INVESTIGATION OF THE BIO DEGRADABILITY OF THE STARCH MODIFIED POLYPROPYLENE WITH THE HELP OF MALEIC ANHYDRIDE AS A COUPLING AGENT

A MAJOR PROJECT REPORT
SUBMITTED FOR THE PARTIAL FULFILLMENT OF THE REQUIREMENT
FOR THE AWARD OF THE
DEGREE OF
MASTER OF TECHNOLOGY
IN
POLYMER TECHNOLOGY
UNDER THE ESTEEMED GUIDANCE OF
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Declaration

I hereby declare that major project entitled "Investigation of the bio-degradability of the starch modified polypropylene with the help of maleic anhydride as a coupling agent" is a record of original work done by me under the guidance of Dr. Anil Kumar (Assistant Professor), during the session 2014-2015.

I also declare that no part of this report has been previously submitted to any University or any examining body for acquiring any degree.

STUDENT SIGNATURE

CERTIFICATE

This is to certify that M.Tech major project entitled "**Investigation of the bio-degradability of the starch modified polypropylene with the help of maleic anhydride as a coupling agent**" submitted by Ashish Virmani for the award of the degree of "**Master of Technology in Polymer Technology"** is a record of the bonafide work carried out by him. Ashish has worked under the supervision and guidance of **Dr. Anil Kumar (Assistant Professor),** and has fulfilled the requirements for the submission of the dissertation. The project work has been carried during the session 2014-2015.

To the best of my knowledge and belief, this work has not been submitted to any other university/institution for the award of any degree or diploma.
No part of this project work has been reproduced elsewhere for any degree or diploma.

PROJECT GUIDE	**HEAD OF DEPARTMENT**
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ABBREVIATIONS

1. PP: Polypropylene
2. PVA: Poly Vinyl Alcohol
3. MAH: Maleic Anhydride
4. Sample 1: Pure PP
5. Sample 2: PP+MAH+STARCH+PVA
6. Sample 3: PP+MAH+STARCH
7. SEM: Scanning Electron Microscopy
8. FTIR: Fourier Transform Infrared Spectroscopy
9. UTM: Universal Testing Machine

ABSTRACT

Polypropylene was modified with starch in 1/20 ratio by adding a coupling agent in the absence and presence of a compatiblizer so as to produce a modified polypropylene with the advantage of bio-degradability in lesser time as compare to normal time span of degradation. As polypropylene a hydrophobic material and starch a hydrophilic material, so maleic anhydride was used as a coupling agent and PVA used as a compatiblizer to produce proper formation of bond. For the proper inter-mixing of the polymers they were swollen by aromatic compound such as toluene at elevated temperature. The material produced was tested in IR Spectroscopy, Universal Testing Machine, Water Absorption Test, Soil Burial Test and Scanning Electron Microscopy for the checking of proper inter-mixing, change in mechanical properties and to check the bio-degradability respectively.

AIM AND OBJECTIVE

AIM

The aim of the project was preparation and characterization of the starch modified PP samples for degradation.

PROJECT OBJECTIVE

Synthesis of starch modified PP: It was carried out in the presence and absence of PVA with Maleic anhydride as a coupling agent.

Mechanical Properties analysis: To know about the change in tensile properties after the addition of starch and maleic anhydride in to the PP.

Bio-degradation analysis: To know the change in weight and different surface properties under normal conditions.

Morphological characterization: To know the change in surface properties at microscopic level.

Introduction

Plastics are used in almost every field due to its excellent properties, easy availability, easy molding and cheap price. It is estimated that all over the world near about 140 million tons of polymers are produced synthetically to replace conventional material.[1,2] Over 70% of post-consumer plastic waste is recycled every year which is produced by households and after every recycling their properties reduced and after some cycles they are unable to recycle. Plastics are compounded to resist the environmental degradation and also more cost effective than other conventional materials in terms of manufacturing cost and energy required. Due to these reasons, plastics which are continuously entering in to the waste stream becoming a great problem in the case of pollution. This continuous increasing of waste plastic has led to the increase volume of plastic waste in the landfill which is used to be one of the main methods for the disposal and is now diminishing due to this continuous hike every year.

In the early phases; reduce, reuse and recycle have become substitutes to overcome the problem of increasing waste but all this have their own limitations. Reduction refers to the reduction of the amount of material entering the waste stream by either source reduction or other reduction method in which pattern of production and consumption is redesigned to reduce the amount of plastic which is entering the waste stream as for example heated molds are invented to reduce the amount of plastic waste of sprue and runner in every cycle which reduces the amount of plastic entering the waste. Reuse strategy refers to use the non-consumed and consumed waste for the production or consumption purpose like as in the case of most of products which can be used as aesthetic materials after their shelf life.

Recycling of plastic mainly refers to three types of recycling in which primary recycling refers to the use of sprue, runner and gate which comes as a waste in every cycle by grinding them into pieces and use them again and secondary recycling refers to the use of consumed plastic waste by adding additives to make them use in production of engineering application articles with the addition of virgin material whereas in tertiary recycling the plastic waste is fully modified with chemical treatment and the resultant products are used for other purposes. Moreover, recycling is a process of sorting, collecting and recycling which is not full developed and consume lot of money and time.

There are also other factors which disturbs the superiority of recycled plastic which are usually the degradation of material during the recycling process and the plastic waste which enter the stream on regular basis are normally contaminated by dirt, Food scraps and other waste whose cleaning is one of the major problem in plastic recycling. The high volume to the weight ratio of plastic is also one of the problems for the collection and transportation of the waste which makes plastic recycling costly. Lastly, the plastics will terminate at the landfill again.

Composting is becoming an appropriate way-out to this as this can reduce the 70% of solid waste produced. However, in landfill the environment is anaerobic and dry not favorable for much reduction where in composting there is a proper environment for waste reduction which are humidity, aeration and high temperatures. Plastics have high volume of solid waste and in these field Bio-degradable polymers can play a significant role.

Biopolymer as a solution

To reduce the increasing environment issues related to polymers the society has directed its research onto bio-degradable polymers. They are the polymers which in natural environment start reducing its chemical properties, mechanical properties and structural properties and finally changes into other smaller compositions which are innocuous in nature. These polymers are usually produced by from natural and renewable resources but the society has directed its effort to produce it from crude oil. There are divided into four divisions which are widely known. The first divisions of bio polymers are the polymers which are made by natural raw material such as Polysaccharides, Polypeptides, Jute, Starch, Cellulose, casein and silk etc. The second division polymers contain those polymers which are chemical synthesized from naturally- derived monomers such as poly lactic acid (PLA). The third division polymers are those which produced by micro-organisms or genetically modified by the help of bacteria such as poly hydroxyl-alkanoates (PHA), poly hydroxyl-butyrate, poly hydroxyl-valerate and pullan etc. The fourth divisions of polymers are those which are produced from crude oil like aliphatic and aromatic polyesters, polyvinyl alcohol and modified polyolefin.

Biodegradability of plastics

A material is said to be bio-degradable if it start reducing in natural occurring phenomena as in the presence of sunlight, oxygen or with the help of micro-organisms. Biodegradation of a material may occurs in various phases such as in the first phase the macromolecule experience a direct enzymatic scission which is followed by the metabolism of split portions and leads to an advanced enzymatic dissimilation of the macromolecule from the chain endings and the chain fragments will become short enough to be converted by micro-organisms.

Bio-degradable polymers are usually manufactured by renewable resources which are mostly in the form of natural polymers like starch and cellulose. These bio-polymers are first disposed in a bio-waste collection centre and finally composted which will ultimately reduce into an environmental friendly by-products.

Factors affecting the bio-degradability of plastics

Chemical and physical properties of polymers plays a great role in the process of bio-degradation. The surface condition, first order structure and high order structure all play a significant role in the bio-degradation process of polymer. Surface area, hydrophobic and hydrophilic properties are the surface condition properties which play a major role as a hydrophilic polymer of a greater surface area will reduce faster as compare to lower surface area and hydrophilic polymer will reduce in a longer time in presence of water. Chemical structure, molecular weight and molecular weight distribution of the polymer are the first order structure properties which play a major role as a high molecular weight will take more time in reduction as compare to a low molecular weight. Glass transition temperature, melting temperature, modulus of elasticity and crystallinity of the polymer are the high order structure properties and they equally affect the biodegradability as like others two. Molecular weight and crystallinity are the two most significant properties which affect the bio-degradability criteria the most as other properties are dependent on it. A high molecular weight and crystalline polymer will have a properly packed structure which cannot be easily break by the enzymes and it will be more resistant to degradation as compare to the amorphous one.

Literature Review

2.1 Polypropylene

Introduction and Structure

Polypropylene is a thermoplastic polymer manufactured by using propylene as a monomer by addition polymerization. It is used in a wide variety of applications like packaging, labelling, housing of electronic items, cookware, laboratory equipment's , automotive components, mobile housing and many more. It usually shows good mechanical strength and chemical resistant to most of the acids and base. PP covers near about 40% of the plastic market and it was estimated that in 2013, the worldwide market for PP reached near about 55 million metric tons. [3]

PP is the second widely used plastic after polyethylene whose market is increasing at a growth rate of 5.8% and will exceed US$145 billion by 2019.[3] PP is synthesized in three forms which are as follows:

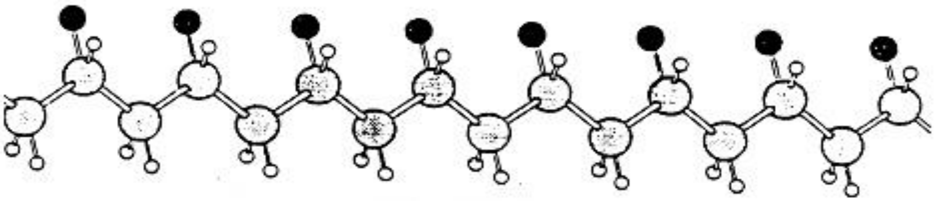


Fig 2.1.1: Isotactic

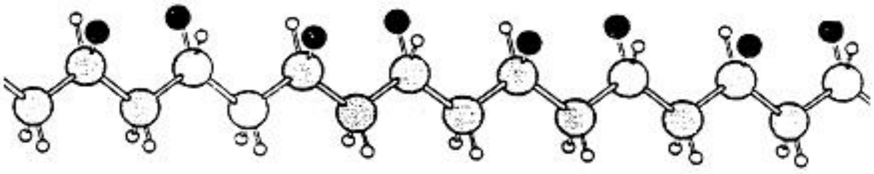


Fig 2.1.2: Syndiotactic

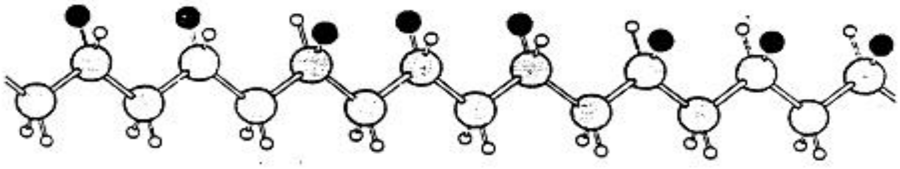


Fig 2.1.3: Atactic

Isotactic are those in which the main group is located on the one side of the plane. Syndiotactic are those in which the main group is located alternatively above and below the plane. Atactic are those in which the main group is located randomly anywhere above or below the plane. Isotactic and syndiotactic polymers are of high melting point and shows less solubility. Atactic polymers are usually used for the coating and copolymerization with other polymers because of its easy solubility.

Isotactic polymers are usually produced in less yield when made by normal process of polymerization by adding benzoyl per oxide as initiator and to increase its yield a new process is induced which uses Ziegler-Natta catalysts and they are able to restrict the linking of monomers to a specific regular orientation and by which all methyl groups are positioned at the same side with respect to the backbone of the polymer chain and Ziegler-Natta catalysts which are made from different materials can also be used for the production of syndiotactic in which the positions of methyl groups are alternate in the planes.

Isotactic PP is mostly produced with two types of Ziegler-Natta Catalysts from which the first one consist of solid catalysts which are mostly used and other one consist of soluble metallocene catalyst which are less used. They facilitate in the coiling of macromolecules into coil shape and achieving the desired properties. New catalysts which are produced for the polymerizing of propylene and other 1-alkene in to isotactic PP usually use $TiCl_4$ as an active part and $MgCl_2$ as support part which helps in activation.[4,5,6]These catalysts also contain organic modifier which can be either aromatic acid di-esters, esters or ethers. These catalyst also require special type of co-catalyst for activation which are usually organoaluminium compounds and second types of modifiers. The two most important processing characteristics of all the supported catalysts are that they able to produce high yield and productivity of the Isotactic PP at 70-80 ^{0}C under normal conditions and does not require any special processing conditions. In industry, the production of Isotactic PP is done in the medium of liquid propylene or either in gas phase reactors.

Syndiotactic PP is mostly produced with different types of metallocene catalysts as compare to those used for Isotactic PP. They also helps in the coiling of macromolecules but in these helices are of different types. This type of catalyst employ bridged bis-metallocene complexes of the bridge type -$(Cp_1)(Cp_2)ZrCl_2$ where the first Cp ligand is the cyclopentadienyl group, in which the second Cp ligand is the fluorenyl group, and the bridge between the two Cp ligands is of $-CH_2-CH_2-$, $>SiMe_2$, or $>SiPh_2$.[7] These complexes also require special type of co-catalyst for their activation which aree usually special organo-aluminum co-catalyst or methyl aluminoxane(MAO).[8]

Chemical and Physical Properties

PP is a tough and flexible polymer which exhibit good mechanical strength and shows resistant to most of the acids and base. It is usually copolymerized with ethylene to enhance its properties and after which it can be used as an engineering plastic. PP is economical and can be produce as translucent when uncolored but cannot be made as much transparent much like acrylic plastics. Pure Isotactic PP have a melting point in the range of 165-171^{0}C but commercial PP has a melting range from 160-166^{0}C depending on the presence of atactic part and crystallinity of the polymer.

Syndiotactic PP with a crystallinity of 30% has a melting range of 125-130 °C.[9] Its density ranges from 0.85 to 0.95 g/cm^3.

Biaxially oriented polypropylene (BOPP)

It is produced when polypropylene film is extruded and stretched in both the X-axis and Y-axis it is called as biaxially oriented polypropylene. Biaxial orientation helps in increasing strength and clarity of polymer. BOPP is widely used as a packaging material in packaging industry such as processed foods, fresh produce and others because of its good tear strength properties. It shows good properties of coating, printing and laminating which makes it more acceptable in packaging Industry as it is easy to give a required appearance to it.

Repairing

Polypropylene is also used in the production of pipes due to its advantageous use of repairing by speed welding technique or by using hot glue guns. There are also some glues available for gluing PP. In the process of repairing it is mostly recommended to roughen the surface with a file, sand paper or other abrasives to provide a better surface for the glue to fix the article and it is also to be taken care that surface where glue has to be applied will be properly cleaned with spirits to remove any oil or dirt present on the surface.

The Speed welding technique for PP is similar to the Iron welding. It is held with a feed tube for the plastic weld rod which has to be mixed with the semi-molten base material which is being repaired. The speed tip heats the rod and substrate simultaneously and at the same movement press the molten weld rod in to position of the joint and then a bead of PP is the put in to joint and the parts and weld rod fuse and it fixes the joints.

2.2 Starch

Starch as a Hydrophilic Polymer: Structure and Properties

Starch is a hydrophilic material and mainly made up of two homo-polymers of D-glucose which are amylase and branched amylopectin. It have the same backbone structure as amylose but with many α-1, 6'-linked branch points, and a mostly linear α-D(1, 4')-glucan. There are many hydroxyl groups present on starch chains such as two secondary hydroxyl groups at C-2 and C-3 of each glucose residue and also a primary hydroxyl group at C-6 when it is not linked to any part. Starch chains potentially shows reactivity specific for alcohols due to the existence of hydroxyl groups which permits it to be oxidized and reduced, and helps in taking part in the formation of hydrogen bonds, ethers and esters. Starch may have different proportions of amylose and amylopectin ranging from about 10–22 % amylase and 78–90 % amylopectin varies due to the source of its production. Amylose is able to dissolve in water and forms a helical structure. Starch naturally found as separate granules as short branched amylopectin chains are able to form helical structures which crystallize naturally. Starch granules shows good hydrophilic properties and strong inter-molecular association due to the presence of hydrogen bonding formed by the hydroxyl groups on the granule surface.

The internal interaction between molecules and surface morphology of starch is readily changed by water molecules due to its hydrophilic property and because of which its properties like glass transition temperature (*Tg*), dimension and mechanical properties depend on the moisture content of the material and humidity in the environment. Glass transition temperature of natural starch may be as low as 62 - 81 °C when the weight fraction of water is in the range 0.12 - 0.14. This increases the ease of process ability of starch polymers in the presence of water. Above all, the hydrophilic property of starch is also able to improve the degradation rate of most of the polyolefin which shows low degradation rate.

Starch is fully biodegradable in most of the environments. It is hydrolyzed into glucose by the action of microorganism or enzymes, and then metabolized by them into carbon dioxide and water. It is also of great importance that same the carbon dioxide will again recycle into starch again by plants and sunshine by the photosynthesis process. However, starch shows poor processing properties, dimensional and mechanical properties to be directly used in products because of which starch is used in integration with other materials.

2.3 Poly Vinyl Alcohol

Introduction

Polyvinyl Alcohol (PVA) is a synthetically produced polymer which shows hydophillic properties and is able to degrade naturally in presence of water. Its formula is $[CH_2CH(OH)]_n$. It is used as emulsifiers in papermaking industry and for polymer production industries and in variety of coatings. It is white (colorless) and odorless. It is usually available in white powder or as a solution in water. [10]

Preparation

PVA cannot be produced by the polymerizing its corresponding monomer, Vinyl Alcohol as it unstable in nature. PVA as an alternative is prepared by first polymerizing vinyl acetate, vinyl formate or vinyl chloro acetate depending on cost and other measures like availability etc. It is then converted in to the PVA. [10] The process of conversion of the polyesters is usually carried done by base-catalysed transesterification with ethanol:

$$[CH_2CH(OAcetate)]_n + C_2H_5OH \rightarrow [CH_2CH(OH)]_n + C_2H_5OAcetate$$

The properties of the produced polymer depend on the quantity of residual ester groups. Even though it shows poor properties as clothing fibre but it is produced because of its bio degradable properties.

Structure and properties

PVA is a random chained polymer which means it is amorphous in nature and is able to use as coatings. In terms of microstructure, it is mainly made up of 1,3-diol linkages $[-CH_2-CH(OH)-CH_2-CH(OH)-]$ and a little amount of 1,2-diols $[-CH_2-CH(OH)-CH(OH)-CH_2-]$ also present depending on the environment for the polymerization of the vinyl ester precursor.[10]

Polyvinyl alcohol shows good film forming, emulsifying and adhesive properties. It also shows resistant to most of the oils, solvents and grease. It also have good tensile strength and flexibility in addition with high oxygen and aroma barrier properties but all these properties are moisture dependent or in other words with moisture content and the water which acts as a plasticizer, will then reduce its tensile strength, but increase its elongation and tear strength.

PVA may have a melting range of 215-230 °C or in between 182–192°C depending on its hydrolyzed grade whether it is fully hydrolyzed or partially hydrolyzed. It decomposes rapidly above 210 °C as it may undergo pyrolysis at elevated temperatures. The Poisson's ratio of PVA is in between 0.42 and 0.48. [11]

2.4 Maleic Anhydride

Maleic anhydride is a synthetically produced organic compound with the chemical formula of $C_2H_2(CO)_2O$. It is the acid anhydride of maleic acid. It may be colorless or white solid with an acrid odor depending on its moisture content or production process. It is synthesized on a large scale because of its applications in coatings and polymers.[12]

In old times, Maleic anhydride was synthesized by the oxidation process of benzene or other aromatic compounds. As of 2006, only few plants use benzene for its production. As an alternative they start producing most of maleic anhydride is syntesized by vapor-phase oxidation of *n*-butane. This overall process helps in changing the methyl groups to carboxylate groups and dehydrogenates the carbon backbone. The selectivity of this process shows the sturdiness of maleic anhydride, with its conjugated double-bond system. Maleic anhydride chemistry is very amusing which shows its readily bi-functional reactivity. It hydrolyzes to produce maleic acid, *cis*-HOOC–CH=CH–COOH. With alcohols, the half-esters are generated, for e.g., *cis*-HOOC–CH=CH–$COOCH_3$. It can easily dimerizes in a photochemical reaction to form cyclobutane tetracarboxylic dianhydride (CBTA) which is used for the production of polyimides and as an alignment film for liquid crystal displays.[13] Around 50% of worldwide maleic anhydride output is used for the production of polymer which is unsaturated polyester resins (UPR).

However, the UPR market shows good market growth as it is used in the many industries like construction, automobile, product housing and marine industries. Maleic anhydride is a low hazard profile chemical. Maleic anhydride rapidly hydrolyzes in the presence of water but usually produce gases at the time of melting which are not environment friendly. Maleic anhydride is easily biodegraded in air in sewage sludge and in soil and water as well.

Chapter 3

Experimental Method

Materials Involved: The Polypropylene pallets were obtained from Indian Oil Corporation Limited. The sago starch and polyvinyl alcohol were obtained from the MERCK and SISCO Research Laboratories. Toluene, maleic anhydride and benzoyl per oxide were obtained from CDH Laboratories.

Lab Equipment's Involved: Three neck flask, Magnetic Stirrer, Magnetic beads, Conical Flask, Beakers, Burette Stand, Condenser, Motor, Filter paper and Thermometer.

Instrumentation: FTIR were recorded on Nicolet 380. Mechanical Tests were done on Instron 3369 Universal Testing Machine and SEM were recorded on the Hitachi 3700 N.

Preparation of samples:

Firstly, the maleic anhydride is added in the toluene in the presence of benzoyl per oxide. To this polypropylene pallets, PVA and starch were added at elevated temperature for two different samples give in Table 1. This solution was then refluxed in toluene. The samples were then put in the presence of air for the removal of volatile gases present in it and collected for the testing.

S. No.	Polypropylene (gm)	Starch (gm)	Polyvinyl alcohol (gm)	Maleic Anhydride (gm)	Benzoyl per Oxide (gm)	Toluene (ml)
Sample1	200	0	0	0	0	0
Sample 2	200	10	10	10	1	200
Sample 3	200	10	0	10	1	200

Table 3.1: Formulation of the samples

Chapter 4

Characterization

4.1 Universal Testing Machine

UTM is a special tool for the analysis of mechanical properties of the samples which may be either tensile, compression, flexural etc. as per the requirement. In this the samples are tested over a high range of load up to the specimen will not break.

Sample Preparation

The samples were prepared by the use of hand injection molding machine. The samples were analyzed by Instron 3369 UTM.

4.2 Water Absorption Test

Water Absorption is a simple test to check the change in weight and other surface properties of a material over a limited period of time in the presence of water. In this method, just the change in weight and color are recorded over a period of time. The data collected can be used to determine the different property changes in material.

4.3 Soil Burial Test

Soil burial test is a simple test to check the change in weight and other surface properties of a material over a limited period of time in the presence of soil. In this method, just the change in weight and color are recorded over a period of time. The data collected can be used to determine the different property changes in material.

4.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a method for the analysis of functional group of both the organic and inorganic samples. It can be used in the analysis of the solid, Liquid and gases. In this method the optical frequency of all the samples are recorded over a period of time. The data collected can convert an interference pattern into a spectrum. The samples are analyzed for the presence of the functional groups.

Sample Preparation

The FTIR spectra of the solid sample can be taken by the help of preparation of the pallets with KBr which is also called as drift sampling. The samples were analyzed by Thermoscientific Nicolet 380.

4.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is an important tool to analyze the surface of almost any material. It uses a focused beam of the high energy electrons to generate the signals from the specimen. SEM is used to analyze the selected point on the samples. The resolution of an image depends on the electron probe and also on the interaction of the sample specimen with the electron probe. The combination of the higher magnification, greater resolution, and crystallographic information makes it an effective method for the study ofsurface morphology.

Results and discussion

5.1 Mechanical testing

The samples were tested on the Instron 3369 Universal Testing Machine to check the change in strength and for this dumb bell shaped specimen were prepared by the use of Hand Injection molding and tested on the machine. After this test it is observed that the samples show less ductility and toughness as compare to the pure polypropylene which is due to the presence of starch as it is a brittle material and reduce ductility and toughness when added in to the polymer for the purpose of modification in properties.

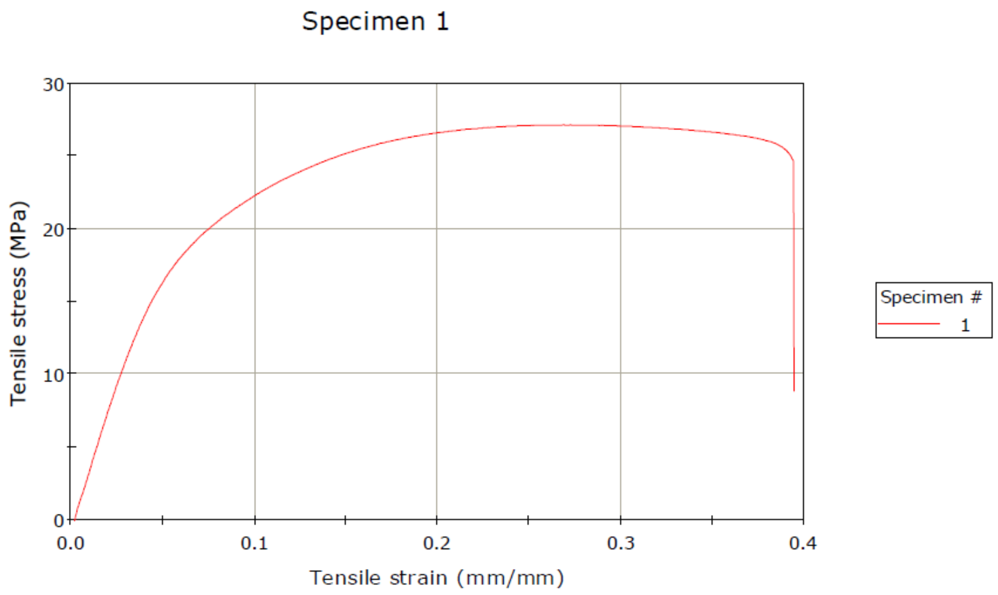
Fig 5.1.1: Instron 3369 Universal Testing Machine (UTM)

Photos of the sample for mechanical testing under UTM

Fig 5.1.2: Sample 1

Fig 5.1.3: Sample 2

Fig 5.1.4: Sample 3



Graph 5.1.1: Stress-Strain curve of Sample 1

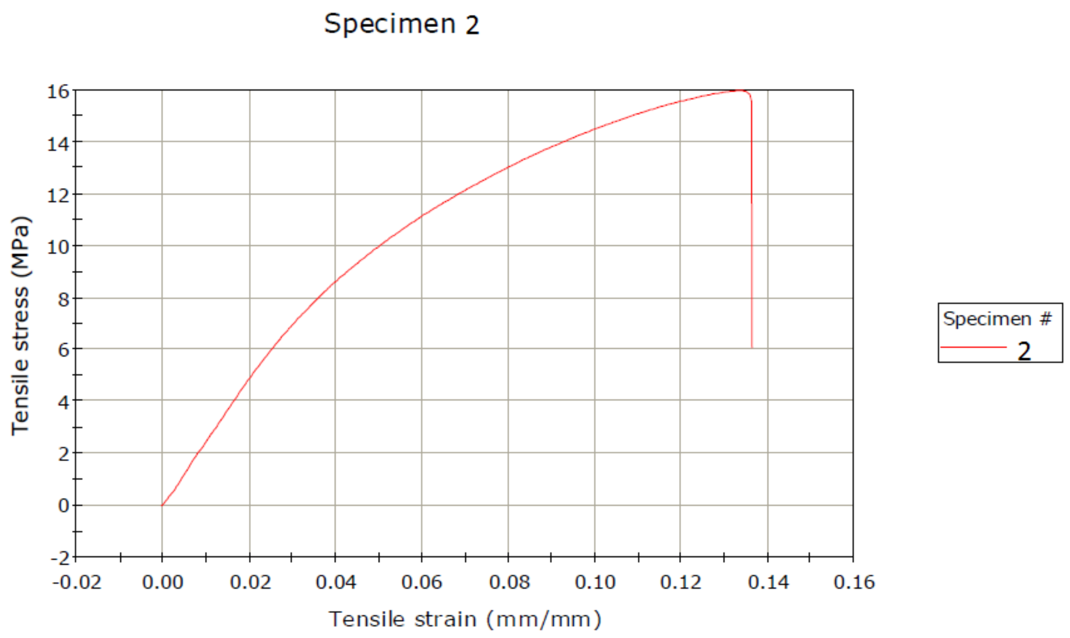
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	1.05811	25.03334	8.89008	93.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	3.00000	13.00000	39.00000	36.46656

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	0.39427	36.48140	346.71323	350.01286

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	350.01286	0.03600

Table 5.1.1: Mechanical Testing of Sample 1



Graph 5.1.2: Stress-Strain curve of Sample 2

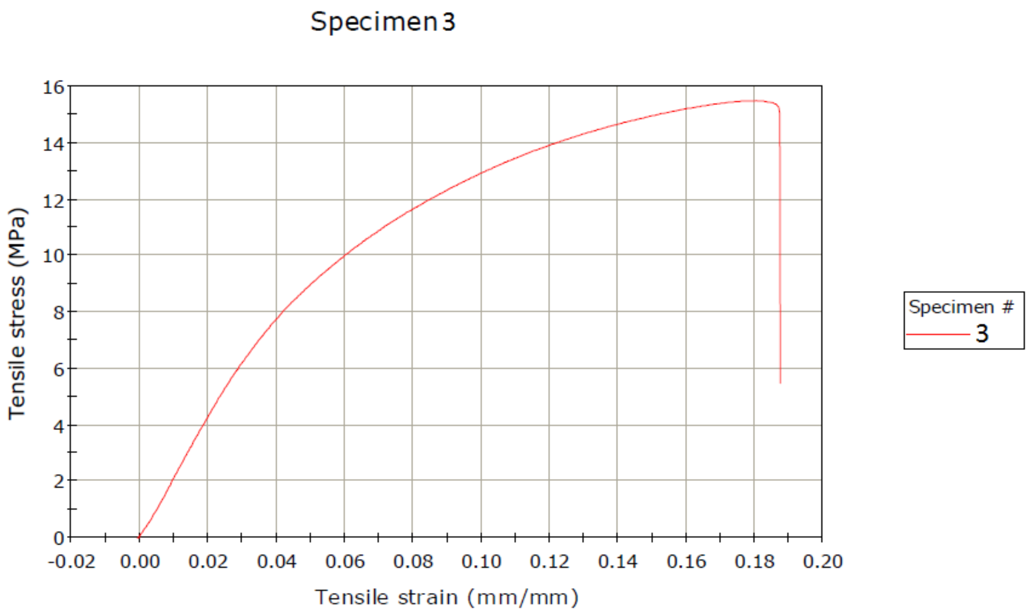
	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.62247	12.80824	6.07050	96.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	3.00000	13.00000	39.00000	13.10015

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	0.13620	13.10922	236.74942	243.43985

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	243.43985	0.03600

Table 5.1.2: Mechanical Testing of Sample 2



Graph 5.1.3: Stress-Strain curve of Sample 3

	Maximum Load (kN)	Tensile extension at Maximum Load (mm)	Tensile stress at Maximum Load (MPa)	Length (mm)
1	0.60300	16.42086	5.47291	91.00000

	Thickness (mm)	Width (mm)	Area (mm^2)	Extension at Break (Standard) (mm)
1	3.00000	13.00000	39.00000	17.10000

	Tensile strain at Break (Standard) (mm/mm)	Maximum Extension (mm)	Load at Maximum Extension (N)	Modulus (Automatic) (MPa)
1	0.18741	17.10968	213.44346	209.88487

	Modulus (Automatic) (MPa)	Final area (cm^2)
1	209.88487	0.03600

Table 5.1.3: Mechanical Testing of Sample 3

5.2 Water Absorption Test

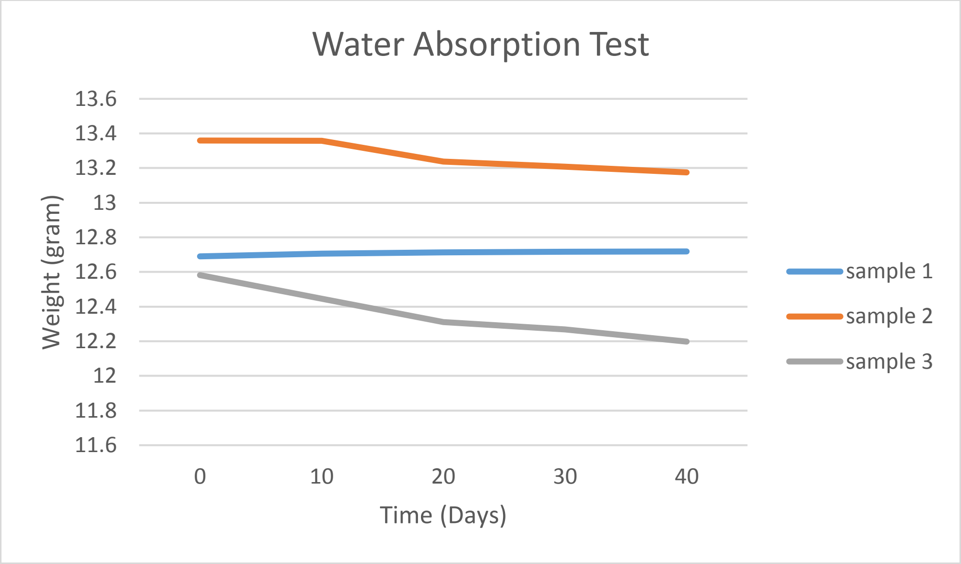
The samples were put in water for 40 days to observe the change in weight as well as size of sample. Observations are recorded in Table . After this test it is observed that the samples weight decreases with time in presence of water and polymer particles are dissociating in the water which is due to the bleeding and blooming phenomena as PVA and starch is coming out from the sample in to the water as it shows high affinity to the water as compare to Polypropylene and can be seen in Figure. [14]

Fig 5.2.1: Beaker in which Water Absorption

Test is carried out

Time	sample 1	sample 2	sample 3
(Days)	Weight in gram		
0	12.6904	13.3593	12.5821
10	12.7061	13.3586	12.4453
20	12.7128	13.2371	12.3112
30	12.7167	13.2087	12.2686
40	12.7189	13.1753	12.1983

Table 5.2.1: Water Absorption Test



Graph 5.2.1: Water Absorption Test

5.3 Soil Burial Test

In this test, samples were deeply buried in the soil for 40 days to observe the change in weight were shown in Table. It was observed that the sample weight increases with time which may be due to the absorbance of moisture by different materials present in the sample as polypropylene itself a hygroscopic material and whereas starch and maleic anhydride were also able to absorb a great amount of moisture. [15]

samples	change in weight	
	Before	After
sample 1	6.3226g	6.3235g
sample 2	3.5464g	3.5669g
sample 3	3.8650g	3.8872g

Table 5.3.1: Soil Burial Test

5.4 Fourier-transform Infrared Spectroscopy

Fourier- transform spectroscopy was used to check and collect the qualitative data related to the chemical character and the functional group of the Polypropylene, Starch, maleic anhydride and PVA and there resultant product. The samples were studied under the drift sampling process by Nicolet 380.

Figure shows typical FTIR spectra for Maleic anhydride, starch, PVA, PP and modified samples of PP. The presence of peaks at 2700-3000 cm-1, and 800 – 1800 cm-1 were the characteristics bands of PP. Sample 2 shows increase in the no. of peaks in between 800 - 1800 cm-1 and decrease in the percentage of transmittance at 2700 - 3000 cm-1 peaks was typically due to the presence of PVA & Maleic anhydride and Starch respectively. Sample 3 shows increase in the no. of peaks in between 800 - 1800 cm-1 and decrease in the percentage of transmittance at 2700 - 3000 cm-1 and 800 – 1800 cm-1 peaks was typically due to the presence of Maleic anhydride and Starch respectively.

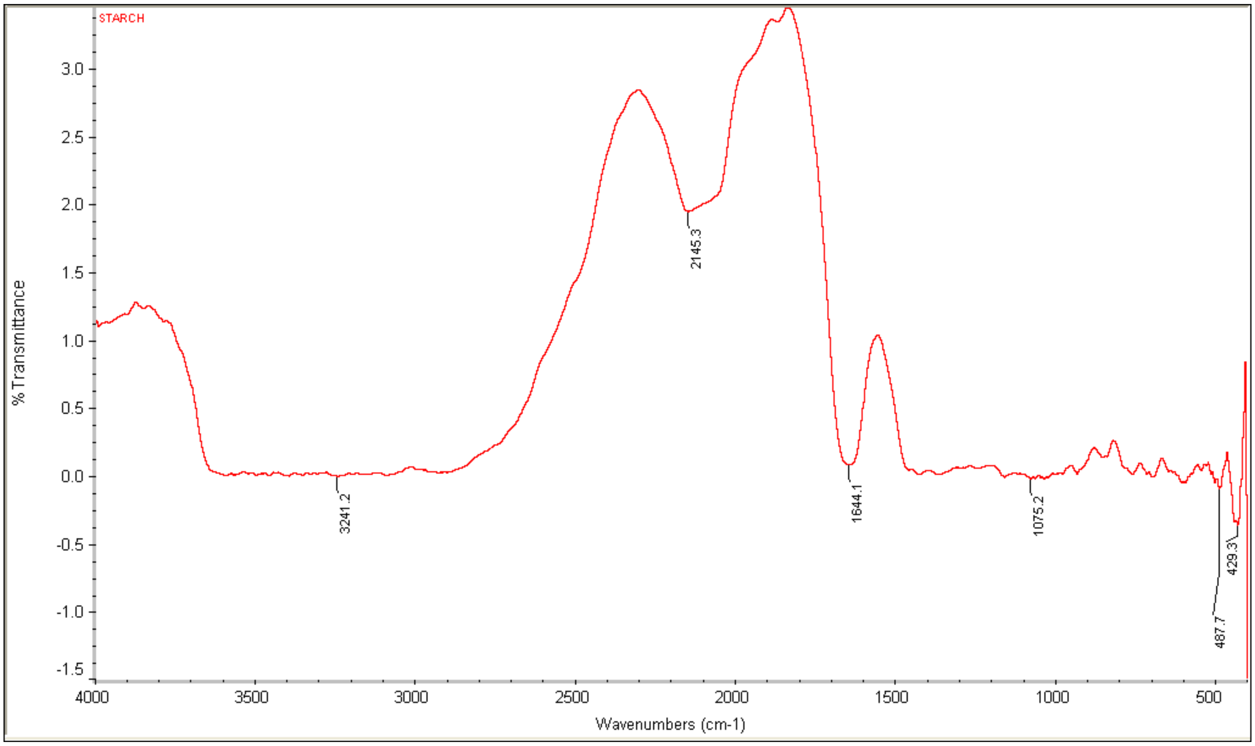


Fig. 5.4.1: FTIR of starch

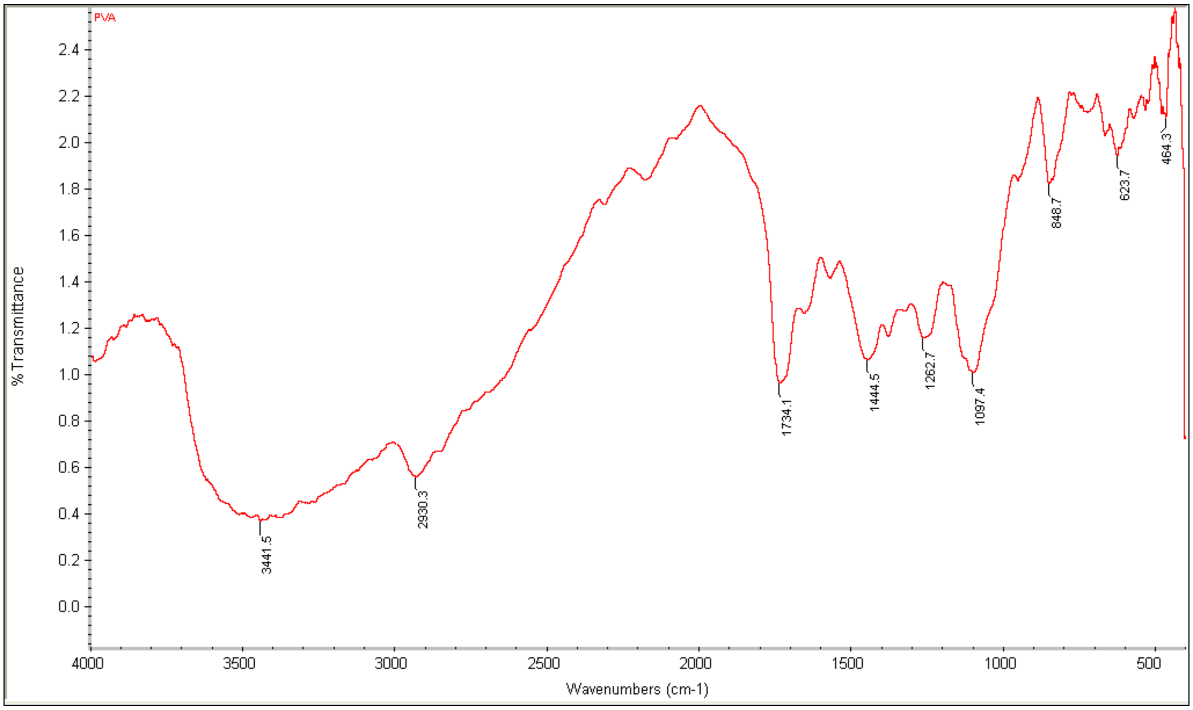


Fig 5.4.2: FTIR of PVA

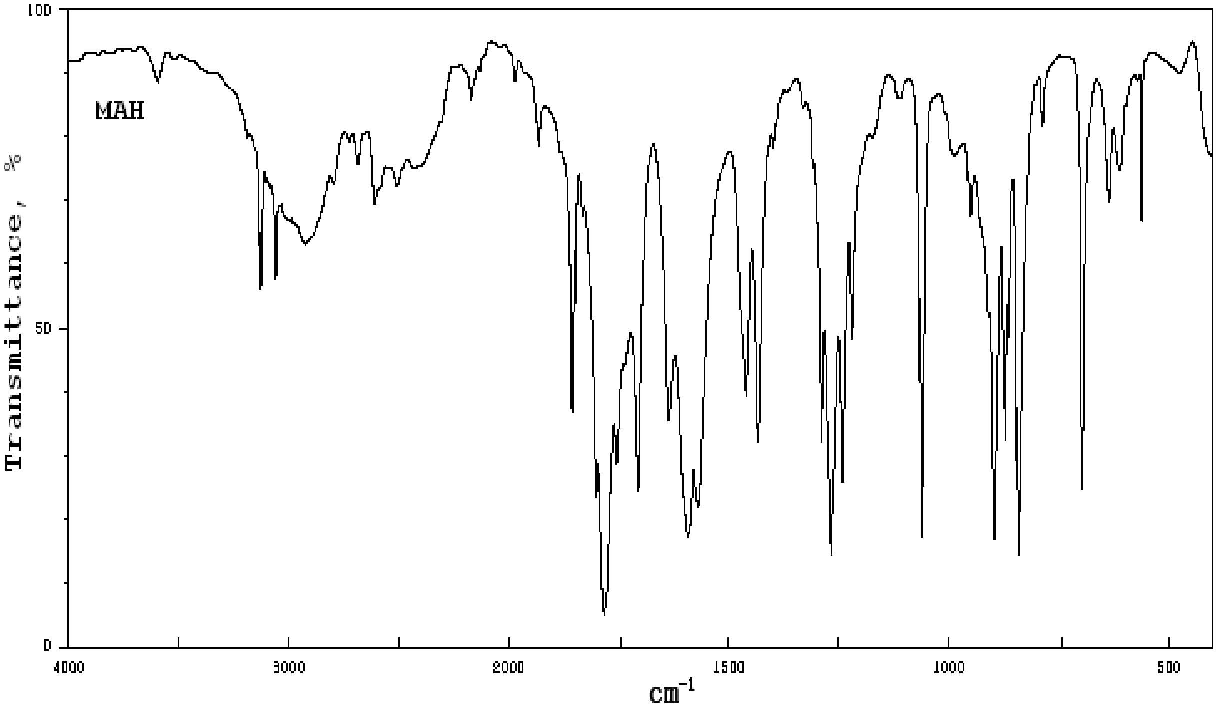


Fig 5.4.3: FTIR of Maleic Anhydride

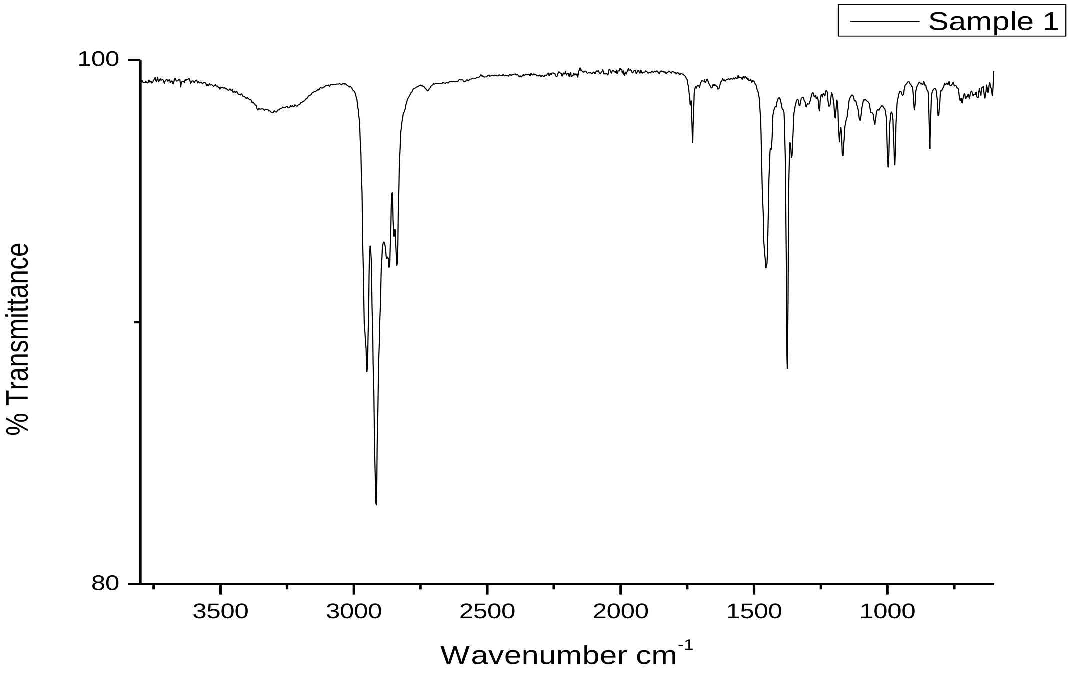


Fig 5.4.4: FTIR OF Sample 1

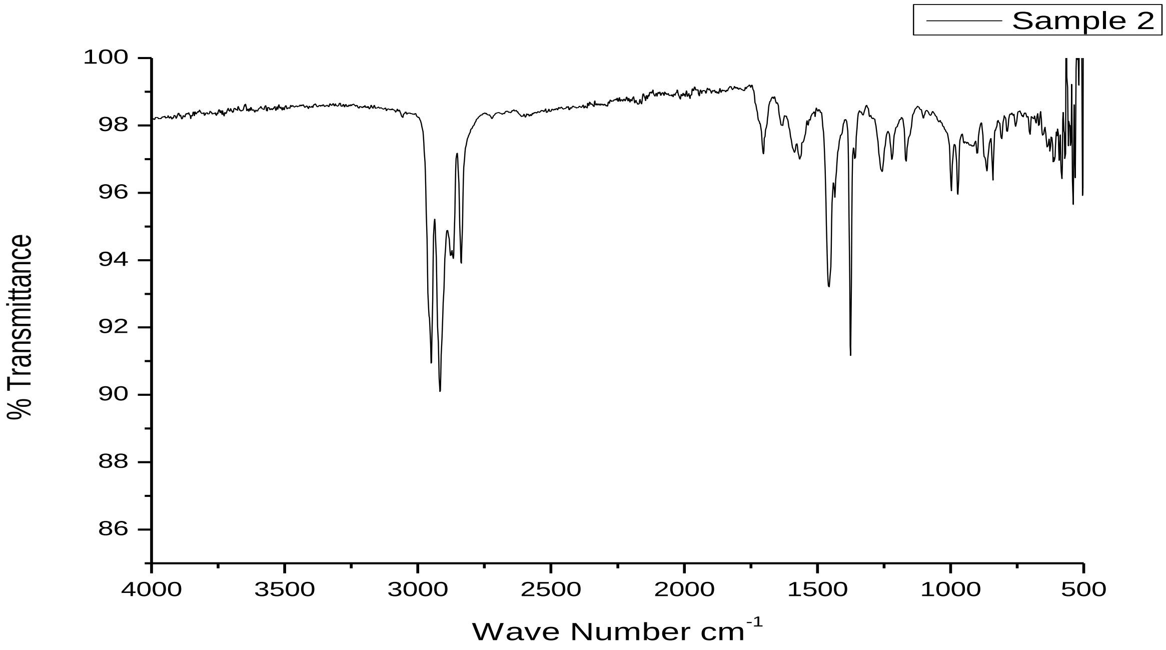


Fig 5.4.5: FTIR of Sample

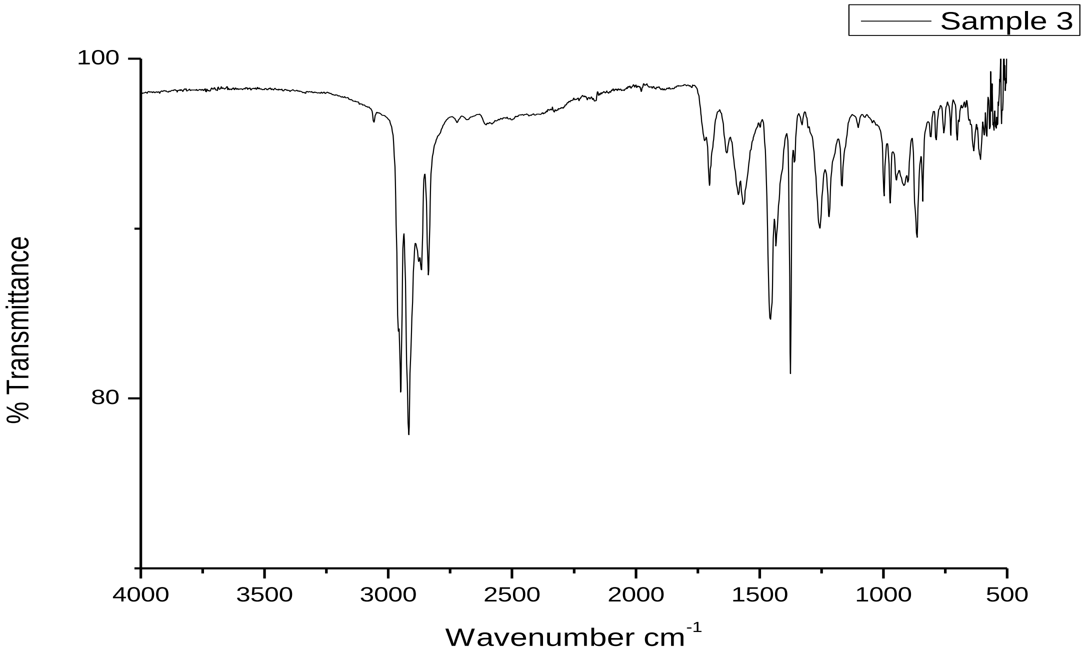


Fig 5.4.6: FTIR of Sample 3

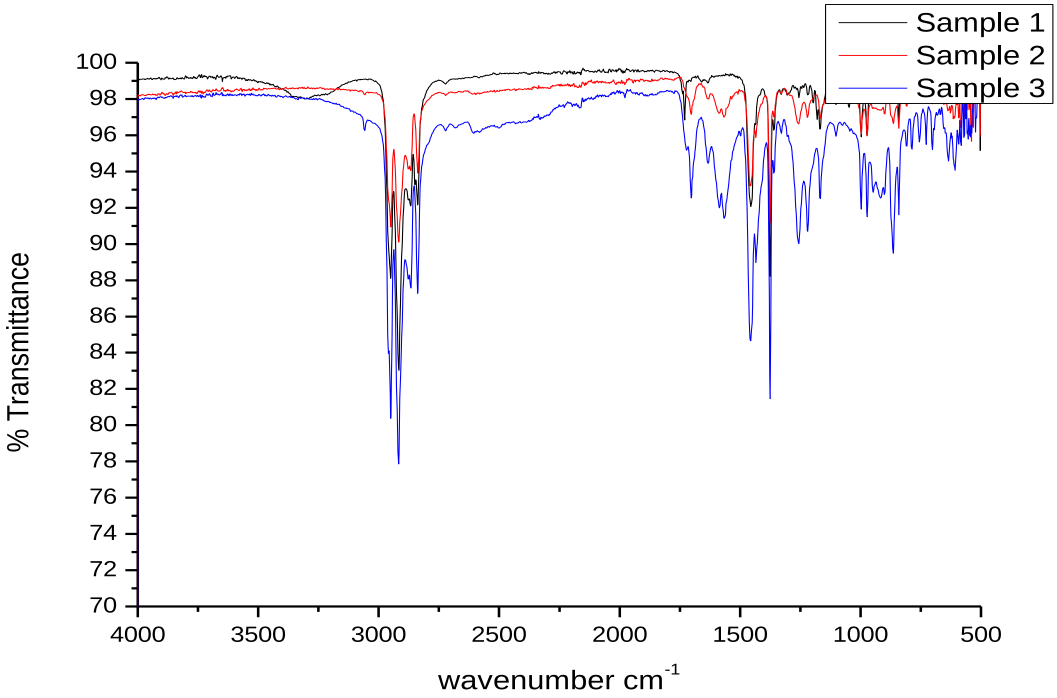


Fig 5.4.7: FTIR of all Samples

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5.5 Scanning electron microscopy

The surface morphology of the solid sheet type samples which passed through 40 days of water absorption test and 40 days of soil burial test were analyzed by the help of scanning electron microscope (SEM). The samples studied at 15kV with proper magnification in Hitachi 3700 N.

The surface morphology of the sample 1 in both the cases of soil burial test and water absorption test shows regular surface and did not show any signs of degradation as pure PP shows good resistance to bio-degradability. The surface morphology of the sample 2 shows irregular surface and it shows good signs of degradation under the soil burial test whereas less signs of degradation under water absorption test as compare to sample 3 as which may be mainly due to the presence of starch and PVA as starch will try to dissociate in water and PVA will try to bind it which will reduce degradation and in soil burial test PVA may help in the growth of bacteria which may result in increased degradation. The surface morphology of the sample 3 shows irregular surface and it shows good signs of degradation under the water absorption test as compare to sample 2 which may be due to the presence of starch whereas less signs of degradation under soil burial test as compare to sample 2 which may be due to the absence of PVA.

SEM test after 40 Days Water absorption Test

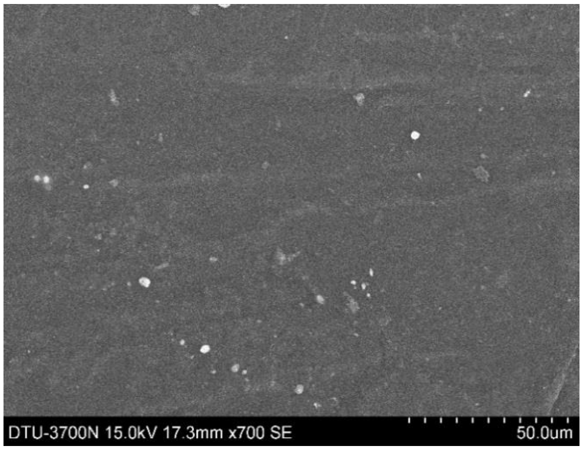

Fig 5.5.1:Sample 1

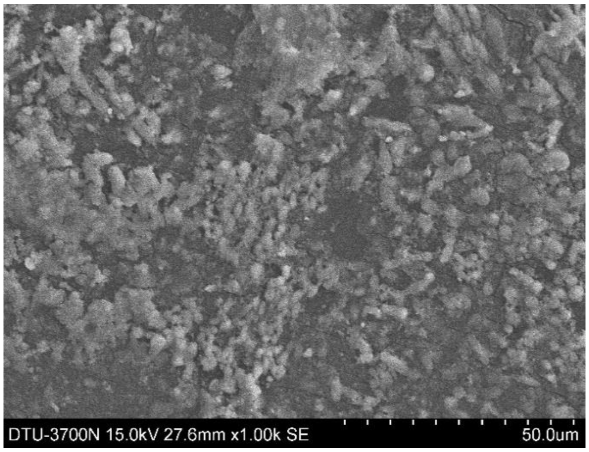

Fig 5.5.2: Sample 2

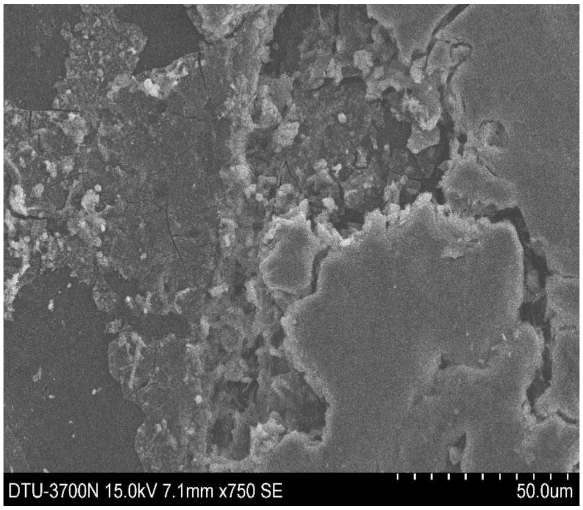

Fig 5.5.3: Sample 3

SEM test after 40 days soil burial test

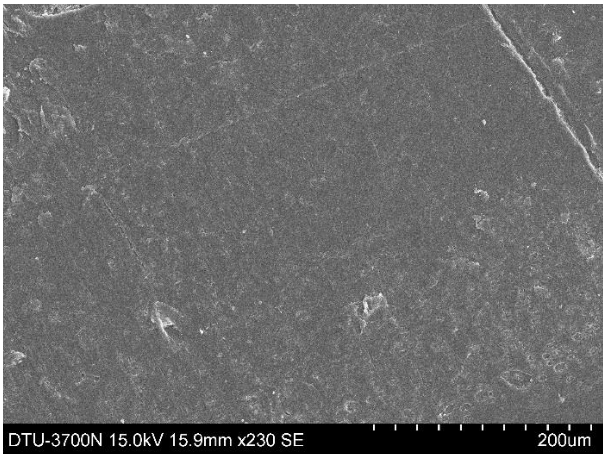

Fig 5.5.4: Sample 1

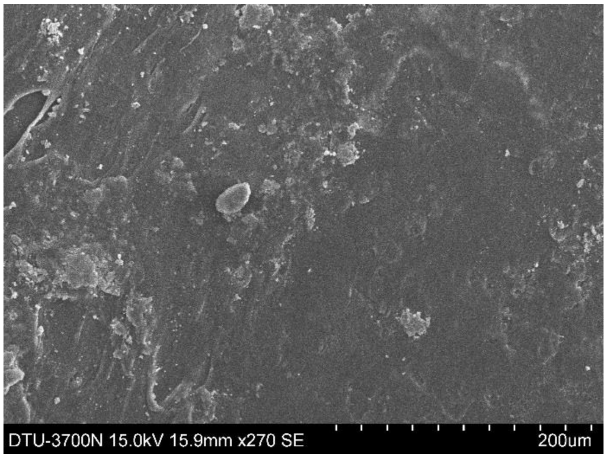

Fig 5.5.5: Sample 2

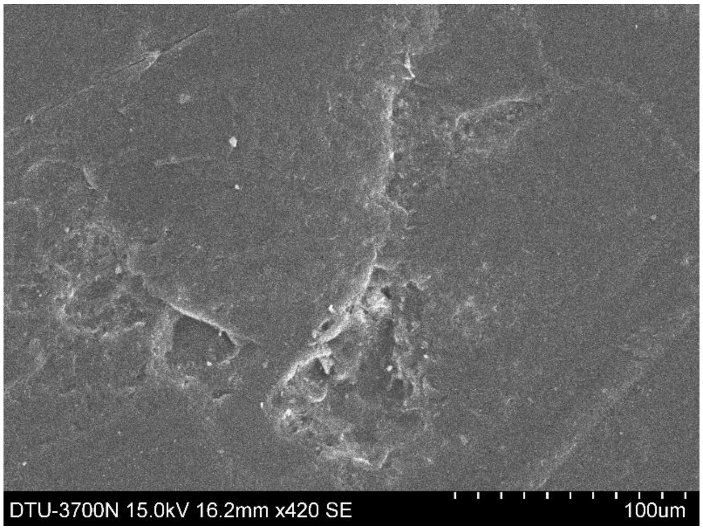

Fig 5.5.6: Sample 3

Conclusion

Modified PP samples were synthesized in the presence and absence of the PVA. The samples were first studied on the FTIR spectroscopy for characterization and it was observed that with the incorporation of Maleic Anhydride as a coupling agent it shows better coupling. The study shows that with the incorporation of the starch in to the polymer reduces its mechanical strength and makes it brittle in nature. These samples were studied for the degradation analysis by 40 days water absorption test and 40 days soil burial test and it was observed that the samples weight decreased in the presence of water and increased in the presence of soil. The same samples which pass through the water absorption test and soil burial test were studied on the SEM and it was observed that the sample in which PVA was added shows less degradation in water absorption test and more degradation in soil burial test as compare to the sample in which PVA is not added. After all this testing's it can be said that the Modified samples will show less span time for degradation as compare to pure PP and before its commercialization for food packaging articles and other applications further testing's were required such as degradation testing in different conditions to check out the better environment for degradation , bacteria growth due to the presence of any material present in the food , effect of the addition of different additives on its degradation & mechanical properties and many more.

Future Prospect

Modified PP have a wide range of applications. This study will help in synthesizing the bio-degradable material with the help of synthetically produced polymers which will show good mechanical properties and can be incorporated in the applications which have short life span. This study will also help in reducing the amount of the material which is incorporated every year for land fill as modified PP after a required amount can be chemically recycled or may be controlled cracked to produce better products. This study will also help in knowing the amount of different materials which should be incorporated in the material to produce modified so that it will show good reliability and durability during shelf life and can be easily degrade during degradation as it was observed during study by adding PVA with different other materials it shows less degradation in the presence of water then the soil.

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