top ten countries which are most active in hybrid composites are China followed by India and USA as shown in Figure 1.3.
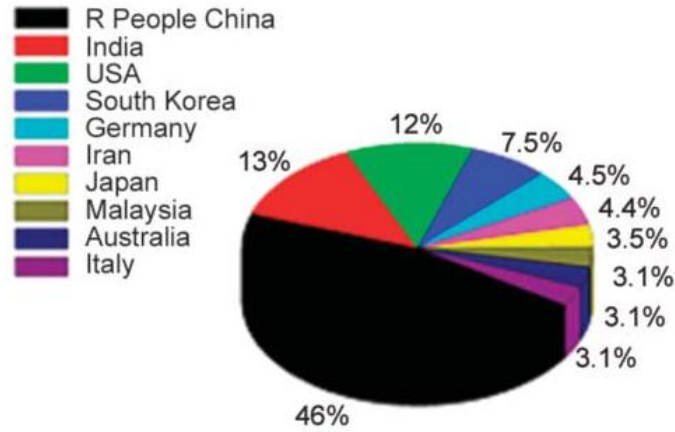
Figure 1.3: Countries wise consumption of hybrid composites

The aim of two or more fillers into a polymer matrix , to ensure that they can learn from each other and match in coordination to give excellent properties at overall low cost. The positive hybrid effect can be explained as better performance obtained from hybridized composites as compared to single reinforced composite. Hybridization offers a new scope to broaden the use of the composites materials in advanced applications. The desired properties can be predicted by using the rule of mixture equation by assuming that there is no chemical/physical interaction between the fillers [Saba N. et al., 2016; Castellanos W.R. et al., 2016].

$$PH=PC_1 \ VC_1+PC_2 \ VC_2$$

Where PH= Resulting properties of hybrid composite

PC_1, PC_2 are properties of respective constituents and

VC_1, VC_2 are volume fraction of respective constituents and

$$VC_1+VC_2=1$$

Natural fibre composite are available at low cost and their friendly environment character, are the main reasons for an increase in interest in their development. Further the natural fibres hybrids composite are recyclable and biodegradable [Taj S. et al., 2007], but as natural fibres are flammable which restrict their various applications. Flame retardants and nano particles can be reinforced into the polymer matrix to enhance flame resistance of hybrid composites. Introduction of flame retardants materials adversely affects the mechanical properties of the composite [El-Sabbagh A. et al., 2016].

1.5.1. Properties of Hybrid Composites:

Mechanical properties of hybrid composites depends strongly on the filler morphology, filler content, dispersion / distribution of filler material into matrix and filler/matrix adhesion, length of individual fibres and fibre orientation, large surface area, high aspect ratio, mechanical properties of fillers, effect of modification [Bisaria H.et al., 2015; Gupta M.K. and Srivastava R.K., 2015; Kureemun U. et al., 2018; Shanmugam D. and Thiruchitrambalam M., 2013; Ramana M.V. and Ramprasad S., 2017]. The quality of hybrid composite is determined by the mechanical, physical and chemical stability of filler/matrix composite. Fillers dispersion into hybrid polymer matrix is an indication of the relatively homogeneous nature of composite. In case of two or more reinforcements, advantage of one filler can complement the disadvantage of filler and thus enhance the properties of the hybrid composite.

There is great expectation from the eco-friendly products in the coming years, to save the energy and environment. We are trying to have new materials with green engineering approaches. These new materials have better wear resistance. Natural fibre filled polymer hybrid composite are fourth generation of the composites since early 1990.

The main criteria for success of eco-friendly sustainable composites based on three features, which are technical criteria of the composite consisting of tensile strength, flexural strength and impact strength to make them fit for engineering applications, environmental effect of composite and economical value of composite, as the majority of the bio composites are inexpensive the cost of hybrid composite will also be economical.

To improve the mechanical properties of natural fibre based hybrid composite nano clay materials are commonly selected for their dimension and high aspect ratio in most of the research work [Babaei I.et al., 2014; Saba N. et al., 2014].

The Hybrid composite with natural fibres reduces health risk and environmental hazard problems as compared to composite based on synthetic fibres as they are characterized by higher pollutant emissions. The low stiffness and strength of polymer can be improved with reinforcement of stiffer and stronger fibres in polymer matrix composite. Addition of fibres increases the tensile modulus, hardness, flexural strength and flexural modulus and decreases the ultimate tensile strength of the matrix.

Application of hybrid polymer composites:

Used in aerospace due to improved strength, durability, corrosion resistance, wears resistance.

Used in chemical industry for producing structural supports, storage tanks, exhaust stacks, blowers, pumps, reactors etc. for tough environment.

Increased use in automobile industry due to light weight, high durability and corrosion resistance, used commonly for interior-exterior panels, gas tanks and bumpers.

Construction Industry- structural panels, building sections due to long lasting, scratch resistant properties.

For producing artificial body parts.

Light weight structural parts, like wind turbine blades, carbon and glass fibres hybrid are the most used fillers for turbine blades.

For ballistic and armour application, natural fibres combined with synthetic fibre hybrids are more suitable for such application due to better impact properties.

Polymer hybrid composites are the future material for packaging industry [El-Wazery M.S., 2017; Dorez G. et al., 2014; Szolnoki B. et al., 2015].

1.6 Objective and Scope of Present Research Work:

The present research work entitled **"Study on Hybrid Composites Reinforced with Nanomaterial, Natural Fibres and Bio-material"** involves with the synthesis of hybrid composite of polypropylene as matrix and natural fibres (Agave Americana), nano-material (nano talc) and bio-material (potato starch) all together as reinforcements. The utmost challenge in the synthesis of hybrid composite is the effective uniform dispersion and adhesion of reinforcement materials with polypropylene matrix. Attempts have been made to synthesize the hybrid composite using various combinations of natural fibre (Agave Americana), nano talc and starch as filler materials. Natural fibres are alkali treated for good adhesion with polymer matrix. Maleic Anhydride grafted polypropylene used as compatibilizer. Hybrid composite produced by melt compounding method on co-rotating twin screw extruder to achieve the uniform dispersion of filler materials within the polypropylene matrix.

The main objectives of this research work are:

1. The main objective of this research work is to reduce the dependency on fossil fuels and hybrid composite development based on renewable and sustainable resources.

2. To synthesizes and optimize the composition of potato starch, nano talc and Agave Americana in hybrid composites based on polypropylene.

3. Studies on mechanical properties to optimize potato starch, nano talc and Agave Americana hybrid composites based on polypropylene.

4. Studies on the effect of content of potato starch, nano talc and Agave Americana hybrid composites based on polypropylene.

5. Study of tensile, flexural, impact and % elongation, thermal properties, morphology etc. of potato starch, nano talc and Agave Americana hybrid composites based on polypropylene.

The prepared hybrid composites have been evaluated for existing applications of bio-based materials in sectors like automotive/ household/ construction/ packaging. The following characterization techniques will be used to establish the findings of this research work:

1. Physio-chemical properties: FTIR

2. Mechanical properties: Tensile strength, Flexural Properties, Impact Properties, %Elongation as per international accepted ASTM Standard

3. Melt Flow Index as per international accepted ASTM Standard.

4. Crystallization Behaviour: DSC, XRD

5. Thermal Studies: HDT & VST

6. XRD

7. SEM

CHAPTER 2

LITERATURE REVIEW:

Hybrid composites are the emerging class of mineral filled polymers that contain small amounts of nano sized inorganic particles. This new class of composite are now an active area of research due to its improved physical, mechanical and thermal properties. Further polymers can be modified by reinforcing natural fibres to suit the high strength requirements. The fibres have various advantages like high specific strength and modulus, low cost, low density, renewable, environmental friendly, wide availability and relative non abrasiveness. In order to improve adhesion between natural fibres and polymer material several fibre surface modification processes have been reported in the literature. A versatile literature review is done before starting the experimental work.

[Liu X. and Wu Q., 2002] studied the mechanical performance of Polyactide 66(PA66) nano composite and found that the tensile strength increased rapidly from 78 MPa for PA66 to 98 MPa for Polyactide 66-clay nano composite (PA66CN), but the magnitude of this increase value diminished when the clay content was above 5%.

[Alshabanat M., 2013] studied the mechanical properties of intercalated talc and polypropylene nano composite and observed that best mechanical properties were obtained at talc content of 10 %. During observation it was found that impact strength of pure polypropylene was 23J/m as compared to talc filled polypropylene was 31.7J/m. They also observed that yield stress also increases from 35 MPa to 39 MPa. Results indicated that composite became tougher and stronger but at the same time it became brittle.

[Shahinur S. and Hasan M., 2021] discussed about various fibre-reinforced polymer composites with different sustainable features, which are technical criteria of composite,

environmental effects of composites and economical value of composites .Features for environmental criteria are water usage, recycle factor, CO_2 emission, cost, availability and health impact.

[Karim M.R.A. et al., 2020] discussed that natural fibres as reinforcement have no harmful impact on the environment and economical also. Interfacial strength between fibres and matrix can be improved by some chemical modification of fibre surface which improves the adhesion between fibre and matrix, with these benefits of natural fibres manufacturers as well as end users switch over to natural fibre based products.

[Ammar O. et al.,2017] studied the thermal properties of polypropylene/talc and found that melting temperature remain unchanged at 165°C, but crystallization temp increased from 120°C to 128°C, indicating that talc is a good nucleating agent, they also observed 100 % increase in elastic modulus value of composite. However the ultimate elongation decreases with the addition of talc from 63% to 10%. Therefore addition of talc reduces the ductility and material became brittle.

[Nafchi H.R. et al., 2015] studied the effects of oxidized polypropylene as a compatibilizer and nano clay particles and concluded that by using oxidized polypropylene thermal properties of the composite improved and releases less energy during thermal degradation and shows more thermal resistance and stability.

[Han G. et al., 2008] studied the composite of bamboo fibre, polyethylene polymer with nano clay particles and found that the addition of 1% nano clay increases the flexural elasticity modulus, dynamic elastic modulus and thermal stability.

Nano composites based on polypropylene and clay modified with two organosilanes as nano filler promoted the covalent bonding between polymer and clay. Nano filler used at

different concentration (1-5 wt %). Resulted in enhanced mechanical characteristics due to better adhesion between the polypropylene and clay, with better spatial dispersion-distribution of these two [Raji M. et al., 2018].

The hybrid composite properties are characterized by using various tests such as: SEM to know about morphology of the composite which give an indication of relatively homogeneous nature of the composite. FTIR illustrates the chemical structural properties and also shows the interaction between the various filler constituents. The mechanical properties are tested by tensile, flexural and impact testing on UTM and impact tester.

The thermal stability of hybrid composite is determined by using TGA. The initial weight loss in the range 100-200°C may be due to the evaporation of water contained in the natural fibre. The thermal decomposition of all natural fibres consist of following steps: hemicellulose degradation in temp range 180-310°C, cellulose decomposition in temperature range 320-340°C, lignin degradation at temperature range 440-480°C. The variation of the thermal degradation peak temperature is due to the variation of the composition of the natural fibres which depends upon season, part of plant, maturity of plant [Essabir H. et al., 2016].

Thermal decomposition and degradation starts at different temperature for differently treated and filled composites. Pure polymers decomposition and degradation starts at 220°C whereas the sample with compatibilizer starts degraded at 270°C, and the same sample with compatbilizer and nano filled particles starts degradation at 300-320°C. Which shows that thermal stability increases with compatibilization and nano particles [Reisi H. et al., 2015].

[Reddy B.M. et al., 2021] developed hybrid composites of cordiadichotoma fibre (20 wt %) with variable amount of granite powder (0, 5, 10, 15 and 20 wt %) and observed that

good filler material (granite powder) enhanced the mechanical properties of composites further filler reduced the water absorption and chemical resistance. Composite is thermally stable up to 430^{0}C.

[Essabir H.et al., 2013] observed that tensile strength of the PP/Doum fibre properly compatibilized with (SEBS-g-MA) improved by 18% as compared to neat PP and achieved a maximum value 28.66 MPa at fibre content 10 wt% with increase of fibre content, tensile strength decreases, whereas tensile modulus improved by 77% as compared to neat PP but at higher fibre content (30 wt %). The degradation temperatures of neat polypropylene increased with fibre content and further increased for chemically treated fibres. The thermal stability increases from 351°C for polypropylene to 360-380°C for Doum /polypropylene and further increased for malic anhydride compatibilized composite to 363 – 400°C.

[Laachachi A. et al., 2005] observed the phenomena of improvement in thermal stability of PMMA/oxide nano composites by reinforcement from ferric oxide zinc oxide nano particles.

[Guo Z. et al., 2009] reported that the thermal stability and decomposition temperature of Fe_2O_3/polypyrol nano composites increased slightly with increasing content of nano particles.

[Horroch A. and Kandola R., 2005] concluded that improved compatibility between the polymer and fibres, enhanced the thermal stability of the composite.

[Song P. et al., 2012] observed that there is a linear relation between the gas permeability, viscoelasticity and flammability performance for polymer nano composite.

[Hotta S. and Paul D.R., 2004] evaluated for the nano composites derived from the organoclays, both melt viscosity and melt tension increased with increased content of clay and linear low density polyethylene grafted maleic anhydride, and gas permeability decreased by the addition of clay.

[Costache M.C. et al., 2006] observed that addition of nano clay fillers increase the thermal degradation temperature and reduce heat release rate. This is due to intercalation structure and creation of barrier structure in composite.

[Arrakhiz F.Z. et al., 2012] studied that tensile strength of alfa fibre/PP decreased by great extent as compared to neat polypropylene, but at the same time reported extensive enhancement Youngs Modulus value, i.e. twice the modulus of neat polypropylene.

[Essabir H. et al., 2016] observed that tensile strength of composite decrease by 8-9% as compared to neat polypropylene, as natural fibre act as defect point under tensile testing. Whereas 20% fibre content composite have maximum Youngs Modulus increased from 1034 MPa to 1650 MPa.

[Sarkar M.C. et al., 2008] observed that polypropylene/clay composite with bentonite with 5 wt % tensile strength improved by 14% and toughness improved by 80%.They also observed that high clay wt % give inferior mechanical properties due to agglomeration and less interaction between clay and matrix.

[Ma X. et al., 2005] studied the effect of fibre contents on the Youngs Modulus of micro winceyette fibre reinforced thermoplastic corn starch composite from 0% to 20 wt %, and find that Youngs Modulus improved three times from 40 MPa to 140MPa.

[Leong Y.W. et al., 2004] observed that for talc filled polypropylene, tensile modulus significantly improved lineally with filler load and maximum up to 0.15 of volume

fraction. They also observed the effect of talc is best as compare to other filler kaolin and CaCO$_3$. Increase in the tensile strength was observed for talc up to maximum at volume fraction 0.12 after which tensile strength decreased.

[Post W. et al., 2021] studied the effect of various fillers (talc, calcium carbonate, kaolin and mica) with biodegradable polymers. Fillers enhanced the mechanical properties of composites and at the same time filler into biodegradable polymers does not hamper the microbial disintegration of these polymers.

[Husein D.A. et al., 2013] observed that polypropylene clay nano composite with addition of 2% and 5% of clay improves the strength and modulus substantially and also improves the scratch resistance properties of the polypropylene.

[Elkhaoulani A. et al., 2013] studied the polymer composite based with hemp fibres and polypropylene, and found that Youngs Modullus reached maximum value 1796 MPa at 20 wt % hemp fibres for compatibilized composite, whereas tensile strength reached 29.5 MPa at 10 wt % hemp fibre while pure PP tensile strength was 24.2 MPa.

[Arrakhiz F.Z. et al., 2012] evaluated the mechanical properties of pine cone fibres reinforced compatibilized polypropylene and observed a gain of 43% and 49% in Youngs Modulus for alkali treated pine cone and pine cone compatibilized with maleic anhydride respectively.

[Begum S. et al., 2021] reviewed that multiple natural fibres reinforcement has lot of potential to fabricate hybrid composites. Further natural fibres are gaining attention over synthetic fibres for reinforcing due to their bio-renewable and eco-friendly behaviour.

[Wambua P. et al., 2003] studied the hybrid composite of sisal, kenaf, hemp, jute and coir fibres in polypropylene and observed that hemp fibres composite displayed the highest

tensile strength while coir has the lowest. Hemp composite also showed the best flexural strength at 54 MPa and it is comparable with glass fibre composite (60MPa)

[Singla A.S. and Thakur V.K., 2008] studied the reinforcement the matrix with the fibres at three levels, like size of particles, short fibre and long fibre. They observed that composite with particle reinforcement shows high tensile properties followed by short and long fibres.

[Mark U.C. et al., 2019] studied the effect of carbonized coconut shell particles from (0-40 wt %) of various sizes and concluded that the reinforced polypropylene composites have enhanced mechanical properties like yield strength, tensile strength, tensile modulus, flexural strength and hardness in proportion to increased amount of filler, however the elongation at break and modulus of resilience decreased with increase of filler loading.

[Gao H. et al., 2012] observed that composite based on polypropylene/polyethylene grafted with maleic anhydride improved the tensile, flexural and impact strength of composite by 216%, 120% and 62.7% respectively relative to unmodified PP/PE composite

[Trinh B.M. et al., 2020] investigated the properties of their structured wood-fibres-polylactic acid bio-composites as well as the effect of modifying polylactic acid through the grafting of maleic anhydride, and observed that grafting of maleic anhydride on polylactic acid increased the hydrophilicity of polylactic acid, which resulted in better interaction with the wood fibre and leads to improved mechanical, thermo-mechanical properties.

[Evora V.M.F. and Shukla A., 2003] observed that the nano composite containing 1, 2 and 3 vol% TiO_2 gives excellent particle dispersion stability. Whereas agglomeration observed

in samples containing higher amount of TiO_2, which results in weak bonding and leads to fall in fracture toughness.

[Bhuiyan M.A. et al., 2011] observed in their study of carbon nanotubes/polypropylene composite that tensile modulus and ultimate tensile strength of composite increases with the content of nanotube.

[Lu C. et al., 2005] studied the mechanical properties of the epoxy composite filled with nanoparticles and found that the addition of nanoparticle enhanced the mechanical properties of the composite, with nanoparticle amount with 1.3 and 2.6 wt %.

[Santosh J. et al., 2014] observed that alkali treatment of banana fibres improves the mechanical properties like tensile strength, flexural strength and impact strength when compared to the untreated fibres.

[Shekeil Y.A.E. et al.,2011] studied the kenaf fibre reinforced thermoplastic polyurethane composite by melt blending process and observed that impact strength has increased with increasing size of fibres.

[Branciforti M.C. et al., 2010] concluded for the study of flexural modulus of polypropylene/talc composite that flexural modulus of the composite increased linearly with the increase of talc content.

[Booplan M. et al., 2013] studied the jute and banana fibre reinforced epoxy hybrid composites and observed that addition of banana fibre in jute/epoxy composite upto 50% by weight results in increasing the mechanical and thermal properties and decreasing the moisture absorption.

[Nunna S. et al., 2012] summarized the main factors affecting the mechanical properties of natural fibre based hybrid composites, the factors are volume fraction of fibres and chemical treatment of natural fibres.

[Nofar M. et al., 2019] studied the effects of processing parameters of injection moulding on the mechanical and thermal properties of composites of polypropylene with talc, and observed that talc addition decreased the melt flow index which made material easy to flow. High mould temperature provided more time for material to get processed, which improves the crystallinity. However impact resistance reduced due to increase of degree of crystallization and barrel temperature.

[Sarasini F. et al., 2018] observed that hybridization with basalt fibres increased the tensile properties of hemp fibre composite. This hybridization also increased the overall crystallinity and vicat softening temperature of the composite.

[Essabir H. et al., 2016] studied the hybrid composite of polypropylene filled with coir fibres and coir shell particles and observed 50% improvement in Youngs Modulus due to homogeneous dispersion/distribution of both fillers into polymer matrix.

[Kumar R. et al., 2020] studied the natural fibre hybrid polymeric composites using two natural fibres (shisham wood powder and rice husk) and found that tensile strength, flexural strength and impact strength increased up to 20 wt % of fibre loading.

[Muraliraja R. et al., 2021] reviewed in their work that fillers used in composites to improve the properties like wear, friction, corrosion, heat conductivity, decrease the thermal expansion. For tribological application short fibres are recommended. Addition of filler improves the thermal, mechanical and tribological properties.

[Borba P.M. et al., 2014] concluded that hybridization involving the use of nano fillers and natural fibre in the polymer matrix results in reduction of water absorption properties and increased mechanical properties.

[Kord B.et al., 2011] studied that nano filler reinforcement to HDPE/Rice husk flour composite system greatly enhanced their mechanical properties.

[Vladimirov V. et al., 2006] observed that dispersion of nanoparticles improved by using maleic anhydride grafted polymer as a compatibilizer. They also noted that agglomeration of nanoparticles increased by increasing the content of nanoparticles and agglomeration decreased at higher PP-g-MA amounts. Crystallization rates were also increased by increasing nanoparticles as well as PP-g-MA content.

[Arrakhiz F.Z. et al., 2013] studied the flexural modulus and strength for different fibres and observed that flexural modulus increase with the increase in fibre content and flexural strength remain constant for all the composites with fibre content from 5wt% and 30wt%.

[Chirholm N. et al., 2005] reported the effect of micro and nano sized SiC reinforcement on the mechanical properties of an epoxy matrix system and found that nano particles based composites have superior mechanical properties compared to micro sized composite.

[Fernandes E.M. et al., 2013] studies the effect of coir fibres into composite of cork and HDPE, and observed that the presence of coupling agent resulted in an increase in tensile strength and tensile modulus when compared with basic composite.

[Mohanty S. et al., 2004] studied the effect of maleic anhydride grafted polypropylene (MAPP) as coupling agent for surface modification of jute fibre/polypropylene composite.

[Ray D. et al., 2001] studied mechanical properties of jute fibre reinforced vinyl ester composite and found that the NaOH treatment of natural fibres increases the impact

strength and fatigue resistance of the composites due to increase in bonding between reinforcement and matrix.

[Su B. et al., 2017] concluded the effect of the fillers on the polypropylene/ low density polyethylene composites. These fillers drastically improve the tensile strength; strain at break and modulus simultaneously.

[Michal S., et al., 2020] observed that scratch resistance increase with content of talc, and degree of crystallinity of surface layer decrease of polypropylene and talc composites.

[Ma X. et al., 2005] studied the effect of fibre contents on the Young's Modulus of micro winceyette fibre reinforced thermoplastic corn starch composite and found that Young's Modulus improved.

[Kocic N. et al., 2012] observed that crystallization as well as crystallization peak temperature shifted to higher temperature with increasing talc concentration. Maximum changes occur up to a maximum of 5% of talc.

[Henrique P. el al., 2009] studied that nano composites creates a very large interaction between the nano-sized particles and polymer matrix. Nano composites exhibit unusual properties, combination and unique multi-dimensional design flexibilities.

[Hotta S. and Paul D., 2004] used small amount of maleic anhydride grafted polypropylene that is miscible with the base polypropylene. It was observed that the polar character of the anhydride causes affinity for the talc which serves as a compatibilizer between the matrix and filler.

[Saleem A. et al., 2020] focussed their research work towards the improvement of mechanical properties of bast fibre reinforced polypropylene composites. Study concluded that mechanical performance improved when bast/basalt hybridization done in maleic

anhydride modified polymer. They also compared bast/basalt hybrid composites with bast/glass fibres hybrid composites and found bast/basalt hybrid have 32% higher specific flexural and tensile strength than glass fibre hybrid.

[Mwaikambo L.Y. and Ansell M.P., 2002] treated hemp fibre, jute, sisal and kapol fibres with sodium hydroxide(NaOH) and observed that the chemically treated fibres showed better fibre-resin adhesion, which leads to an increase of thermal and mechanical properties of the composite.

[Kord B., 2011] studied the effect of layered nanoparticles on various properties of polypropylene/hemp fibres and observed that the tensile modulus, tensile strength and elongation at break of composite increased with an increase of nanoparticles loading up to 3% and then decreased while impact strength decreased with the increase in nano clay loading. Crystallization is one of the effective processes to control the extent of intercalations of polymer chains into silicate galleries, which further control the mechanical and other properties of nano composites [Ray S.S. and Okamoto M., 2003]. Reduced crystallization time is desirable for industrial applications as it results in shorter cycle time which results in economical production and saving in energy. Various minerals filler as nucleating agents are talc, calcium carbonate, sepiolite and mica [Sterzynski T. and Oysaed H., 2004].

[Shazra S. et al., 2021] investigated the nucleation effect of polylactic acid, filled with cellulose nano fibres at different levels of loading (1-6 wt %). It is observed that filled polylactic acid had the highest crystallinity of 44.2% with an increment of 95%, when compared to neat polylactic acid. They suggested that cellulose nano fibre at 3 wt % is more effective for enhancing the crystallization rate and the mechanical properties.

Nanoparticles can significantly improve the stiffness, heat distortion temperature, dimensional stability, gas barrier and flame retardancy of polymers with small addition 0.1- 10% of dispersed nano phase [Wu Z.G.et al., 2002; Li J. et al., 2004].

[Khalili P. et al., 2019] studied the natural fibre –reinforced composites with nano-hydroxyapatite and found that composite having higher quantity of nano-hydroxyapatite, achieved more flame resistivity with no burn rate. Also observed that the increase in tensile strength, tensile modulus and flexural modulus with introduction of flax fibres.

Polymer composite materials have ease of processing, productivity and cost reductions [Sanjay M.R. and Suchant S., 2019] and are tailor made materials which have a unique quality where the properties can be altered by varying the different reinforcement and matrix phase [Yogesha B., 2017].

Natural fibres as fillers have low thermal stability and highly flammable, during processing thermal degradation can be reduced by inclusion of thermal stable synthetic fibres or flame retardants. The most frequently used flame retardants include phosphoric acid, zinc borate, dicyanodiamide, expandable graphite (EG), sodium borate, nano clay, maleic anhydride etc. with natural fibres [Brostow W.et al., 2016; Sakthivel M. et al., 2014; Hao A.et al., 2013; Schirp A. and Su S., 2016; Amir N.et al., 2017].

Hybridization of synthetic fibres and natural fibre (jute) resulted in improvement of the tensile and flexural properties and reduction of water absorption of the hybrid composite [Kureemun U. et al., 2018; Ramana M.V. and Ramprasad S., 2017; Akil H.H.et al., 2014].

[Balasubramanian K. et al., 2020] investigated the mechanical properties of bio-hybrid composites with natural fibres (flax, aloe vera and sisal) with epoxy resin, and found that

tension, flexural, impact and hardness of bio-composites improves and results are in agreement with the analytical results with deviation around 2-6%.

[Badyankal P.V. et al., 2020] studied the hybrid composites of banana and sisal fibres with thermoset epoxy resin and confirmed that with increasing sisal fibres percentage the compression and water absorption properties improves.

Hybridization of natural fibres and nano materials also leads to increase the stiffness but at the same time values for tensile strength remains unaltered or decreased [Arrakhiz F.Z. et al., 2013; Piekarska K. et al., 2016; Essabir H. et al., 2016], whereas hybrid nano composites displayed improvement in mechanical properties and reduction in cost when compared to natural-natural fibre hybrids [Essabir H.et al., 2016; Saba N.et al., 2016].

[Gilberto G.D.P. et al., 2020] evaluated the mechanical properties of epoxy composite reinforced with curaua fibres and organophilic clay, treated with NaOH solution at three levels(2.5, 5, 10%) and nano clay also at three levels(2.5, 5, 10 wt %) and observed that tensile strength, flexural strength and impact resistance are better for treated fibres. The highest tensile and flexural strengths are achieved with 5 wt % of nano clay, 20 wt % of curaua fibres when treated with 5% NaOH for 4 hours.

Addition of natural fibres could improve the flammability resistance of neat polymers, but the addition of nano particles reduces the main drawbacks of natural fibres composite which are highly flammable and resulted in the advanced application in engineering fields [Saba N.et al., 2016].

Nano clay is regarded as good flame retardant to minimize the combustion of polymer composites [Yu T.et al., 2017], further the addition of 1% nano clay decreased the burning rate, which is attributed to the formation of a protective layer of char on the matrix. The

nano clay prevents oxygen from entering the substrate and also prevents its exit from substrate into flame [Karunakaran S. et al., 2016].

[Queiroz H.F.M. et al., 2021] studied the single lap adhesively bonded joints made of natural, synthetic and hybrid reinforced polymer composites and observed that significant variation of joint behaviour due to the adhered material. The joint efficiency can be achieved by hybrid 3-layer adhered joints.

Natural fibre reinforced composites can be used in acoustic panels, for controlling the sound by absorbing it, which are prepared by additive manufacturing which is also known as 3D printing. The 3D printed composites have very small voids formation between deposition lines which improves acoustic properties of the composites [Chin D.D.V.S. et al., 2018; Sekar V.et al., 2019].

[Olcay H. and Kocak E.D., 2020] studied the composites of rice plant waste reinforced with polyurethane for acoustic applications. Sound absorption performance evaluated by studying the cell and pore structures and densities of the composites, they concluded that agricultural waste can be utilized to improve the sound absorption coefficient without changing the thickness of material.

SUMMARY OF LITERATURE REVIEW

- Natural fibre as reinforcement is environmental friendly and is an economical option.

- Chemical treatment of fibres improves the desired properties due to better adhesion with the matrix.

- Maleic Anhydride polypropylene as compatibiliser improves thermal properties and mechanical properties.

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- Nano particles in smaller percentage are found to increase thermal stability, strength and scratch resistance.

- Hybridization increased the overall crystallinity and mechanical properties.

RESEARCH GAP

- Agave Americana leaves as natural fibres very rarely used whereas, it can grow well in neglected areas as decorative plant with very small amount of water.

- Nano talc used as nucleating agent instead as a filler, to reduce the weight of the composites.

- Hybridization with natural fibres (Agave Americana) and Nano talc with starch very less explored.

- The foremost challenge in the synthesis of hybrid composite is the effective dispersion of reinforcement in the polymeric polypropylene matrix to realize the full potential of the hybrid composites.

- Two or more reinforcement delivers combination of properties as desired.

Chapter 3

Materials and Experimental

This chapter gives information about raw materials used, experimental setup and processing techniques involved with the preparation of hybrid composites, specimen preparation for testing and characterization. The detail of various materials and polymers used is followed by the processing techniques and characterization technique, which used for the study of identification and characterization:

3.1. Materials:

3.1.1. Polymer (used as matrix for hybrid composites):

Manufacturer	Material	Grade	M.F.I.
Reliance Industries Ltd., India	Polypropylene Homo-polymer	PP H 350 FG	35 g/10 min. 230°C/2.16 Kg load

3.1.2. Bio-material Starch (used as reinforcement for hybrid composites):

The starch molecule structure is quite complex and partly non-linear. Starch suffers from the phenomenon of retro-gradation i.e. a natural increase in crystallinity over time, leading to increased brittleness. Starch is an important material of choice as approximately 75% of all organic material on earth is present in the form of starch (i.e. polysaccharides). Polysaccharides are the world's most abundant polymers as well as a renewable and sustainable, which are biodegradable and environmental friendly materials. Starch is a natural polymer consisting of anhydroglucose (AHG) monomer. The representative structure of starch is shown Figure 3.1.

Figure 3.1: Structure of Starch molecule

In present research work we used starch as per details given in Table no. 3.1.

Table no. 3.1: The details of starch used.

Manufacturer	Material	Chemical formula	Molecular Weight	Chemical composition
M/s LobaChemie, Mumbai, India	Potato Starch	$(C_6H_{10}O_5)_n$	162.14	Amylose app. 30% and Amylopectin app. 70%

3.1.3. Natural fibre-(used as reinforcement for hybrid composites):

Agave Americana, commonly known as a Century plant, is an exotic plant which is widely cultivated in the world for aesthetic purposes. It is belongs to the family

Agavaceae and one of the abundant source of strong natural fibre as shown in Figure 3.2.
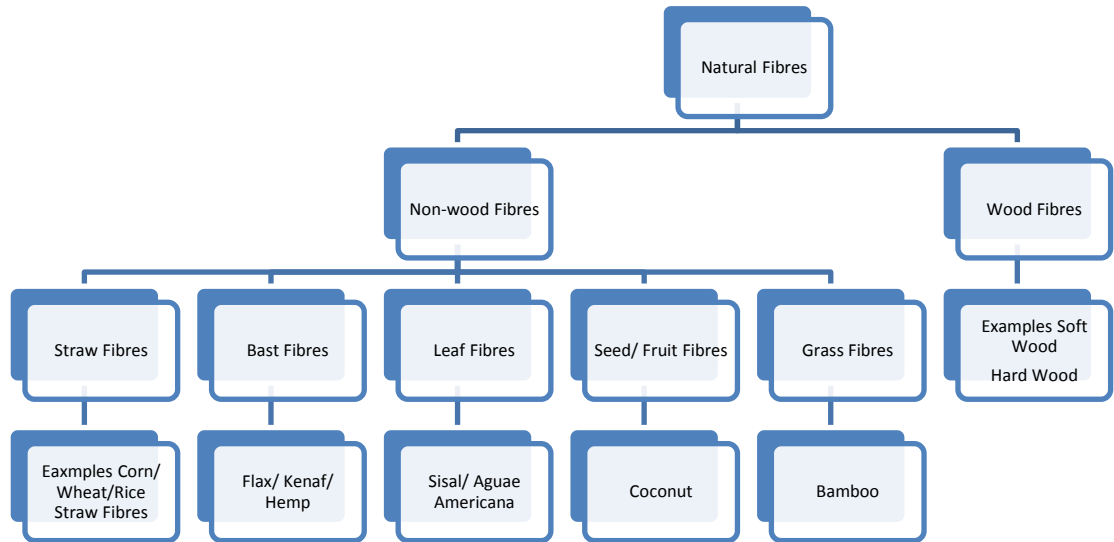
Figure 3.2: Classification of Natural Fibres

Natural Fibres (Agave Americana) were extracted in Laboratory by retting process. After proper washing, drying fibres was cut into approximately 2 mm length piece for the preparation of hybrid composites as in Table no. 3.2.

Table no. 3.2. The details of Agave-Americana used in research.

Natural Fibre	Type of Fibre	Source	Shape
Agave Americana	Leaf Fibre	Extracted by retting process in Laboratory	Cut in app. 2mm in length

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Figure 3.3: Photograph of plants and fibres extracted (in chopped form) of natural fibres (Agave Americana).

3.1.4. Nano Talc (used as reinforcement in hybrid composite):

The pure talc, the softest of all minerals with a Mohs hardness of 1, is an organophilic water repellent and chemically inert mineral. It is characterized as a hydrated magnesium sheet silicate with the formula $Mg_3\ Si_4O_{10}\ (OH)_2$. Talc consists of a layer or sheet of brucite $(Mg(OH)_2)$ sandwiched between two sheets of silica (SiO_2) shown in Figure 3.4. Weak Van der Waal's forces bond the crystal lattice of talc. Thus, talc undergoes cleavage very readily, is very soft and has a soapy feel.
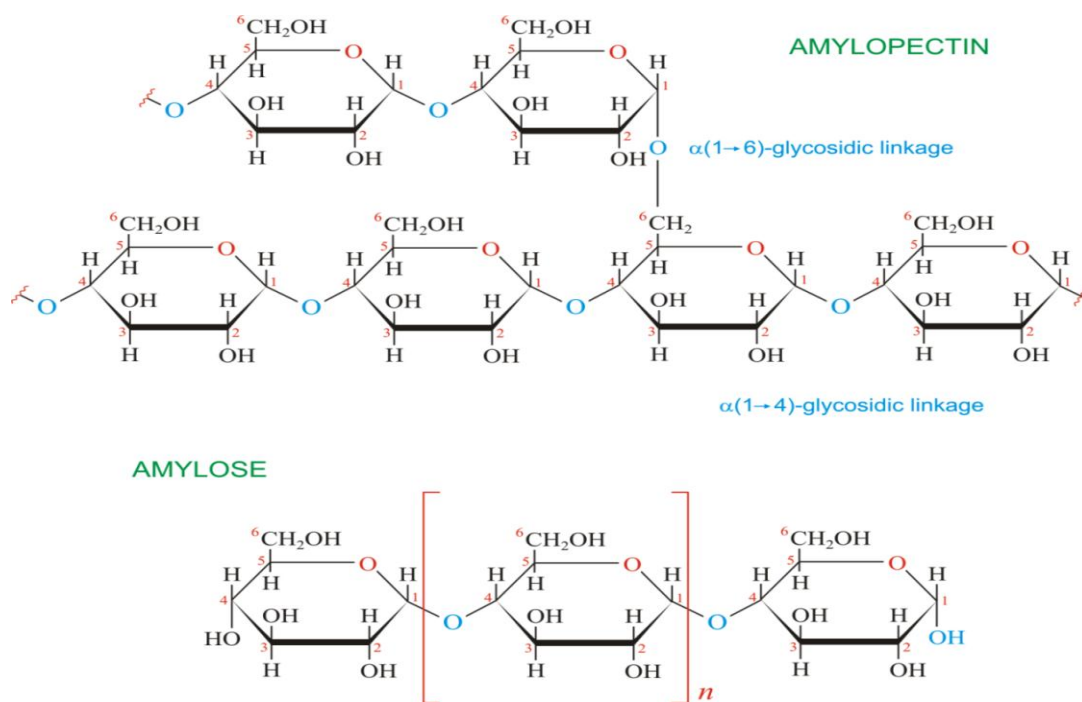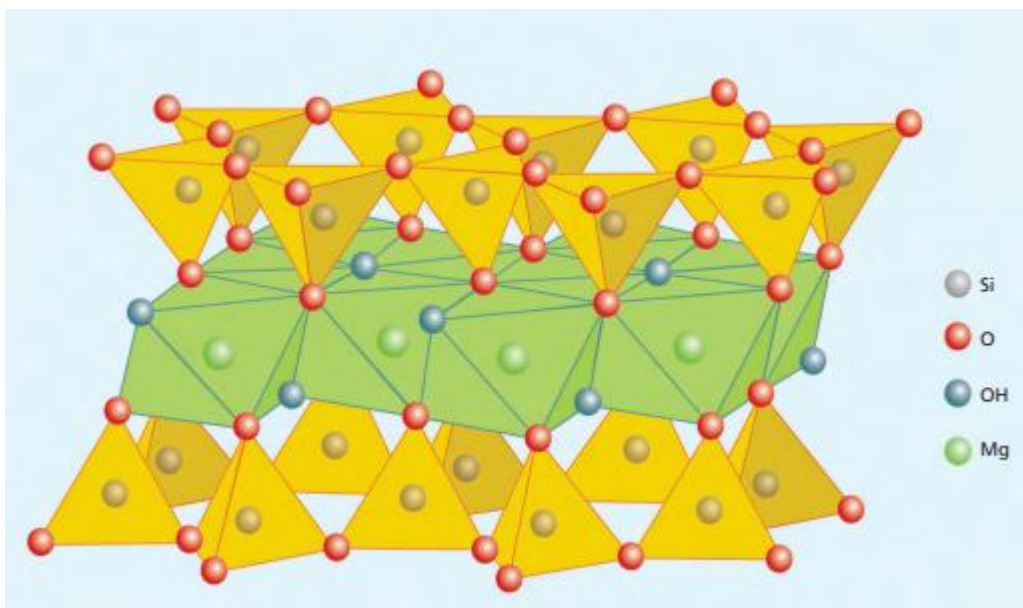
Figure 3.4: Structure of talc

In this work we used talc as per details given in Table no. 3.3.

Table 3.3.: The details of talc used in research

Manufacturer	Material	Grade	Chemical Composition	Particle Size
Soapstone Pvt. Ltd., Jaipur (India)	Nano Talc	EI-GT0.7WG	$3MgO.4SiO_2.H_2O$	Under 100 nm

3.1.5. Compatibiliser-Maleic anhydride grafted Polypropylene:

The maleic anhydride grafted PP in this research work used as per details given in Table no. 3.4.

Table no. 3.4.: The details of compatibilizer used in research work.

Manufacturer	Material	Grade	Chemical Composition	Particle Size/shape
Eastman	Maleic	EpoleneG-	Maleic	granule

Chemical Products Co. USA	anhydride grafted Polypropylene	3015	anhydride cross linked	

3.2. Material Preparation:

3.2.1. Preparation of Hybrid Composites by Melt Extrusion:

The polypropylene as polymeric matrix, and reinforcement i.e. starch (Bio-material), natural fibre (Bio-material) and nano talc (inorganic material) were mixed homogeneously in high speed mixer and melt blended by melt extrusion process by using co-rotating twin screw extruder make Steer extrusion, Mumbai as shown in Figure 3.5. After proper extrusion in twin screw extruder hybrid composite so obtained was in granules forms.

Figure 3.5: Lab Scale Co-rotated Twin Screw Extruder Steer India make.

3.2.2. Preparation of Specimens on Injection Moulding process:

Dumbbell shape test specimen (as mentioned in ASTM D 638) and plaque specimen of 0.5 mm thickness and 2x2 inch size were moulded on an injection moulding machine as shown in Figure no. 3.6., by using granules obtained from above hybrid composites.
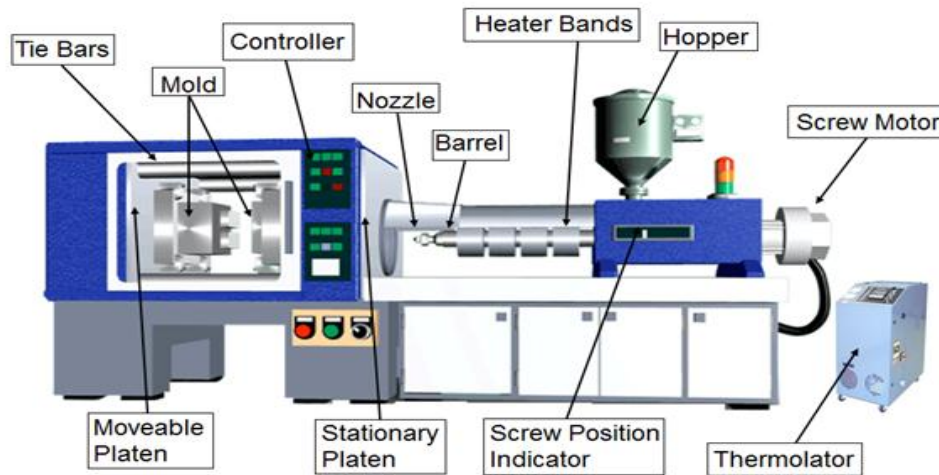
Figure 3.6: Injection Moulding machine used for the preparation of Test Specimens.

3.3. Characterization Techniques:

The details of various characterization techniques which were used for the study of the functional group, mechanical properties, structural properties, thermal behaviour, crystallographic nature, and morphological properties etc. of the prepared samples.

Mechanical Testing:

3.3.1. Tensile Properties

Tensile test were carried out on dumbbell shaped injection moulded sample using an Instron Universal Testing machine model 3369 as per international accepted test method ASTM D 638:2014. The Universal Testing Machine is of constant rate extension meter (CRE) type with cross head speed of 50 mm/min was taken for testing. The specimen samples were pre-conditioned at 23+/- 2 °C and 50+/-10% RH for 40 hours. Tensile test is a measurement of the ability of composite materials to withstand forces that tend to pull it

apart and to determine to what extent the material stretches before breaking. The area under stress-strain curve is considered as the toughness of the polymeric composite. Five specimens were used to obtain the average value of tensile strength and percentage elongation at breaking point.

Figure 3.7:   Universal Testing Machine (UTM) makes Instron model 3369

3.3.2. Flexural Properties

Flexural properties of hybrid composites were conducted in three point bending mode according to ASTM D 790:2015 using Instron UTM model 3369. The crosshead speed taken as 5 mm/min for testing. The test specimens were prepared by injection moulding and dimensions were according to ASTM standard. Flexural strength is the ability of material to withstand bending forces applied perpendicular to its longitudinal axis. The maximum strain in the outer fibre of specimen reached 5%. The loading nose and support

must have cylindrical surfaces of radius about 3.17mm. A strain gauge type mechanism called deflectometer is used to measure deflection in specimen. Injection moulded specimen usually shows higher flexural value than compression moulded specimens. Five samples were used to obtain the average value of test.

3.3.3. Impact Strength

The notched Izod impact testing was performed using Ceast spa (ResilImpactor), a pendulum impact tester according to ASTM D 256:2010. The hammer that was used to strike the sample was 2.75J. Notch provided on specimens provides stress concentration area that promotes brittle fracture and prevents the plastic deformation. Impact strength directly related to the overall toughness of the material, and toughness is the ability of the material to absorb applied energy. Impact strength is calculated by dividing impact values obtained from scale by the thickness of the specimen. Five samples were used to obtain the average value of impact strength.

Figure 3.8: Impact Tester make Ceast spa model ResilImpactor

3.3.4. Scanning Electron Microscopy

The SEM is used to study the morphologies of the compounds and phase domains. Studies on the morphology of the tensile fractured surface of the hybrid composites were carried out under high vacuum with operating at 15KV, using HITACHI model S3700 N.

Figure 3.9: Scanning Electron Microscopy (SEM) makes Hitachi-Japan Model no S-3700N

The samples have been first dried in an oven to remove the moisture and then the fractured end of the sample were mounted and sputter coated with thin layer of gold to avoid electrical charging during examination procedure. SEM is one of the popular ways to identify micro structural characteristics of the composite as it gives indirect information about the particle size. SEM provides high resolution images of the fibres and other fillers when scanning by an electron beam focused across the surface of specimen. It also provides information about phase morphology, distribution and fracture characteristics of the specimen.

3.3.5. X-Ray Diffraction

The crystalline structure of hybrid composite was characterized by XRD on M/s Bruker D8-Advance Diffracto-meter using Cu-Kα radiation of wavelength (0.15406 nm) in

transmission technique. Scattered radiations have been detected at the angular region 2ø of 2° to 60° at a scanning rate of 2 /min. Nickel foil is employed to filter Kb radiation. XRD is a non-destructive and rapid analytical technique to identify the crystallographic structure of the composites. The degree of talc intercalation in the hybrid composite is determined by this technique.

Figure 3.10: X-ray Diffractro meter makes Bruker D8-Advance

The XRD is used to characterize the structure of composites; by this method we determine the spaces between the structural layers by using Bragg's Law;

$$Sin\ \theta = n\lambda/2d$$

Where θ is measured diffraction angle, λ is wavelength of X-Ray radiation. XRD also shows type of material and dispersion quality of various constituents of the composite. Sharp diffraction peaks in XRD measurements is an evidence of good exfoliation.

3.3.6. Fourier Transmission Infrared Spectroscopy

The chemical structure analysed by FTIR technique. It shows the interaction between the polymer and other reinforcement materials of hybrid composites. It helps to identify types of chemical bonds in a molecule. The all hybrid composites have been scanned from 4000 to 550cm^{-1} range. FTIR is considered a non-destructive test that can provide quantitatively and qualitative details of natural fibres and other constituents. It gives various peak values and its corresponding chemical stretching mode vibrations on the fillers. The IR spectra of sample recorded, by passing beam of IR light through the sample. Observation of the transmitted light reveals the amount of energy absorbed at each corresponding wavelength. It can be performed with a monochromatic beam, which changes in wavelength over time. The test was conducted according to ASTM E 1252:2013 with ATR by using Perkin Elmer model Spectrum 100 spectro meter, on injection moulded plaque of hybrid composites.
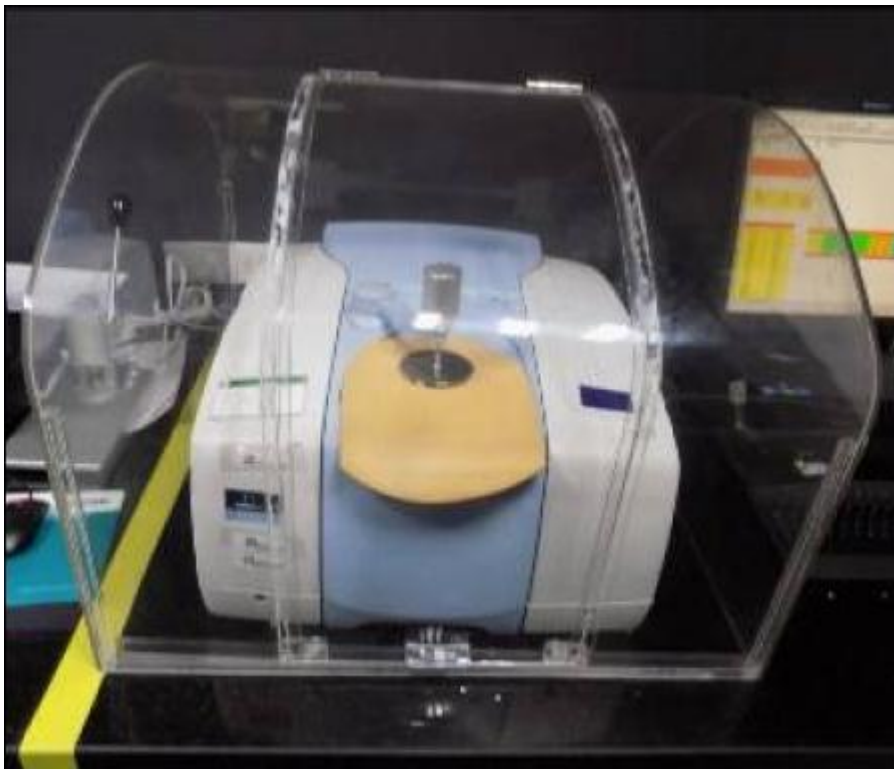
Figure 3.11: Fourier Transmission Infrared Spectroscopy (FTIR) makes – Perkin Elmer Model – Spectrum 100

3.3.7. Differential Scanning Calorimetry

The DSC test method used to study crystallization and melting behaviour of PP and hybrid composites. It is used to determine the specific enthalpy and temperature of melting and crystallization. Experiments were performed by heating from -50°C to 200°C at a heating rate 10°C/min. Samples of 5+/- 0.1 mg were used in tests. They were sealed in Aluminium pans. The sample and reference are placed in a sample holder and heated as per above mentioned range and rate in an inert atmosphere of nitrogen. The changes are recorded graphically for measurement of either temperature or energy differential against temperature or time. Two heating cycles were realized to neutralise the processing conditions. It measures the quantity of energy absorbed or evolved by a sample in calories as it temperature is changed. DSC test conducted according to test method ASTM D 3418:2015 on DSC equipment Make – NETZSCH model Model – DSC 214 Polyma.

3.3.8. Heat Deflection Temperature

The HDT is a single point measurement and does not indicate long term heat resistance of composite material. HDT is defined as the temperature at which a standard test bar deflects 0.254mm under a stated load of 0.45MPa. This temperature gives the relative service temperature of polymers when used under loading conditions.   The test conditions are that specimens preconditioned at 23°C +/-2°C & 50+/-10% RH for 40 hrs, stress used (0.45MPa) and heating rate 120°C/hr. This test is performed under ASTM D 648:2016 on HDT and VSP equipment HDT & VST make CEAST model – HV3.

Figure 3.13: Heat Deflection Temperature (HDT) and Vicat Softening Temperature (VSP)
make Ceast model HV3

3.3.9. Vicat Softening Point

VSP used in comparing the heat softening quality of composite material. This test is conducted as per ASTM D 1525:2009. VST is adopted to establish the service temperature of composites. VST is the temperature of the bath at which a flat ended needle of 1mm circular cross section will penetrate a thermoplastic specimen to a depth of 1mm under a specified load using a uniform rate of heating. The test conditions are that specimens preconditioned at 23°C +/-2°C & 50+/-10% RH for 40 hrs. load used (10+/-0.2N) and ramp as 50+/-5 C/hr.

3.3.10. Melt Flow Index

The MFI for the composite has been conducted according to ASTM D 1238. The test conducted at 230°C at 2.16 Kg load with pressure around 298.2 KPa on Ceast Spa Equipment. Five tests were done to obtain the average value of melt.

Figure 3.14: Melt Flow Index Tester Ceast Spa

The MFI is used as a means of measuring the flow rate of the composite material. It is the most accepted practical method to relate the molecular weight and viscosity of the composite material and widely used in industry. The melt index test measures the rate of extrusion of a material through an orifice of specific length and diameter under above mentioned conditions of temperature and pressure. The initial extrudate is generally discarded as it may contain air bubbles and other contaminants. The extruded material cut out at different fixed time intervals. It helps to distinguish different grades of polymers.

Chapter 4

Synthesis of Hybrid Composites:

4.1. Raw materials

Polypropylene (H350FG) in powder form purchased from Reliance Industries Ltd. (India) was used for the production of hybrid composites as matrix in research work. It is revealed from the technical data sheet that melt flow rate of this material is 35 g/10 min at 230°C /2.16Kg (ASTM D 1238) and density 0.9gm/cm^3.

Starch is used to reduce the carbon footprints of conventional polymer as they are the better alternate having degradable property. Further starch is one of the most abundant and easily available biopolymer which is inexpensive, renewable and can be modified chemically. Potato starch having molecular weight 162.14 was purchased from Loba Chemie, India. Starch has hydrophilic nature i.e. it has tendency to absorb water.

The maleic anhydride grafted PP (MAPP- Epolene G-3015) was supplied by Eastman Chemical Products Co (USA), is used as a compatibilizer i.e. coupling agent. The coupling agent having active sites suitable to bind with organic and inorganic compounds hence works as bridge between polymer matrix and reinforcement (either organic or inorganic).

The Agave Americana natural fibres were extracted from Agave Americana plant by water retting process in our institute laboratory. Density of agave fibre 1.36 gm/cm3 and its chemical composition, cellulose 68-80%, hemicellulose 15%, lignin 5-17%, wax 0.3% and water around 8%. Chemical composition of fibres depends on the age, conditions of growth and method of fibre extraction.

Nano talc having chemical composition $3MgO.4SiO_2.H_2O$ (EI-GT0.7WG), with particle size under 100nm was supplied by Soapstone Pvt. Ltd., Jaipur (India).Talc is chemically

inert and water repellent and is an inorganic nanoparticle. Talc is stable up to 900°C in thermal degradation test.
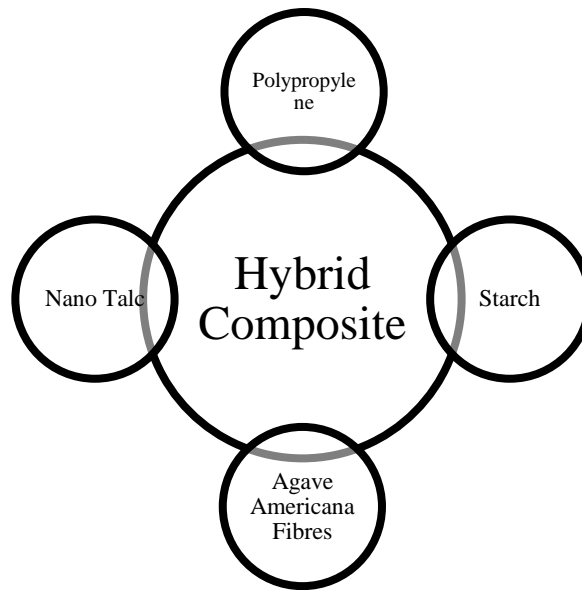
Figure 4.1: The hybrid composites

4.2. Fibre Extraction Process:

Agave Americana fibres used for experiment as it have maximum cellulose content as compares to other natural fibres and it effectively absorbs CO_2 from the atmosphere and have minimal environmental impact. Its fibre is 100 % biodegradable. Agave is truly a no waste plant, which enable its production and processing for a well sustainable industry. The water requirement for agave Americana is 4/5 times less when compared to sugarcane. This is attributed to agave ability to store large volumes of water in its leaves. Agave Americana fibres chemical composition is very similar to the commonly used fibres like hemp, jute, and sisal [Hulle A. et al., 2015].

Figure 4.2: Agave Americana and its leaf fibres

Agave Americana leaf fibres have properties of low density and high tenacity. These fibres are long and biodegradable. These fibres have some common name like Pita fibres, Century plant, Maguey or American aloe. It is originally belongs to Mexico, Arizona and Texas. But now it's cultivated worldwide as an ornamental plant. It grows well even in neglected conditions. It can grow on dry soils unfit for cultivation. Natural fibre extracted from Agave Americana plant by retting process, which was available in our university campus. Quality of fibres extracted by water retting process is better than dew retting. Retting process took 2-3 weeks and this process is cheaper when compared with mechanical extraction process. In water retting process Agave leaves immersed in water for approximately 2 weeks, water penetrates the stalk and swells the inner cells of the leaves, causing the outermost layers of the leaves to burst. It gives high quality fibres.

The fibres so extracted, further undergoes surface treatment to reduce the hydrophilic nature of fibre, modify the fibre surface and increase the fibre strength.

Alkali Treatment: Crushed fibres washed with plenty of water and kept in sodium hydroxide aqueous solution. After treatment fibres finally cut into an approximately 2mm length size and oven dried in vacuum overnight and packed in air tight plastic bag till melt blending in co-rotated twin screw extruder. In this process lignin waxes and resin removed from fibres external surface.

Alkali treatment of natural fibres increases the surface roughness which results to form new hydrogen bonds between the cellulose, further this treatment increases the amount of cellulose exposed on the fibre surface [Ku H.et al., 2011; Essabir H. et al., 2016; Arrakhiz F.Z. et al., 2012], which leads to better bonding between matrix and reinforcements [Essabir H. et al., 2016].

4.3. Preparation of Hybrid Composites using twin screw extruder:

The potato starch, Agave Americana natural fibres and talc were mixed with polypropylene, with experimental formation as shown in Table no. 4.1. All the constituents were mixed in a high speed mixer for 2 min. and composites were prepared by melt extrusion techniques.

Table 4.1.: Formulation of Hybrid Composites based on Polypropylene

Sample No.	Sample Name	Polypropylene (PP)%	Starch (ST)%	Nano Talc(TL)%	Natural Fibre(NF)%
1	PP	100	00	00	00
2	PPST20TL01NF05	100	20	01	05
3	PPST20TL03NF03	100	20	03	03
4	PPST20TL05NF01	100	20	05	01
5	PPST00TL05NF00	100	00	05	00

Various Processing Techniques:

To transform the blended materials to the final shape, without causing any defect in the product various processing techniques are as follows

1. Intercalation process- is used for preparing polymer nano composites which contain layered silicates. In this process solvent is used in which polymer is soluble. Different types of nano composites prepared with interaction of layered silicates and polymer depending on the degree of penetration e.g. micro composites, intercalated nano composites and exfoliated nano composites [Muller K. et al., 2017]. In micro composites polymer is unable to intercalate between the silicates layers. In intercalated nano composites polymer enters between silicates layers in regular pattern. In exfoliated nano composite polymer enter between the silicates layers in zigzag form.

2. In situ polymerization- involves the dispersion of nano silica in the polymer at first stage and then polymerization is carried out to get the resulted mixture.

3. Melt intercalation process- in this process mixture of polymer and nano particles are annealed above the softening temperature of the polymer under the shear action, diffusion of polymer into the nano layers during the annealing process.

4. Sol-gel Process- in this process the nano particles and polymer dissolved in a solution, results in the formation of interpenetrating in between each other at mild temperatures. This leads to builds strong interfacial interaction between the two constituents.

5. Blending- the simplest process for synthesis of polymer/inorganic nano composites is direct mixing of nano particles into the polymer. The mixing can be done in two ways solution blending and melt blending. In solution blending methods nano particles are added in polymer solution by using solvents like toluene, chloroform

and aceto nitrite to integrate polymers and fillers. Due to use of solvents this process is not environmental friendly. Melt blending process involves dispersion of nano particles into a polymer melt and polymer/nano composite then obtained by extrusion [Kango S. et al., 2013]. Extrusion allows melting a polymer with high energy input during short duration, friction between the screws results in melting of mass and it became formable and pressed through the extruder die. During this process mass can be compressed, mixed, plasticized, homogenized, chemically transformed degsificated or gasificated. Dispersion quality depends upon screw rotation speed of extruder and screw configuration.

The reactive melt blending process is used to produce the hybrid composite as this process is most effective, economical and environment friendly as no organic solvents are needed in this process, and more importantly this process is directly scalable for industrial mass production [Bhuiyan Md.A. et al., 2011; Aftab A., 2018]. This process is compatible with the commonly used industrial process, giving end user numerous degree of freedom related to the specifications of end product like polymer grade, types of filler, reinforcement level etc. [Qaiss A.E.K. et al.,2015]. The composite were prepared by using co-rotating twin screw extruder of diameter 13mm and length 520mm. The co-rotating twin screw extruder consists of appropriate screw elements in order to introduce polypropylene melting and particle fine dispersion in polymer melt. The processing was done in such a way to obtain minimum degradation of polypropylene and other constituents of hybrid composites to get maximum characteristic properties of each ingredient. The temperature profile of the twin screw extruder was 170°C to 190°C, screw rpm was 275, and melt Pressure was 25 MPa during extrusion. The melt extruded composite were cooled in a water bath and then pelletized into small granules of size 2-3 mm.

Figure 4.3: The co-rotating Twin Screw Extruder used for melt reactive blending.

The detail of preparation process is shown by flow chart in Figure 4.4.
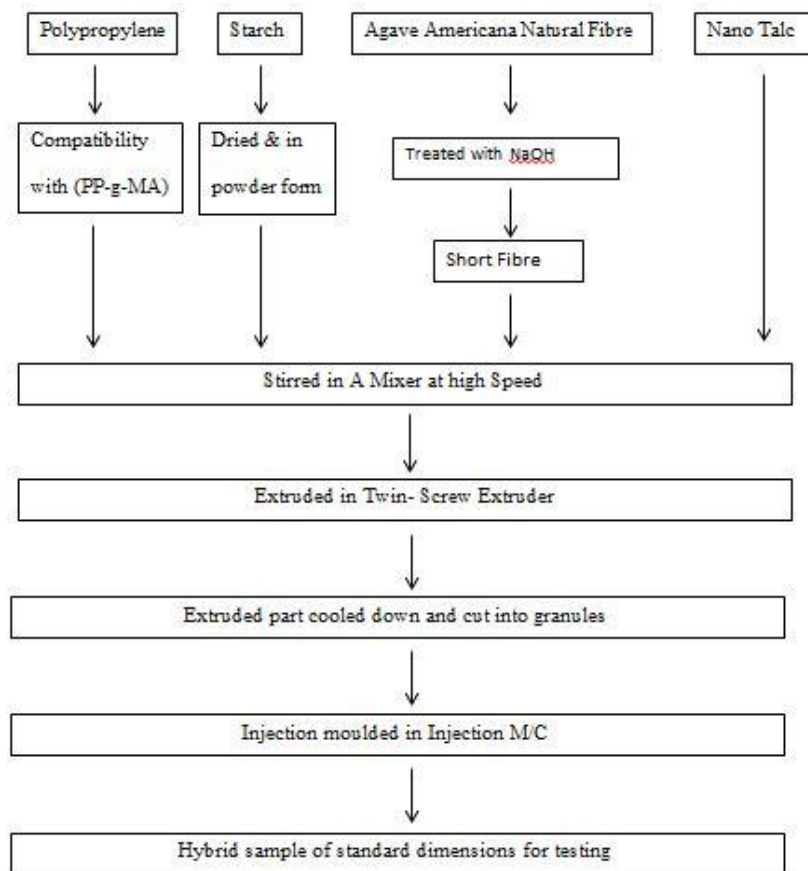
Figure 4.4: Flow Chart for preparation of hybrid composite

The composite produced by this method may perform better in mechanical properties, have less agglomeration and contain fewer defects. Further this method is simple as it does not require specialized equipment and versatility with materials which can be used. Melt compounding is capable of facilitating chemical reaction between the constituents during process [Aftab A., 2018].

The screw rotation speed corresponds to the applied shear stress and the residence time of molten material during compounding process in the extruder. Increasing the screw speed generates a higher shear stress in the polymer melt and is sufficient to delaminate the nano layers [Kord B. and Kiakojouri S.M.H., 2011; Mohan T.P. and Kanny K., 2011]. High screw speeds above 90 rpm leads to inadequate residence time of melt in the extruder which is inadequate to achieve complete compounding. Incomplete mixing of the composite materials leads to poor intercalations in polymer matrix [Chen R.S.et al., 2017].

4.4. Test specimen preparation by Injection Moulding:

The granules of hybrid composites so obtained by melt extrusion were injection moulded into standard mechanical test specimen for tensile strength and flexural strength as defined in ASTM standards (used for SEM also), and plaque (square plate) of 0.5mm thickness and 2x2 inch were moulded (used in FTIR and XRD testing) on an injection moulding machine. The Injection Moulding process parameters were given in Table no. 4.2. The injection temperature was kept lower than the degradation temperature of hybrid composite i.e. 190°C to retain properties of composite, because at higher temperature natural fibre and starch may degraded, which affects the test values. At the same injection temperature should not be less than 150°C to have proper melting of matrix [Li X et al., 2009].

Table 4.2. The process parameters for Injection Moulding of Specimen for Testing

Temperature (Z 1) 155 °C	Temperature (Z 2) 153 °C	Temperature (Z 3) 150 °C	Temperature (Z 4) 150 °C
Melt Temperature 165 °C	Screw Speed (rpm) 55	Injection speed (rpm) 45	Injection Time (Sec) 8
Mould Cooling (Sec) 15	Hold Time (Sec) 2	Cycle Time (Sec) 35	

4.5. Challenges with natural fibre composites-

Natural fibres are hydrophilic and their polar hydroxyl group increase the amount of water absorbed into the composite.

Polymer have non polar characteristic which creates difficulty in compounding with polar fibres.

Limited thermal stability, processing temperature of natural fibres is limited to 200°C. This problem overcome by addition of nano particles to the composite.

During processing at high temperature water evaporates from composite melt, evaporation of water leads to bubble formation and causes the porosity of the composite. Therefore many apparatus equipped with degassing units which allows the water vapours to exit the machine during processing.

Chapter 5

Results and Discussions:

5.1.Mechanical Properties:

The Figure no 5.1 shows the tensile strength and tensile graph of sample no. 1

Table 5.1: Tensile strength of sample No.1

Sample No.1	Tensile Strengh (MPa)	Elongation at break (%)
Specimen 1	32.985	290.167
Specimen 2	32.825	296.000
Specimen 3	32.938	250.333
Specimen 4	32.507	400.000
Specimen 5	32.703	150.167
Average	32.792	277.433
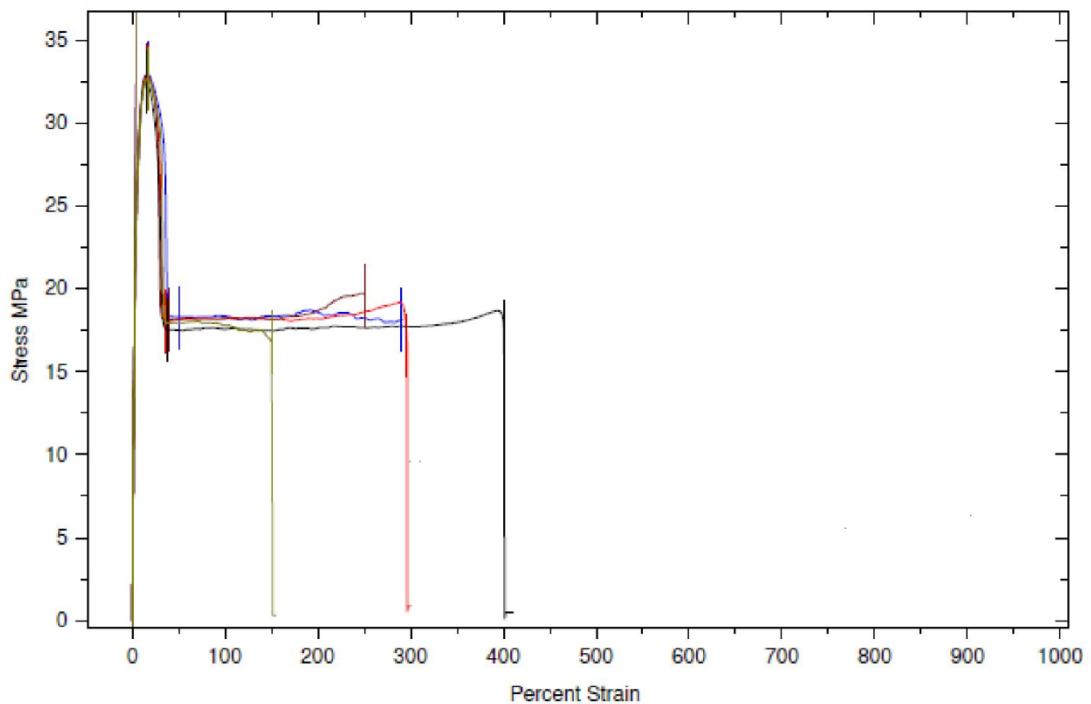
Figure 5.1: Tensile Strength and Graph of Sample No. 1

I.e. PP contains pure polypropylene. In all testing a dumbbell shape injection moulded specimen as defined in ASTM Standard was taken and 5 samples were tested and their

average value was considered for evaluation. The tensile strength of hybrid composites of sample no.1 (i.e. pure polypropylene) shows average tensile strength 32.79 MPa and elongation at breaks was 277.43 %. These values clearly reflected the pure polymeric curves as shown in tensile graph.

The Figure 5.2 shows the tensile strength and tensile graph of sample no. 2

Table 5.2: Tensile strength of sample no.2

Sample No.2	Tensile Strength (MPa)	Elongation at break(%)
Specimen 1	31.717	13.000
Specimen 2	30.789	12.667
Specimen 3	30.470	13.333
Specimen 4	31.378	13.000
Specimen 5	30.819	13.500
Average	31.035	13.100

Figure 5.2: Tensile Strength and Graph of Sample no. 2

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i.e. PPST20TL01NF05 contains 20% starch, 1% nano Talc and 5% Agave Americana. The tensile strength of hybrid composites of sample no. 2 shows average tensile strength 31.05MPa and elongation at breaks was around 13%. These values clearly reflected that the addition of potato starch, nano talc and Agave Americana, as reinforcement maintains the tensile strength at the cost of elongation.

The Figure no 5.3 shows the tensile strength and tensile graph of sample no. 3

Table 5.3: Tensile strength of sample no.3

Sample No.3	Tensile Strength (MPa)	Elongation at break(%)
Specimen 1	27.685	8.333
Specimen 2	27.805	9.333
Specimen 3	28.229	8.500
Specimen 4	28.159	9.167
Specimen 5	27.936	9.833
Average	27.963	9.133

Figure 5.3: Tensile Strength and Graph of Sample no. 3

i.e. PPST20TL03NF03 contains 20% starch, 3% nano Talc and 3% Agave Americana. The tensile strength of hybrid composites of sample no.3 shows average tensile strength 27.96MPa and elongation at breaks was around 9.13%.

The Figure no 5.4 shows the tensile strength and tensile graph of sample no. 4

Table 5.4: Tensile strength of sample no.4

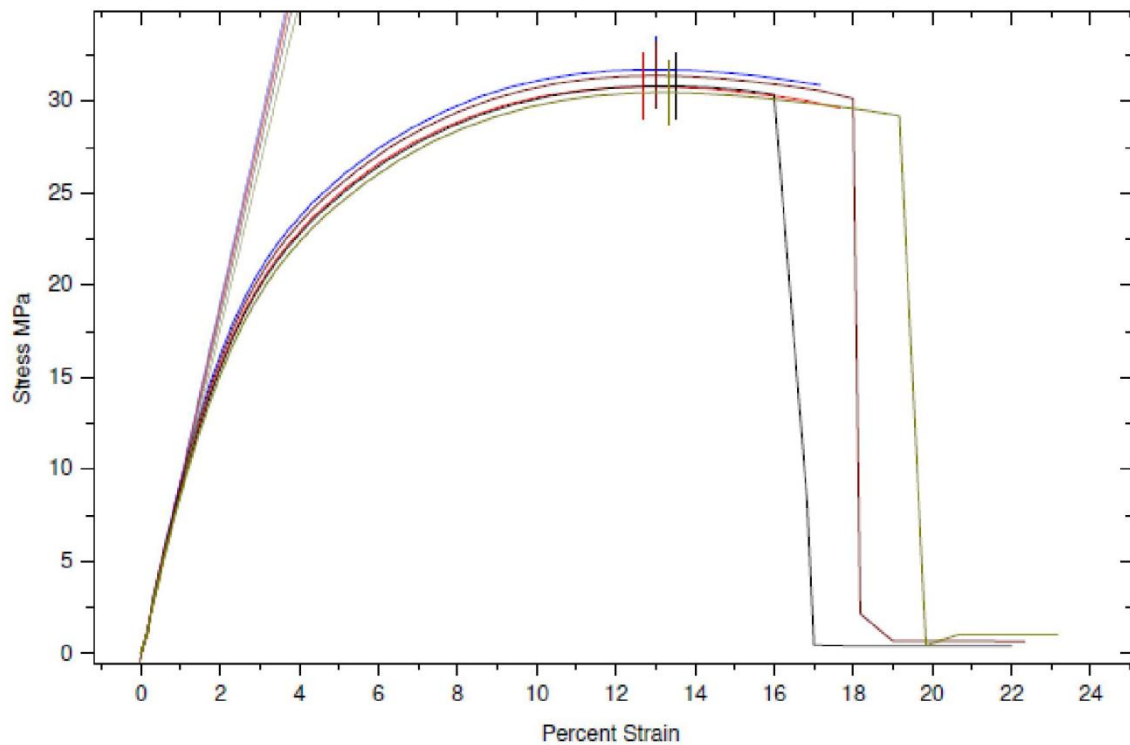| Sample No.4	Tensile Strengh (MPa)	Elongation at break(%)
Specimen 1	29.010	11.000
Specimen 2	29.432	11.833
Specimen 3	27.717	11.500
Specimen 4	29.079	11.500
Specimen 5	29.574	11.666
Average	29.362	11.500

Figure 5.4: Tensile Strength and Graph of Sample no. 4

73

i.e. PPST20TL05NF01 contains 20% starch, 5% nano Talc and 1% Agave Americana. The
tensile strength of hybrid composites of sample no.4 shows average tensile strength 29.36
MPa and elongation at breaks was around 11.5%.

The Figure no 5.5 shows the tensile strength and tensile graph of sample no. 5

Table 5.5: Tensile strength of sample no.5

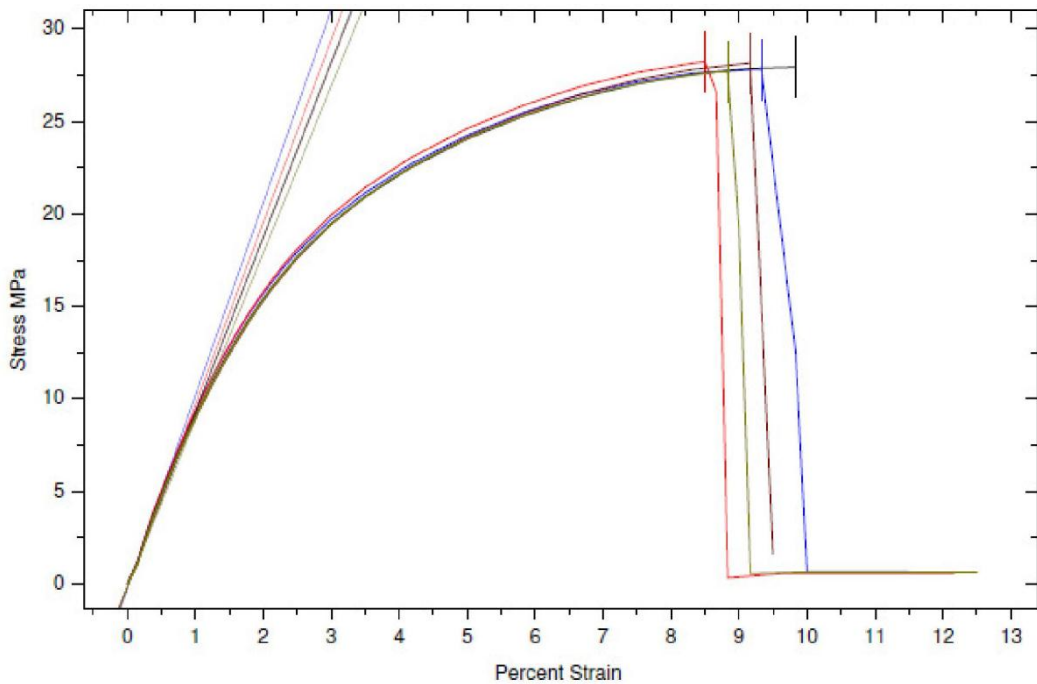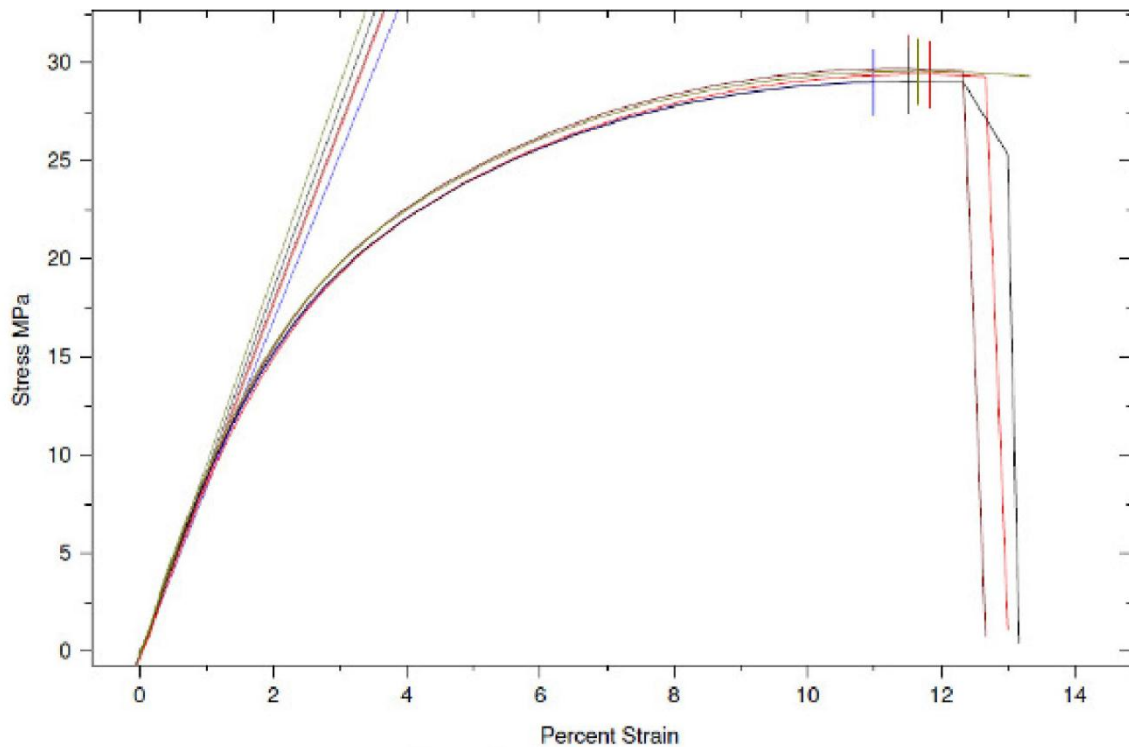| Sample No.5	Tensile Strength (MPa)	Elongation at break(%)
Specimen 1	30.042	14.167
Specimen 2	29.354	13.500
Specimen 3	29.974	13.500
Specimen 4	29.110	14.167
Specimen 5	29.600	13.833
Average	29.616	13.833
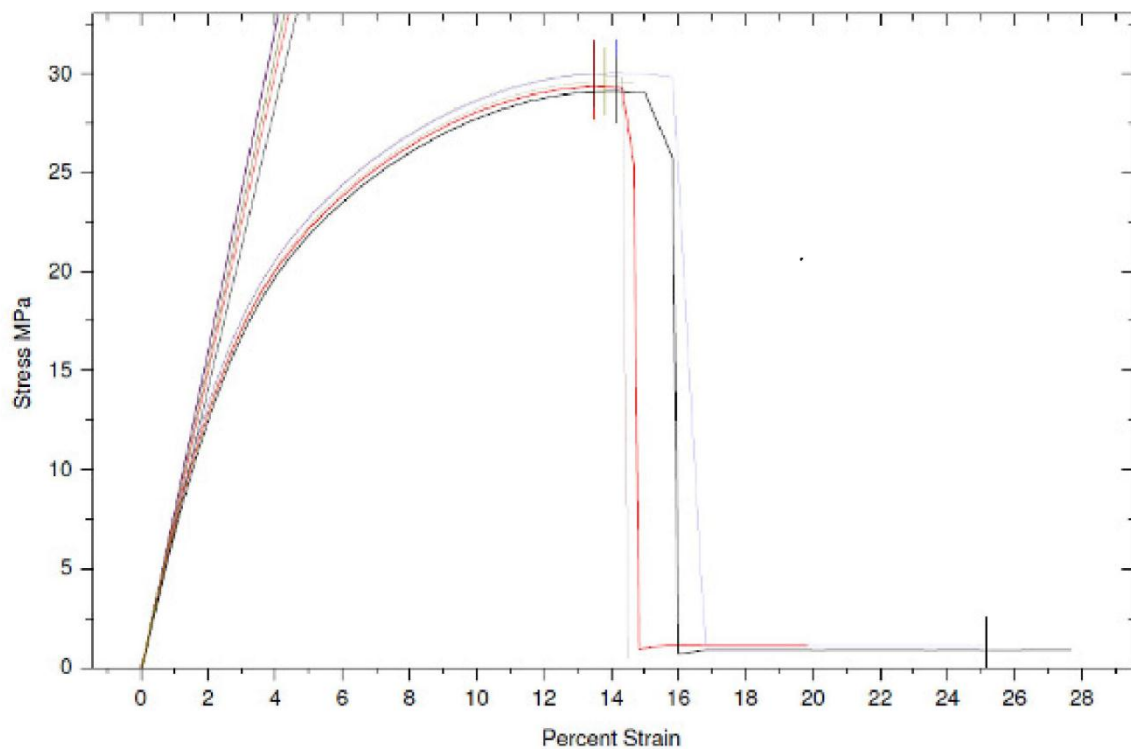
Figure 5.5: Tensile Strength of Sample no. 5

i.e. PPST00TL05NF00 contains 0% starch, 5% nano Talc and 0% Agave Americana. The tensile strength of hybrid composites of sample no.5 shows average tensile strength 29.61MPa and elongation at breaks was around 13.83%.

Due to the improved interfacial bonding in the presence of compatibilizer and plasticization of starch, a considerable enhancement in mechanical properties of the hybrid composite is expected. The sample no.2 is the most suitable composite which is having the tensile strength equal to pure polypropylene but its lost ductility as the elongation at break abruptly reduces. This may be attributed to that polypropylene being filled with more rigid fillers. This confirms that the addition of fillers specially starch and fibres restricts the motion of polymer chains and hence elongation decreases sharply. Incorporation of filler changes the failure of polypropylene from ductile to brittle behaviour [Leong Y.W. et al., 2004]. This sample verifies that nano materials presence is more effective at low content, after it fillers started to form agglomerates due to high surface energy of nano materials [Akinci A., 2009; Premalal H.G.B. et al., 2002]. These results suggested that optimum level of talc and natural fibres gives better mechanical performance as tensile strength is sensitive to the degree of dispersion level. The results are shown in Table no 5.6 and Figure 5.6.

Table 5.6: The Tensile Strength and Elongation at break for PP and Hybrid Composite

S. No.	Sample	Tensile Strength(MPa)	Elongation at Break %
1	PP	32.792	277.433
2	PPST20TL01NF05	31.035	13.100
3	PPST20TL03NF03	27.963	9.133
4	PPST20TL05NF01	29.362	11.500
5	PPST00TL05NF00	29.616	13.83
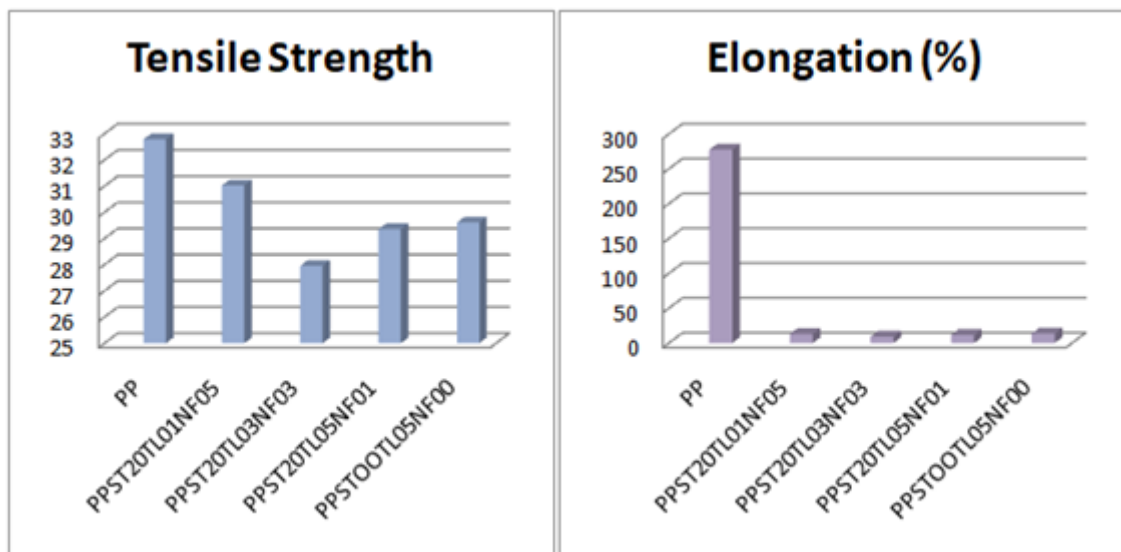
Figure 5.6: The Tensile Strength and Elongation at break of PP and Hybrid Composites

5.2. Flexural Strength:

The Figure no 5.7 shows the tensile strength and flexural strength and flexural strength graph of sample no. 1 i.e. PP contains pure polypropylene. In all testing a dumbbell shape injection moulded specimen as defined in ASTM standard was taken and 5 samples was tested and their average value was considered for evaluation.

Table 5.7: Flexural Strength of sample no.1

Sample No.1	Flexural Strength (MPa)
Specimen 1	40.408
Specimen 2	41.312
Specimen 3	41.494
Specimen 4	41.113
Specimen 5	41.918
Avg.	41.249
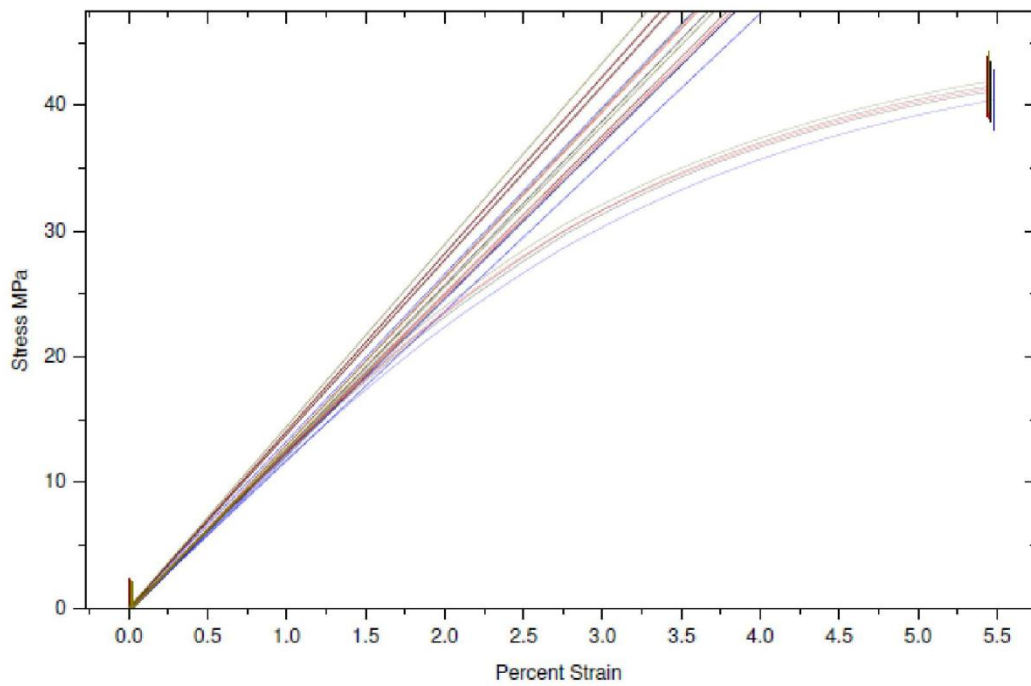
Figure 5.7: Flexural Strength - Graph of Sample no.1

The Figure no 5.8 shows the flexural strength and flexural strength graph of sample no. 2 i.e. PPST20TL01NF05 contains 20% starch, 1% nano Talc and 5% Agave Americana.

Table 5.8: Flexural strength of sample no.2

Sample No.2	Flexural Strength (MPa)
Specimen 1	42.774
Specimen 2	41.935
Specimen 3	42.442
Specimen 4	41.465
Specimen 5	43.178
Avg.	42.359
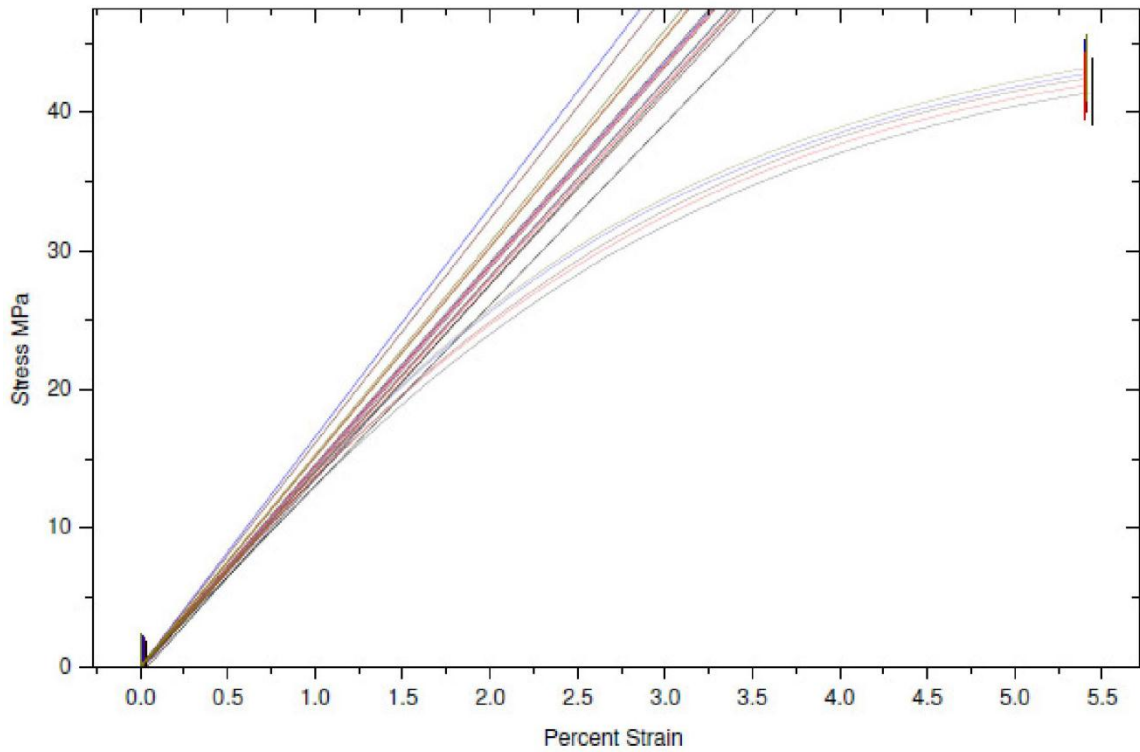
Figure 5.8: Flexural strength - graph of Sample no.2

The Figure no 5.9 shows the flexural strength and flexural strength graph of sample no. 3 i.e. PPST20TL03NF03 contains 20% starch, 3% nano Talc and 3% Agave Americana.

Table 5.9: Flexural strength of sample no.3

Sample No.3	Flexural Strength (MPa)
Specimen 1	39.884
Specimen 2	40.392
Specimen 3	40.702
Specimen 4	40.041
Specimen 5	40.357
Avg.	40.275
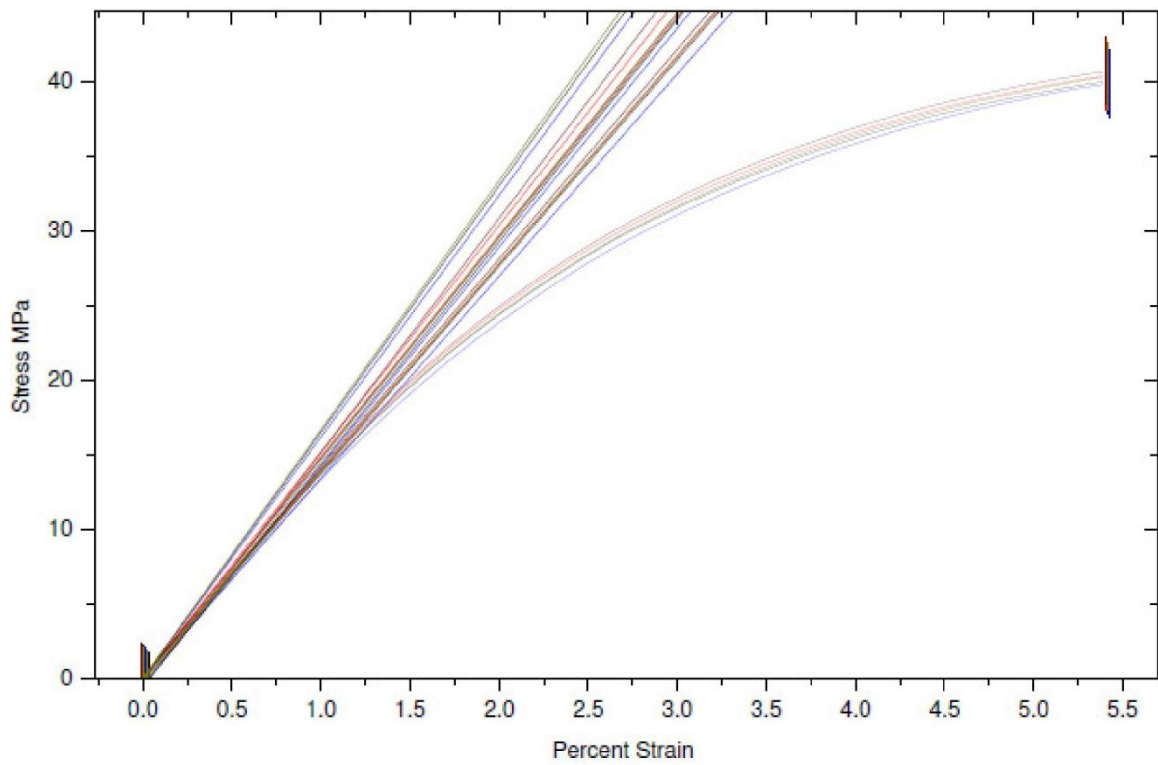
Figure 5.9: Flexural Strength - Graph of Sample no.3

The Figure no 5.10 shows the flexural strength and flexural strength graph of sample no. 4 i.e. PPST20TL05NF01 contains 20% starch, 5% nano Talc and 1% Agave Americana.

Table 5.10: Flexural Strength of sample no.4

Sample No.4	Flexural Strength (MPa)
Specimen 1	39.941
Specimen 2	40.034
Specimen 3	40.659
Specimen 4	39.905
Specimen 5	39.953
Avg.	40.098
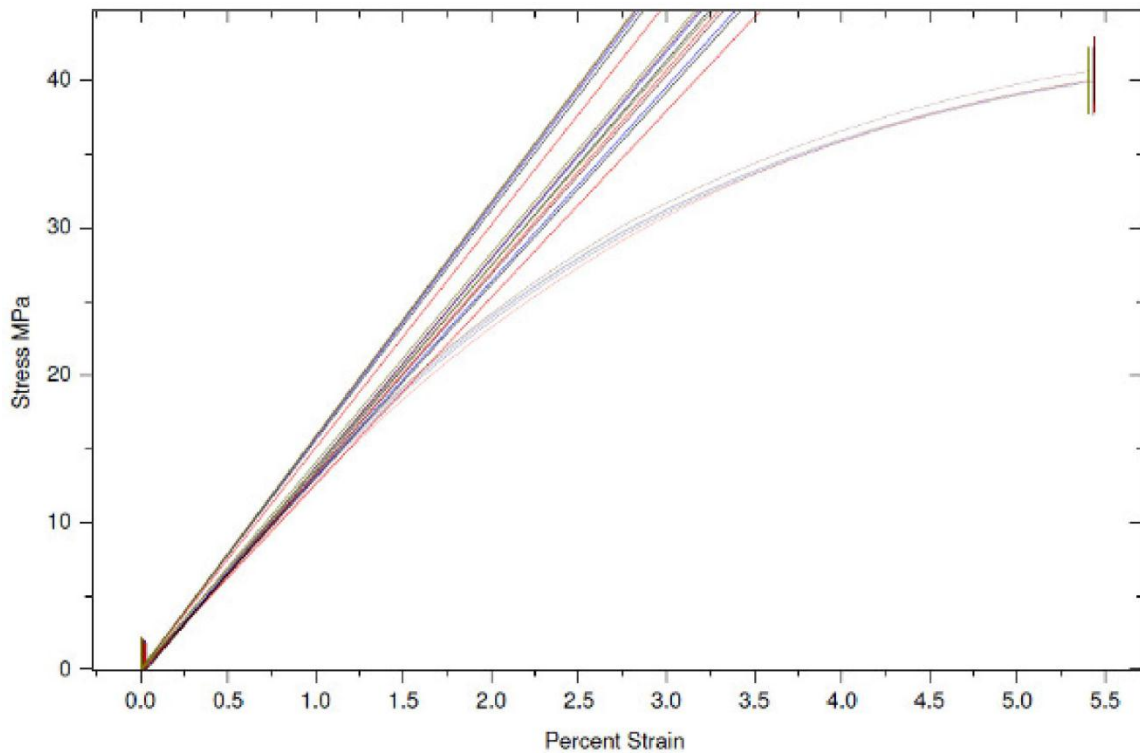
Figure 5.10: Flexural Strength - Graph of Sample no.4

The Figure no 5.11 shows the flexural strength and flexural strength graph of sample no. 5 i.e. PPST00TL05NF00 contains 0% starch, 5% nano Talc and 0% Agave Americana.

Table 5.11: Flexural Strength of sample no.5

Sample No.5	Flexural Strength (MPa)
Specimen 1	38.951
Specimen 2	40.281
Specimen 3	40.306
Specimen 4	39.420
Specimen 5	39.868
Avg.	39.765
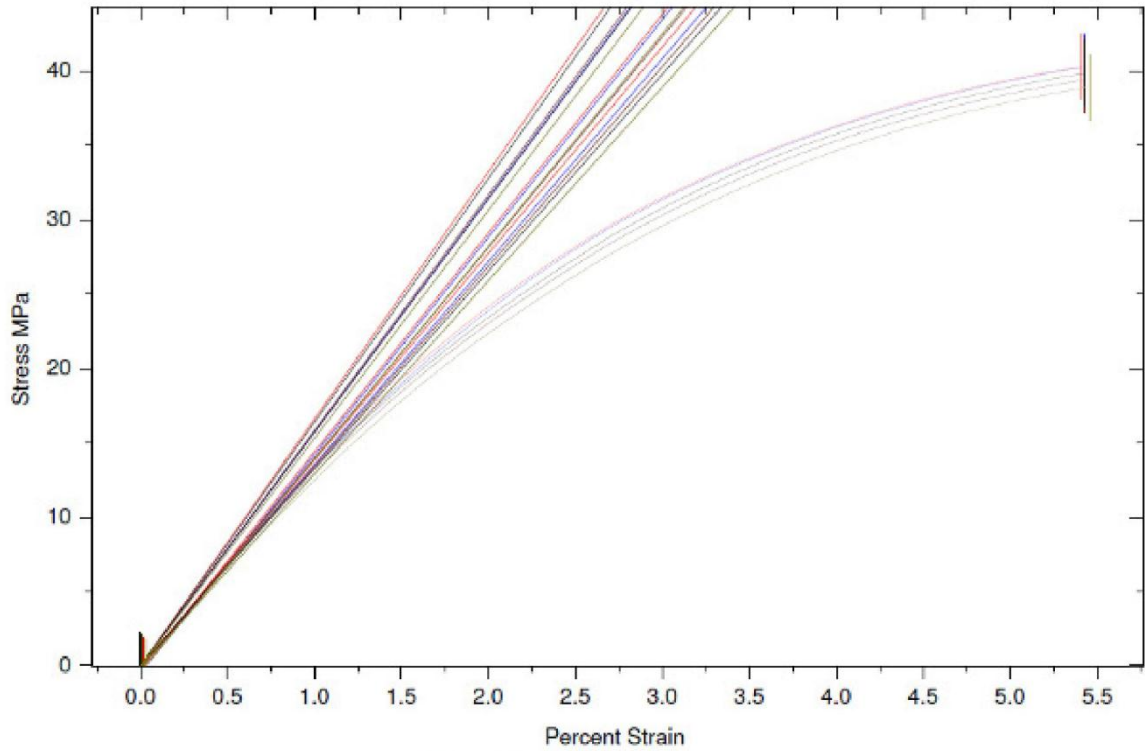
Figure 5.11: Flexural Strength - Graph of Sample No.5

The flexural strength for sample no. 2 is slightly improved as compare to the pure polypropylene. As this sample consists of highest level of fibres loading and fibres contributes against bending forces, and hence flexural strength improved. High amount of talc have the tendency to agglomerates and thus produces negative effect on the mechanical properties [Bikiaris D.N. et al., 2005]. These results are given in Figure 5.12 and Table no. 5.12.

Table 5.12: The Flexural Strength of PP and Hybrid Composites

S. No.	Sample	Flexural Strength(MPa)
1	PP	41.249
2	PPST20TL01NF05	42.359
3	PPST20TL03NF03	40.275
4	PPST20TL05NF01	40.098
5	PPST00TL05NF00	39.765
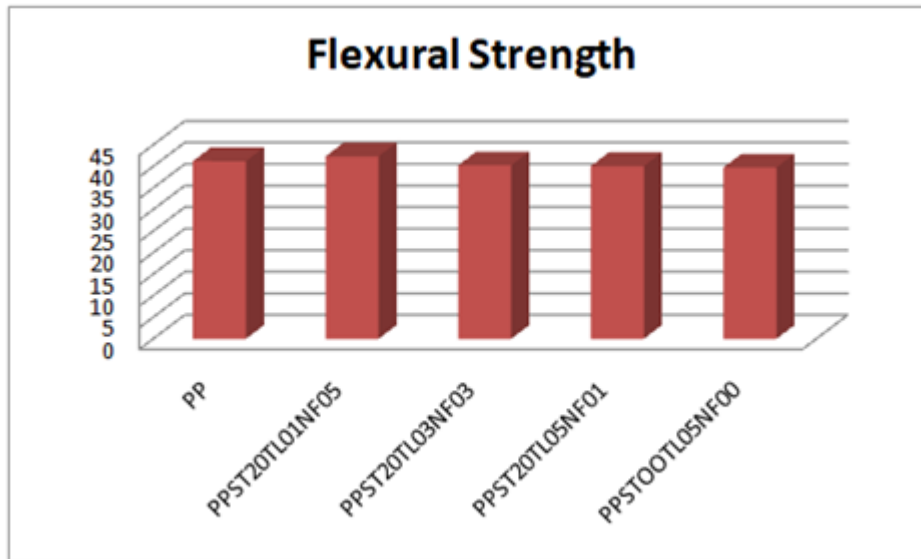
Figure 5.12: The flexural Strength of PP and its Hybrid composites

5.3. Impact Strength:

The Table 5.13 shows the impact strength of sample no.1 i.e. PP contains 100% polypropylene and 0% starch, 0% nano talc and 0% Agave Americana. The average impact strength was 1.80 KJ/m^2.

Table 5.13: Impact Strength of Sample No. 1

Sample No.1	Impact Strength (kJ/m^2)	Type of failure
Specimen 1	1.70	Complete
Specimen 2	1.73	Complete
Specimen 3	1.96	Complete
Specimen 4	1.76	Complete
Specimen 5	1.85	Complete
Avg.	1.80	

The Table 5.14 shows the impact strength of sample no. 2 i.e. PPST20TL01NF05 contains 20% starch, 1% nano talc and 5% Agave Americana. The average impact strength was 1.81 KJ/m^2.

Table 5.14: Impact Strength of Sample no. 2.

Sample No.2	Impact Strength (kJ/m^2)	Type of failure
Specimen 1	1.94	Complete
Specimen 2	2.09	Complete
Specimen 3	1.67	Complete
Specimen 4	1.76	Complete
Specimen 5	1.61	Complete
Avg.	1.81	

The Table 5.15 shows the impact strength of sample no. 3 i.e. PPST20TL03NF03 contains 20% starch, 3% nano talc and 3% Agave Americana. The average impact strength was 2.01 KJ/m^2.

Table 5.15: Impact Strength of Sample no. 3

Sample No.3	Impact Strength (kJ/m^2)	Type of failure
Specimen 1	1.96	Complete
Specimen 2	2.01	Complete
Specimen 3	2.06	Complete
Specimen 4	2.16	Complete
Specimen 5	1.85	Complete
Avg.	2.01	

The Table 5.16 shows the impact strength of sample no. 4 i.e. PPST20TL05NF01 contains 20% starch, 5% nano talc and 1% Agave Americana. The average impact strength was 2.04 KJ/m^2.

Table 5.16: Impact Strength of Sample no. 4

Sample No.4	Impact Strength (kJ/m^2)	Type of failure
Specimen 1	1.95	Complete
Specimen 2	2.07	Complete
Specimen 3	2.06	Complete
Specimen 4	2.04	Complete
Specimen 5	2.11	Complete
Avg.	2.04	

The Table 5.17 shows the impact strength of sample no. 5 i.e. PPST00TL05NF00 contains 00% starch, 5% nano talc and 0% Agave Americana. The average impact strength was 1.88 KJ/m^2.

Table 5.17: Impact Strength of Sample no. 5

Sample No.5	Impact Strength (kJ/m^2)	Type of failure
Specimen 1	1.77	Complete
Specimen 2	1.79	Complete
Specimen 3	2.01	Complete
Specimen 4	1.75	Complete
Specimen 5	2.07	Complete
Avg.	1.88	

The impact strength of hybrid composites increases slightly in sample no. 2 then it increased sharply in sample no. 3 & 4. To understand this behaviour one needs to consider that when a crack is generated due to an impact it propagates towards the poor interfacial sites, while in case of sample 3 and 4 the presence of Agave Americana fibres bears the load and improves impact strength drastically about 15% [Premalal H.G.B et al., 2002]. It can be explained because at low filler content stress concentration points are also less and the interfacial adhesion is stronger, further at low filler content uniform distribution

achieved easily which leads to intercalation or exfoliation of nano composites. The results are shown in Figure 5.13 and Table no. 5.18.

Table 5.18: The Impact Strength of PP and Hybrid Composites

S. No.	Sample	Impact Strength(kJ/m²)
1	PP	1.80
2	PPST20TL01NF05	1.81
3	PPST20TL03NF03	2.01
4	PPST20TL05NF01	2.04
5	PPST00TL05NF00	1.88
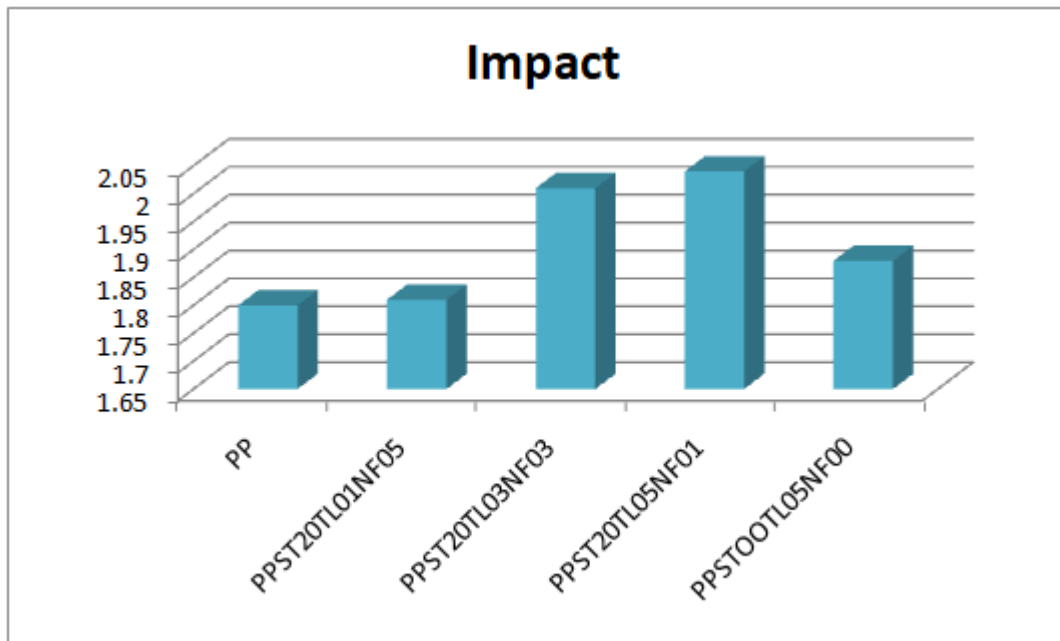
Figure 5.13: The impact strength of PP and its hybrid composites.

5.4. Morphology analysis:

The SEM micrographs of polypropylene and its hybrid composite are given in Figure 5.14. These images with different percentage of filler by weight revealed that fillers are being continuously and uniformly mixed throughout the polypropylene matrix and form a homogeneous phase. Results show that fillers are properly dispersed due to the use of

compatibilizer and extrusion conditions. The maleic anhydride facilitates the strong ester bonds between the polypropylene chains and OH group on the fibres which is identified in our previous FTIR test [Bajwa G.S. et al., 2019].
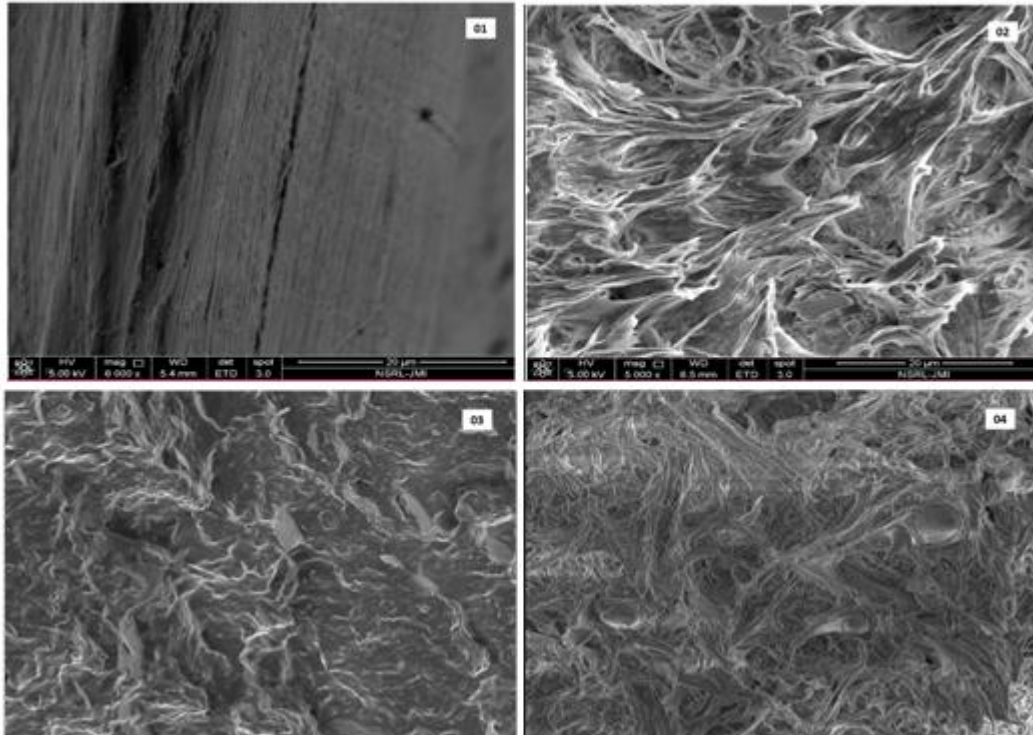
Figure 5.14: The SEM images of polypropylene based hybrid composites

5.5. X-ray diffraction:

The XRD pattern of PP and its hybrid composites is given in Figure 5.15. The sample no. 1 (Pure PP) shows the crystalline peaks at 2θ values of 14.3^0, 17^0, 18.7^0 and 22^0 corresponding to the (110), (040), (130), and (041) planes respectively for pure polypropylene system [Sarkar M.C.et al., 2008; Kocic N. et al., 2012]. These crystalline peaks were also presents in other hybrid composites i.e. sample no. 2 to 5, confirms the presence of PP as polymer matrix in all composites. The sample no. 2, 3 and 4 shows an extra peak at 25.5^0, which confirms the presence of starch. The existence of talc in the hybrid composites sample no. 2, 3, 4 and 5 could easily be characterize by the diffraction

peak at 2θ values 9.3^0 and 28.62^0 corresponding to the (002) and (113) plane respectively [Stemple I.S. and Brindley G.W., 1960]. 2θ values are decreased as compared to pure polypropylene indicating that distance between the filler components had become greater and hence intercalation structure between the hybrid composites [Alshabanat M., 2013].
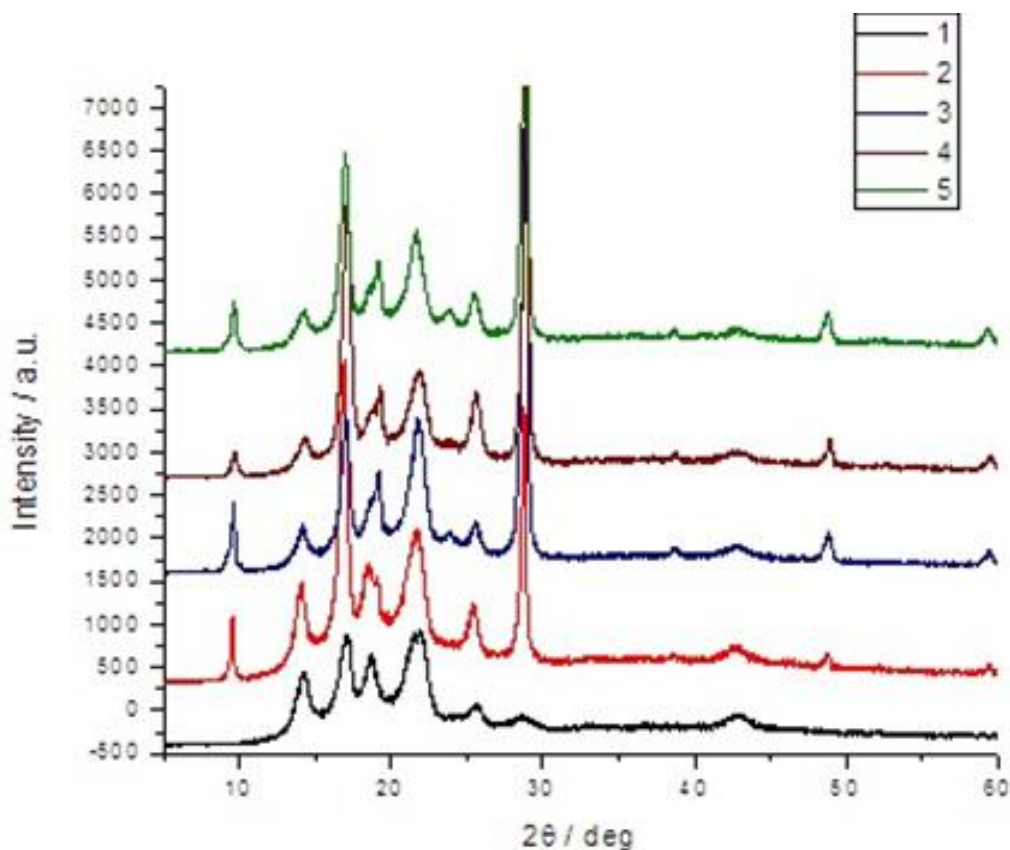
Figure 5.15: The X-ray Diffractograph of PP and its Hybrid Composites

5.6.Fourier Transform Infra-Red Spectroscopy:

The FTIR spectra of polypropylene and its hybrid composites were shown in Figure 5.16. All five spectrums show very sharp crystalline peaks. These spectrum peaks were utilized to confirm the existence of reactive melt blending and results with the bond formation between polypropylene and its fillers i.e. starch, Agave Americana and nano talc through compatiblizer MAPP, which ultimately leads to the developments of hybrid composites. All five spectrums shows peaks of polypropylene at 2951 cm^{-1}, 2868 cm^{-1} and 1376 cm^{-1} (-CH$_3$ groups), 2917 cm^{-1}, 2837 cm^{-1} and 1457 cm^{-1} (-CH$_2$ groups), and three characteristic

isotatic peaks at 1167 cm^{-1}, 997 cm^{-1}, and 973 cm^{-1} [Alshabanat M., 2013; Devasahayam S. et al., 2013]. This confirms the presence of polypropylene in all composites as matrix. Peaks at 1746 cm^{-1} confirms anhydride group of MAPP in backbone of polypropylene, which can be assigned to carbonyl group through which all fillers becomes the part of structure and contributes their properties in hybrid composites [Gupta A.P.et al., 2010]. The existence of starch in formulation 2, 3, and 4 confirms by very dim hump like structure at 3600 cm^{-1} to 3100 cm^{-1} (OH), 1746 cm^{-1} (C=O), 1257 cm^{-1} (-O-C=O) and1017 cm^{-1} (C-O) [Gupta A.P. et al., 2010; Wang S.J.et al., 2005]. The sharp peaks observed at 668 cm^{-1} stretching vibration of -OH confirms the presence of talc materials and same has been evident from the intensity level of the peaks increases as loading of talc increases in sample no. 2, 3, 4 and 5 respectively [Alshabanat M., 2013]. The peaks at 668cm^{-1}, 808cm^{-1}, 841cm^{-1} attribute to presence of sacharides structure due to the presence of Agave Americana fibres. Peaks at 1456cm^{-1}also confirms the presence of glycerol which is used as plasticizer.
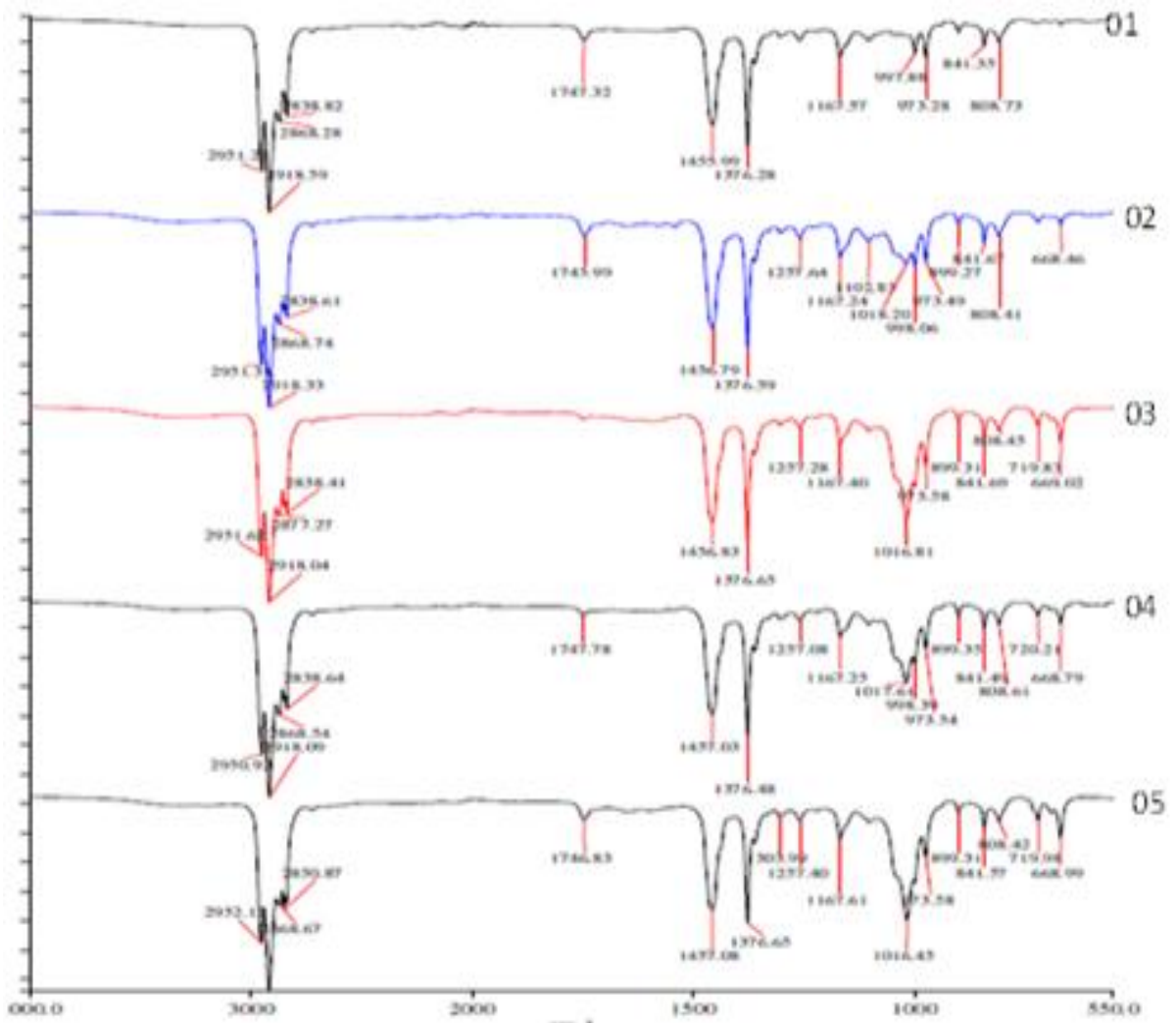
Figure 5.16: FTIR of PP and its hybrid composites

5.7. Differential Scanning Calorimetry:

The Figure no. 5.17 shows the thermal behaviour of sample no. 1 i.e. PP, contains 100% polypropylene, 00% starch, 00% nano talc and 0% Agave Americana. The thermal curves shows the heating and cooling curves between temperature $-50\,^{\circ}C$ to $200\,^{\circ}C$ at a standard rate of cooling and heating. The readings show that melting point $168\,^{0}C$, crystallization temperature $123\,^{0}C$, enthalpy of melting 97.33 J/g and enthalpy of crystallization 114.7 J/g.
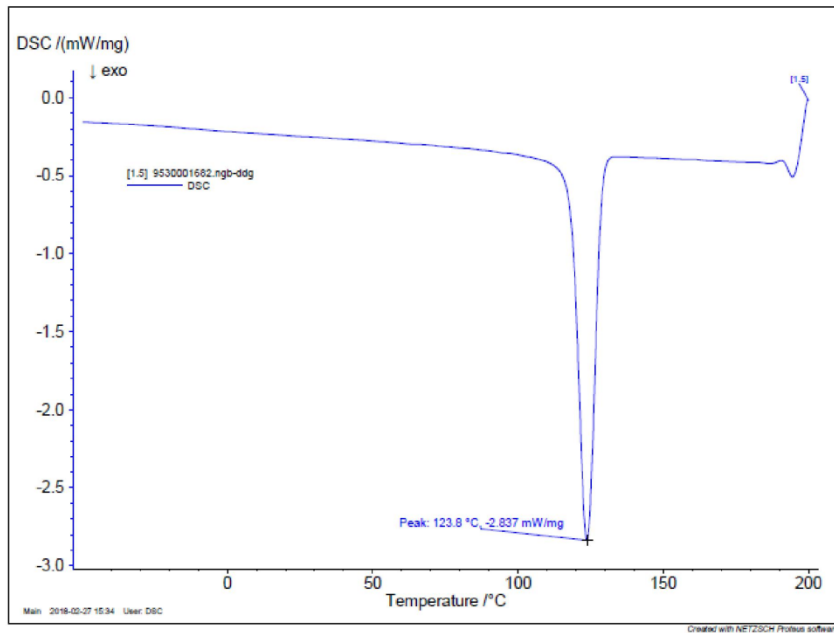
(a)
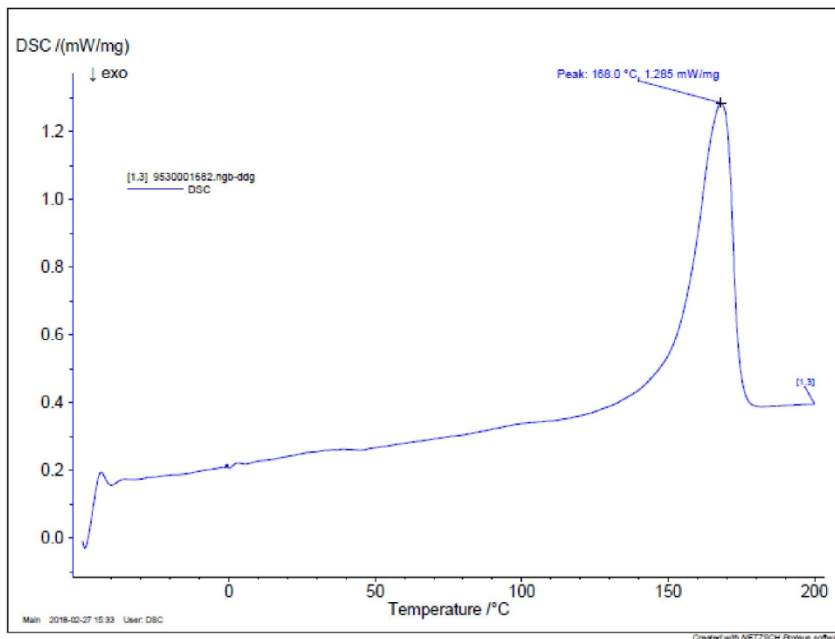
(b)

Figure 5.17: Thermal Curves of Sample 1: (a) Cooling and (b) Heating pattern

The Figure no. 5.18 shows the thermal behaviour of sample no. 2 i.e. PPST20TL01NF05, contains 20% starch, 01% nano talc and 05% Agave Americana. The thermal curves shows the heating and cooling curves between temperature -50°C to 200°C at a standard rate of cooling and heating. The readings show that melting point 165.9^{0}C, crystallization

temperature 119.2^{0}C, enthalpy of melting 93.59 J/g and enthalpy of crystallization 106.4 J/g.

(a)

(b)

Figure 5.18: Thermal Curves of Sample 2: (a) Cooling and (b) Heating pattern

The Figure no. 5.19 shows the thermal behaviour of sample no. 3 i.e. PPST20TL03NF03, contains 20% starch, 03% nano talc and 03% Agave Americana. The thermal curves shows

the heating and cooling curves between temperature -50°C to 200°C at a standard rate of cooling and heating. The readings show that melting point $167.2\ ^{0}$C, crystallization temperature $124.4\ ^{0}$C, enthalpy of melting 104.9 J/g and enthalpy of crystallization 101.2 J/g.
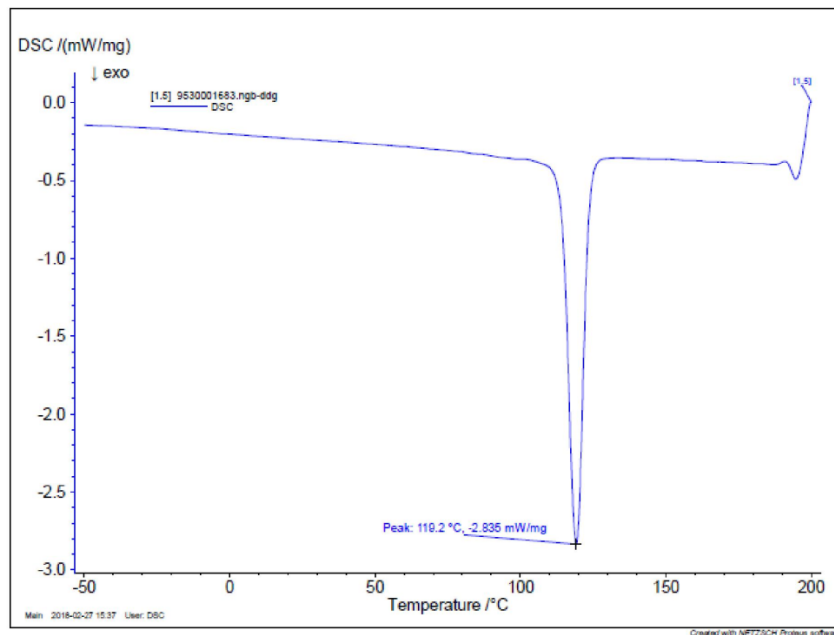
(a)
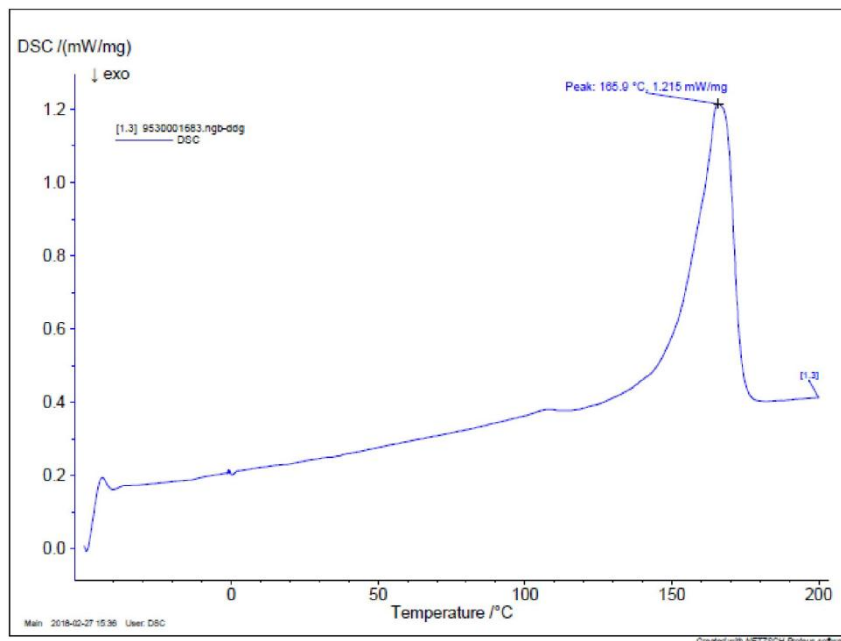
(b)

Figure 5.19: Thermal Curves of Sample 3: (a) Cooling and (b) Heating pattern

The Figure no. 5.20 shows the thermal behaviour of sample no. 4 i.e. PPST20TL05NF01, contains 20% starch, 05% nano talc and 01% Agave Americana. The thermal curves shows the heating and cooling curves between temperature -50°C to 200°C at a standard rate of cooling and heating. The readings show that melting point 166.9⁰C, crystallization temperature 122.4⁰C, enthalpy of melting 90.6 J/g and enthalpy of crystallization 102.6 J/g.
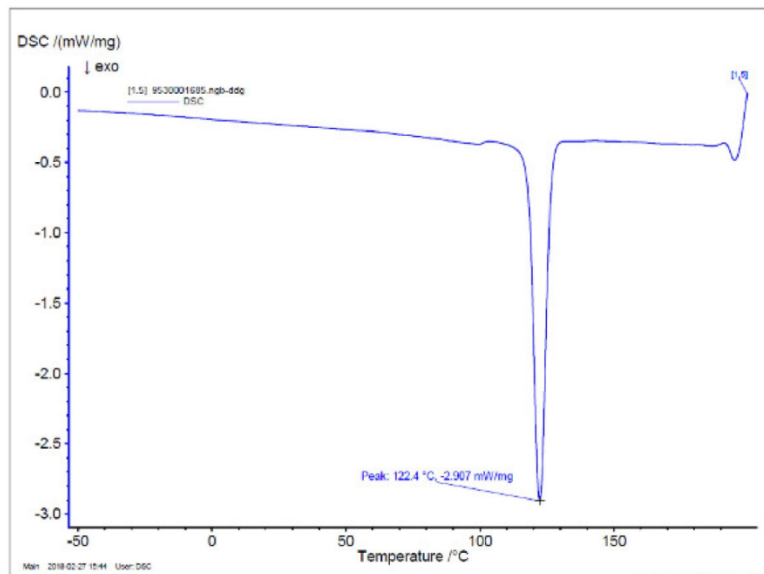
(a)
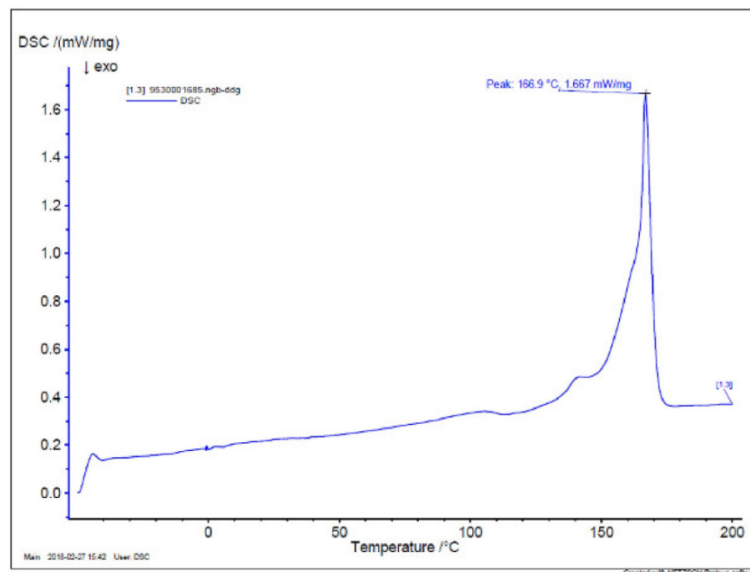
(b)

Figure 5.20: Thermal Curves of Sample 4: (a) Cooling and (b) Heating pattern

The Figure no. 5.21 shows the thermal behaviour of sample no. 5 i.e. PPST00TL05NF00, contains 00% starch, 05% nano talc and 00% Agave Americana. The thermal curves shows the heating and cooling curves between temperature -50°C to 200°C at a standard rate of cooling and heating. The readings show that melting point 167.8^{0}C, crystallization temperature 122.2^{0}C, enthalpy of melting 99.32 J/g and enthalpy of crystallization 103.4 J/g.
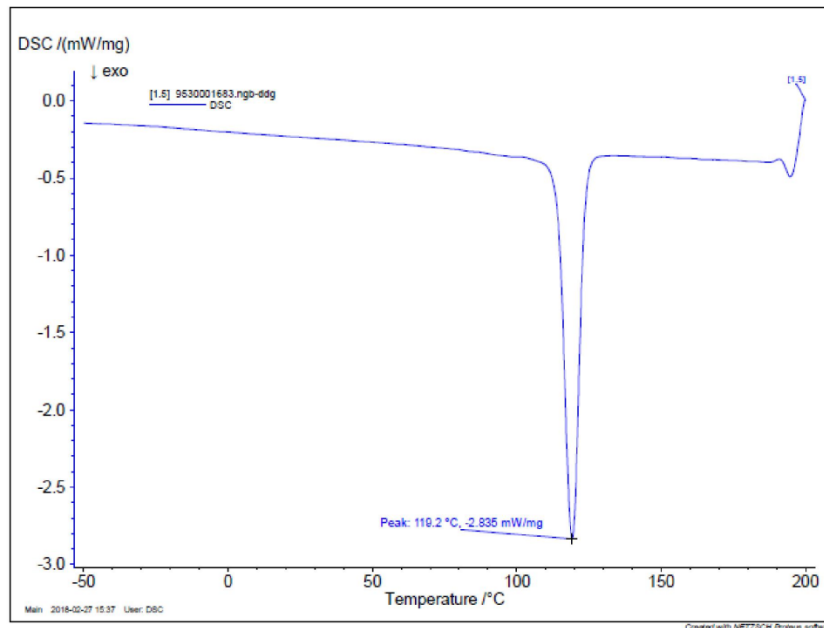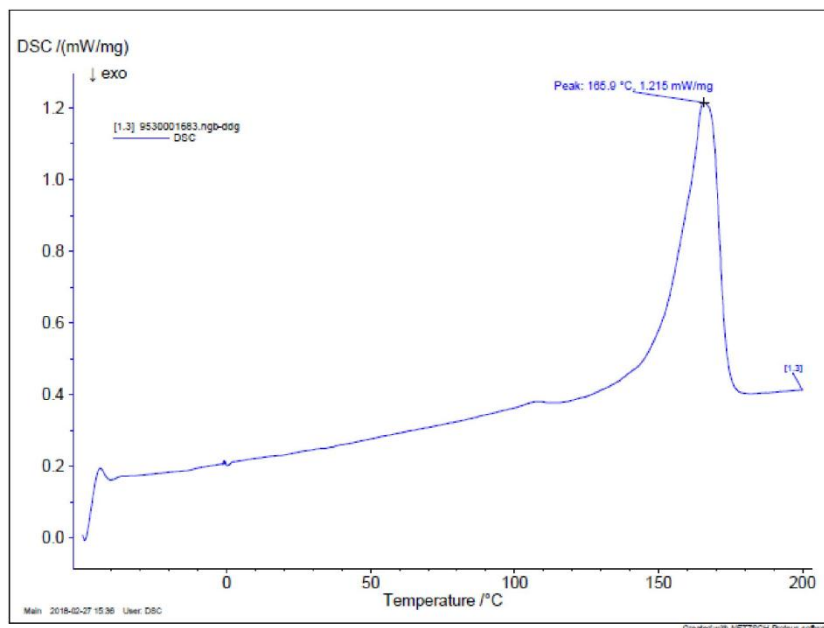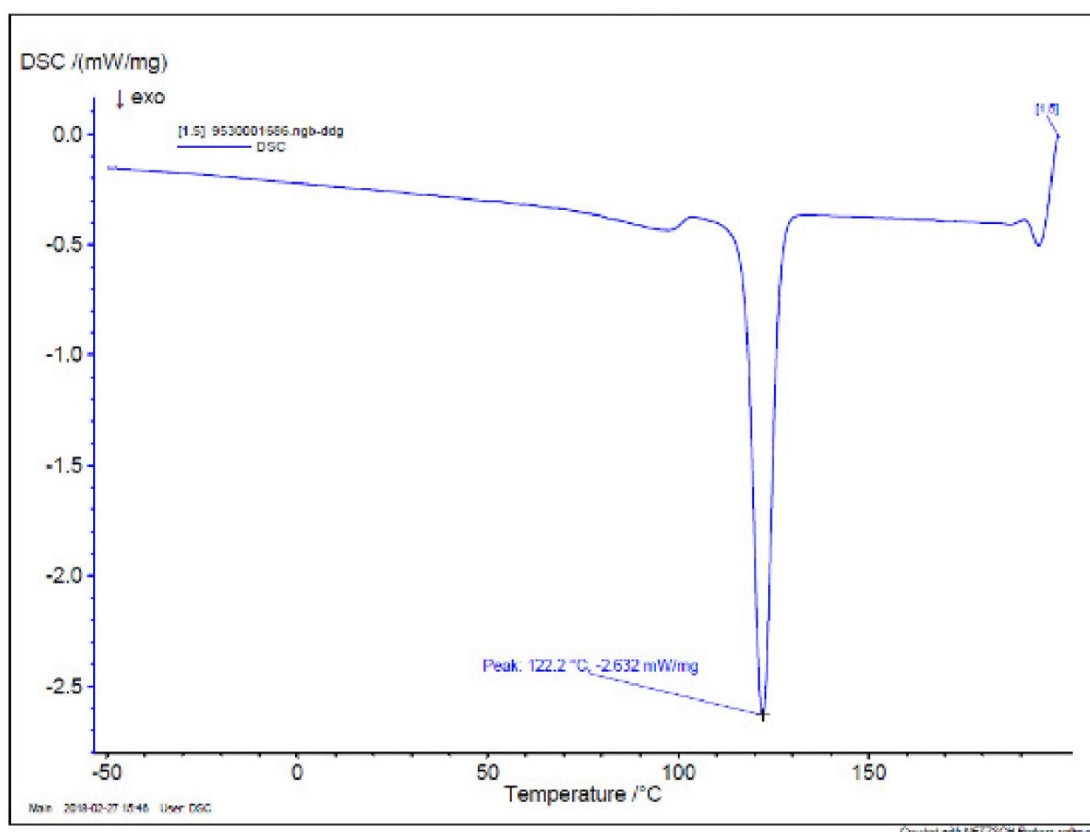

(a)
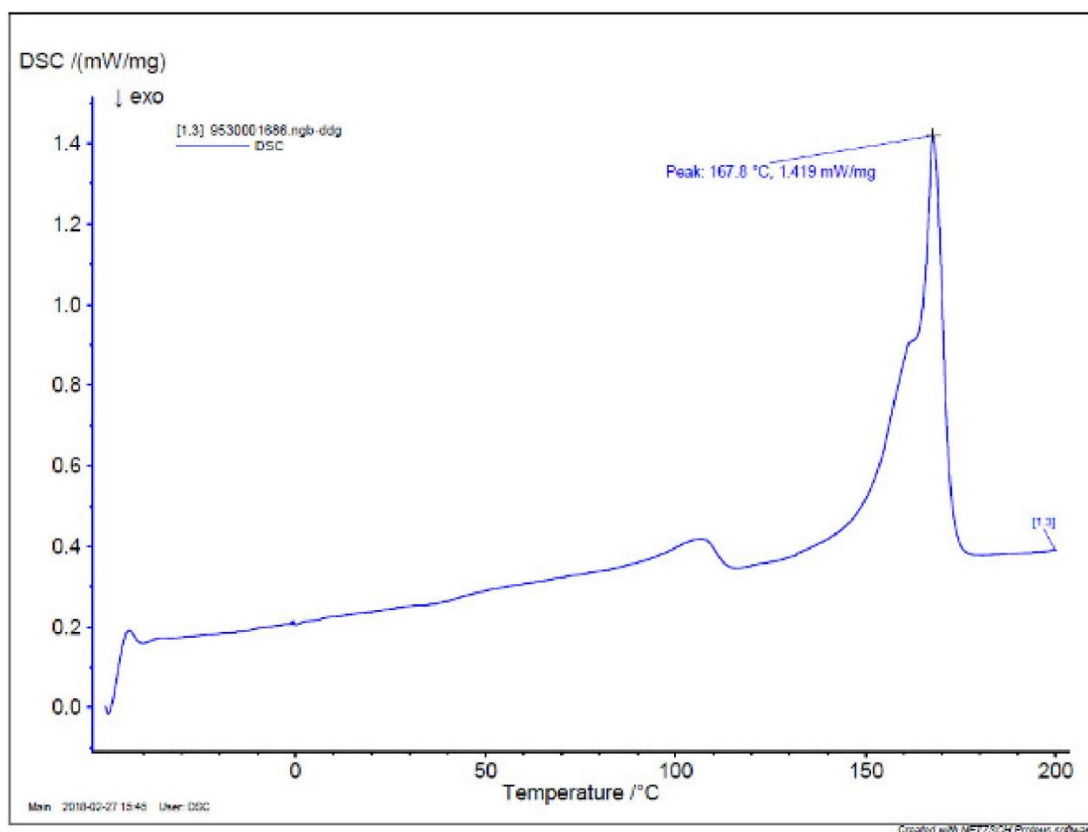
(b)

Figure 5.21: Thermal Curves of Sample 5: (a) Cooling and (b) Heating pattern

DSC thermo grams in Figure No. 5.22 and 5.23, shows the heating and cooling curves between temperature -50°C to 200°C at a standard rate of cooling and heating .The readings show that melting temperature does not modified with different composites, the crystallization temperature slightly increase in case of sample 3 as shown in Figure 5.23. It is also observed that enthalpy of melting is also maximum for sample 3 at value 104.9 J/g. In this study it is observed that talc's nucleating property is subdued in the presence of natural fibre and starch. However the results shows a uniformity in hybrid composite which indicates proper and uniform adhesion and stability of the composite the details of test summarize in Table 5.19

Table 5.19: The Melting, Crystallization and Enthalpy of Polypropylene based hybrid composites

S.No.	Sample	Melting Point (°C)	Crystallization Temp(°C)	ΔH melting(J/g)	ΔH of crystallization(J/g)
1	PP	168.0	123.8	97.33	114.7
2	PPST20TL01NF05	165.9	119.2	93.59	106.4
3	PPST20TL03NF03	167.5	124.4	104.9	101.2
4	PPST20TL05NF01	166.9	122.4	90.62	102.6
5	PPST00TL05NF00	167.8	122.2	99.32	103.4
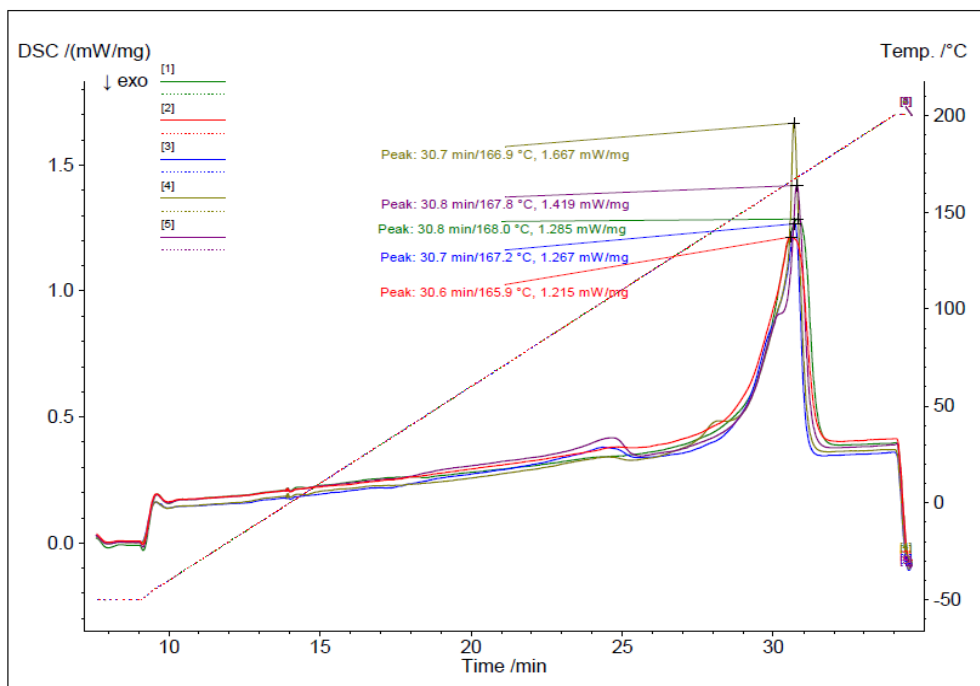
Figure 5.22: The melting point temperatures of polypropylene based hybrid composites.
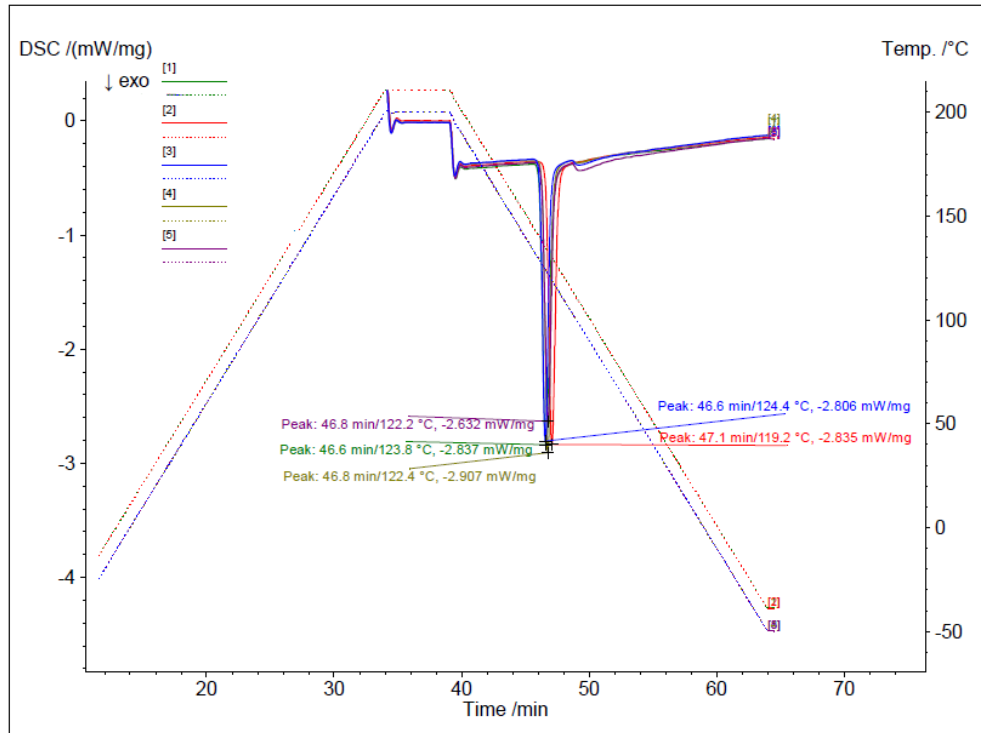
Figure 5.23: The Crystallization temperatures of polypropylene based hybrid composites.

5.8.Heat Deflection Temperature:

The HDT of all sample are preconditioned at 23+/- 2°C and 50 +/- 10% RH for 40 hrs. The stress for each sample is kept constant at 0.45MPa and employing heating rate of 120°C/hr. For HDT calculation deflection is 0.25 mm for each sample for each reading we took the average of two samples for more reliability. The values for each sample illustrated in Table 5.20. The incorporation of nano talc increased the hardness of hybrid composites and hence sample no. 4 and 5 shows highest level of heat deflection temperatures [Guo Z.et al., 2009; Horroch A. and Kandola R., 2005].

Table No.5.20: The Heat Deflection Temperatures of polypropylene based hybrid composites

S.No.	Sample	HDT($^\circ$C)	Deflection(mm)
1	PP	123.95	0.250
2	PPST20TL01NF05	107.25	0.250
3	PPST20TL03NF03	109.50	0.250
4	PPST20TL05NF01	117.05	0.250
5	PPST00TL05NF00	115.60	0.250

5.9.Vicat Softening Temperature:

For VST all samples are preconditioned at 23 +/- 2°C and 50 +/- 10% RH for 40 hrs. Load during testing kept constant at 10-0 +/- 2N and heating rate employed is 50 +/- 5°C/hr. Deflection during test kept constant at 1mm. VST temperature for sample 3 and 5 is constant at 142.80, maximum VST temperature for pure PP is 149.35 $^\circ$C .The results are in line with the conclusion of [Zhang V. et al., 2012]. For each reading we took average of two samples. Values for each sample is shown in Table No 5.21

Table No.5.21: The Vicat Softening Temperature of polypropylene based hybrid composites

S.No	Sample	VST($^\circ$C)	Deflection(mm)
1	PP	149.35	1
2	PPST20TL01NF05	147.80	1
3	PPST20TL03NF03	142.80	1
4	PPST20TL05NF01	145.50	1
5	PPST00TL05NF00	142.80	1

VST is a parameter usually adopted to establish the service temperature of the thermoplastic polymers and can be interpreted as a temperature at which the modulus has reached a particular level, being related to the fundamental properties of the material [Nambata S.P. et al., 1990].

Vicat temperature was found to increase with fibre content and the effect is more evident in compatibilized systems, due to increased modulus and fibre /matrix interaction [Zhang V.et al., 2012; Yu T.et al., 2010].

5.10. Melt Flow Index:

The MFI is used as a means of measuring of the flow rate of the thermoplastic polymers. It is the most accepted and widely used practical method to relate the molecular weight and viscosity of the polymer and widely used in industry. The MFI value of different compositions of bio composites were shown in Table 5.22. The MFI value of sample no. 5 was slightly increased by as compared with pure PP, which indicates the uniform distribution of nano talc in the polypropylene matrix. The addition of natural fibres to hybrid composites resulted in lower values of MFI, as the addition of natural fibres hindered the flow of polymers due to the surface roughness of natural fibres.

Table 5.22: The Melt Flow Index of hybrid composites

S.No.	Sample	Melt Flow Index
01	PP	35.4
02	PPST20TL01NF05	26.4
03	PPST20TL03NF03	27.8
04	PPST20TL05NF01	32.7
05	PPST00TL05NF00	36.3

Chapter 6

Conclusion:

- The hybrid composite based on polypropylene reinforced by starch, Agave Americana natural fibres and nano talc were prepared and investigated. Four sets of composites prepared by reactive melt blending using MAPP as coupling agent, and its composition was kept constant at 10% in all composites with 20% starch in sample no. 2, 3, and 4. The composition of Agave Americana and nano talc was varied from 1, 3 and 5%. The mechanical, morphological and thermal properties of composites were studied.

- The mechanical characterization has shown that flexural strength almost remains constant throughout the all samples, but has maximum value for sample no.2, which have maximum amount of natural fibre i.e., 5%. And at the same time tensile strength for this sample is also maximum amongst all prepared hybrids and is nearly equal to pure PP. The impact strength increased in sample no. 3 and 4, this reflect that the incorporation of Agave Americana fibres increased impact strength as expected. The tensile strength and % elongation decreased by the addition of Agave Americana, starch and nano talc in sample no. 2, 3, 4 and 5.

- The morphological characterization based on SEM has confirmed that natural fibres, starch and nano talc were distributed uniformly, indicating a good dispersion of natural fibres, nano talc and thermoplastic potato starch in the PP/PP-g-MA matrix. It has been observed that starch and talc participated in hybrid composition as particulate materials, and this was confirmed by sharp and crystalline peaks in FTIR and XRD. In XRD graph 2θ values are decreased for hybrid composite as compared to pure PP values indicating that distance between the filler composites increased indicating good intercalation between the hybrid composites.

- Vicat softening temperature has been utilised to indicate the service temperature of polymer based hybrid composites. The VST was increase with fibre loading and effect is proven in sample no. 2 having highest content of natural fibres i.e. Agave Americana.

- Heat deflection temperature confirms that with increase of talc (nano level inorganic filler) content, the thermal stability improved for the hybrid composite. The presence of low level of natural fibres in sample 4 with 5% nano talc content shows highest level of HDT. DSC test shows that crystallization temperature slightly improved for sample no.3. In hybrid composite talc's nucleating property subdued due to natural fibre and starch, whereas melting temperature does not modified for the composite.

- The addition of natural fibres to hybrid composites resulted in lower values of MFI, as the addition of natural fibres hindered the flow of polymers due to the surface roughness of natural fibres.

- Homogeneous mixing of the filler is a positive indication which will help to replace the synthetic fibres. This hybrid composite can further be tested for various properties in future. This will help to produce light weight, thermal resistant and tough durable environmental friendly material. These results confirm and provide a scope of new development of hybrid composites, which require less energy during processing, reduced CO_2 emissions, easily degradable and easy to dispose due to presence of bio-materials (Starch and Agave Americana). These materials will reduce the burden on the petroleum products.

- Agave Americana leaf fibre is a new sustainable alternative for petroleum derived and ecologically unfriendly substituents. Agave Americana leaf fibres have better physical properties that make it suitable material to replace conventional materials

as reinforcement. This not only provides a biodegradable resource but also provide opportunity for economic development in rural areas.

- The hybrid composite finds extensive use in automobile sector due to advanced properties and low density. Further it can be used for any type of environment in hazardous chemical industry. This material can also be used for constructional and furniture items due to their toughness.

FUTURE PROSPECTIVES:

- This work shows the possibility of application of this type of hybrid mixing in plastic processing industry. The future of natural fibres hybrid composites appears to be bright because they are economical, light weight, sustainable nature and environmentally superior. The new composite structure offers new technology and commercial prospects for different sectors.

- Biodegradation offers a lot of advantages such as the reduction of plastic waste and reduction in the cost of waste management. However this can't be implemented for every material but can be helpful to reduce the harmful effects on the environment with the use of biopolymers to some extent.

- Future research should hence focus on achieving superior technical performance and component life. The less explored aspects of hybrid composites such as the electric resistance and acoustic insulation properties can be the point for future research and development, to expand new areas of application.

- Adhesive bonding is the preferred joining method for composites and increasingly used in the automotive industry, however natural fibre reinforced polymer composites adhesive joints needs further investigation in future. The other use of this hybrid material can be in additive manufacturing.

- We must use the fibre that is easy in production and require less amount of water and care, further it should not belong to food chain; Agave Americana seems to be the desired fibre from these points of view.

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B. Research Papers Published in International / National Conference Proceedings

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[3].   **Bajwa G.S.**, Ranganath M.S., Mishra R.S. and Aftab A.; "Recent Development in Polymeric Hybrid Composites: Opportunities and Challenges" in International Conference on Advanced Production and Industrial Engineering at Delhi Technological University, Bawana Road, New Delhi on October, 2017.