A
Ph.D. Thesis
on

PROCESSING TECHNIQUES AND DEGRADATION BEHAVIOR OF SUSTAINABLE POLYMERIC COMPOSITES

Submitted by

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CHAPTER 1

INTRODUCTION

Development of sustainable materials is an area where efforts are being put worldwide for ensuring judicious as well as optimal utilization of available resources. Composite materials signify a class of materials with abundant opportunities and possess the tremendous potential to be exploited in various applications such as; aerospace, automobile, building and construction [1]–[5]. The use of composite materials has multiplied manifold owing to their superior combination of properties, usually difficult to achieve using traditional/conventional engineering materials. However, the non-biodegradability, non-recyclability and non-renewability of most of the currently used composite materials is a major limitation and is motivating the researchers and scientists to explore the feasibility of conceptualizing, designing and developing composite materials based on sustainable resources. The research community has identified the natural fibers as an alternative to overcome the challenges associated with the biodegradability, recyclability and sustainability. Now-a-days, the research effort have been focused on the various challenges associated with the processing of these materials. The current chapter presents an overview of composite materials, natural fibers, challenges with composite materials, different techniques that have been developed world wide for processing of short fiber based composites. The outcome of various processing parameters on the performance of the injection molded composites has also been highlighted

1.1 COMPOSITE MATERIALS

Composite materials have gained significant attraction towards the replacement of conventional materials like metals, polymers, ceramics and wood due to their numerous advantages such as stiffness and specific strength [6]–[9]. Day by day the use of composite materials is becoming very common in our lives. Composite materials can also be considered as today’s material because their application areas have now spread in various industries and are ranging from aircraft body to children’s toys [10]–[13]. However, they have potential to be called as tomorrow’s materials due to the properties they can offer in the future, such as nano-composites and smart materials. The composite materials can be classified based on different aspects such as matrix and reinforcing materials, size and shape of materials. The classification of composite materials is shown in Fig.1.1.

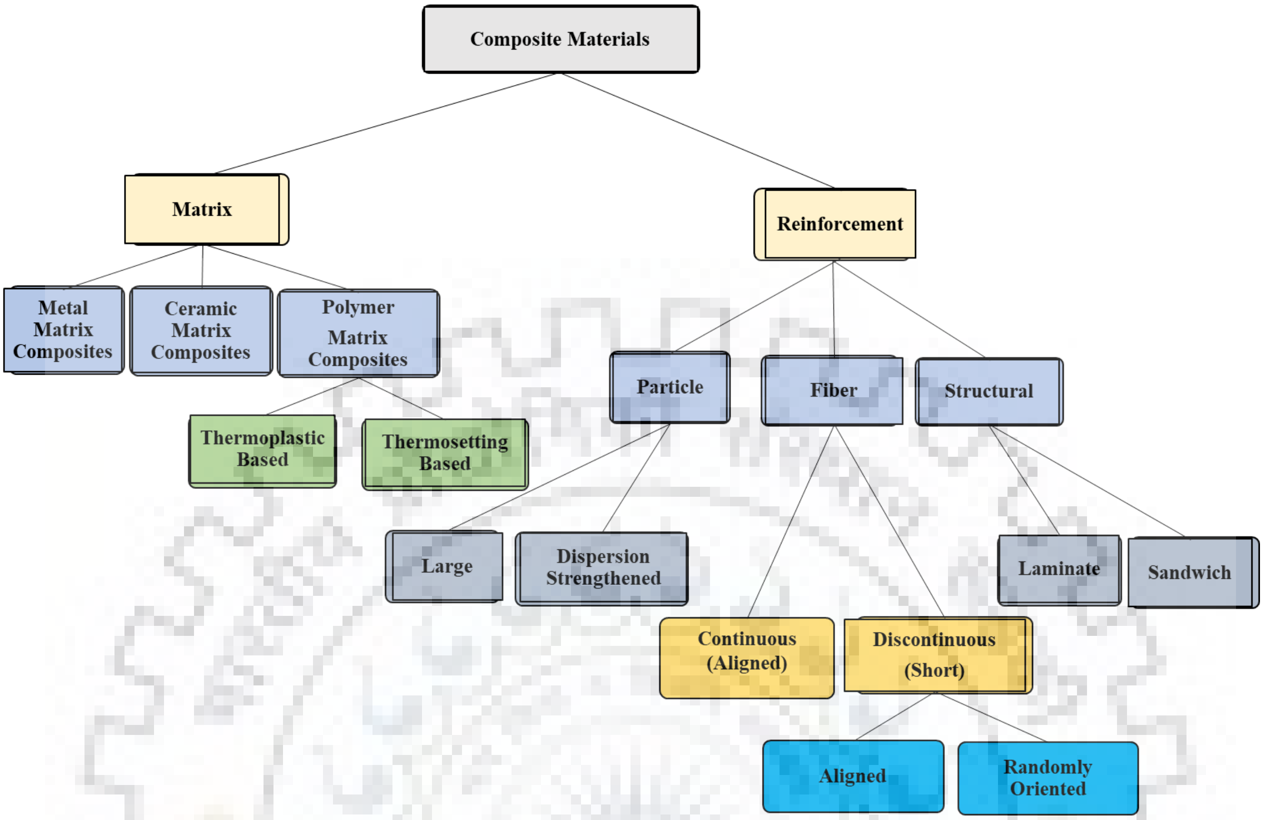

Fig. 1. 1 Classification of composite materials

Now-a-days polymer matrix composites are gaining importance due to their low weight and affordable cost [14]–[17]. They have the potential to replace the conventional material in many specific areas. Their corrosion resistance makes them suitable for the use in marine and construction fields. They are light in weight and have good vibration damping properties which makes them suitable for use in sports equipment, automobile, and space industry. In polymer matrix composites, the most common fibers are glass fiber, carbon fiber and aramid fibers. But the growing environmental rules and ecological concerns demand for renewable composites. Therefore, in the present scenario the researchers are striving to develop natural fiber reinforced composites. Natural fibers are derived from animals or plants. These fibers are categorized as environment friendly and have comparable properties to synthetic fibers [18], [19]. They are light in weight, biodegradable, cheap and abundantly available in nature. The classification of natural fibers is shown in shown Fig. 1.2. Natural fiber based composites (sometimes biocomposites), have revealed comparable or sometimes even better properties than synthetic fiber based composites. Biocomposites can also be tailored easily to meet the specific requirements of products for different engineering applications [20].

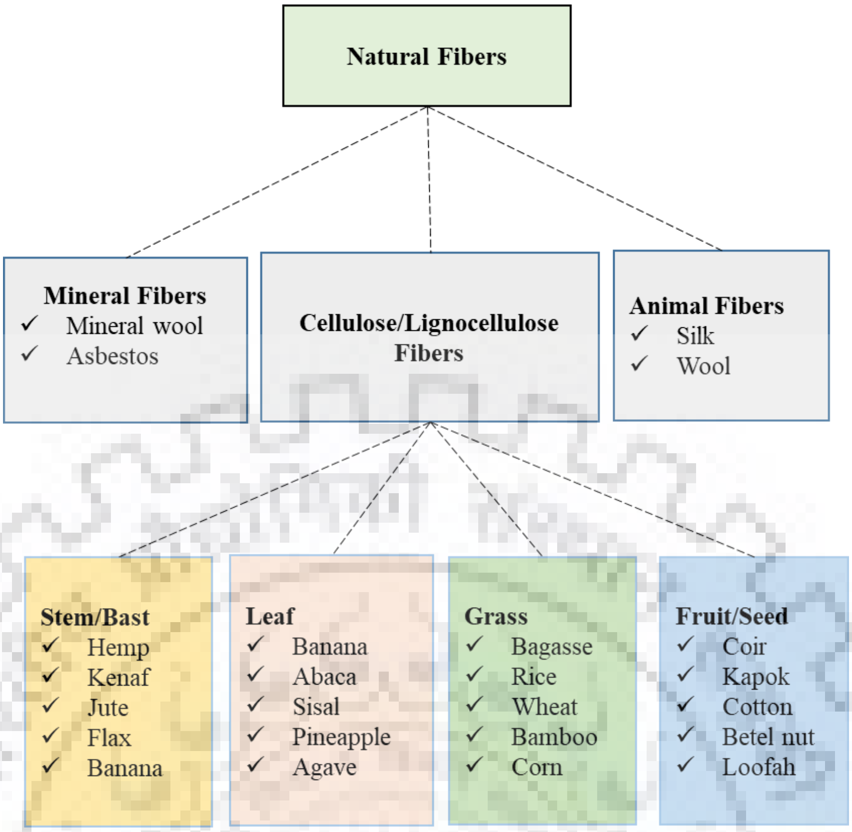

Fig. 1. 2 Classification of natural fibers

The comparative analysis depicting the properties of few natural fibers and synthetic fibers is shown in Table 1.1.

Table 1. 1 Natural fibers vs synthetic fibers [21]–[25]

Type	**Name**	**Density (g/cm^3)**	**Tensile strength (MPa)**	**Young modulus (GPa)**	**Elongation at break (%)**
Synthetic fibers	Glass	2.5-2.6	2200-3600	65-75	3
	Carbon	1.4-1.8	3000-4000	250-500	1-1.5
	Aramid	1.4	3000-3150	63-67	3.3-3.7
Natural fibers	Hemp	1.4-1.6	550-900	70	1.6
	Sisal	1.3-1.5	600-700	38	2-3
	Jute	1.3-1.5	200-800	10-30	1.8
	Ramie	1.5	500	44	2
	Cotton	1.5-1.6	290-490	12	3-10
	Flax	1.4-1.5	800-1500	60-80	1.2-1.6
	Coir	1.2-1.5	180-220	6	15-25
	Pineapple	0.8-1.6	400-627	1.44	14.5
	Kenaf	1.45	930	53	1.6
	Bagasse	1.25	290	17	-
	Bamboo	0.6-1.1	140-230	11-17	-
	Abaca	1.5	400	12	3-10

Polymer composites based on the natural fibers are either partially or fully biodegradable in nature depending upon their constituents. Natural fiber reinforced non-biodegradable polymeric composites are called as partially biodegradable composites. When natural fibers are used to reinforce the biodegradable polymers, these can be termed as biodegradable composites or simply biocomposites. Fig. 1.3 depicts the classification of polymer composites based on their disposal characteristics.

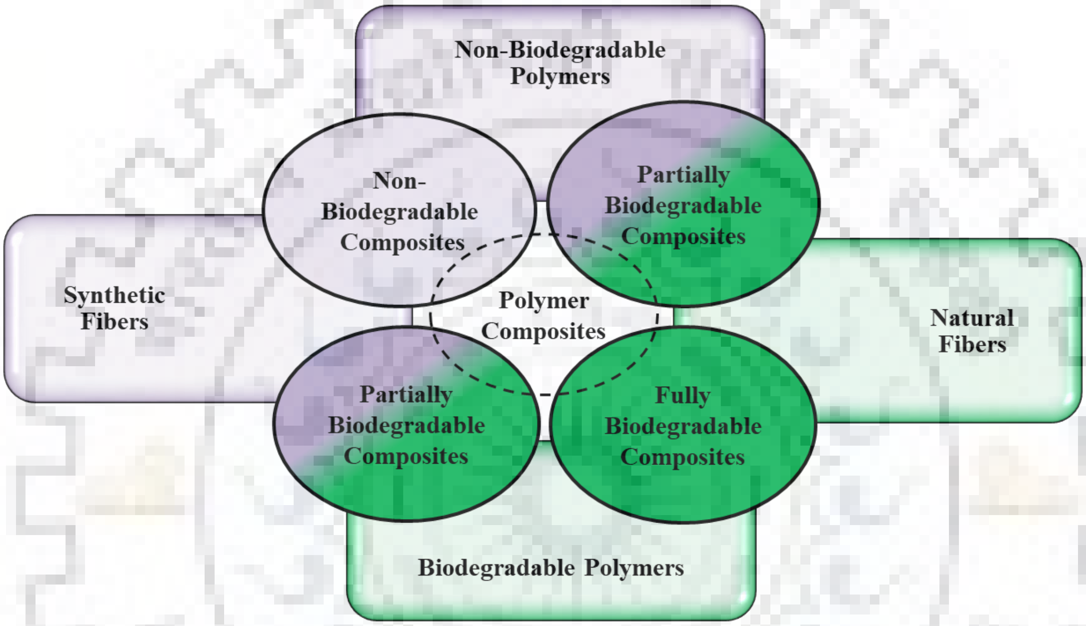

Fig. 1. 3 Classification of polymer matrix composites

1.2 CHALLENGES WITH COMPOSITE MATERIALS

The composites possess several favorable characteristics like high strength-to-weight ratio, comparable mechanical properties and corrosion resistant. However, there are various challenges associated with the composite materials which becomes necessary in order to fabricate the composite products with excellent properties. Some of these challenges have been discussed here;

- Composites are tailor-made materials i.e. it can be engineered according to the requirement. However, it is very challenging task to select the best processing technique with optimized processing parameters in order to meet the specific requirements.
- The properties (physical, chemical, thermal and mechanical) of both the constituents (reinforcement and matrix) are completely different. Therefore, the blending/melt

mixing of these significantly different materials is a key in order to achieve the required properties.

- The interfacial characteristics between the constituents play a crucial role in governing the overall properties of the composite materials. The interfacial zones are prone to failure under loading and it is a challenge to control these characteristics. There are number of approaches that have been tried worldwide to improve the interfacial characteristics between the constituents such as treatment (physical and chemical) and coating of fibers, inclusion of fillers, additives and catalyst during blending.
- As compared to conventional materials, the constituents of composites are completely distinct and their properties are also different. Therefore, the machines and tooling requirements are entirely distinct from conventional materials. The tooling and operating parameters for reinforcement may not be suitable for the matrix or vice-versa.

1.3 PROCESSING OF POLYMERIC MATRIX COMPOSITES

The behavior and performance of the composite products depend upon the properties, size and shape of its constituents, processing techniques, operating parameters, the distribution and orientation of fibers and the interfacial characteristics between the constituents [26][27]–[29]. In polymeric matrix composites, the matrix material can be either thermoplastic or thermosets. Generally, thermosets and thermoplastics are available in the form of resin and granules, respectively. There are number of processing techniques (hand lay-up, injection molding, resin transfer molding and compression molding) which can be used for converting these matrix materials into the final products.

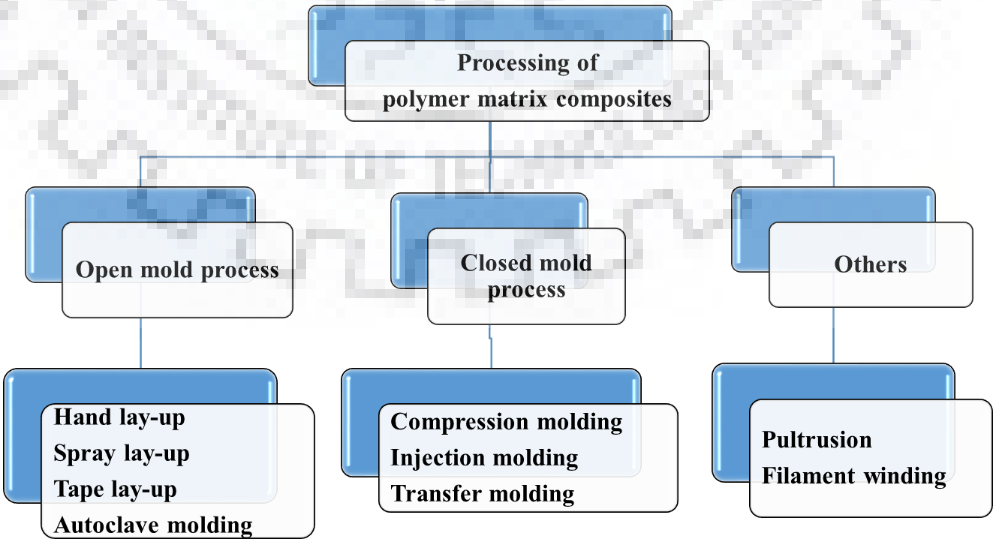

Fig. 1. 4 Processing techniques of polymer based composites

The processing techniques of polymer based composites can be mainly categorized as open mold and closed mold processes (Fig. 1.4). Each process has its own benefits and limitations based on the materials, part accuracy, wastage and cost.

1.3.1 Selection of Processing Techniques

The selection of appropriate techniques for the fabrication of polymer composites involve several factors to be taken into account. Some of these factors are:

- The size, shape, orientation and characteristics of the constituents (fibers and matrix)
- The size, shape and properties of the resultant composites
- Manufacturing limitations of fibers and matrix
- The manufacturing cost

The choice of processing method plays a significant role during the development of composite materials. The geometry required for the composite parts also plays a vital role in selection. Pultrusion and direct-extrusion processes are employed for the development of long products having uniform cross-sectional profile. Pultrusion process is generally used for the development of composites reinforced with continuous strands of natural fibers while extrusion process can be employed for the development of products incorporating short fibers as a reinforcement. In case of thermoplastic based composites, these processes have been reportedly used as pre-compounding processes before injection or compression molding [30].

Compression molding is usually employed to develop products with simple geometries while, the composite parts of complex geometry with high precision, and dimensional accuracy are usually made by injection molding process. Moreover, owing to its excellent production rate, this is the most widely used processing route for the manufacturing of plastic parts in the industry. As natural fibers are derived from various parts of the plant, they have the limitation of maximum fiber length that can be extracted from the plant source.

Therefore, their use in the form of continuous fibers is usually fulfilled by spinning the fibers into yarns. These yarns are then used to feed the pultrusion machine or in case of compression molding process, these spun yarns are weaved into the desired orientation and then hot-compressed between the polymer sheets to produce natural fiber based composites. The use of long or continuous fibers increases the cost of fiber production as well as adds to the process complexity.

Table 1. 2 Comparison of processing techniques

Characteristics	**Injection molding**	**Compression molding**	**Resin transfer molding**
Properties	• Composites based on the thermosets and thermoplastics can be easily processed. • Small to large size products with complex geometries and high dimensional accuracy can be easily produced. • Production rate is high. • Excellent dimensional accuracy can be achieved.	• Composites based on the thermosets and thermoplastics can be easily processed. • Good dimensional accuracy can be achieved. • Good flexibility in part design is possible. • Extra features like inserts, bosses and attachment can be molded during the processing.	• High injection pressure is not required during processing. • Material wastage is minimal • The parts having excellent dimensional accuracy and surface finish can be produced. • Any combination of reinforced materials in any orientation can be achieved. • Ability to incorporate inserts and other attachments into molding.
Limitations	• Mainly suitable for short fiber type of reinforcement. • Excessive damage to the fibers and matrix may take place during the processing. • High initial tooling and operational cost.	• Production rate is slow • Large curing time. • Defects such as uneven parting lines can be present in the final product. • It is a labor intensive process.	• Mold cavity limits the size of the composite products. • High tooling cost. • Composites based on short fiber reinforcement may not be suitable for processing.
Applications	• The process is well suited for high production volume at low cost specially for automotive parts. • It can easily be used for making automotive door panels, air	• This process can be used for producing the variety of products such as toys, kitchen goods, automotive, airplane and electrical parts.	• Complex structures can be produced. • Automotive body parts, containers, bathtubs are generally manufactured.

	spoilers, fenders and body panels.		

Short fiber extraction is rather easier and cheaper compared to long/continuous fibers. Short fibers are easier to mix and blend with the polymer matrix and can be processed using extrusion and injection molding processes. A comparative analysis of some of the most widely used processing routes is depicted in the Table 1. **2.** A brief review on different processing technique employed for the fabrication of natural fiber based composites is shown in Table 1. 3.

Table 1. 3 Fabrication techniques

Reinforcement	Matrix	Processing routes	Reference
Microcrystalline cellulose, cellulose fibers and wood flour	PLA	Extrusion-injection molding	[31]
Corn husk flour	PLA	Extrusion-injection molding	[32]
Banana fiber	PP	Extrusion followed by injection molding	[33], [34]
Bagasse fiber	Unsaturated polyester	Vacuum bagging	[35]
Sisal fibers	PP	Melt-mixing and solution-mixing	[29]
Hemp	PLA	Microniser + compression molding	[36]
Banana and sisal fibers	PLA	Extrusion-injection molding	[37]

*PP –Polypropylene, **PLA- Poly-lactic acid

It has been observed that the injection molding process has been used extensively for the fabrication of natural fiber based polymeric composites.

1.4 MOTIVATION

The use of composite materials has multiplied manifold owing to their superior combination of properties, usually difficult to achieve using traditional/conventional engineering materials. However, the non-biodegradability, non-recyclability and non-renewability of most of the currently used composite materials is a major limitation and is motivating the researchers and scientists to explore the feasibility of conceptualizing, designing and developing composite materials based on sustainable resources. The research community has identified the natural fibers and biopolymers as an alternative to overcome the challenges associated with the biodegradability, recyclability and sustainability. The commercial viability of the biocomposites depends on the manufacturing method with less processing time, simplicity in operation with exceptional dimensional properties and repeatability. The literature reveals that one of the most commonly used processing technique for the fabrication of short fiber-based polymeric composites is injection molding [38]. It is a quick process and offers flexibility in product design variation. However, the lack of information regarding the processing of biocomposites, the poor interfacial bonding between the natural fibers and polymeric matrices, the tendency of natural fibers to absorb moisture and the degradation characteristics of the biocomposites during the service period are limiting the application spectrum and commercial viability of these biocomposites.

Hence, there is an imminent need to focus on the development of partially and fully biodegradable composites. In order to improve the interfacial interaction between the fibers and polymeric matrices, eco-friendly route of chemical treatment can also be explored. In order to investigate the recycling behavior, the recyclability assessment of partially and fully biodegradable composites can be investigated. The challenges in the development of natural fiber reinforced composites lie in making them structurally and functionally stable during their service life as well as easily degradable on disposal at the end of service life. These materials may be exposed to different environmental conditions during their service life such as exposure to sunlight, moisture and acids, and soil [39], [40]. Hence, there is an imminent need to investigate, in-service performance and the degradation behavior at the end of service life, the environmental aging and degradation behavior of the composites can also be explored. This type of investigation gives an insight in the development and degradation behavior of the partially and fully biodegradable composites for the industrial and research community working in the area of development of sustainable biocomposites.

1.5 OUTLINE OF THE THESIS

The present research endeavor has been organized into the following chapters:

Chapter 1: Introduction

This chapter presents an overview of the polymer-based composite materials. A brief classification of the matrices and natural fibers along with the challenges associated with the development of polymer composites has been outlined.

Chapter 2: Literature Review

This chapter presents an in-depth review of the literature in a wide area of development of the polymer composites. The review also emphases on the fiber surface modification routes that have been tried globally. It also provides an exhaustive review of the literature focusing on the recycling and degradation behavior of the natural fiber-based composites. Based on the gaps in the literature, the identification of research opportunities and the objectives of the present research endeavor has been discussed.

Chapter 3: Materials and Methods

This chapter deals with the materials and methods used for the development of polymer composites. The details of the machine setups used for the development of polymer composites and conducting the degradation analysis have been discussed. The characterization techniques employed to investigate the behavior of the natural fibers and developed composites are also reported in detail.

Chapter 4: Development of Polymer Matrix Composites

This chapter deals with the effect of three processing routes on the performance of the developed composites. The performance of composites has been investigated in context of their thermal and mechanical as well as dynamic mechanical behavior. This chapter also explores the effect of different types of chemical treatments of the fibers on the behavior of the fibers and developed composites.

Chapter 5: Recyclability Assessment of the Banana and Pineapple Fiber Reinforced PP and PLA based Composites.

This chapter explores the recyclability assessment of the developed composites. The performance of the recycled composites has been reported in terms of the fiber aspect ratio, mechanical, thermal and dynamic mechanical behavior as well as the crystallinity.

Chapter 6: Environmental Aging of the Natural Fiber Reinforced PP and PLA based Composites.

In this chapter, the environmental aging behavior of the developed composites in various environments has been reported. The effect of environmental aging on the behavior of the developed composites has been reported in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.

Chapter 7: Degradation Behavior of the Natural Fiber Reinforced PP and PLA based Composites.

The chapter highlights, the degradation behavior of the neat polymers and developed composites exposed in different mediums for a period of 6 months with an analysis interval of

2 months. The degradation behavior has been reported in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.

Chapter 8: Summary and Conclusions

This chapter concludes the findings of the research work. The future direction of the current research endeavor has also been outlined.

CHAPTER 2

LITERATURE REVIEW

The current chapter deals with the materials and methods used for the development of polymer composites. The details of the machine setups used for the development of polymer composites and conducting the degradation analysis have been discussed. The characterization techniques employed to investigate the behavior of the natural fibers and developed composites are also reported in details.

2.1 PROCESSING OF COMPOSITES

Ramesh et al. [41] evaluated the mechanical properties of Banana Fiber Reinforced epoxy Composites. In this study, banana fiber reinforced epoxy composites were fabricated with different fiber volume fractions using the hand lay-up process and by applying pressure at room temperature. Three different types of samples were fabricated; 40% banana fiber + 60% Epoxy resin, 50% banana fiber + 50% Epoxy resin and 60% banana fiber + 40% Epoxy resin. The mechanical properties of the fabricated composites were evaluated. The prepared samples were subjected to mechanical testing like tensile test, flexural test and impact loading. 50% banana fiber and 50% epoxy resin composite samples recorded the maximum tensile strength of 112.58 MPa. The same combination i.e, 50% banana fiber + 50% epoxy resin samples possess the maximum flexural strength of 76.53MPa. For analyzing the fractured surface morphology and evaluation of matrix fiber interface, Scanning electron microscope (SEM) analysis was carried out.

Subramonian et al. [42] studied the effect of change in weight percentage of bagasse fiber in the polypropylene composites. They incorporated the alkali treated bagasse fiber in Polypropylene (PP) to prepare a short fiber reinforced composite using hot pressing method. The composites were prepared at 10%, 20%, 30% and 40% of fiber concentration. It was observed that PP with 30% filler has the highest tensile strength of 15.1MPa. Although it was found to be lower than the neat PP (19.6MPa). The tensile strength was recorded to be minimum at 10% fiber loading but at 10% fiber loading, flexural strength was found to be highest (57MPa). It was noticed that with increase in fiber content, the hardness of composite increases.

Aji et al. [43] studied the variation of fiber length and fiber loading on the mechanical properties of pineapple and kenaf reinforced HDPE composites. In this study, they focused on the tensile, impact and flexural strength of the composites. The test specimens were cut out from the compression molded sheets of the composites. It has been found that the smaller fiber (0.25mm) reinforced composites showed better tensile and flexural properties. On the other hand, impact strength showed increment with larger (0.75mm to 2mm) fiber length. Fiber load was varied from 10% to 70% and the lengths of the fibers were kept at 0.25, 0.5, 0.75 and 2 mm. At 0.25 mm fiber length the tensile and flexural properties were found to be best and the properties increased linearly up to the fiber loading of 60%. While with 0.75 and 2 mm length of the fiber, impact strength was found to be better. Scanning electron microscopy was used for analyzing the morphology of the tested composite samples.

Dhakal et. al [44] investigated the effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites. It shows that moisture uptake increase with fibre volume fraction increases due to increased voids and cellulose content. The water absorption pattern of these composites at room temperature is found to follow Fickian behaviour, whereas at the elevated temperature the absorption behaviour is non-Fickian.

There are various factors (fiber loading, fiber aspect ratio, the distribution and orientation of fibers, interfacial characteristics between the constituents, processing routes) which governs the mechanical performance of natural fiber based composites [45]. A brief review on mechanical performance of injection molded composites is shown in the Table 2.1

Table 2. 1 Mechanical properties of injection molded composites

Materials	Findings	Reference
Abaca fibers (30 wt. %) + PLA	Enhancement in tensile modulus and strength of the composite by 140% and 20% , respectively.	[46]
Kenaf fiber (20 and 30 wt. %) + PLA	As compared to neat PLA, the tensile modulus of the composites incorporating 20 and 30 wt. % of kenaf fiber increases by 21 and 31%, respectively.	[47]

Wood flour (20, 30 and 40 wt. %) + PLA	The tensile modulus of the composite increased by 77%, 96% and 133%, respectively.	[48]
Cordenka (30 wt. %) + PLA, flax fibers (30 wt. %) + PLA	The impact strength of cordenka fiber reinforced composite was found to be higher.	[49]
Kenaf fiber (20 wt. %) + PLA, rice husk fiber (20 wt. %) + PLA	The flexural and impact strength of the kenaf fiber based composites exhibited superior properties.	[50]
Banana fiber (10, 20 and 30 wt. %) + PP	The tensile modulus, flexural strength and modulus increases with respect to fiber loading.	[34]

2.2 FIBER SURFACE MODIFICATION

Natural fibers pose compatibility issues with the matrix during development of polymer composites. Natural fibers comprise of cellulosic fibrils, attached together by the non-cellulosic content like hemicellulose, lignin and pectin [51]. The properties of the natural fibers mainly depend upon their lignocellulosic content. Excessive wax and hemicellulose causes the formation of week interfacial interaction among the fibers and matrix. Moreover, these non-cellulosic content is also responsible for the hydrophilic nature and early thermal degradation of the fibers during processing. To overcome these challenges, several preprocessing approaches have been suggested in the literature such as modification of the surface of fibers and compounding of fibers and matrix [52].

The aim of this approach is to improve the interfacial interaction between the fibers and matrix by removing the non-cellulosic content from the surface of the fibers using any surface modification technique. This technique can be generally divided into the physical and chemical treatments [53]. Physical treatment includes heat treatment, calendaring and the use of electric discharge [54]. Electric discharge treatments (corona and plasma treatment) of natural fibers has attracted a lot of attention worldwide as these techniques demonstrate the ability to alter the surface energy of the fibers without affecting the bulk properties.

The modification of fiber surface using chemical treatment is the most widely explored technique by the researchers. Chemicals such as sodium hydroxide, silane, acetic acid, permanganate are some of the most widely used chemicals for the chemical treatment of fibers. The chemical treatment removes the excessive non-cellulosic constituents from the surface of the fibers that results in enhancement in interfacial characteristics between the polymers and matrix [23], [28], [35], [55]. A brief information of the widely explored surface modification techniques is shown in Table 2. 2.

Table 2. 2 Surface modification techniques

Reinforcement	Matrix	Processing routes	Fiber treatment/ Compatibilizer/ Filler	Reference
Banana fiber	PLA	Melt blending followed by compression molding	Alkali (NaOH) treatment and silane coupling	[56]
Hemp	PLA	Hot press	Alkali (NaOH) treatment	[57]
Banana fiber	PP	Extrusion-injection molding	Sodium hydroxide (NaOH) treatment	[33]
Bagasse fiber	Unsaturated polyester	Vacuum bagging	Sodium hydroxide (NaOH) and acrylic acid	[35]
Sisal fibers	PP	Melt-mixing and solution-mixing	Sodium hydroxide, maleic anhydride and permanganate	[29]
Wood flour	PLA	Extrusion followed by injection molding	Methylenediphenyl-diisocyanate and poly(ethylene–acrylic acid)	[58]
Banana and sisal fibers	PLA	Extrusion-injection molding	Alkali (NaOH) and benzoyl peroxide treatment	[37], [59]

Prasad et al. [60] made an attempt to use banana fiber as reinforcement with low density polyethylene for development of environment friendly composite materials. Banana fiber reinforced LDPE composites were fabricated with the use of compression molding technique at different fiber loading 10,15,20,25 and 30 wt %. On the basis of biodegradability and mechanical properties, 25 wt % banana fiber loading was found to be optimum. Further, the effect of surface treatment on banana fiber with alkali and acrylic acid was studied. The mechanical properties and water resistance property of the composite was enhanced as a result of alkali and acrylic acid treatment of banana fiber.

Dong et al. [61] studied the effect of fiber loading and alkali treatment on morphological, mechanical, thermal and biodegradable properties of coir fiber reinforced PLA composites. Alkali treatment was performed to modify the surface of fibers. Composites were fabricated by compression molding technique with fiber content of 5, 10, 20 and 30 wt. %. Tensile and flexural modulus of coir/PLA composite was improved as compared to neat PLA and was found to be maximum at 5% fiber content. Tensile and flexural strength of all the composites treated or untreated were less than the neat PLA. But for all fiber loading, the treated fiber composites had higher tensile and flexural strength compared to untreated fiber composites. Thermal stability of both treated and untreated fiber composites decreased. Biodegradability of composites was good for all the composites.

Amir et al. [62] investigated the effect of fiber configuration on mechanical properties of Banana Fiber Reinforced Polypropylene Composites. In this research, they developed PP composites using compression molding method. Continuous banana fiber was used as reinforcement and polymer to fiber weight percent ratio was taken as 70:30. To improve bonding between the polymer and the natural fiber, a coupling agent maleic anhydride grafted polypropylene (MAPP) was added to the composites. The banana fiber configuration were varied, and the performance of composites was tested. The banana fiber configuration was varied by three different ways; banana fiber mat, raw banana fiber, and banana fiber yarn. Mechanical properties of the samples were assessed using tensile and flexural testing. To explain the failure mechanisms and behavior of the composites, micro-structural analysis was performed using scanning electron microscope. They found that PP/Banana yarn composites yielded highest tensile strength of 77.74 MPa followed by PP/Raw banana fiber composites and PP/Banana mat composites. The flexural strength of PP/Banana Yarn was found to be maximum (52.88 MPa) followed by PP/ Banana Mat and PP/Raw Banana Fiber.

Majhi et al. [63] conducted an experimental work on banana fiber reinforced PLA composites. The composites were developed by melt compounding technique. The influence of mercerization and use of maleic anhydride as a compatibilizer and glycerol triacetate ester (GTA) on banana fiber reinforced PLA composite was investigated. Tensile modulus was improved by 62% for maleic anhydride compatibilized composites whereas for GTA plasticized composites showed improvement of 143% in impact strength. TGA ensured the increase in thermal stability of Maleic anhydride incorporated composites.

Mohanty et al. [64] studied the mechanical properties and biodegradability of the resulting composites after addition of jute fabrics as reinforcement in biopol. They used two varieties of jute fabrics, i.e. carpet backing cloth (CBC) and hessian cloth (HC). For surface modification of jute fabrics, dewaxing, cyanoethylation, alkali treatment and grafting have been made in a view of better adhesion bonding between reinforcing agents and biodegradable polymer matrix, Biopol. The chemically treated fibers were characterized by thermo gravimetric analysis (TGA) and Fourier-transform infrared spectroscopy (FTIR). An investigation was made on the amount of fiber content and effect of different surface treatments on the performance of resulting biocomposites. As a result of jute fiber reinforcement, the mechanical properties of the resulting composites such as tensile strength, impact strength and bending strength improved in comparison to pure biopol. In comparison to pure biopol, more than 50%, 30% and 90% improvement was observed in tensile strength, bending strength and impact strength of the composites, respectively. The images got from scanning electron microscopy (SEM) confirmed that the surface modification of fibers improved the fiber matrix bonding. From degradation analysis by compost burial of 150 days of the composite specimens, it was found that more than 50 % weight loss of the composites occur while only 34% weight loss was observed in pure biopol.

Mofokeng et al. [65] made a comparison on the morphological, thermal and thermo-mechanical properties of sisal fiber reinforced polypropylene and poly-lactic acid composites. Fiber and matrix was melt blended using extruder and pellets were prepared. These pellets were fed to injection molding machine to form composites. SEM micrographs revealed that the bonding between PLA and sisal fiber was better than the bonding between PP and sisal. Incorporation of fiber in both matrices enhances the thermal stability of composites. But, increase in thermal stability in case of sisal/PP composite is more significant. In this article, they further describe the basic observations on the biodegradability of the composites. Degradation of sisal/PLA composite through hydrolysis was studied and it was reported that incorporation of sisal in PLA enhance the degradation rate of composite as compared to neat PLA. The results from hydrolysis test of sisal/PP composites and sisal/PLA composites were compared. From this result, it was found that the loss in mass of PLA and its composites was higher than that of PP/sisal composites.

Chaitanya and Singh [66] had experimentally examined the behaviour of aloe vera reinforced biopolymer composites and compared it with the biocomposites of sisal fibre. They studied the effect of alkaline treatment on mechanical and thermal properties of sisal and aloe vera fiber reinforced PLA composites. Composites were prepared by extrusion followed by injection molding. Enhanced mechanical properties were reported for both types of treated fibers. Tensile and flexural modulus of treated aloe vera fiber composite was increased by 177% and 114% and for treated sisal fiber composite increased by 237.9% and 135% respectively. Degradation temperature of treated fibers was higher than the untreated fiber indicating that the thermal stability of both fibers increases on alkali treatment. Moreover, it was evident from the results that the characteristics of both the bio-composites made from aloe vera and those made from sisal fibers are comparable.

Rosa et al. [67] investigated the effect of various chemical treatments on the mechanical, thermal and water absorption properties of okra fiber. Treatments performed were: bleaching followed by alkalization and acetylation, sodium sulphite and sulphuric acid with potassium permanganate. Tensile strength was found to be highest for sodium sulphite (82.6 MPa) followed by acetylation treatment (82.4 MPa). All the treatments lead to decrease in tensile strength of fibers as compared to untreated fibers. Same decreasing trend was observed for tensile modulus. There was significant improvement in water absorption profile after all the applied treatments.

2.3 RECYCLING OF POLYMER COMPOSITES

Duigou et al. [68] studied the effect of recycling on mechanical properties of bio-compostable flax fiber reinforced poly(L-lactide) composites. Now a day bio-composites are becoming an attractive alternative for glass fiber reinforced petrochemical polymers. The aim of the work was to study the capacity of flax/PLLA composites (20 and 30 wt% of fibers) to be recycled. The flax fiber reinforced PLLA composites were fabricated by Injection molding method with varying composition of 20% and 30% by weight of flax fiber. Mechanical properties of the composites were evaluated initially. It was found that the mechanical properties of the fabricated composite samples are similar to glass/PP composites and superior to sisal/PP and hemp/PP composites. Then after repeated injection cycle, until the third cycle, the tensile properties of the specimens were conserved. Fiber aspect ratio and matrix degradation were followed by the help of molecular weight measurements, section image analysis, rheological and thermal analysis, and SEM morphology. These techniques revealed lowering of glass transition temp, fiber length reduction, lower molecular wt. and separation of the fiber bundles with repeated injection cycles. The retention of the properties after three repeated cycles and under the extreme recycling conditions indicates that these materials have good recyclability.

Gourier et al. [69] explored the recycling behavior of Flax fiber reinforced Polyamide and PP composites. The composites having 59 wt.% of fiber reinforcement were first ground and then mixed with neat polymers in a way that final reinforcement content becomes 21wt.%. This mixture was then injection molded to develop the test specimens. It has been reported that, compared to petroleum derived plastics like PP, biopolymers like PLA have lower thermal stability which restricts their recycling ability. The recycling of neat PLA following mechanical recycling route has been reported by few researchers.

Zenkiewicz et al. [70] conducted the behavioral analysis of up to 10 recycles of PLA using multiple extrusion and subsequent injection molding process. They reported a slight decrease in the tensile strength while the impact strength declined with increasing recycling number. In a different study by Taubner et al. [173], it was reported that the multiple extrusion of PLLA at higher processing temperatures can lead to severe reduction in its molecular weight. Moreover the presence of moisture further escalates the molecular weight degradation. Hence, care must be taken while selection of recycling processing temperature and moisture uptake must be kept under check.

Badia et al. [71] studied the recycling behavior of PLA for up to five extrusion cycles. They reported a severe loss of molecular weight of PLA after 5 recycles. Nascimento et al. [175] also investigated the mechanical and thermal behavior of recycled PLA in comparison to PLA before recycling. They reported no significant change in the mechanical and fracture behavior of PLA post recycling.

2.4 ENVIRONMENTAL AGING OF THE POLYMER COMPOSITES

Jumaidin et al. [72] studied the effect of Seaweed on biodegradation, mechanical and thermal properties of Sugar Palm Starch reinforced Agar Composites. The aim of the study was to investigate characteristics of thermoplastic sugar palm Starch /agar (TPSA) blend which contains biofiller as eucheuma cottonii seaweed waste. The composites were fabricated by melt-mixing and hot pressing for 10 minutes at 140˚C temperature. The biodegradation, mechanical and thermal properties of TPSA/seaweed composites were characterized. The addition of seaweed from 0 to 40 wt % significantly improved tensile, impact and flexural strength of the TPSA /seaweed composites. Homogeneous surfaces with the cleavage plane formation were shown by the Scanning electron microscope images of the tensile fracture of the composites. It was also confirmed from the TGA results, that thermal stability of the resulted composites was improved with the addition of seaweed. After conducting a soil burial test for 2 and 4 weeks, it was found that the biodegradation properties of the composites were enhanced with addition of the seaweed. Overall, addition of the seaweed into TPSA improves the TPSA properties for short life product applications like plates, trays etc.

Zaaba et. al [73] investigated the degradation of peanut shell powder based recycled composites due to natural weathering. The weight loss of the uncompatibilized RPP/PSP composites was reported higher than that of the compatibilized composites after the degradation period. The compatibilized RPP/PSP composites were more resistant to weathering degradation compared with the uncompatibilized RPP/PSP composites.[18]

2.5 DEGRADATION BEHAVIOR OF THE POLYMER COMPOSITES

Huq T. et al. [74] experimentally investigated the effect of soil burial on jute- PET composites and reported a significant reduction (≈25%) in tensile and flexural strength after 6 months. The major effect was observed on the interface of the composites, which led to reduction in mechanical properties.

In a similar type of experiment, Kumar et al. [75] fabricated the Flax-PLA specimen incorporating various biodegradation accelerator (1%) and subjected to soil burial test for different time durations. Neat PLA exhibited faster degradation as compared to fibers, while composites with Mandelic Acid accelerator exhibited higher rate (20-25%) of degradation within 50-60 days. SEM images also confirmed the removal of PLA from the surface of the composites in presence of Mandelic acid. Ethylene Propylene copolymer specimen reinforced with NaOH treated and microcrystalline cellulose fibers were subjected to accelerated weathering as well as composting [76]. Neat EPC was found to be highly stable than all the composites with increasing UV irradiation. It was also reported that the composites are less durable under both abiotic and biotic conditions in comparison to the neat polymer. Microcrystalline cellulose fiber reinforced exhibited superior mechanical properties, Bio disintegrability as well as photo resistance. The composites made from microcrystalline cellulose showed higher weight loss than the alkali-treated fibers.

Fukushima et al. [77] studied the decomposition behaviour of Neat and organically modified PLA and reported that the bacteria Bacillus licheni formis is mainly responsible for PLA biodegradation in compost and reinforcement of nanoclay significantly affect the degradation behaviour of PLA.

Cheung et al [78] reported that reinforcement of animal silk in PLA results in increased stiffness and ductility of the developed composites. Faster degradation rate was observed in reinforced PLA within 4 month of exposure to PBS solution.

Experimental investigation by Iwanczuk et al [79] revealed higher biodegradation rate in flax fiber reinforced composites as compared to neat polymer when immersed in anaerobic sludge. For PHB/PHV based composite the degradation was observed so fast that the samples could not transfer tensile stress at all. Water absorption capacity was reported as directly proportional to temperature and fiber content in Sisal- PHBV biocomposites [80].

Gunning et al [81] studied mechanical and degradation behaviour of different fibers reinforced PHB composites and reported a huge increase in flexural properties of developed composites. Weight loss was reported as maximum in Jute reinforced PHB composites after 12 week, when exposed to compost which was attributed to higher rate of dispersion.

Cameron et. al [82] reported that NaOH treated Maple fibers reinforced PLA exhibits quickest and higher peak rate of biodegradation compared to the other composites containing treated and untreated bores. It was also reported that NaOH treatment not only caused an increased rate of degradation in the PLA through increase fibre porosity, but also caused an increased rate of degradation in the fibre from the lack of surface waxes and hemicellulose.

Ahn et al. [83] developed biocomposites by reinforcing poultry feather in different bioplastics and studied its biodegradability by measuring CO2 emission when subjected to Dairy compost for 60 days. Biodegradability of Neat PLA was observed very less (13 ± 3%) as compared other bioplastic used in the study. Near infrared spectroscopy (NIRS) results also revealed that poultry feather were not degraded during composting for the time duration.

Stromberg et al [84] studied the effect of biodegradation on surface and bulk properties of different biocomposites and reported that hydrolysis affect only the surface properties in PP and PE composites while surface and bulk were affected in PLA composites. Mechanical properties of recycled PP and PE remain unaffected by hydrolysis.

Bayerl et al [85] studied the effect of flax fiber length in PLA composites when subjected to industrial compost. It was reported that incorporation of flax fibers promote the degradation process by hydrolysis and maximum weight loss was reported in unidirectional fiber reinforced composites as compared to long and short fibers reinforced composites.

Wei et al [86] reported that potato peel fermentation residue reinforced PHB composites completely degrade in 8 months in a mixture of fertile garden top soil and organic potting mix, when the reinforcement is 50%. Also the biocomposites with more than 15% reinforcement exhibited higher degradation rate as compared to neat PHB.

Liu et al [87] studied the effect of fiber diameter and fiber surface modification of Jute-PBS composite by measuring weight loss when subjected to compost soil. It was reported that direction composite with untreated fibers exhibits higher degradation rate followed by alkali treated and coupling agent treated jute fiber reinforced composites. Weight loss was also reported as increasing with increase in fiber diameter.

Kanemura et al [88] investigated the reprocessing of biodegradable polymers (PBS, PLA) after immersion in water for different time durations. Very less degradation in the mechanical properties of PBS up to the third reprocessing cycle, while its bending strength decreased as the immersion time increased when immersed in water at high-temperature. The bending strength of the reprocessed material after immersion was reported higher than that of the immersed material due to removal of cracks and voids. The molecular weight of the immersed PBS was observed higher after reprocessing which was not observed in PLA. In a similar study,

Fortunati et al [88] investigated mechanical properties and chemical structures of biodegradable poly(butylene-succinate) for material reprocessing. It was reported that addition of EVA-GMA to PLA retarded the PLA degradation, but after 21 days in composting conditions, the blends and composites resulted more easily degradable than PLA itself. The addition of cellulose microfibers in PLA/EVA-GMA system modified the rheological behavior.

Kalka et al [89] studied the biodegradation behaviour of Rayon- PLA and all cellulose composites in soil and reported that untreated all cellulose composite exhibits severe degradation after 70 days, while untreated fiber composite shows higher degradation as compared to treated composites.

Sain et al [90] studied the effect of modified cellulose fibres on the biodegradation behavior of in-situ formed PMMA/cellulose composites in soil environment and reported that chemical modification of cellulosic fillers and their incorporation in a synthetic matrix like PMMA by in-situ polymerization method is an effective way to make them environmentally friendly and partly degradable.

Kim et al [91] experimentally investigated the Biodegradability of bio-flour (rice husk flour) filled biodegradable poly(butylene succinate) bio-composites in natural and compost soil and reported a maximum reduction in tensile strength and izod impact strength after 80 days, when subjected to compost soil.

Lee et al. [92] reported that addition of LDI coupling agent results in lower degradation rate in bamboo fiber reinforced PLA/ PBS composites. Addition of LDI also result in improved tensile properties, water resistance and better interfacial adhesion.

Kim et al [93] studied the degradation behavior of PLA and PHBV films when treated with CO2-plasma and reported that exposure of the polymer surfaces to CO2- plasma led to the formation of polar groups and oxidation on the surfaces and subsequently results in increased roughness, wettability and degradability.

Petinakis et al [94] studied the biodegradation and thermal decomposition of poly(lactic acid)-based materials reinforced with hydrophilic fillers (starch and wood flour) in mature compost and reported that the degradation rates of both, PLA/starch blends and PLA/wood-flour composites, were lower than that of pure cellulose but higher than pure PLA. It was also reported that the biodegradation rate increased from about 60% to 80% when the starch content increased from10%to 40%.

Barkoula et al [95] investigated the biodegradation behaviour of Flax-PHB composite copolymerized with HV in open soil and reported that tensile properties drops significantly in the initial stage of degradation and then become stagnant. Increase in PHB brittleness was also reported after addition of HV.

Chlopek et al [96] investigated the influence of different environment on the degradation behaviour of various composites and analyzed the degradation in terms of pH and mass change. It was reported that the degradation process in the natural biological environment is much faster than under simulated conditions while strength is unaffected in pure PLA during composting of 3 months but in case of water incubation strength is decreases by 20 % of initial strength. Water absorption and degradation behaviour of treated sisal fiber reinforced TPS/ PCL/ blend was analyzed by Campos et al [26] and it was reported that blend with 10% fiber reinforcement exhibit increased crystallinity and lower absorption, while fiber agglomeration was reported at higher fiber reinforcement. TPS samples without any additives had the highest rate and extent of degradation whereas the neat PCL samples had the lowest degradation rate. Biodegradation tests also revealed that initially, most samples, with or without fibers, showed a rapid rate of degradation for about 100 h.

Bourmaud et al [68] investigated the effect of recycling on hemp and sisal fiber reinforced composites using mechanical grinding and injection molding processes and reported that reprocessing does not show significant effect on the mechanical properties of PP/hemp or sisal composites. Using coupling agent exhibits an improvement in elongation only up to 3 cycles.

Fakhrul et al [97] examined the degradation behaviour of different biocomposites in various environment and reported that addition of sawdust and wheat flour to PP has evidently increased its biodegradability while order of degradation is observed maximum when exposed to brine solution as compared to moist soil, water or open environment. PP-sawdust composites exhibited greater biodegradability than the PP-wheat flour composites due to the high water absorption ability of sawdust in comparison to wheat flour.

Sapuan et al. [98] studied mechanical properties of kenaf fiber reinforced thermoplastic polyurethane (TPU) composites before and after soil burial. The composites were fabricated by melt mixing method using a Hake Polydrive R-600 internal mixer. The fiber loading in the composite was taken as 30%. To study the moisture absorption effect on the mechanical properties of the composites, soil burial test was performed. Tensile and flexural properties of composites were studied before and after the soil burial for 20, 40, 60 and 80 days. After the soil burial test, the percentage of moisture uptake and weight gain was recorded. After 80 days of soil burial test, the tensile strength of kenaf /TPU composites dropped to 16.14 MPa. It means after soil burial there was a reduction in the tensile properties of the composite. There was no significant change observed in flexural properties (flexural strength and modulus) of the soil buried specimens of kenaf / TPU composites after 80 days. The results show that as a matrix, TPU needs more time to degrade. The poor absorbability of the composites was shown by the low moisture content and low weight gain after soil burial tests. The reduction in tensile strength of the composites is significantly influenced by the degradation process, temperature, weather and humidity.

Huang et al. [99] prepared biodegradable composites from sugarcane rind fiber (SRF) and poly (butylene succinate) (PBS) by melt blending process. An investigation was made on the effect of the content of SRF and the soil burial time on the biodegradability of SRF reinforced PBS composites. Under natural soil conditions, the soil burial test was conducted for 100 days. The evaluation of the biodegradability of pure PBS and SRF reinforced PBS composites was made by analyzing the weight loss, change in mechanical properties and morphological properties, crystallization and melting behavior of the composites and the thermal stability of the composites after the soil burial test. The loss in weight and mechanical properties of the composites were found to be higher than that of the pure PBS, and it reaches a maximum value at the SRF content of 5wt% after the soil burial of 100 days. By Scanning electron microscopy (SEM), it was observed that degree of erosion of the SRF/PBS composites was higher as compared to the pure PBS. Thermo gravimetric analysis (TG) and Differential scanning calorimetry (DSC) showed an increase in crystallization temperature (Tc), maximum weight loss rate temperature (T-max) and degree of crystallinity (χc) after the soil burial of 100 days except for 5wt% SRF reinforced PBS composites. It indicates that the addition of 5wt% SRF to the PBS has maximum impact on the accelerated degradation of PBS.

Salehpour et al. [100] made a study on biodegradation impact of cellulose nano-composites in municipal solid waste composting. They made biodegradable nano-composites from cellulose nano-fiber (CNF) and polyvinyl alcohol (PVA) with the help of liquid nitrogen, freeze drying and hot press technique. For investigating the effect of CNF content on biodegradability of the composites, visual observation was made and scanning electron microscopy (SEM) test, CO2 evolution, differential scanning calorimetry test and weight loss analysis were performed. The results obtained confirm that the loss in weight of nanocomposites was lower as compared to neat PVA because of the zig-zag pathway of microorganisms in CNF presence. The initiation of biodegradation is confirmed by the SEM analysis which shows extensive surface roughness and cracks for all the samples. With increasing the CNF content from 0 % to 10 % , the CO2 evolution decreased and then, it increases with further increase in the CNF content (up to 30 %). Because of the amorphous parts degradation, the crystallinity of PVA and its nano-composites increased as a function of time.

Bootklad and Kaewtatip [101] prepared thermoplastic starch (TPS) composites using compression molding method. They used chicken eggshell as a filler. The effects of addition of eggshell powder (EP) on the TPS properties were compared with the effects of addition of commercial calcium carbonate (CC). It was confirmed by the SEM micrographs that the organic compounds that are present on the surfaces of the eggshell powder act as a coupling agent, which results in a strong adhesion bonding between the TPS matrix and eggshell powder. The biodegradation property of the composites was examined by the soil burial test. The results from surface morphology after the soil burial of 15 days and weight loss showed that the addition of commercial calcium powder and egg shell powder both delayed the biodegradation of the TPS. The degradation of the TPS/EP composites was more rapid than that of TPS/CC composites. It was observed that the thermal stability and water resistance property of the TPS is improved by the addition of eggshell powder. The lowest water absorption was shown by the TPS/EP composites. The improvement of thermal stability by the addition of eggshell powder is shown by TGA curves. Thus the eggshell powder is confirmed as better filler than that of commercial CaCO3 to improve the properties of TPS.

2.6 IDENTIFIED GAPS AND OPPORTUNITIES

The literature review reveals the following knowledge gaps;

- In the last few years, a number of experimental investigations have been conducted focusing on the development and characterization of new composites and findings reported based only on their mechanical behavior. But only a handful have reported the influence of processing route on the mechanical behavior of the fabricated biocomposites.
- The researchers have recommended the various types of fiber surface modification techniques such as physical, chemical, and enzymatic treatment of fibers. The use of these treatments is costly and harmful for the environment when used on commercial scale. Therefore, it becomes necessary to explore alternate economical and environment-friendly chemical treatment route for the natural fibers.
- The literature focusing on the recycling behavior of the natural fiber-based partially and fully biodegradable composites is rarely available.
- The research work is available focusing majorly on the effect of moisture absorption and degradation on tensile properties of the composites. However, the effect of different environments such as acids, bases, salt solution, etc. on the flexural and impact

properties as well as crystallinity of the natural fiber-based composites has not been experimentally investigated in detail.

- The number of research articles available focusing on the degradation behavior of the composites at the end of service life. However, the effect of different degradation mediums such cow manure, organic compost and farmland soil on the tensile, flexural and impact properties as well as the crystallinity of the natural fiber-based composites have not been exhaustively investigated.

2.7 OBJECTIVES OF THE PRESENT WORK

The objectives of the present research work have been outlined as follows:

- To investigate the effect of processing routes (direct injection molding, extrusion-injection molding and extrusion-compression molding) on the behavior of the fabricated polymer composites.
- To explore the effect of eco-friendly treatment of natural fibers on the behavior of the PP and PLA based composites.
- To study the recycling behavior of the natural fiber reinforced PP and PLA based composites.
- To investigate the environmental aging of the natural fiber reinforced PP and PLA based composites.
- To investigate the degradation behavior of the natural fiber reinforced PP and PLA based composites in different environments.

CHAPTER SUMMARY

The chapter has provided the following information:

- A state of the art review on the various aspects of development, recycling, degradation and characterization of natural fiber based polymer composites.
- The knowledge gap in earlier investigations
- The objectives of the present experimental investigation.


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CHAPTER 3

MATERIALS AND METHODS

The current chapter deals with the materials and methods used for the development of polymer composites. The details of the machine setups used for the development of polymer composites and conducting the degradation analysis have been discussed. The characterization techniques employed to investigate the behavior of the natural fibers and developed composites are also reported in details.

3 MATERIALS

3.1.1 Matrix

The PP (1110MAS) of injection molding grade was procured from Indian Oil Corporation Limited, India. The polymer was supplied in pellet form having density and melt flow rate of 0.91 g/cm^3 and 11 g/10 min (230°C, 2.16 kg), respectively. The PLA of injection molding grade (grade 3052 D) in pellet form was supplied by Nature Tech. India Pvt. Ltd., Chennai, India. The PLA is hygroscopic is nature. Therefore, the pellets were dried at 60^{o}C for 6 hours to remove the moisture prior to use. The key properties of the neat PP and PLA are mentioned in Appendix (Table A1). The procured PP and PLA pellets (Fig. 3.1a and 3.1b) were observed to be partially opaque and opaque, respectively. The chemical structure of PP and PLA is shown in Fig. 3.2 (a)-(b)

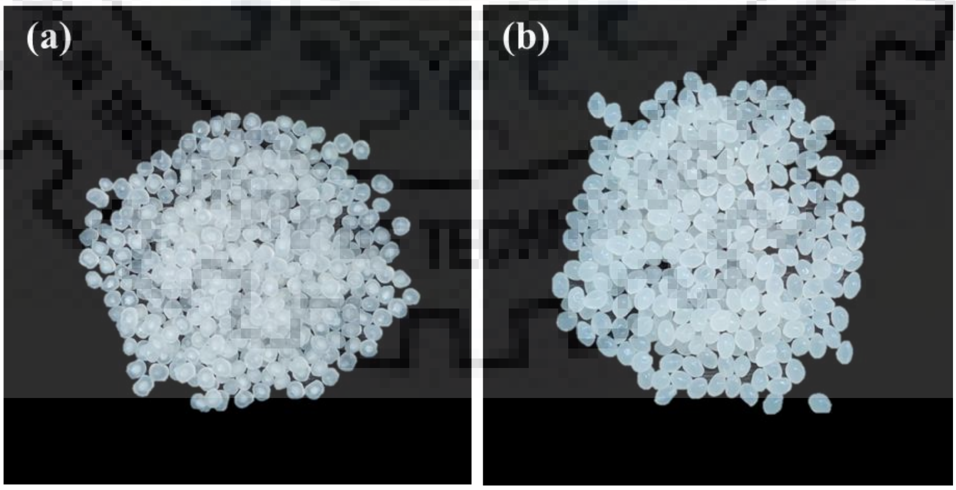


Fig. 3. 1 (a) PP and (b) PLA pellets

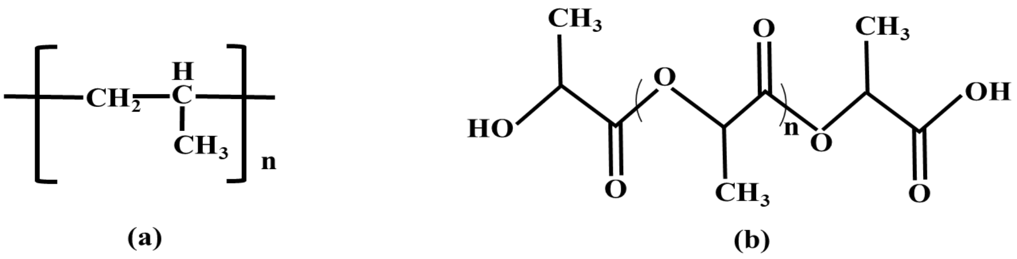


Fig. 3. 2 Chemical structure of (a) PP and (b) PLA

3.1.2 Reinforcement

In the present experimental work, two types of natural fibers (Banana and Pineapple) are used as reinforcement into PP and PLA matrices. The Banana fibers were procured from Sri Achu Fibers, Erode, Tamil Nadu, India. The Pineapple fibers were supplied by Jolly Enterprises, Kolkata, India. Both the fibers were supplied in raw form (long strand), the raw fibers were cut into the short form (average length of 4-5 mm). The short fibers were immersed in water for 24 hours to eliminate the pith/dirt and other contaminants and then dried in sunlight for 24 hours. The dried fibers were screened through a sieve (Mesh No: 60) and finally dried in an oven. Fig. 3.3 depict the steps involved in processing of fibers.

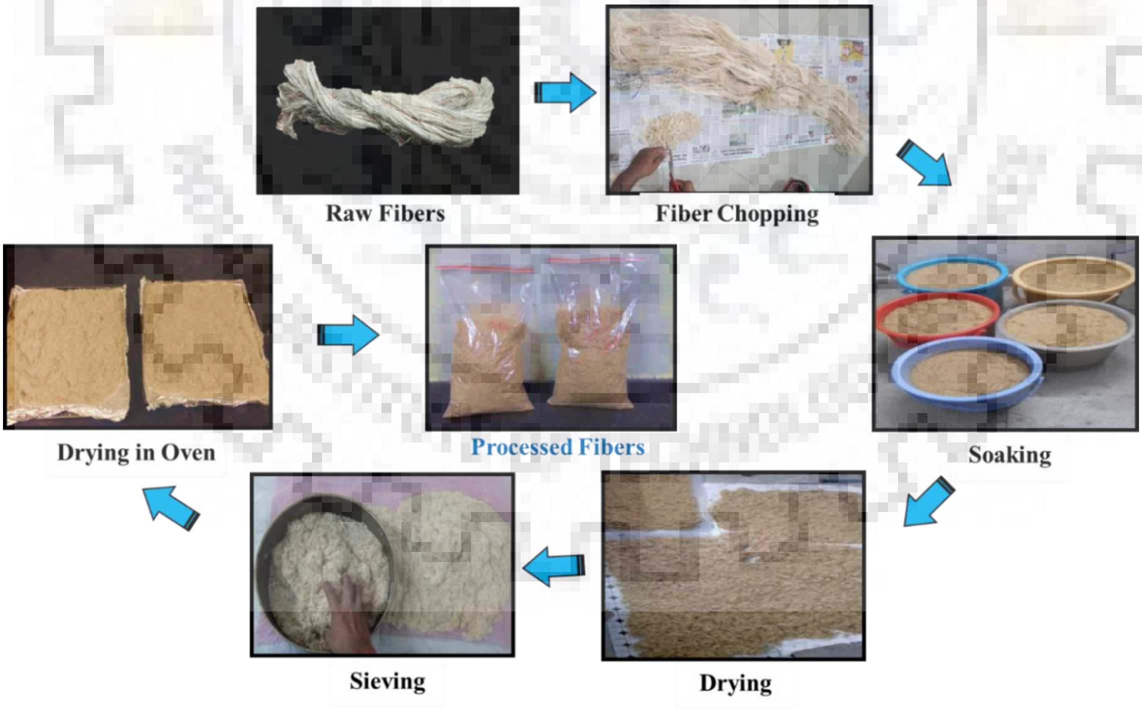


Fig. 3. 3 Processing of Banana fibers

The images of raw and processed Banana and Pineapple fibers are shown in Fig. 3.4 (a)-(d).

Fig. 3. 4 (a) Raw Banana fibers, (b) processed Banana fibers, (c) raw Pineapple fibers and (d) processed Pineapple fibers

3.1.2.1 Surface Modification of Fibers

As discussed in the previous chapter, the surface modification of lignocellulosic fibers is usually recommended to improve the interfacial interaction between the fibers and polymeric matrix. In the current experimental investigation, the surface of the fibers was modified by using different chemical treatments such as Potassium Permanganate ($KMnO_4$), Sodium Bicarbonate ($NaHCO_3$) and Borax Decahydrate ($Na_2[B_4O_5(OH)_4]\cdot 8H_2O$). All the chemicals were supplied in powder form by Sisco Research Laboratories Pvt. Ltd., India.

3.2 CHARACTERIZATION OF FIBER

3.2.1 Thermal Characterization

Thermal properties of the fiber were experimentally investigated by using a Thermo-Gravimetric Analyzer (EXSTAR TG/DTA 6300) under nitrogen atmosphere. The nitrogen flow rate and specimen heating rate were kept as 200 ml/min and 5°C/min., respectively.

3.2.2 FTIR Spectroscopy

The infrared spectrum of fibers was recorded using Fourier Transform Infrared (FTIR) spectroscopy (Make: Thermo Nicollet, Model Magna 760). The fibers were converted into fine powder form by grinding action. The powder was then mixed vigorously with Potassium Bromide (KBr) in the proportion of 1:200 by weight. The thin pellets for testing were obtained by compressing the mixture in the die. The spectra were recorded in the range of 4000 cm^{-1} to 500 cm^{-1} in the transmittance mode.

3.2.3 Morphological Characterization

The effect of chemical treatments on the surface of the untreated and treated fibers was observed by using Scanning Electron Microscope (SEM) (Make: LEO 1550). For the better resolution, a thin layer of gold was coated on the surface of the fiber prior to SEM observation.

3.2.4 Lignocellulosic Analysis

The lignocellulosic content of the untreated and treated fibers was measured experimentally using Laboratory Analytical Procedure (LAP) as reported by Mishra et al. [102]. The lignocellulosic content was measured in terms of total solid, moisture content, ash content, acid-insoluble lignin, acid-soluble lignin, hemicellulose and cellulose.

3.2.4.1 Total Solid and Moisture Content

Total solid and ash content of the fibers were measured using LAP as reported by Sluiter et al. [103]. A fixed weight of dried fibers was taken in a dried and pre-weighted (using SHIDMADZU, ATY224 weighing balance) crucible and kept in muffle furnace at 105°C. The final weight was measured at regular interval until the constant weight was obtained. The total solid and moisture content was calculated using Eq. 3.1 and Eq. 3.2, respectively.

$$\text{Total Solid (\% w/w)} = \frac{\text{Final Weight (Sample +Crucible)} - \text{Crucible Weight}}{\text{Initial Weight of Sample}} \times 100 \tag{3.1}$$

$$\text{Moisture Content (\% w/w)} = \frac{\text{Initial Weight (Sample +Crucible)} - \text{Final Weight (Sample +Crucible)}}{\text{Initial Weight of Sample}} \times 100$$

(3.2)

3.2.4.2 Ash Content

A pre-measured weight of dried fibers was kept in a crucible and placed in a muffle furnace (Yamato, FO 100) at 550 °C for 6h. After incineration, the sample was cooled down and placed in a desiccator and weight of the crucible containing ash was measured. The ash content of the fiber was measured using Eq. 3.3

$$\text{Ash Content (\% w/w)} = \frac{\text{Initial Weight (Sample +Crucible)} - \text{Final Weight (Sample +Crucible)}}{\text{Initial Weight of Sample}} \times 100$$

(3.3)

3.2.4.3 Acid Insoluble Lignin Content

Lignin content of the fibers was measured using LAP as reported by Sluiter et al. [104]. Initially, 0.3 ± 0.001 g of fiber was weighted (W_1) and kept in a test tube containing 30.01 mL of 72% Sulfuric acid (98% w/w H_2SO_4) and mixed thoroughly. The test tube was kept in a water bath at 30 °C for 2 h and stirred at an interval of 15 min. The sample was then transferred in a flask and diluted to reduce the acid concentration from 72% to 4% by adding the 84 mL of deionized water. The flask was then covered and placed in an autoclave at 121 °C for 1 h. The sample was then allowed to cool till the room temperature is reached and filtered using whatman filter paper. Solid residue was then washed using deionized water repeatedly and 20 mL of filtrate was stored at 4° C for further measurement. The solid residue was kept in a crucible and dried at 105° C and measured till the constant weight (W_2) was achieved. The crucible containing solid residue was then transferred to the furnace at 550°C for 4 h of incineration. After cooling, the weight (W_3) of the crucible containing ash was measured. The insoluble lignin of the fiber was measured using Eq. 3.4.

$$\text{Acid Insoluble Lignin (\% w/w)} = \frac{W2 - W3}{W1 \times \text{Total solid (\%)}} \times 100$$

(3.4)

3.2.4.4 Acid Soluble Lignin

The absorbance of filtrate obtained in the previous section was recorded at 205 nm against 4% H_2SO_4. Acid soluble lignin of the fibers was calculated using Eq. 3.5.

Acid Soluble Lignin (% w/w) = $\frac{\left(\frac{\mathrm{A}}{\mathrm{b}\times\mathrm{a}}\right)\times \text{Dilution factor} \times \left(\frac{\mathrm{V}}{1000}\right)}{\mathrm{W1} \times \text{Total solid (\%)}} \times 100$

(3.5)

Where, A = Absorbance at 205 nm

b = Path length of cell (1 cm)

a = Absorptivity (110 L/g× cm)

V = Filtrate volume (87 mL)

W_1 = Initial weight of fiber

3.2.4.5 Cellulose and Hemicellulose

The filtrate stored during the calculation of acid insoluble lignin was neutralized using $Ca(OH)_2$ between 6-7 pH and filtered again to remove any precipitate. Total reducing sugar (TRS) contains glucose and xylose and it was estimated using (Dinitrosalicylic acid) DNS method given by Miller [105]. Approximately, 90% of the total glucan represents the cellulose content of the lignocellulosic fibers and 90% of total xylan represents the hemicellulose content of the fibers.

The cellulose and hemicellulose can be determined using Eq. 3.6 and 3.7, respectively.

$$\text{Cellulose} = 0.9 \times \text{Total glucan} \tag{3.6}$$

$$\text{Hemicellulose} = 0.9 \times \text{Total xylan} \tag{3.7}$$

3.2.5 Tensile Behavior of Fibers

The tensile behavior of the fibers was investigated in context of strength and modulus. The test was performed on small scale tensile testing machine (Bose, Model: Electroforce 3200, Load Cell 225N) as per ASTM D3822-14 at a crosshead speed and gauge length of 0.1 mm/min., and 25 mm, respectively. A total of 25 test specimens were prepared per sample and average values have been reported. The test specimens were prepared by pasting the fibers on paper frame with adhesive to avoid the misalignment of fibers during testing (Fig. 3.4). After fixing the specimen between the upper and lower jaws, the paper frame was cut from the middle of the gauge length prior to start of the testing.

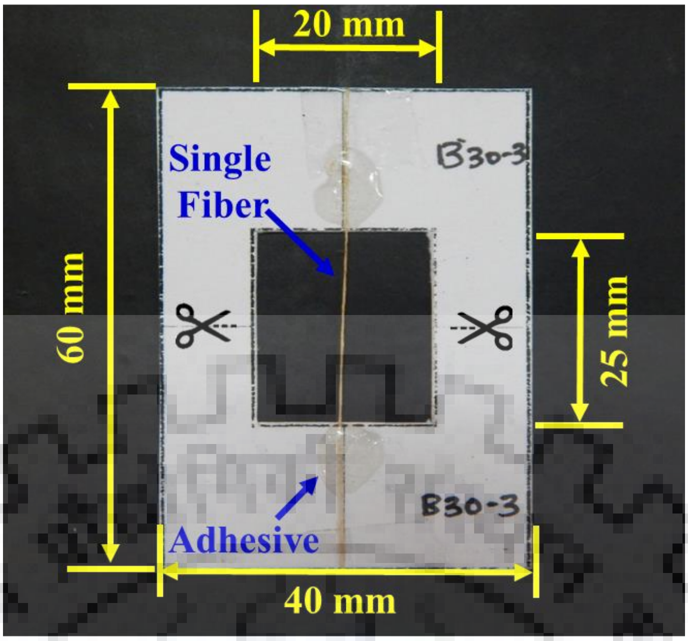


Fig. 3. 5 Tensile test specimen for fibers

3.3 EXPERIMENTAL SETUPS

3.3.1 Extrusion Set-up

The compounding of fibers and polymeric pellets is usually recommended to achieve the uniform distribution and alignment of fibers within the polymeric composites. There are various compounding methods prior to final fabrication that have been suggested in the literature. The most widely used methods are extrusion, pultrusion and melt blending. These methods are generally used for the compounding of thermoplastic based composites. The extrusion method has been suggested as the most widely used compounding method in the literature. Depending upon the number of screws used, the extruder can be a single screw extruder or twin screw extruder. The extrusion setup used in the present work is shown in Fig. 3.6. The specifications of the extrusion setup are listed in Table 3.1

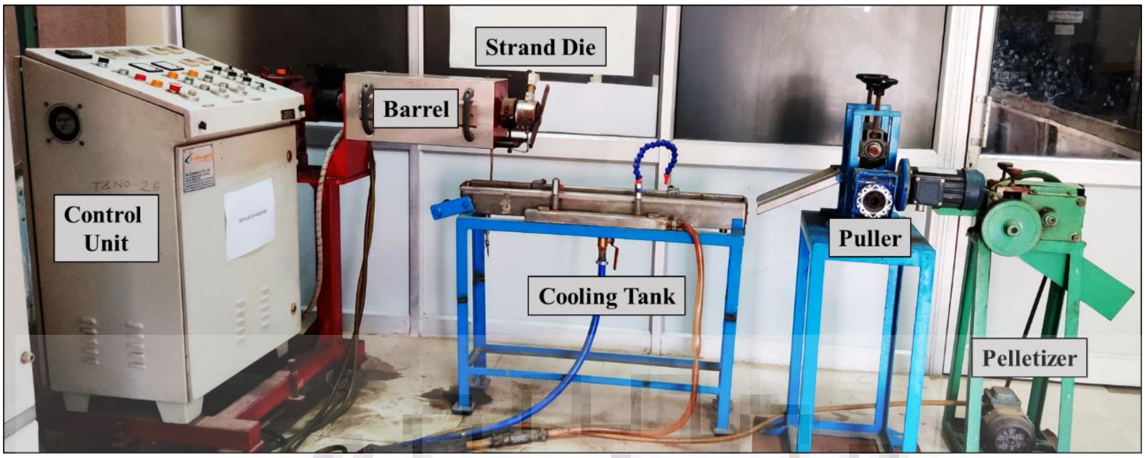


Fig. 3. 6 Extrusion setup

Table 3. 1 The specifications of extrusion setup

Specifications	**Values**
Maximum Temperature (°C)	400
Maximum Screw Speed (rpm)	200
Screw Diameter (mm)	30
Screw Length to Diameter Ratio (L/D)	21
Die Opening Diameter (mm)	04

For compounding, the polymeric (PP and PLA) pellets and fibers (Banana and Pineapple) were mixed rigorously and fed into the hopper of the extruder. The mixture is then carried inside the barrel with the help of rotating screw. As the mixture travel toward the die, the pellets melt and compounding with fibers take place due to heating and rotating action of the screw. The composite strand in the form of wire is then passed through the water bath for cooling and then pelletized using pelletizer. The pellets were dried in hot air oven at 90°C for 6 hours and stored in air tight container for further use.

The quality of the composite pellets depends upon the processing parameters such as barrel temperature, screw speed and fiber loading. The selection of barrel temperature and screw speed depends upon the thermal degradation behavior of the individual constituents. The barrel is divided into feed zone, melt zone, compression zone and metering zone (hopper to die end).

The temperature of these zones can be judiciously selected and controlled to avoid the thermal degradation of the constituents (polymer and fiber) during processing. The barrel temperature should be kept above the melting point of the thermoplastic polymers but lower than the degradation temperature of fibers. The screw speed should be selected considering the attrition characteristics of the fiber. Pilot experiments revealed that the maximum fiber loading that can be achieved with the existing setup was 30 wt.%. However, there were several challenges occurred during processing such as, choking of nozzle and fiber burning. Therefore, fiber loading of 20 wt.% was selected as optimum. These processing parameters were optimized during pilot experiments. In the present work, the barrel temperature and screw speed was kept as 170 ^{o}C and 400 rpm, respectively for PP based composites and 155 ^{o}C and 400 rpm for PLA based composites.

3.3.2 Injection Molding Machine

It is one of the most widely used fabrication techniques for the polymeric and polymer based composite products. The working principle of injection molding machine is same as extrusion process. The fibers and polymers or composite pellets were fed into the hopper of the injection molding machine. The mixture is then carried inside the barrel with the help of rotating screw which can rotate as well as reciprocate. As the pellets enter into the barrel, softening of materials take place due to heating. As the screw rotates, mixing of fibers and polymers takes place and at the same time, the melted composite compound is forced towards the converging section of the barrel. At the end of the barrel, the nozzle is connected which is used to inject metered amount of mixture into the mold cavity with high pressure. The clamping unit is provided to clamp the mold together under high pressure to prevent the defects during injection. After injection, the cooling take place in the mold cavity. The variety of cooling medium (air, water and oil) can be used as per the requirement. After cooling, the composite part is ejected by giving a slight tap with the help of ejector pins. In the current experimental study, the PP and PLA based composites were fabricated using commercial scale injection molding machine (Make: Electronica-Endura-60). The specifications of injection molding machine are mentioned in Table 3.2. The main components of a typical injection molding machine are depicted in Fig. 3.7.

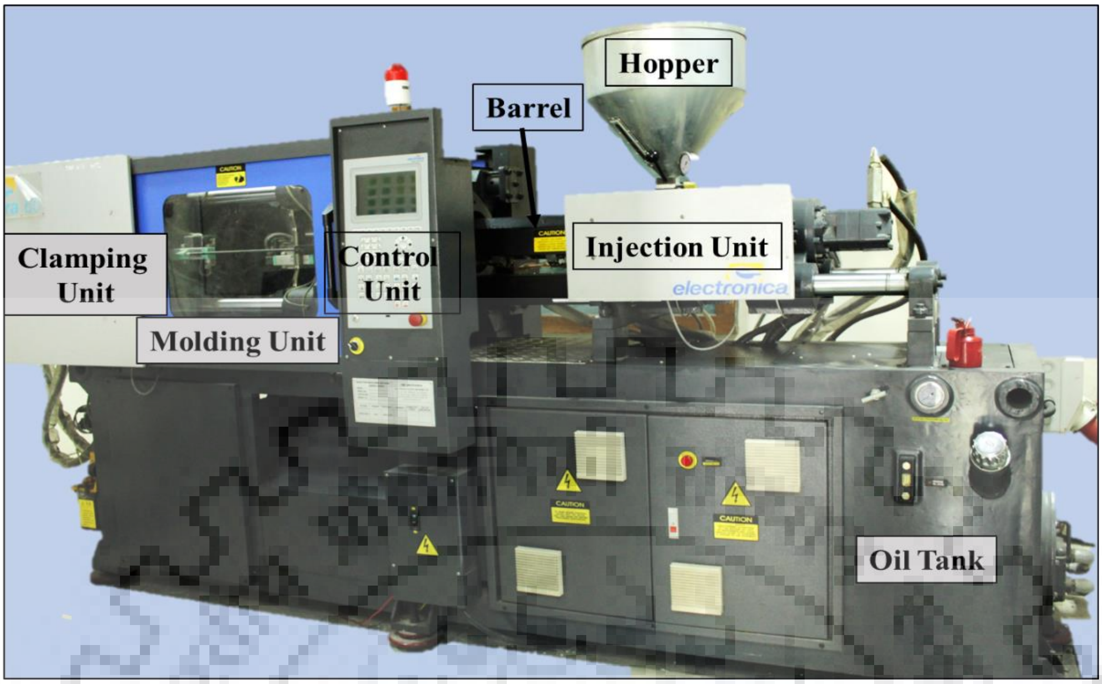


Fig. 3. 7 Injection molding machine

Table 3. 2 Specification of injection molding machine

Specifications	**Values**
Maximum Temperature (°C)	400
Maximum Screw Speed (rpm)	235
Screw Diameter (mm)	28
Screw Length to Diameter Ratio (L/D)	21
Maximum Injection Weight (gm)	64
Maximum Injection Pressure (MPa)	189
Maximum Clamping Force (kN)	600
Mold Opening Stroke (mm)	300

The elements of a typical injection molding cycle are shown in Fig. 3.8. Usually the cycle starts with empty mold in closed position. The clamping unit is provided to clamp the mold together under high pressure to prevent the defects during injection. At this position, the screw that is in retracted position, start moving forward which forces the melt compound and finally inject with the help of nozzle in to the mold cavity.

Post injection, the shrinkage of melt compound take place during solidification and to compensate that, the screw is kept in forwarded position with the help of holding pressure. After holding period, the cooling of the injected compound take place and at the same time the screw start moving backward and at the end of cooling period the screw reaches to its maximum backward position. During backward movement of the screw, the existing melt compound in the barrel moves forward and fresh mixture enters in to the barrel. At the end of cooling, the part is ejected with the help of ejectors. After ejection, the mold closes and cycle repeats.

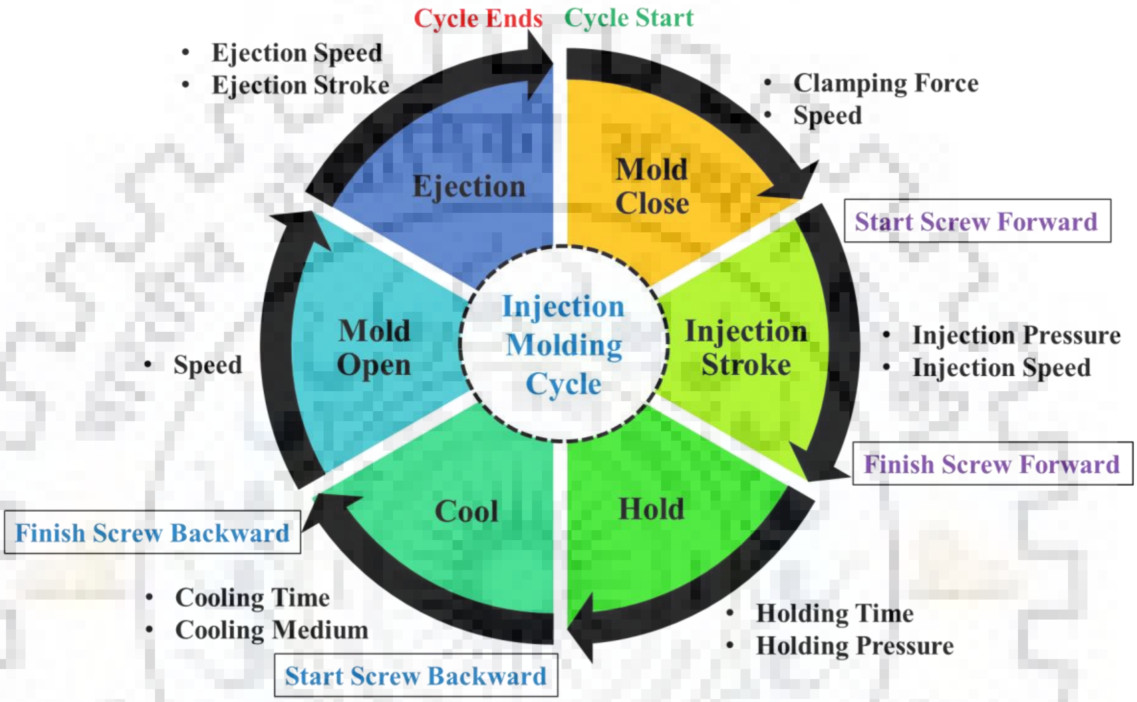


Fig. 3. 8 Injection molding cycle

3.3.2.1 Operating Parameters

A typical injection molding machine can generally be used for the fabrication of thermoplastics and thermoplastic based composite products. In injection molding process, the short fibers (chopped) and matrix are either pre-compounded or directly fed into the hopper of the injection molding machine. During injection molding, the natural fibers have to travel from hopper to nozzle where excessive fiber damage may take place due to heating and shearing action. In order to encounter such type of challenge, researchers have recommended the use of separate hopper (for feeding the natural fibers) near the nozzle. The behavior (physical, chemical and thermal properties) of the fibers and matrix are entirely different from each other. The operating parameters selected for reinforcement may not be suitable for the matrix or vice-versa. Therefore, sound understanding of the effect of these processing parameters on the quality and performance of the composites and judicious selection of processing parameters is necessary to produce the composite parts with exceptional properties. The important processing parameters involved during injection molding process are discussed in the following section;

- Barrel Temperature
- Screw Speed
- Injection Speed
- Injection Pressure

The temperature of barrel is a crucial parameter and has significant effect on the behavior of the final products. The melt-mixing of fibers and matrix take place in the heated barrel. The barrel can be divided in to different zones (from feeding zone to nozzle). The temperature in these zones have to be controlled judiciously. Inside the barrel, the heat is generated in two ways; external heating due to heaters and internal heating due to shearing action of screw during plasticizing. To increase the flow ability (reduction in viscosity) of mixture, the temperature of the barrel must be higher but at the same time excessive heating can degrade the polymers and natural fibers.

The speed of the screw is an another important parameter. The optimum speed is necessary to achieve the uniform distribution of fibers within the composites. Higher speed of the screw leads to the higher heat generation and fiber attrition due to increased shear force. Sometimes, it can degrade the properties of the polymer also. In order to overcome these challenges, an optimum balance between the screw speed and back pressure is required.

Injection speed plays a vital role during processing of thermoplastic based composites. The injection speed has the direct influence on the viscosity of melt compound. As the fiber loading increase, the viscosity of the melt compound also increases and to inject the melt compound and to fill the mold cavity totally, the higher injection speed is required. Higher speed increases the shear force and excessive speed may degrade the properties of fibers and polymers. Higher injection speed is recommended for the processing of parts having thin cross-section where high precision and accuracy are required.

Injection pressure is one of the most important parameter during injection molding. It is the pressure by which the melt compound is forced to flow. Lower injection pressure leads the short shot type of defect in the molded part while the higher pressure may lead to the formation of flash type of defect. Hence, the optimum injection pressure is required to achieve the desired product without any defects. The operating window for injection molding process is depicted in **Fig. 3.9**

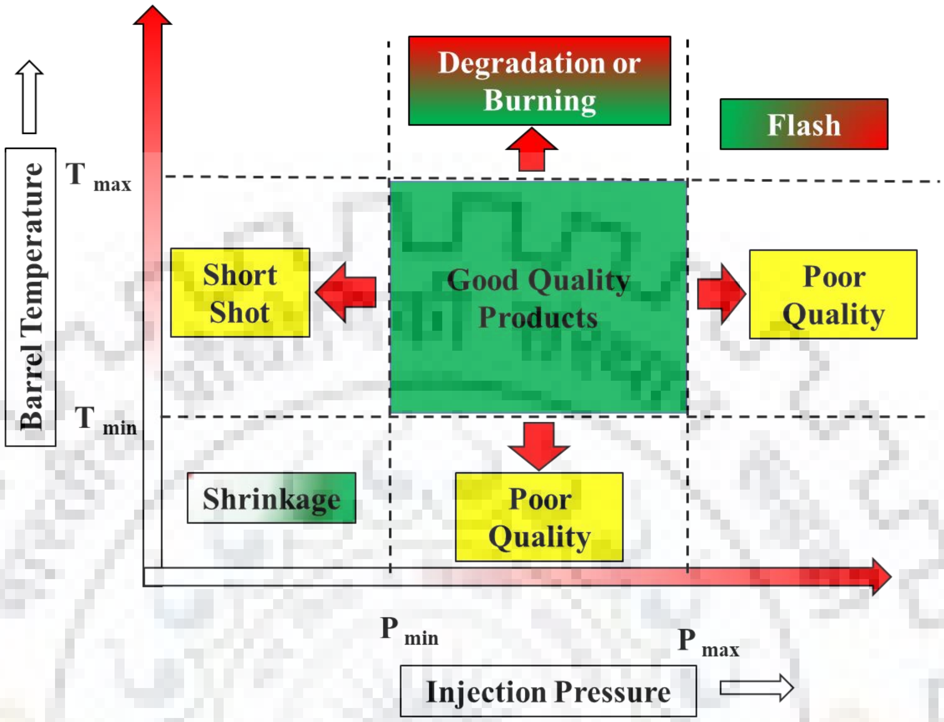


Fig. 3. 9 Operating window for injection molding process

In the present experimental work, the operating parameters for fabricating the composite specimens were decided considering the above mentioned guidelines.

The mold cavity of the injection molding machine is designed (Fig. 3.10) in such a way that, in a single injection, the test specimens for conducting different tests can be fabricated. The dimensions of the cavity in the mold are given in Table 3.3.

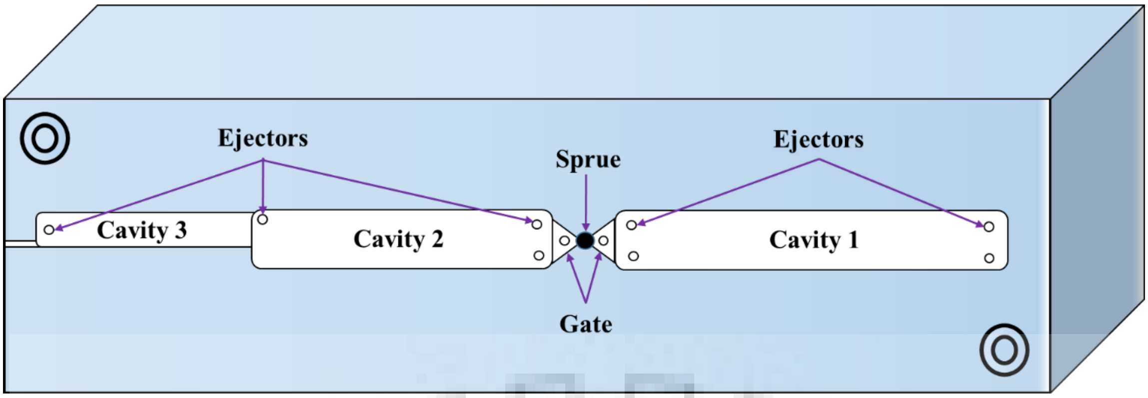


Fig. 3. 10 Schematic of mold cavities of injection molding machine

Table 3. 3 Dimensions of mold cavities

Test Specimens	Cavity	Cavity Dimensions (mm)	ASTM Standard
Tensile Test	Cavity 1	150 X 15 X 4	ASTM D3039M
Flexural Test	Cavity 2	100 X 15 X 4	ASTM D7264
Impact Test/Dynamic Mechanical Analysis	Cavity 3	55 X 15 X 4	ASTM D256/ASTM D 4065

3.3.3 Compression Molding Machine

Compression molding is the most common and one of the oldest technique for the fabrication of composite parts. It is a high pressure closed mold process. It can be used for the processing of both, thermoplastics and thermosetting based composite products. The reinforcement in the variety of forms such as unidirectional, bidirectional, mat of randomly oriented fibers and short fibers can be easily used. Two matched plate type metal molds are used to fabricate the composite product, the upper mold and the lower mold, the lower mold is generally fixed while the upper mold is movable. The reinforcement and the matrix or pre-compounded mixture of fibers and polymers in the form of pellets or loaf are kept in between the metallic molds of the desired shape at elevated temperature and pressure. The molds are kept in closed position for the predefined period of time as per the requirement. The material placed in between the upper and lower mold takes the shape of the mold due to the application of pressure and heat. The shape, size, accuracy, and design of the composite products depend upon the mold design. The polymerization can be done either at room temperature or at elevated temperature as per the processing guidelines of the materials. After polymerization, the molds are opened and the composite product is removed for further processing. The most important processing parameters which need to be controlled to get good quality composite products are; mold heating and cooling rate, applied pressure and curing time. In the current experimental work, the compression molding machine (UNI-100, Unimech, Mumbai, India) used for the fabrication of composites is shown in Fig. 3.11. The specifications of the machine are given in Table 3.4.

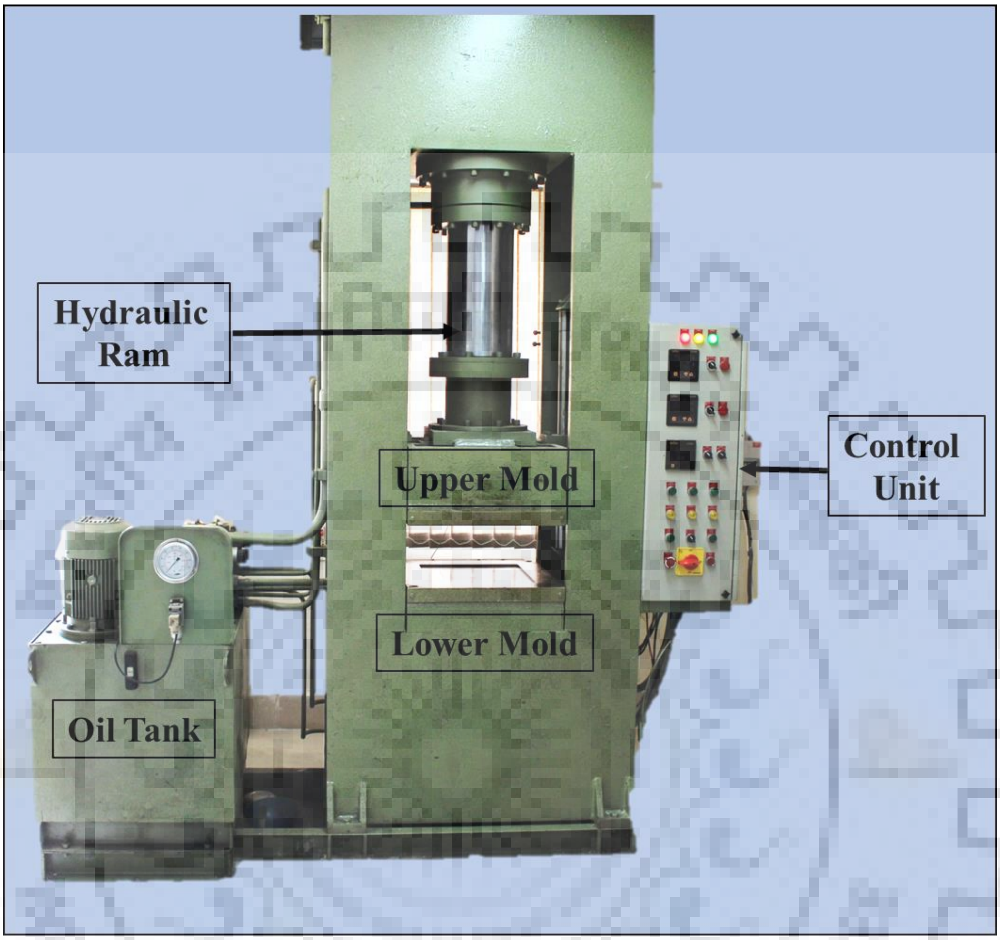


Fig. 3. 11 Compression molding machine

Table 3. 4 Specifications of the compression molding machine

Specifications	**Value/Type**
Type	Hydraulic Press
Capacity (kN)	980
Maximum Temperature (^{o}C)	400
Maximum Pressure (MPa)	17.65

3.4 CHARACTERIZATION OF COMPOSITES

3.4.1 Thermal Characterization

Fibers and polymers as well as composite materials can be subjected to various thermal conditions during their processing and applications. This necessitates the understanding of their thermal characteristics. Thermal degradation behavior of the composites was experimentally investigated by using a Thermo-Gravimetric Analyzer (EXSTAR TG/DTA 6300) under nitrogen atmosphere. The nitrogen flow rate and specimen heating rate were kept as 200 ml/min and 5°C/min., respectively. The alumina (Al_2O_3) powder was used as reference material.

3.4.2 FTIR Spectroscopy

In order to investigate the presence and kind of interfacial interaction in the composites, FTIR analysis was conducted. The infrared spectrum of composites was recorded using Fourier Transform Infrared (FTIR) spectroscopy (Make: Thermo Nicollet, Model Magna 760). The composites were converted into fine powder form by grinding action. The powder was then mixed vigorously with Potassium Bromide (KBr) in the proportion of 1:200 by weight. The thin pellets for testing were obtained by compressing the mixture in the die. The spectra were recorded in the range of 4000 cm^{-1} to 500 cm^{-1} in the transmittance mode.

3.4.3 XRD Analysis

The structure and crystallinity of the developed composites were investigated using X-ray diffraction machine (Bruker, D8-Advance) using Cu as the target material. The crystallinity has been measured by using the Ruland-Wonk method [106]. The expression used for the calculation of crystallinity is given in Eq. (3.1).

$$\text{Crystallinity (\%)} = (\text{Crystalline area} \times 100)/\text{Total area under the curve} \quad (3.1)$$

3.4.4 Mechanical Characterization

The mechanical characteristics in context of tensile, flexural and impact properties of the developed biocomposites were tested and analysed.

3.4.4.1 Tensile Testing

The tensile testing was performed on Universal Testing Machine (Instron: 5982, USA) in accordance with ASTM D3039. During tensile testing, the gauge length was kept as 50 mm and the crosshead speed was fixed at 2 mm/min. Tensile properties were evaluated in terms of strength and modulus.

Fig. 3. 12 Tensile testing of the composite specimens

3.4.4.2 Flexural Testing

The flexural test was performed in accordance with ASTM D7264 using 3-point bending fixture. The span length and thickness of the specimens were 60 and 4 mm, respectively. The testing was performed at a crosshead speed of 2 mm/min. The flexural properties were also investigated in terms of strength and modulus.

Fig. 3. 13 Flexural testing of the composite specimens

3.4.4.3 Impact Testing

The impact test was conducted with a low energy impact tester (Make: Tinius Olsen-IT504) according to ASTM D256-10. For each test, five test specimens were tested and the average value is reported.

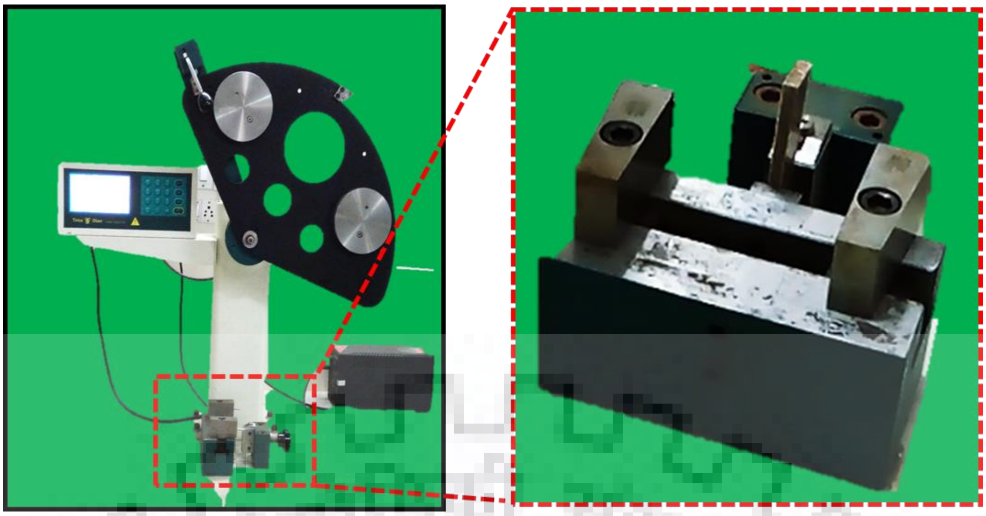


Fig. 3. 14 Impact testing of composite specimens

3.4.5 Morphological Characterization

3.4.5.1 Stereo-Microscopic Analysis

In order to investigate the attrition of fibers during the processing and their effect on the properties of the PLA based composites, the fibers were extracted from the PLA based composites by liquefying the composite specimens in the chloroform solution, the extracted fibers were then observed under a stereo microscope (Nikon, Model: SMZ-745T).

To investigate the distribution and alignment of fibers within the developed composites, the composites were cut normal to the direction of flow of fibers and observed under stereo microscope. This type of study is useful in determining and correlating the effect of orientation of fibers on the behavior of the developed composites.

3.4.5.2 Scanning Electron Microscope Analysis

The morphology of the fractured tensile and impact specimens was observed by using Scanning Electron Microscope (SEM) (Make: LEO 1550). For the better resolution, a thin layer of gold was coated on the surface of the biocomposite specimens before the SEM observation.

3.4.6 Dynamic Mechanical Analysis

The dynamic mechanical properties of the composites were evaluated using Dynamic Mechanical Analyzer (TA-DMA-Q800). The dual cantilever fixture was used for holding the specimen during the testing. The test was conducted at a sinusoidal frequency of 1 Hz, between the temperature range of 30ºC to 90ºC with a temperature ramp of 3ºC/min. The dynamic mechanical behavior of the composites was investigated in context of storage modulus, loss modulus and tan delta.

3.5 DEGRADATION BEHAVIOR OF THE COMPOSITES

3.5.1 Environmental Aging

The challenges in the development of natural fiber reinforced composites lie in making them structurally and functionally stable during their service life as well as easily degradable on disposal at the end of service life. These materials can be exposed to different environmental conditions during their service life such as exposure to sunlight, moisture and acids. This necessitates the understanding of their environmental ageing characteristics. In the current experimental study, the effect of environmental ageing on the behavior of the developed composites was investigated. The developed composite specimens were exposed to different environments [alkaline solution (5% NaOH), acidic solution (5% H_2SO_4), brine solution (5% NaCl), tap water and outdoor weather] for the period of 6 months with an interval of 2 months. The effect of environmental ageing on the behavior of the developed composites were investigated in terms of variation in weight, mechanical properties and crystallinity.

3.5.2 Degradation Behavior

In order to evaluate the effect of different environments (farm land soil, organic compost and cow manure) on the degradation behavior of the composite specimens, the degradation test was carried out by burying the specimens for the period of 6 months with an interval of 2 months. The test was conducted in a compost bin [(20 x 5 × 1) (cubic feet)] (pH 7 and RH 70–80%). RH was maintained throughout the burial time by sprinkling the water at regular interval. The composite specimens were buried at 5 cm depth from the top surface, the average temperature during the exposure time was 30°C. The specimens were taken from the compost bin after every 2 months and washed with tap water. Degradation behavior was measured in terms of the variation in weight, mechanical properties and crystallinity.

CHAPTER SUMMARY

The chapter has provided the following information:

- The description of the lignocellulosic fibers and polymeric matrices used for the development of the composite test specimens.
- The description of the processing techniques (extrusion, compression and injection molding) used for the development of polymer composites.

- The details of the techniques used for the characterization of lignocellulosic fibers.
- The details of the various characterization techniques used to investigate the behavior of the developed composites.
- The description of various techniques used for the morphological examination of the developed, fractured and degraded specimens.

The next chapter presents the effect of three processing techniques and chemical treatments on the behavior of the developed composites.

CHAPTER 4

DEVELOPMENT OF POLYMER MATRIX COMPOSITES

In this chapter, polymer composites based on two types of natural fibers (banana and pineapple fibers) and two types of matrices (PLA and PP) were fabricated using three different processing techniques, namely direct injection molding (DIM), extrusion injection molding (EIM) and extrusion compression molding (ECM). The thermal and mechanical characterization as well as dynamic mechanical analysis has been performed to understand and compare the performance of the developed composites. Moreover, the behavior of the composites has been analyzed in context of extracted fiber morphology as well as the distribution and orientation of fibers within the developed composites. This chapter also explores the effect of different types of chemical treatments of the fibers on the behavior of the developed composites.

4.1 EFFECT OF PROCESSING ROUTES ON THE BEHAVIOR OF THE POLYMER COMPOSITES

Due to ecological and environmental concerns, the research interest is shifting from synthetic fiber-based polymeric composites to the natural fiber-based composites. Synthetic fibers (kevlar, glass and carbon etc.) have been used as reinforcement in various petroleum-based thermoplastic and thermoset matrices due to their excellent physical and mechanical properties [107], [108]. But at the same time, the requirement of high energy during their processing, their non-renewability, non-biodegradability and non-recyclability has forced researchers and engineers to develop sustainable and eco-friendly composites [24], [109], [110].

It has been reported that the properties of natural fiber-based composites are comparative or better than the synthetic fiber-reinforced composites [111], [112]. Overall, characteristics of composites are governed by various factors such as the manufacturing process, processing parameters, distribution and alignment of fibers and the interfacial characteristics between the constituents [27], [28], [113], [114]. In the last few years, a number of experimental investigations have been conducted focusing on the development and characterization of new composites based on their mechanical behavior [66], [107], [115]. But the literature focusing on the effect of processing route on the behavior of the composites is rarely available. A judicious selection of processing route is necessary as it has a significant influence on the overall characteristics of the fabricated composites. The development of composites with uniform distribution and orientation of fibers with high fiber aspect ratio is the key objective of any manufacturing technique to obtain optimal mechanical properties. The commercial viability of the composites depends on the manufacturing method with less processing time, simplicity in operation with exceptional dimensional properties and repeatability. The literature reveals that one of the most commonly used processing technique for the fabrication of short fiber-based polymeric composites is injection molding [38], [116]. It is a quick process and offers flexibility in product design variation. Yet, most of the researchers reported the use of extruder for mixing the fibers and polymers before injection molding for pre-compounding of fibers and matrix material [78], [81], [83], [86]. This process of mixing causes severe fiber attrition due to heating at elevated temperature, shearing action during fabrication and subsequent pelletizing. In the current investigation, three processing techniques were used to fabricate the composites based on two types of natural fibers (banana and pineapple) and two types of matrices (PLA and PP). The effect of these processing techniques on the behavior of the developed biocomposites has been experimentally investigated. The fiber attrition, orientation and alignment of the fibers in the composites were examined and investigated under stereo microscope.

The aim of the current experimental investigation was to study the effect of processing routes on the behavior of the developed composites and to identify the best processing route for the development of short fiber based composites. Therefore, all the characterization conducted was only for the PLA based composites. However, the mechanical characterization was conducted for both PLA and PP based composites.

4.1.1 Fabrication of Composites

Composites incorporating fiber of varying fiber loading (10%, 20%, and 30% wt. %) were developed during pilot experimentation. At 30 wt. % and above, the various problems such as choking of nozzle and fiber burning occurred. Moreover, mechanical testing revealed that the tensile strength of all the composites was found to decrease marginally with an increase in fiber loading up to 20 wt.%. Beyond 20 wt.%, the tensile strength decreased substantially. Furthermore, the flexural strength of composite incorporating 20 wt.% of fibers was found to be maximum. Hence, the fiber weight % of 20 % was found to be optimum and was selected for further investigation. The composites based on two types of fibers (BF and PF) and two types of matrices (PLA and PP) were fabricated using three processing techniques; DIM, EIM and ECM.

4.1.1.1 Direct Injection Molding

Fig. 4.1 depicts the schematic of DIM technique, in which polymer pellets and fibers were mixed vigorously and fed directly into the hopper of injection molding machine and composite test specimens were manufactured as per the ASTM standard. The parameters used for fabricating the specimens are shown in Table 4.1. These optimized parameters for processing were selected based on the pilot experiments.

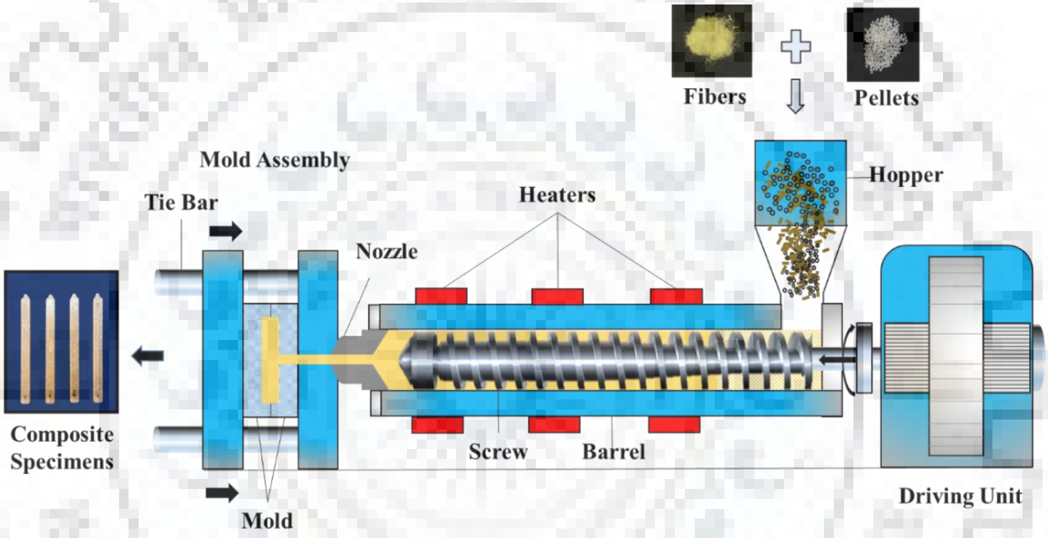


Fig. 4. 1 Schematic of the DIM Process

Table 4. 1 Processing parameters used for the fabrication of composite specimens

	Temperature profile (Nozzle-feed zone)	**Injection pressure (MPa)**	**Holding pressure (MPa)**	**Holding time (Sec.)**	**Cooling time (Sec.)**	**Back pressure (MPa)**
PLA based Composites	170-165-165-160°C	60	40	15	25	10
PP based Composites	185-180-175-170°C	70	40	15	15	10

4.1.1.2 Extrusion Injection Molding

Fig. 4.2 depicts the EIM technique, in which the polymeric pellets and processed short fibers were initially fed into the hopper of extrusion machine (Sai Extrumech, Faridabad, India) and compounded at a temperature and speed of 155°C and 400 rpm for PLA based composites and 170°C and 400 rpm for PP based composites, respectively. Thus, the output in the form of composite strands was obtained. These composite strands were passed through the water bath for cooling. After cooling, the composite strand was converted into the composite pellets using pelletizer. The composite pellets were then transferred and dried in the oven prior to injection molding. These composite pellets were used as raw material and fed into the hopper of the injection molding machine and composite specimens were fabricated. The processing parameters used for fabricating the composite specimens were the same as DIM.

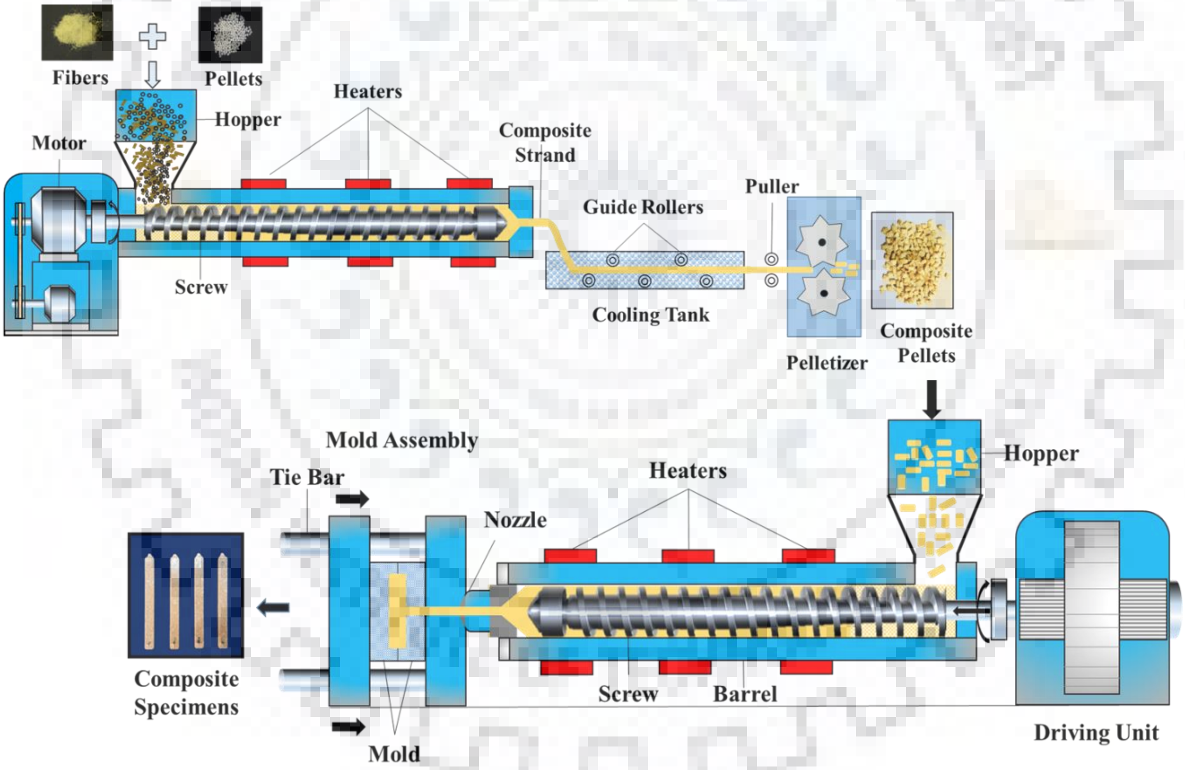


Fig. 4. 2 Schematic of the EIM process

4.1.1.3 Extrusion Compression Molding

Fig. 4.3 shows the schematic of the ECM process, in this process, the compounding of polymer pellets and fibers was done similar to EIM technique. The melted compound was collected in a preheated mold. This mold was then immediately shifted to the compression molding machine and hot-pressed between two preheated molds at a temperature and pressure of 170°C and 40 bar for PLA based composites and 185°C and 40 bar for PP based composites, respectively. Hence, the melted compound takes the shape of the mold due to the application of pressure and heat. When the temperature of the upper and lower molds drops to 50°C, the composite plate was removed from the mold. The composite plate thus obtained was then cut into the test specimens. The polyester sheet was used to facilitate the easy removal of fabricated composite from the mold.

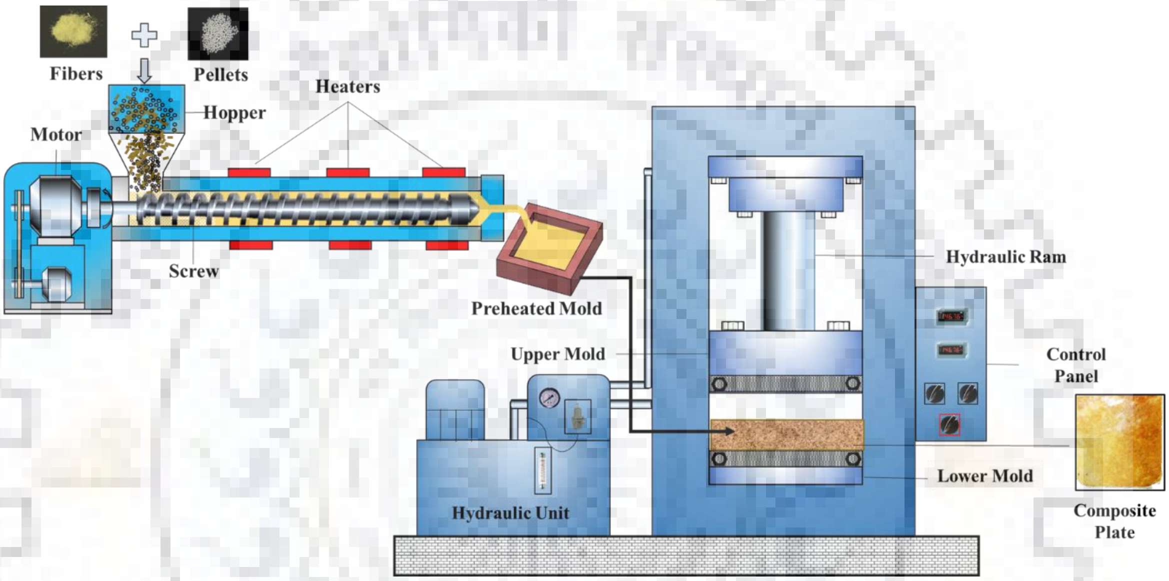


Fig. 4. 3 Schematic of the ECM process

The designation of the composites fabricated using direct injection molding, extrusion injection molding and extrusion compression molding are given in **Table 4.2.**

Table 4. 2 Designation of the developed composites

S.N.	Designation	Details	Process
1	DIM-PLBF	PLA + Banana Fiber	Direct Injection Molding
2	EIM-PLBF		Extrusion Injection Molding
3	ECM-PLBF		Extrusion Compression Molding
4	DIM-PLPF	PLA + Pineapple Fiber	Direct Injection Molding
5	EIM-PLPF		Extrusion Injection Molding
6	ECM-PLPF		Extrusion Compression Molding
7	DIM-PPBF	PP + Banana	Direct Injection Molding

8	EIM-PPBF	Fiber	Extrusion Injection Molding
9	ECM-PPBF		Extrusion Compression Molding
10	DIM-PPPF	PP + Pineapple Fiber	Direct Injection Molding
11	EIM-PPPF		Extrusion Injection Molding
12	ECM-PPPF		Extrusion Compression Molding

4.1.2 Results and Discussion

4.1.2.1 Analysis of Extracted Fiber Morphology

During processing, the natural fibers are exposed to high temperature and pressure as well as high shearing action, which causes fiber attrition and ultimately influence the characteristics of the composites. Therefore, it becomes necessary to investigate the effect of processing routes on the attrition of fibers.

In order to investigate the attrition of fibers during the processing and their effect on the properties of the developed composites, the fibers were extracted from the PLA based composite by liquefying the composite specimens in the chloroform solution. The extracted fibers were then observed under a stereo microscope and images are presented in Fig. 4.4 (a – d) and Fig. 4.5 (a – d). It can be seen that during DIM, the attrition of fibers is mostly in the form of bending and twisting (Fig. 4.4b and Fig. 4.5b). Comparatively longer fibers and absence of interfacial bonding between constituents prior to injection molding may be the main reasons for the bending and twisting of fibers in the developed biocomposites.

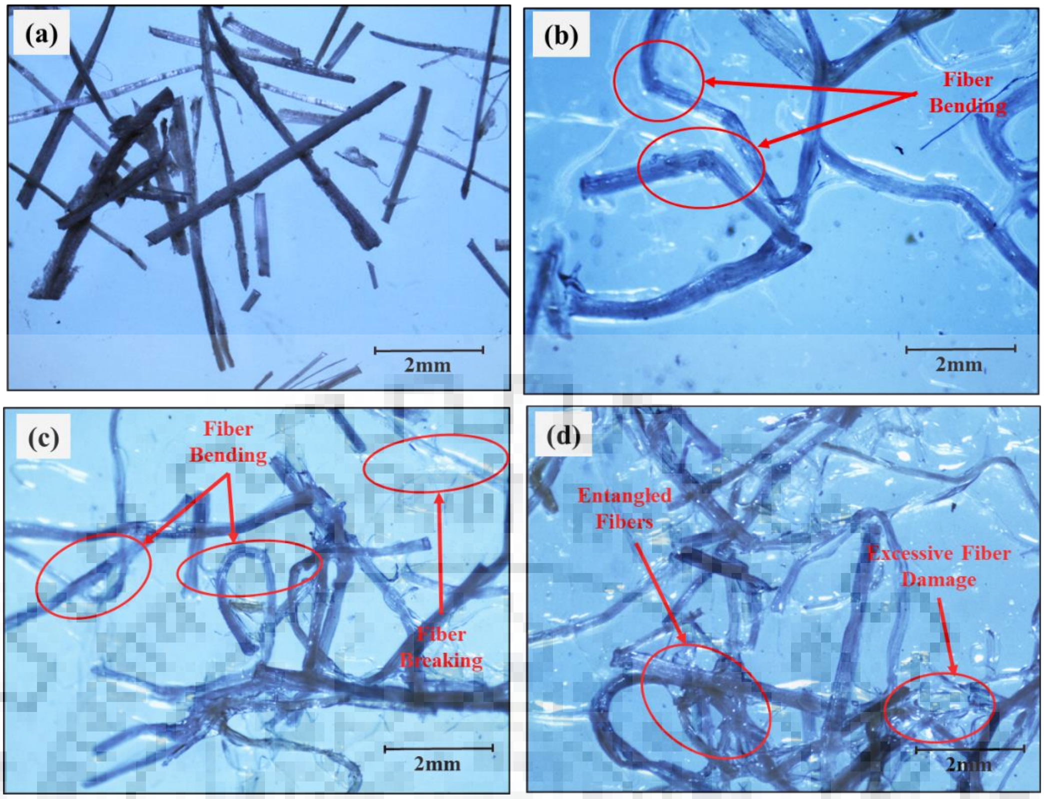


Fig. 4. 4 Stereo microscope images depicting the morphology of extracted banana fibers (a) Raw fibers (b) DIM-PLBF (c) EIM-PLBF and (d) ECM-PLBF

Fig. 4.4 (c) and Fig. 4.5 (c) depicts the morphology of extracted fibers after EIM. It can be seen that the attrition in the form of the breaking of fibers was observed more prominent. It is attributed to the shearing action during blending of fibers and polymers during extrusion followed by pelletizing of composite wire after extrusion. Moreover, high shearing action during injection molding further causes the breaking of fibers. When the composite melt is being forced to flow through the narrow sections (nozzle, sprue and runner) under high pressure and temperature before entering into the mold cavity, the fiber undergoes a severe shearing action.

In ECM, the attrition of fiber in the form of delamination of micro fibrils, fiber bending, entanglement of fibers and sometimes fiber burning was observed (Fig 4.4d and Fig 4.5d). It can be attributed to the comparatively longer fiber (as there is no attrition) and way of the collection of extrudate before compression molding due to which the fibers were entangled with each other during collection stage itself. Furthermore, excessive fiber damage was observed due to extensive exposure of biocomposite plate to high pressure and at elevated temperature during compression molding.

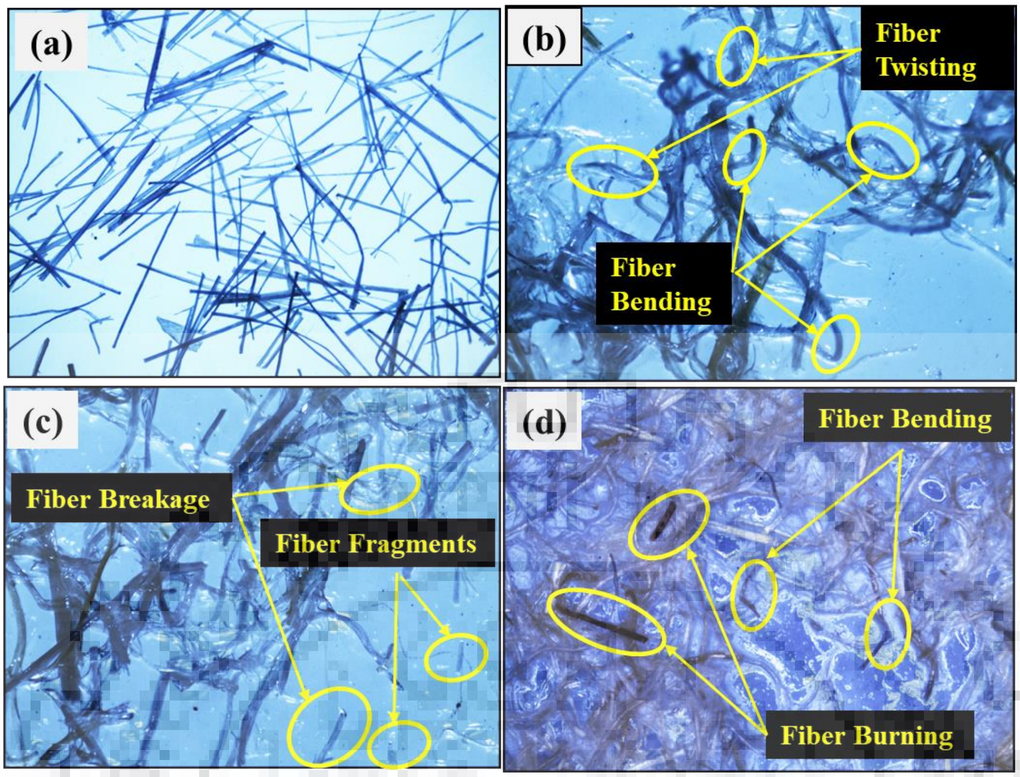


Fig. 4. 5 Stereo microscope images depicting the morphology of extracted pineapple fibers (a) Raw fibers (b)DIM-PLPF (c) EIM-PLPF and (d) ECM-PLPF

4.1.2.2 Distribution and Orientation of Fibers

One of the major aspects, which rules the characteristics of the composites is the distribution and orientation of fibers in the matrix [117]. In order to ensure better load sharing and stress transfer among the fibers, the distribution of fibers should be uniform and orientation should be along the direction of the applied load. Therefore, to investigate the distribution and alignment of fibers within the developed composites, the composites were cut normal to the direction of flow of fibers and observed under stereo microscope. Fig. 4.6 showing the schematic of the distribution and alignment of fibers within the developed composites. Fig. 4.7 and Fig. 4.8 shows the distribution and orientation of fibers, near the surface and at the cross-section of the developed biocomposites. In the composites developed using DIM, fibers depict the complex distribution and orientation. It can be seen that near the surface (mold walls) the alignment of fibers is in the flow direction while at the core region, the fibers are distributed randomly.

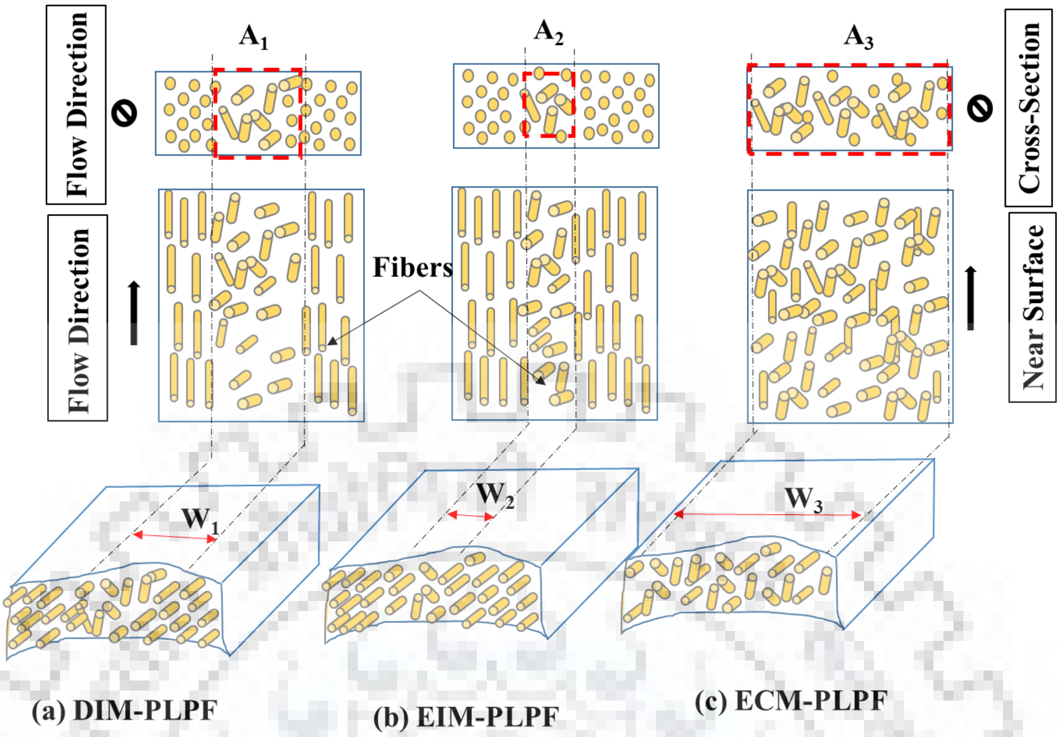


Fig. 4. 6 Schematic diagrams showing the distribution and alignment of fibers in the developed composites

The alignment of the fibers near the mold surface is attributed to the lower flow speed of fibers due to higher frictional force. The random distribution of fibers at the core region is attributed to the higher flow speed of fibers due to lower frictional force [118]. It can be seen that the fibers are oriented randomly at the core region of the composites. The area (A) and width (W) of the randomly oriented region depend on the processing technique. In the composites developed using EIM (Fig. 4.7b and Fig.4.8b), the area (A_2) and width (W_2) were found to be lowest, indicating an enhancement in the orientation of fibers in the flow direction. During injection molding, when the molten composite compound is being injected, the melted compound forces the short fibers to align in the direction of flow and due to interfacial bonding (among the constituents) created during the blending (extrusion), the orientation of fibers and molecular orientation of polymer improves further, resulting in an enhancement in the orientation of fibers in the flow direction [33].

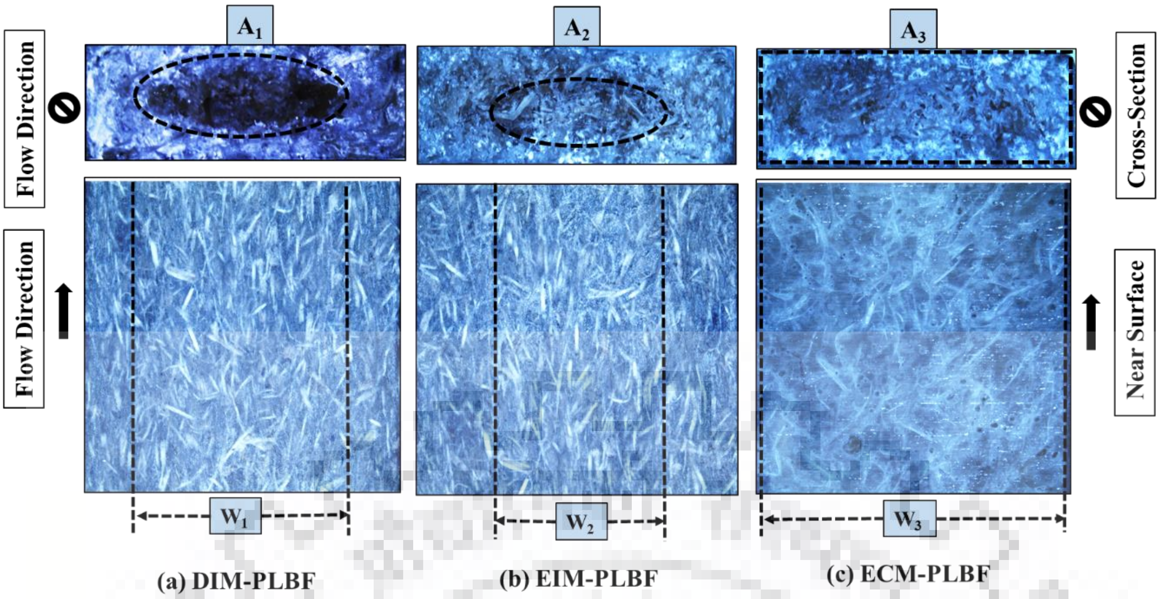
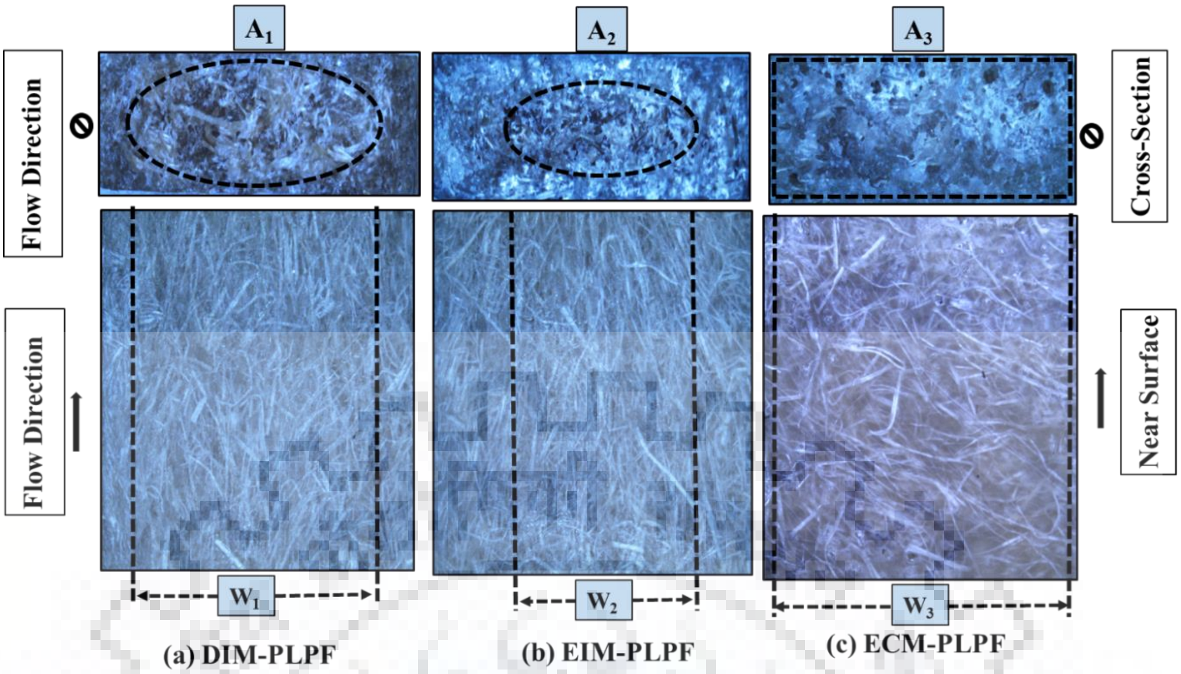


Fig. 4. 7 Stereo micrographs depicting the distribution and orientation of banana fibers in the developed composites

Additionally, during blending (extrusion) the polymer molecules may enter into the pores of banana fibers which may remain solid (do not melt) during injection molding resulting in an increase in stiffness of the individual fiber which prevents the bending of fiber and may improve the orientation of fibers in the flow direction. Moreover, it has been observed that the fiber length during EIM reduces due to pelletizing. It was observed that the smaller fiber has a lower tendency to bend as compared to the long fiber during injection molding which further improves the orientation of fibers in the flow direction.

In the composites developed using ECM, the area (A_3) and the width (W_3) of randomly oriented fiber region were found to be maximum. It can be due to the way of the collection of extrudate (output of the extrusion process) in the mold. The extrudate was in the form of strand/wire and was collected randomly in a mold, leading to the non-uniform orientation of fibers. Moreover, the fibers were independent to flow in any direction when the melted compound was pressed between the heated molds under high pressure and temperature during compression molding. Therefore, the mechanical properties recorded for the composites fabricated by various processing routes are also significantly different.



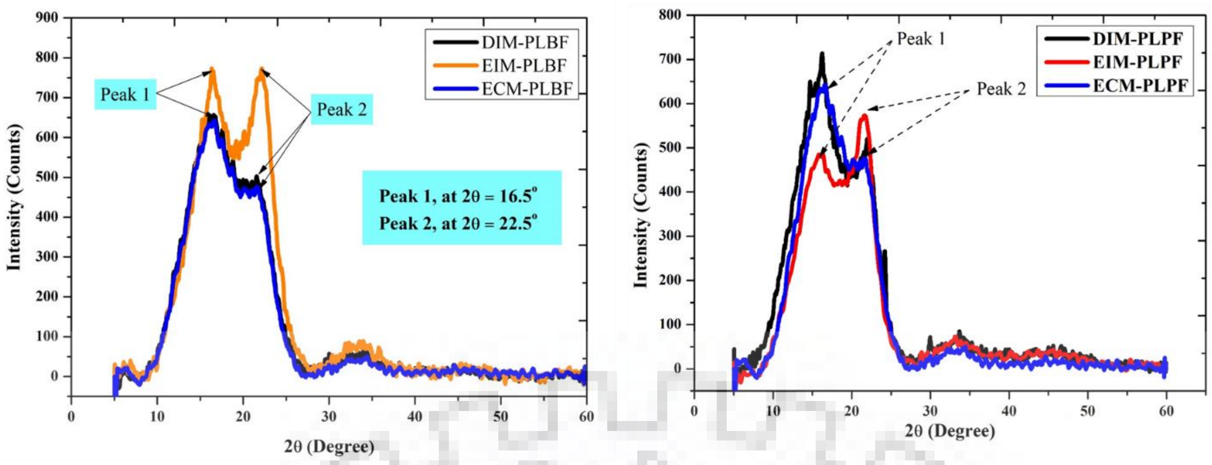
(a) DIM-PLPF (b) EIM-PLPF (c) ECM-PLPF

Fig. 4. 8 Stereo micrographs depicting the distribution and orientation of pineapple fibers in the developed composites

4.1.2.3 XRD Analysis

The properties of the composites are highly dependent on the degree of crystallinity [38]. The effect of processing techniques on the degree of crystallinity of the composites was measured using XRD analysis. Fig. 4.9 shows the XRD spectra for the surface of the PLA based composites. The data obtained has been analyzed and the total area, as well as the crystalline area under the curve, were measured using the software Origin (Ver. 8.5).

In the XRD spectra, the two main peaks were observed, 1st at $2\theta = 16.5^{o}$ and 2nd at $2\theta = 22.5^{o}$ representing the cellulose-I which also confirm that the structure of composites is polymorph (solid material that exist in more than one crystal structure) [119]. The crystallinity of the DIM-PLBF, EIM-PLBF and ECM-PLBF composites was observed as 17%, 22% and 16%, respectively, whereas the crystallinity of the DIM-PLPF, EIM-PLPF and ECM-PLPF composites was observed as 17%, 18% and 16%, respectively. The crystallinity of the developed using EIM was found to be maximum. Compounding of fibers and polymer pellets during extrusion lead to the formation of an interface between the fibers and matrix and further processing (injection molding) may result in improvement of interfacial characteristics among the constituents resulting in improvement in crystallinity.



(a) (b)

Fig. 4. 9 XRD spectra of PLA based composites

Moreover, an improvement in the orientation of fibers and molecular orientation of polymers in the flow direction due to reprocessing during the injection molding leads to the formation of more crystalline regions resulting in improvement in crystallinity. This can also be confirmed from the stereo microscope images (Fig. 4.7b and Fig.4.8b) indicating the smaller zone of randomly oriented fibers in the composites fabricated using EIM.

4.1.2.4 Dynamic Mechanical Analysis

Fig. 4.10 - 4.12 depict the variation in storage modulus (E'), loss modulus (E'') and tan delta of the developed composites as a function of temperature. Fig. 4.10 shows the different regions where physical states of the composites changes with respect to temperature. In the glassy region, the composites are generally hard and rigid. Beyond this region, the stiffness starts to decrease and finally the material is converted into the completely rubbery state. In between these regions, there is a transition region where the physical state of the material is converted from hard and rigid to a rubbery state.

The E' signifies the energy stored in the material. It can be termed as the elastic response of the material. Incorporation of fiber into PLA matrix results in substantial improvement in E', which may be attributed to the improved load sharing and load transfer between the fibers and matrix [120]. At a temperature range of 55 to 65°C, a rapid drop in the E' was observed for all the composites. This is attributed to the reduction in stiffness in the transition region [35], [121]. E' of the composite fabricated using EIM was found to be maximum followed by composites fabricated using DIM and ECM, respectively. This can be due to the enhancement in interfacial bonding between the constituents due to reprocessing of the composite compound during injection molding. Moreover, the improvement in crystallinity of the composites also promotes the improvement in storage modulus. The improvement in crystallinity means the increase in the crystalline region which acts as physical crosslinks or reinforcements to the amorphous region leading to an improvement in the values of storage modulus.

Fig. 4.11 shows the variation in E" of composites as a function of temperature. E" is related to the rheological properties of the materials or the melt viscosity of the materials or in general, the viscous response of the material. It is related to the movement of polymer chains [122], [123]. Incorporation of fibers into the PLA matrix causes the formation of interfaces between the fibers and matrix which causes the restriction in the mobility of polymeric chains resulting in enhancement of the viscosity of the melt [124]. The loss modulus was found to be maximum for the composites fabricated using EIM. It can be attributed to the enhancement in interfacial characteristics between the constituents due to reprocessing of the melted compound during injection molding. The similar observation was also reported by Chaitanya et al. [125]. The melt blending (extrusion) of fibers and polymeric pellets lead to the formation of interfaces between the constituents and reprocessing (injection molding) further strengthens the interfacial characteristics between the constituents. The loss modulus was found to be minimum for the composites fabricated using ECM. It may be due to the degradation of fibers and matrix during manufacturing (compression molding), as the composite was kept under high pressure and at elevated temperature for a longer period of time. Moreover, the reduction in crystallinity can be another reason for the reduction in loss modulus.

Tan delta is related to the damping characteristics of the material. It is also associated with the movement of small groups and polymer chains inside the polymer structure. It is termed as the ratio of loss modulus to the storage modulus [28].

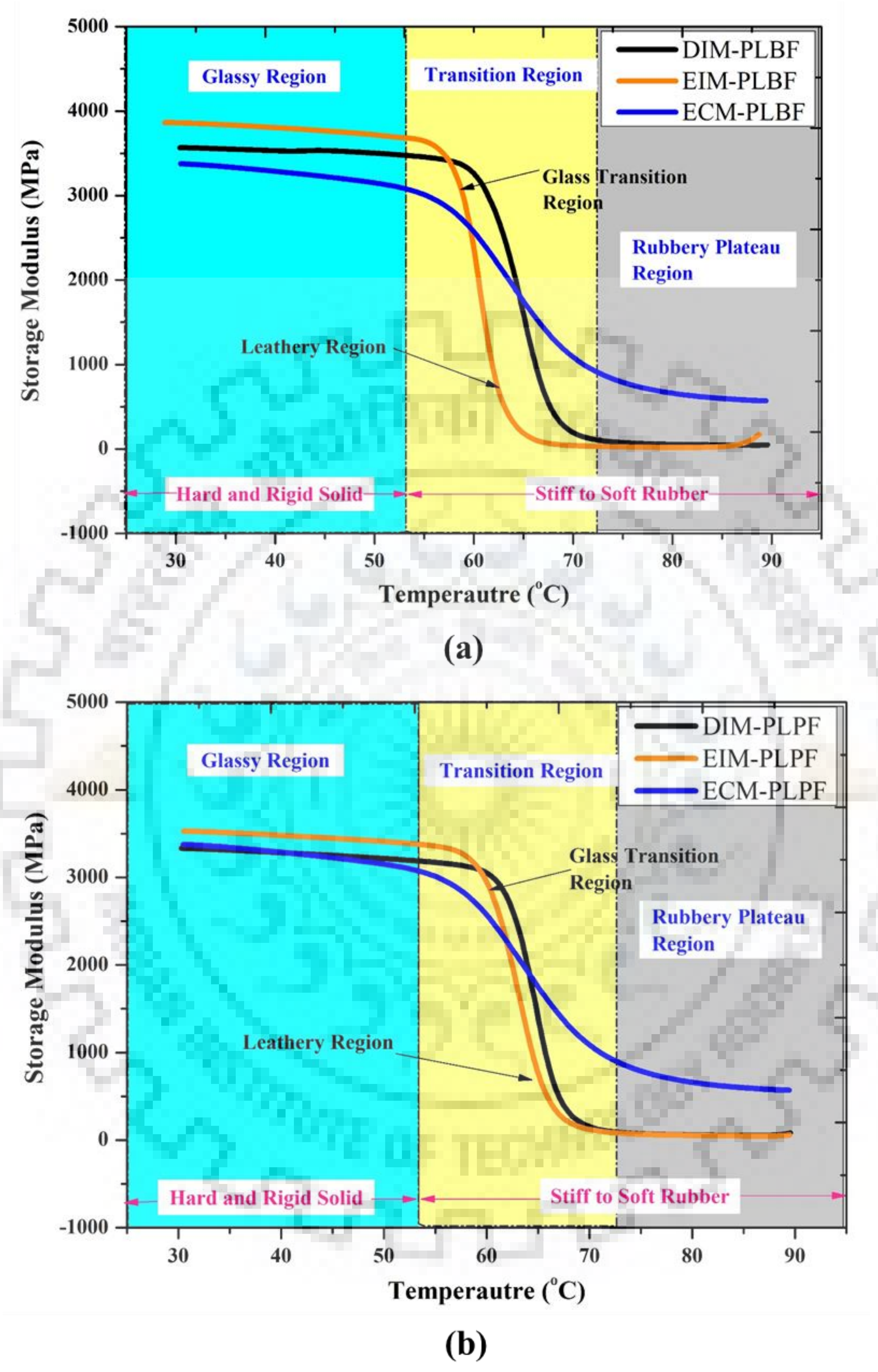


Fig. 4. 10 Variation in storage modulus of the composites as a function of temperature

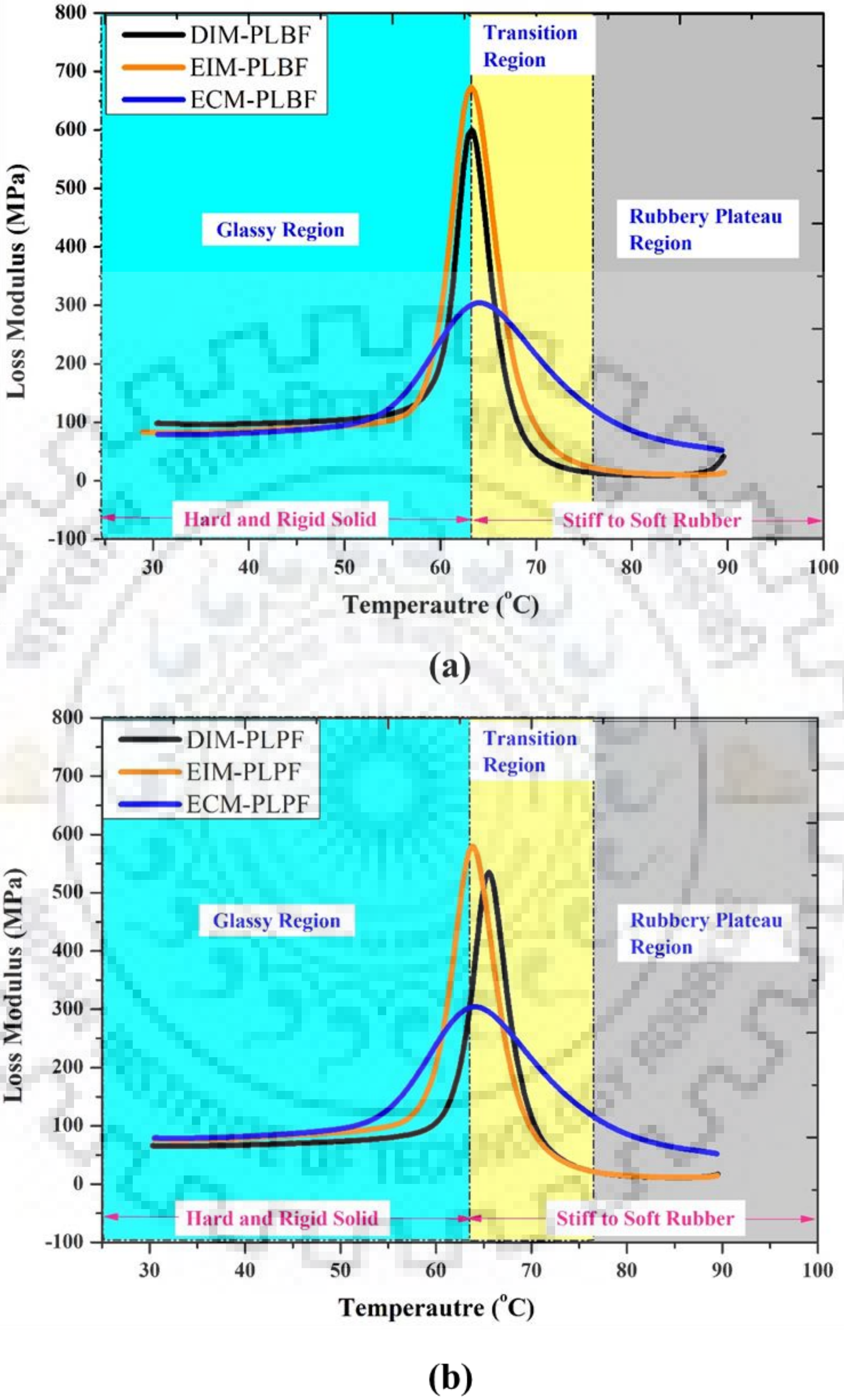


Fig. 4. 11 Variation in loss modulus of the composites as a function of temperature

Fig. 4. 12 depicts the variation in tan delta values with respect to temperature. It can be seen that the glass transition temperature of all the composites lies in the range of 68-69°C indicating that, processing techniques have no significant effect on the glass transition temperature of the composites.

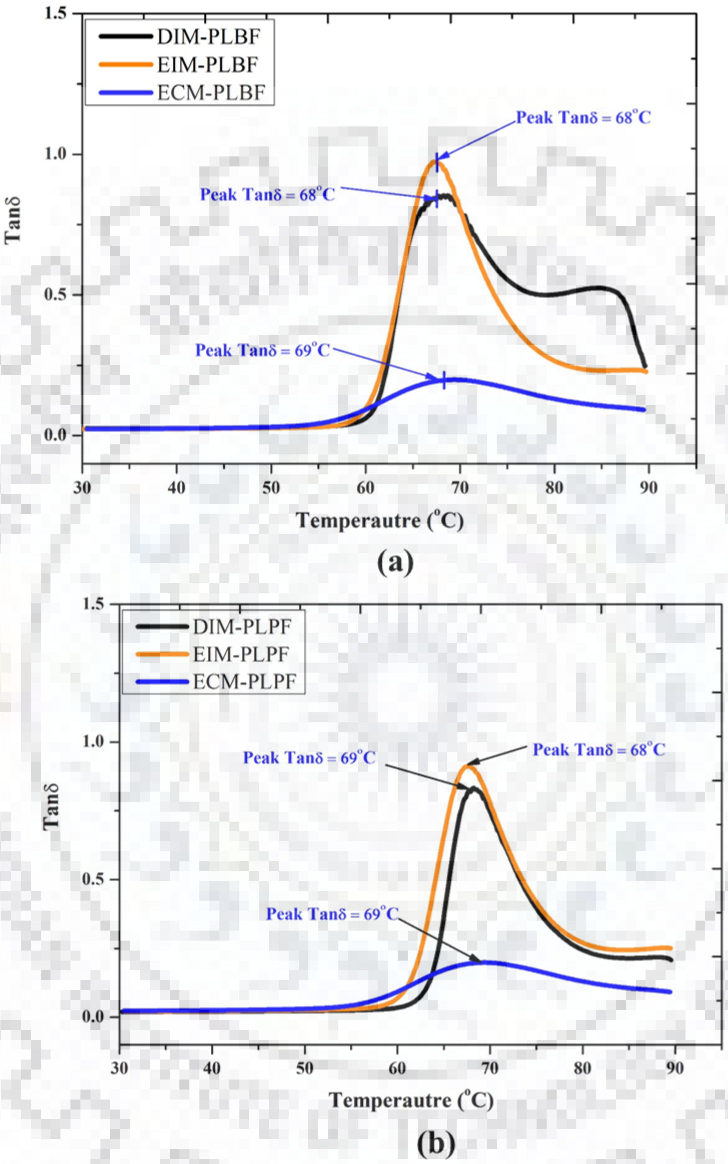


Fig. 4. 12 Variation in tan delta as a function of temperature

It has been reported that incorporation of fibers into the polymer causes the obstruction in the mobility of polymer chains during the transition and results in the decrease in the peak of tan delta curve [28], [126]. The tan delta peak for the composites fabricated using EIM was found to be highest. It is attributed to the reduction in fiber size due to pelletizing and scission of the polymeric chain due to reprocessing during injection molding resulting in improvement in the mobility of the molecular chain. The lowest peak was observed for the composites fabricated using ECM. It may be due to the accumulation of fibers in the form the of fiber clusters during processing (compression molding) leading to obstruction in the movement of polymer chains. The broadening of the peak indicates a reduction in molecular relaxation.

4.1.2.5 Mechanical Properties

Comparative graphs showing the variation in tensile, flexural and impact properties of the PLA based composites are represented in Fig. 4.13 - 4.15. It can be seen that the tensile and flexural properties (strength and modulus) of the composites fabricated using EIM were found to be maximum.

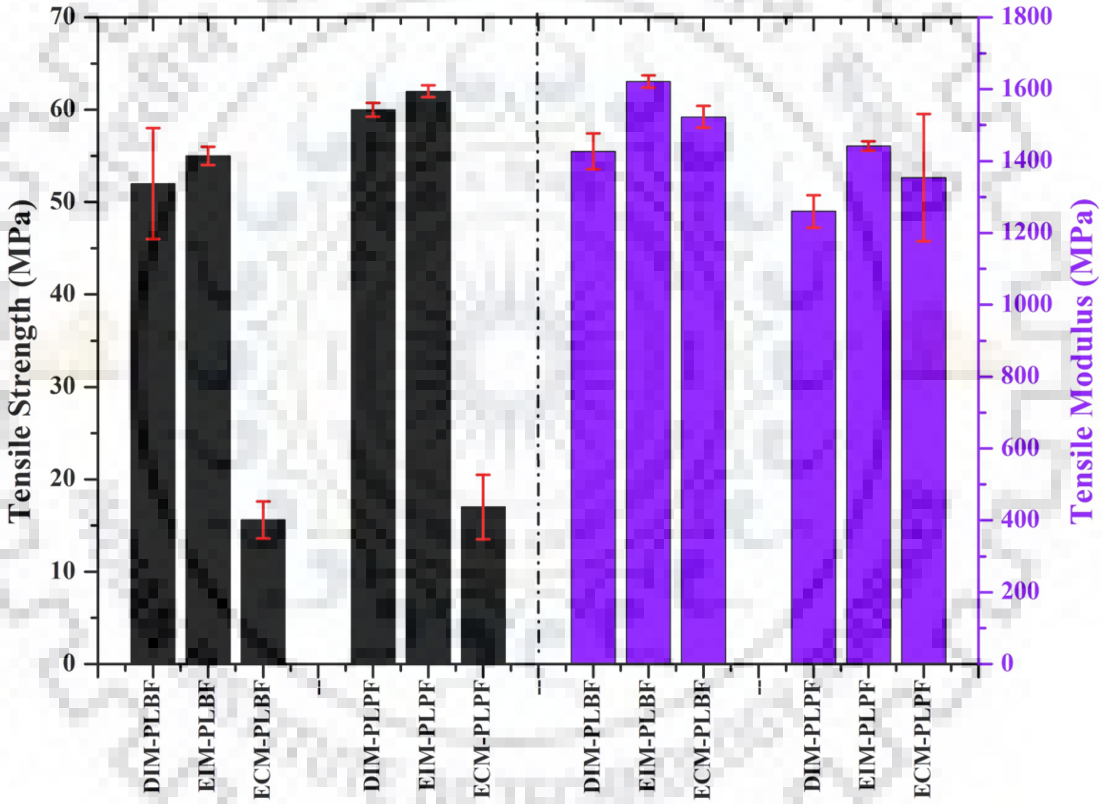


Fig. 4. 13 Variation in tensile properties of the PLA based composites

It is attributed to the improvement in interfacial characteristics between constituents. During extrusion, an interface between the fiber and matrix is formed. This interface gets strengthened due to reprocessing of melt compound during injection molding leading to improvement in interfacial interaction between the fibers and matrix as well as the crystallinity of the composites. Moreover, the development of good interfacial bonding during the melt compounding (extrusion), forces the fibers and polymer molecules to align in the direction of load resulting in an improvement in the orientation of the fibers in the direction of applied load leading to improvement in tensile and flexural properties [127]. It has been reported that the reprocessing further strengthens the initially developed interfacial bonding between the constituents [128], [129].

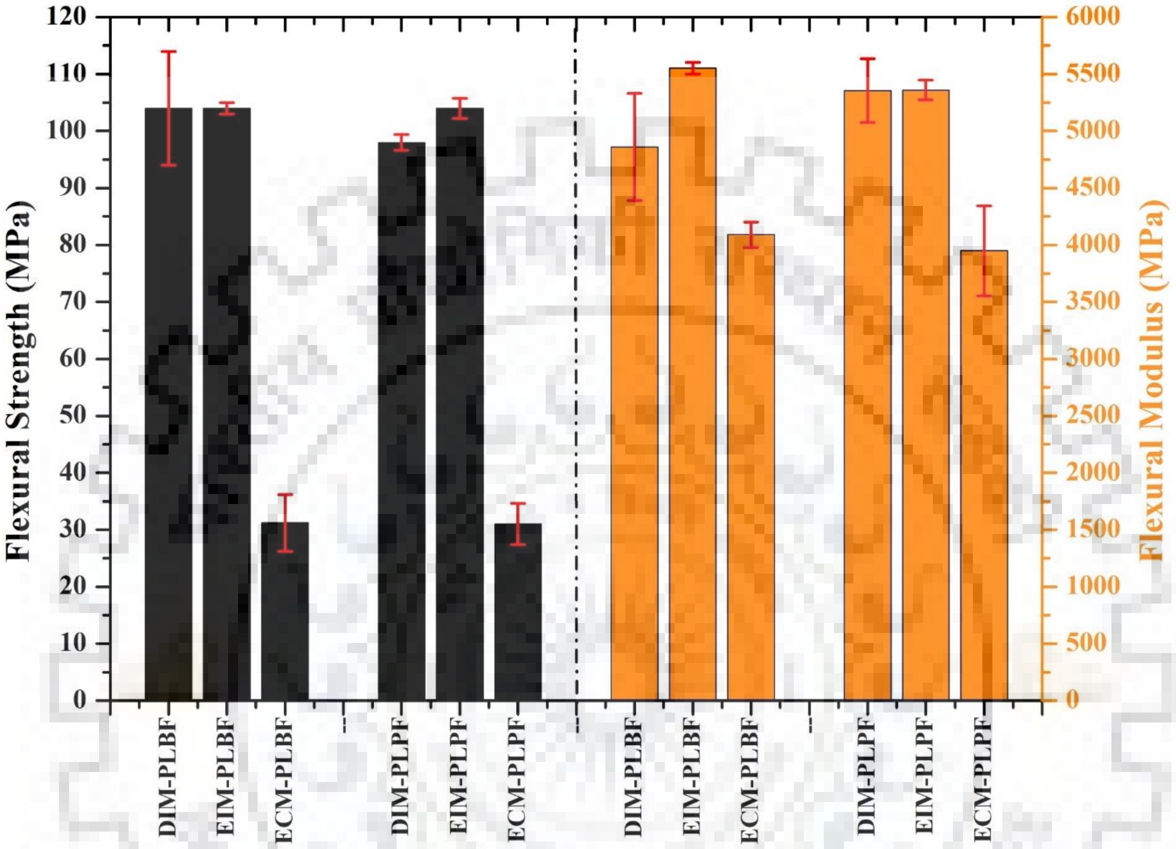


Fig. 4. 14 Variation in flexural properties of the PLA based composites

It has already been discussed (section 4.1.2.4) that the improvement in interfacial bonding, increases the viscosity of the composites. Therefore, the viscosity of the composites developed using EIM was found to be higher as compared to composites fabricated using DIM and ECM, respectively. The flow speed of the melt decreases with an increase in viscosity of the melt, which leads to an improvement in the orientation of fibers in the flow direction. Normally the orientation of fibers in the flow direction increases with a decrease in flow speed inside the mold cavity [51]. Hence, an improvement in the interfacial bonding further improves the orientation of fibers in the direction of load which further improve the tensile and flexural properties. Furthermore, during injection molding, when the melted compound is being injected, the melt is forced to flow through the narrow sections (nozzle, sprue and runner) under high pressure, this encourages the fiber to align in the flow direction which further result in an enhancement in the orientation of fibers

The tensile (Fig. 4.13) and flexural properties (Fig. 4.14) of the composites fabricated using DIM were found to be lower as compared to composites developed using EIM. It may be due to the comparatively longer fibers and bending and twisting of fibers during DIM. The twisting and bending of fibers further results into disruption in the orientation and agglomeration of fibers and act as a stress concentration zone during loading. Moreover, the poor adhesion between the hydrophilic fibers and hydrophobic matrix results in a reduction of tensile and flexural properties.

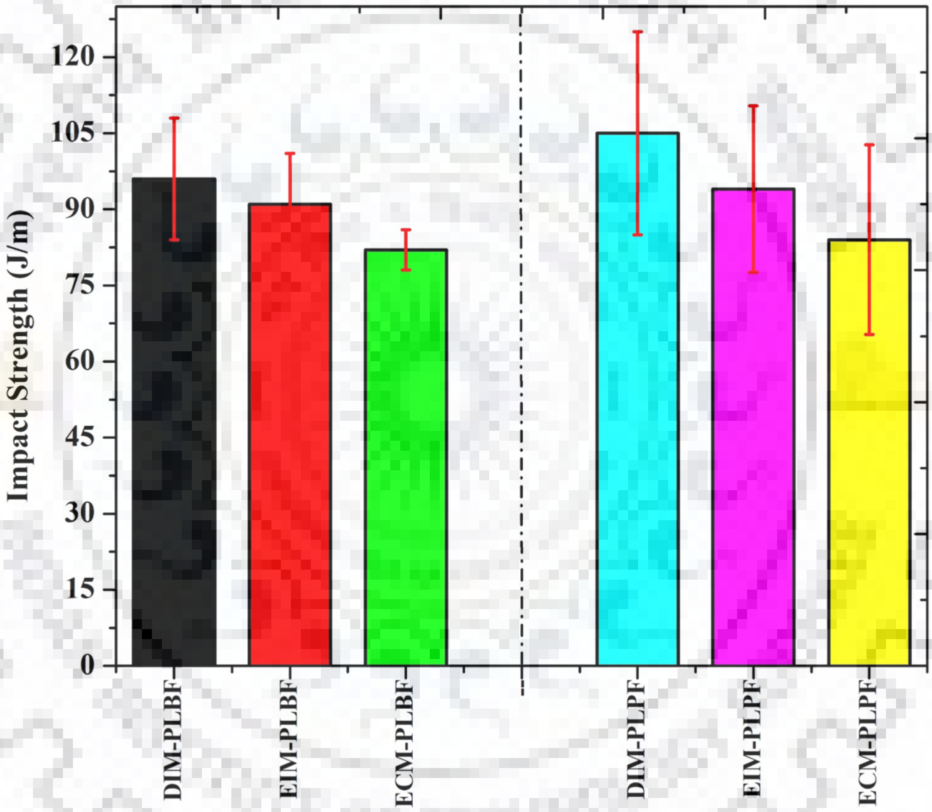


Fig. 4. 15 Variation in impact strength of the PLA based composites

Fig. 4. 15 also depict the effect of processing routes on the impact strength of developed composites. The impact strength of composites developed using DIM was found to be higher. The impact loading causes the failure of composites either due to fiber pull out or the breaking of fibers. It has been reported that the amount of energy required to pull out the fiber from the matrix is more as compared to the breaking of fibers [46], [130]. It was observed (Fig. 14 a) that the major failure mechanism in the composites fabricated by DIM is the fiber pull out. It indicates that the impact strength of the composite developed using DIM is higher. The impact

strength of the composites developed using EIM composite was found to be lower as compared to composites fabricated using DIM. The major failure mechanism of this composite under loading is fiber breakage, this justifies the reduction in impact strength of the composite. The reduction in impact strength can also be attributed to the reduction of fiber length due to pelletizing after extrusion. It has been already reported that the impact strength of composite decreases with the decrease in fiber length [131]. The reduction in fiber length means an increased number of fibers for the same weight fraction, within the developed composites. This facilitates the propagation of crack through the inter-fiber gaps during impact loading. When the smaller fiber comes in the path of crack propagation, the probability of restriction of crack propagation decreases. Moreover, the fiber ends sometimes act as a stress concertation zone which further facilitates the propagation of crack leading to a decrease in impact strength of composites fabricated using EIM.

The tensile, flexural and impact properties of the composites developed using ECM were found to be minimum. It can be due to the poor alignment and distribution of fibers during compression molding. During compression between the heated plates, the fibers were unrestricted to align in any direction and at random location, the formation of a fiber cluster was also observed which resulted in the generation of stress concentration zones. During the testing, the cluster of fibers promotes the initiation and development of crack which ultimately leads to the failure of the composite. Furthermore, the excessive exposure of composite plate under high pressure and temperature causes the degradation of matrix and fibers leading to lower mechanical properties composite.

The similar effect of processing routes on mechanical behavior was observed for the PP based composites also. The tensile (Fig. 4.16) and flexural (Fig. 4.17) properties of the composites fabricated using EIM were found to be maximum followed by composites fabricated using DIM and ECM, respectively.

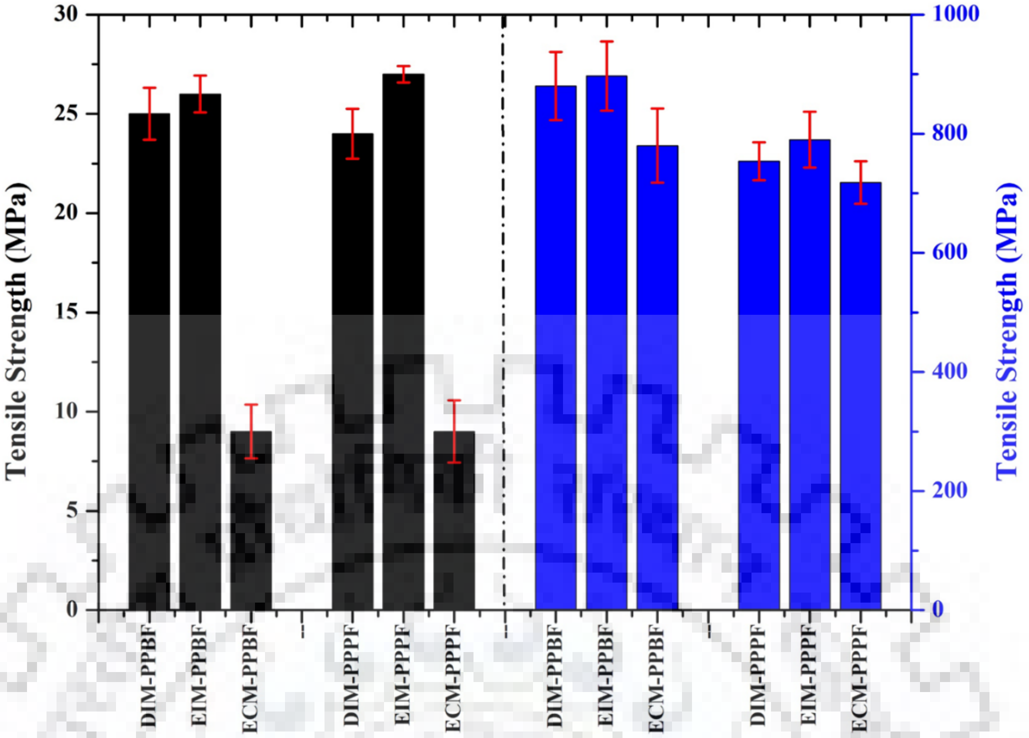


Fig. 4. 16 Variation in tensile properties of the PP based composites

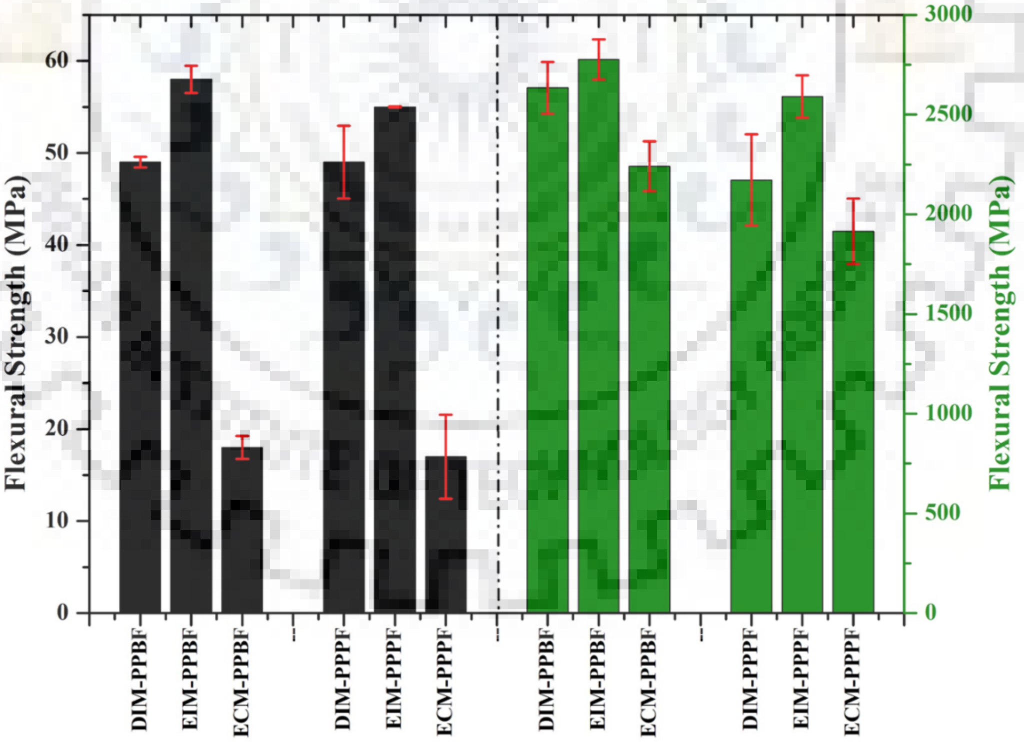


Fig. 4. 17 Variation in flexural properties of the PP based composites

Similar to PLA based composites, the impact strength of the PP based composites fabricated using DIM was found to be higher as compared to composites fabricated using EIM and ECM, respectively.

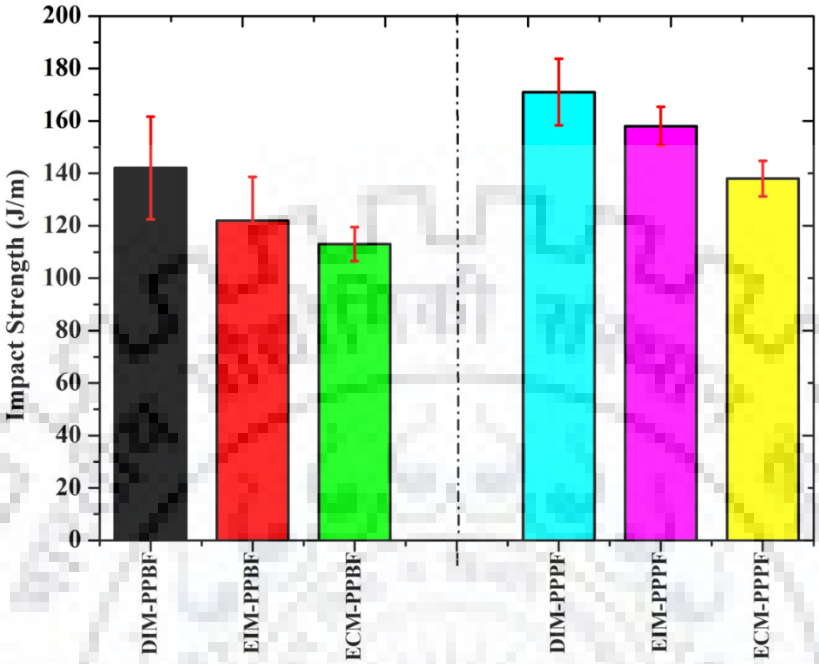


Fig. 4. 18 Variation in impact strength of the PP based composites

4.1.2.6 Morphological Analysis

The fractography of failed tensile specimens and mode of fracture was analyzed using SEM micrographs (Fig. 14 a-c). In the case of DIM-PLBF biocomposites, the fiber pull-out can be seen as the foremost cause for the rupture of DIM-PLBF biocomposites. It can be due to the poor adhesion between the constituents. Fig. 14 (b) depicts the improvement in interfacial adhesion between the fibers and matrix, which further leads to the breaking of fibers instead of pull out. The enhancement in adhesion between the constituents may be due to the improvement in earlier developed interfaces (during extrusion) and wettability of fibers due to reprocessing during injection molding. Fig. 14 (c) depicts the mode of fracture of ECM-PLBF biocomposites under tensile loading. The random distribution of fibers has already been seen (Fig. 8 c). The processing of randomly oriented fibers leads to the formation of fiber clusters and agglomeration which further causes the stress concentration zone leading to fracture of the biocomposites.

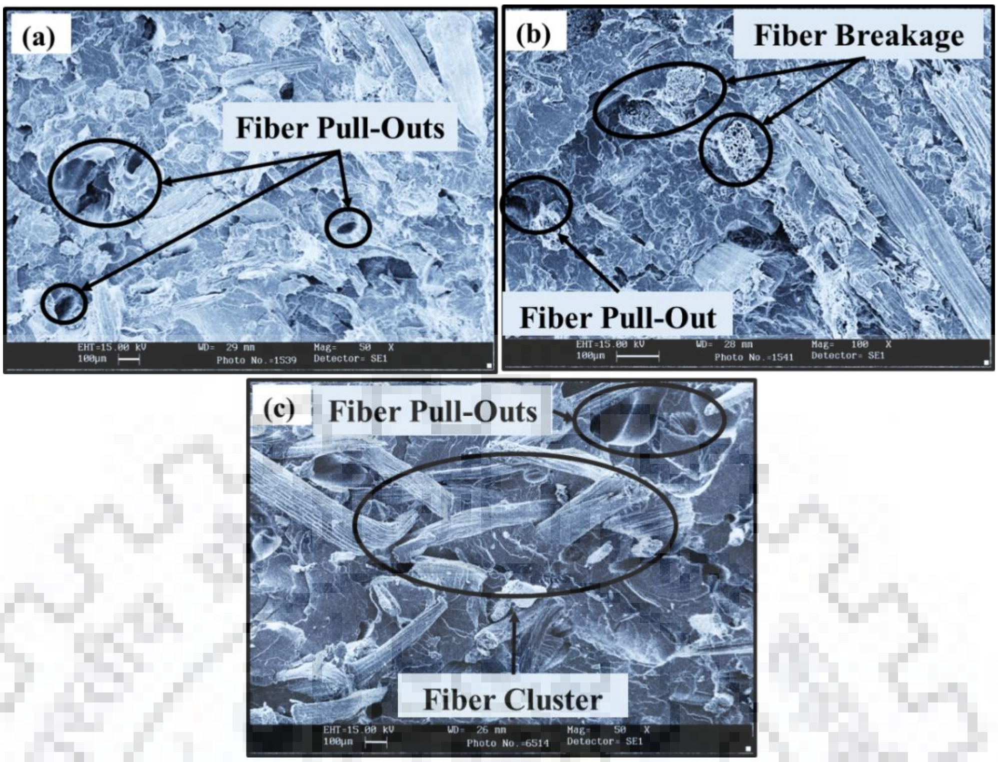


Fig. 4. 19 SEM micrographs depicting the fractography of tensile tested (a) DIM-PLBF, (b) EIM-PLBF and (c) ECM-PLBF biocomposite specimens

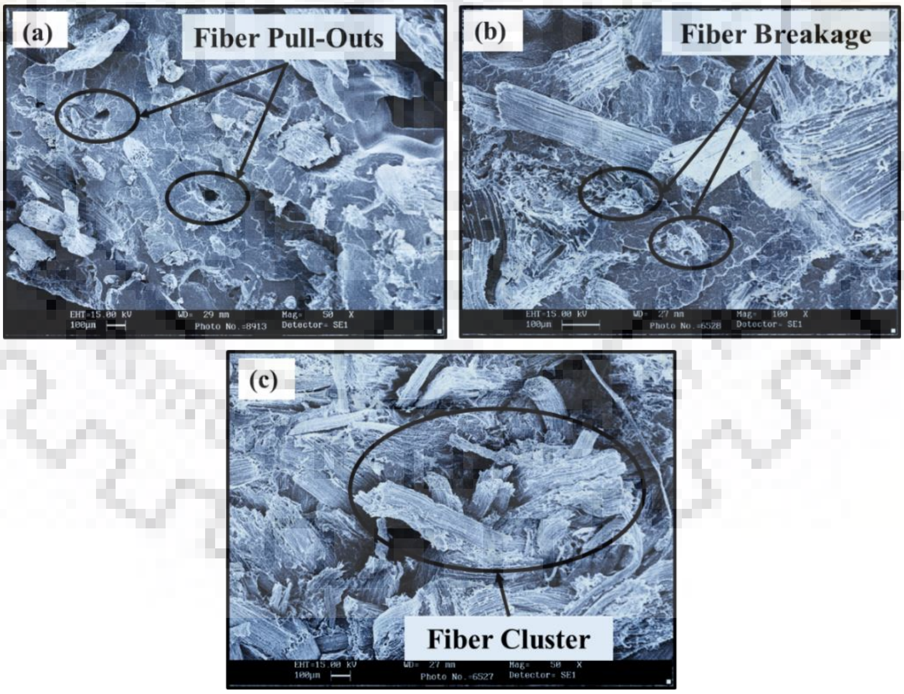


Fig. 4. 20 SEM micrographs depicting the fractography of tensile tested (a) DIM-PPBF, (b) EIM-PPBF and (c) ECM-PPBF biocomposite specimens

Based on the distribution and orientation of fibers as well as the crystalline and mechanical properties of the developed composites, it can be concluded that the EIM technique was found to be superior processing route for the development of short fiber based polymer composites. It can also be concluded that one of the major reasons for the failure of composites under loading is the fiber pull out. It is attributed to the poor interfacial interaction between the hydrophilic fibers and hydrophobic matrices. The interfacial interaction between the constituents can be improved by fiber surface modification techniques. Therefore, the effect of chemical treatment on the behavior of the developed composites is discussed in the following section;

4.2 EFFECT OF CHEMICAL TREATMENT ON THE BEHAVIOR OF THE COMPOSITES

4.2.1 Introduction

It has already been mentioned that the properties of the composites based on natural fibers depend upon the interfacial characteristics between the fibers and polymeric matrix. The researchers have reported that the natural fibers (jute, sisal, pineapple, banana, flax and hemp) have potential to act as substitutes to synthetic fibers due to their unique characteristics i.e. low density, biodegradability, non-corrosive nature, abundant availability, non-toxicity and low carbon emissions [132], [133]. However, the challenges associated with natural fibers are; lower thermal stability, hydrophilic nature and incompatibility when blended with hydrophobic polymers resulting in poor interfacial bonding between the fibers and matrix. Natural fibers contain cellulose fibrils bonded together by the non-cellulosic substances such as hemicellulose, lignin, wax and pectin. The characteristics of individual fibers depend on these lignocellulosic contents. However, the excessive existence of the non-cellulosic contents on the surface of the fiber increases the hydrophilicity as well as causes the poor interfacial bonding when blended with polymeric matrices.

To overcome these challenges, the researchers have recommended the various types of fiber surface modification techniques such as physical, chemical, and enzymatic treatment of fibers [134], [135]. The surface modification of the fibers using chemical treatment has been reported as the most popular among other techniques [136]. The researchers have reported the several types of chemical treatments such as alkali treatment, peroxide treatment, permanganate treatment, silane treatment, sodium chloride treatment, isocyanides treatment etc. Though, the use of these treatments is costly and harmful for the environment when used in commercial scale. Therefore, it becomes necessary to explore other alternate economical and environment-friendly chemical treatment of the fibers. Recently, the use of sodium bicarbonate has been reported as the economical and eco-friendly treatment of lignocellulosic fibers. Some researchers have investigated the effect of sodium bicarbonate treatment of fibers on the behavior of the polymer composites and reported a significant improvement in mechanical properties. However, this treatment was used for the surface modification of sisal and alove vera fibers only [137], [138]. Researchers have explored some other environment-friendly route like borax (borax decahydrate) for the treatment of lignocellulosic fibers. Borax has been used as the environment-friendly thermal retardant. However, this treatment was mainly used to investigate the fire retardant behavior of the polymer composites [139]–[141]. The literature focusing on the effect of this treatment on the mechanical behavior of the polymer composite is rarely available.

Therefore, the current experimental investigation focuses on the feasibility of using sodium bicarbonate and borax for the treatment of banana and pineapple fibers whereas the potassium permanganate treatment was conducted for the reference. The effect of these chemical treatments on the behavior of the fibers as well the composites have been studied.

4.2.2 Experimental Procedure

4.2.2.1 Fiber Surface Modification

Borax Treatment

The chopped raw banana and pineapple fibers were soaked in borax decahydrate ($Na_2B_4O_7\cdot10H_2O$) aqueous solution (5, 10 and 15% (w: v)) for 30 min. at 100°C. The maximum amount of borax that is soluble in water is 15% (w: v). Therefore, the treatment was conducted up to this concentration. The fibers were then washed under running tap water until the pH of the soaked fibers stabilized at 7. After drying for 24 h at room temperature, the fibers were then dried in a hot air oven at 90°C for 6 h and stored in an air tight package for the further use. The borax breakdown into sodium ion and tetraborate anion which further breakdown into boric acid and hydroxide ion in the presence of water.

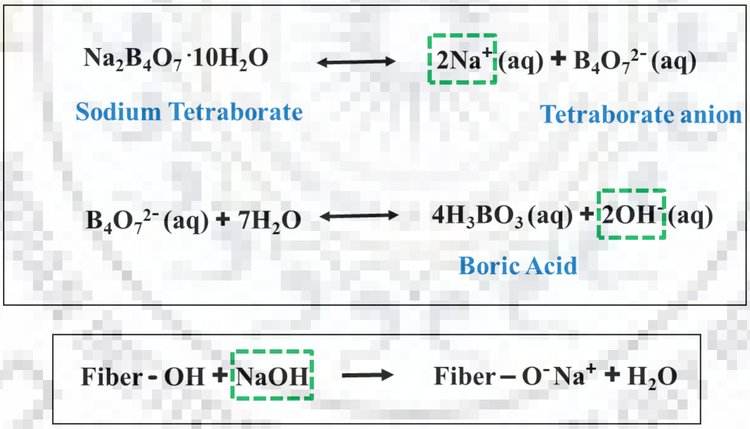


Fig. 4. 21 Chemical reactions during borax decahydrate treatment of fibers

Therefore, the borax behaves like mild NaOH in the presence of water which reacts with the hydroxyl group of the lignocellulosic contents of the fiber and finally separates them from the cell wall. In order to accelerate the chemical reaction, the treatment was conducted at 100°C. The chemical reaction taking place during the borax treatment of fiber is shown in Fig. 4.21.

Sodium Bicarbonate Treatment

The raw fibers were soaked into the aqueous solution (10% (w: v)) of sodium bicarbonate ($NaHCO_3$) at room temperature. The fibers were removed from the solution at an interval of 48, 72 and 96 h. The soaked fibers were then neutralized under running tap water. After drying at room temperature for 24 h, the fibers were finally dried in a hot air oven at 90°C for 6 h and the fibers were packed in the air tight pouch for further use. During this treatment, the sodium bicarbonate is breakdown into sodium ion and bicarbonate ion which further breakdown into carbonic acid and hydroxide ion in the presence of water (Fig. 4.22). Thus, the sodium bicarbonate behaves like mild NaOH, similar to borax treatment which react with the hydroxyl group of the lignocellulosic contents of the fiber. As the treatment was conducted at room temperature and being a mild alkaline in nature, it takes longer time to get the desired results.

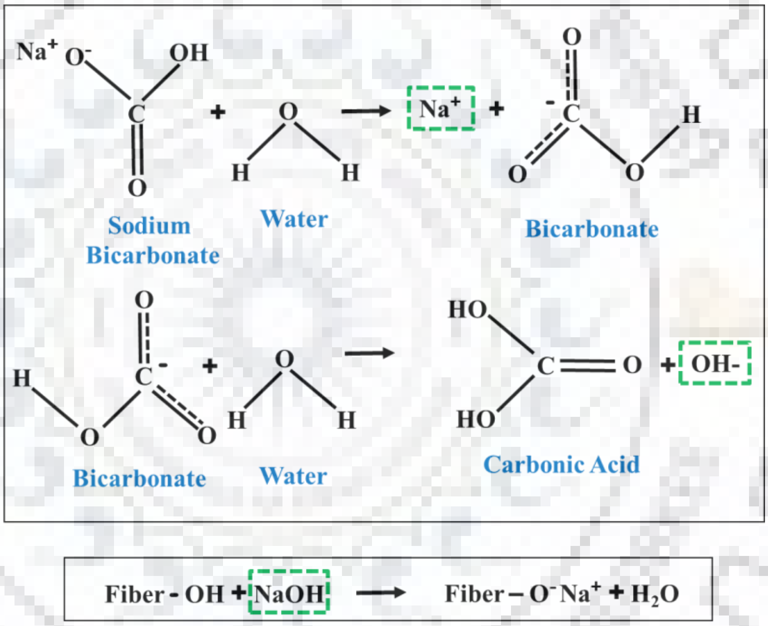
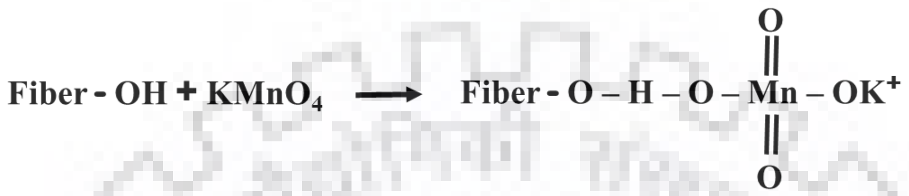


Fig. 4. 22 Chemical reaction during sodium bicarbonate treatment of fibers

Potassium Permanganate Treatment

Permanganate treatment of fibers was conducted by using potassium permanganate ($KMnO_4$) in acetone solution (0.5% (w: v)). The banana and pineapple fibers were soaked in acetone solution for the period of 30 min. at room temperature. The soaked fibers were then washed under running tap water until the pH of fiber stabilized at 7. Similar to borax and sodium bicarbonate treatment, the fibers were first, dried in room temperature and then in a hot air oven and finally stored in a sealed package for further use. During this treatment, the highly reactive ion (Mn^{3+}) reacts with the hydroxyl group of hemicellulose, cellulose and lignin and finally separate them from the cell wall resulting into the reduction in hydrophilicity of the fibers [55]. Increasing the concentration of $KMnO_4$ and treatment time causes the excessive removal of cementing substances within the cellulose which leads to the fibrillation and reduce the properties of the fibers [135], [142]. The chemical reaction taking place during the treatment is shown in Fig. 4.23.



$$\text{Fiber - OH} + KMnO_4 \longrightarrow \text{Fiber - O – H – O – }\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Mn}}\text{ – O}K^{+}$$

Fig. 4. 23 Chemical reaction during potassium permanganate treatment of fiber

4.2.2.2 Fabrication of the Composites

As discussed in the previous part of this chapter (4.1), the composites incorporating untreated and treated banana and pineapple fibers were fabricated using EIM. The designation of the fibers before and after the chemical treatment as well as the developed composites is given in Table 4.3.

Table 4. 3 Designation of the fibers and developed composites

Details	**Percentage/ Treatment Time**	**Banana Fiber**	**Pineapple Fiber**	**PLA Based Composites**		**PP Based Composites**	
				Banana Fiber	**Pineapple Fiber**	**Banana Fiber**	**Pineapple Fiber**
Untreated		BF	PF	PLBF	PLPF	PPBF	PPPF
Borax	5%	TBF-B5	TPF-B5	PLBFT-B5	PLPFT-B5	PPBFT-B5	PPPFT-B5
	10%	TBF-B10	TPF-B10	PLBFT-B10	PLPFT-B10	PPBFT-B10	PPPFT-B10
	15%	TBF-B15	TPF-B15	PLBFT-B15	PLPFT-B15	PPBFT-B15	PPPFT-B15
Sodium Bicarbonate	48 h	TBF-S48	TPF-S48	PLBFT-S48	PLPFT-S48	PPBFT-S48	PPPFT-S48
	72 h	TBF-S72	TPF-S72	PLBFT-S72	PLPFT-S72	PPBFT-S72	PPPFT-S72
	96 h	TBF-S96	TPF-S96	PLBFT-S96	PLPFT-S96	PPBFT-S96	PPPFT-S96
Potassium Permanganate	30 min.	TBF-K30	TPF-K30	PLBFT-K30	PLPFT-K30	PPBFT-K30	PPPFT-K30

4.2.3 Results and Discussion

4.2.3.1 Characterization of Fibers

4.2.3.1.1 Morphological Evaluation of Fibers

The surfaces of untreated and treated banana and pineapple fibers are depicted in Fig. 4.24 and Fig. 4.25, respectively. The presence of hemicellulose, lignin, and other non-cellulosic content on the surface of untreated fibers can be observed in Fig. 4.24 (a) and Fig. 4.25 (a), these non-cellulosic contents are responsible for hydrophilic nature of the fiber, which causes the poor interfacial bonding with the hydrophobic polymer matrix [138]. However, after removing these non-cellulosic contents by chemical treatment, the surface of fiber became rougher and textured as observed in Fig. 4.24 (b-h) and Fig. 4.25 (b-h). The rough surface improves the mechanical interlocking between the fibers and matrix resulting in improved adhesion between them [60]. Fig. 4.24 (b) and Fig. 4.25(b) shows the surface of the fibers after treatment in borax solution (5%). The effective removal of non-cellulosic content from the surface of the fibers can be seen. Fig. 4.24 (c-d) and Fig. 4.25 (c-d) shows that increasing the concentration of borax (10 and 15%) lead to the excessive removal of the non-cellulosic content from the surface of the fibers resulting in fibrillation of fibers.

Similar to borax treatment, the effective removal of non-cellulosic contents can be observed (Fig. 4.24 (e-f) and Fig. 4.25 (e-f)) when the fibers were treated up to 48 and 72h in sodium bicarbonate solution. However, post 72 hours, the fibrillation of fiber starts due to excessive removal of non-cellulosic contents from the surface of the fibers. When the fibers were treated with $KMnO_4$ solution (Fig. 4.24h and Fig. 4.25h), the surface of fiber becomes rough and textured indicting the effective removal of non-cellulosic contents from the surface of the fibers.

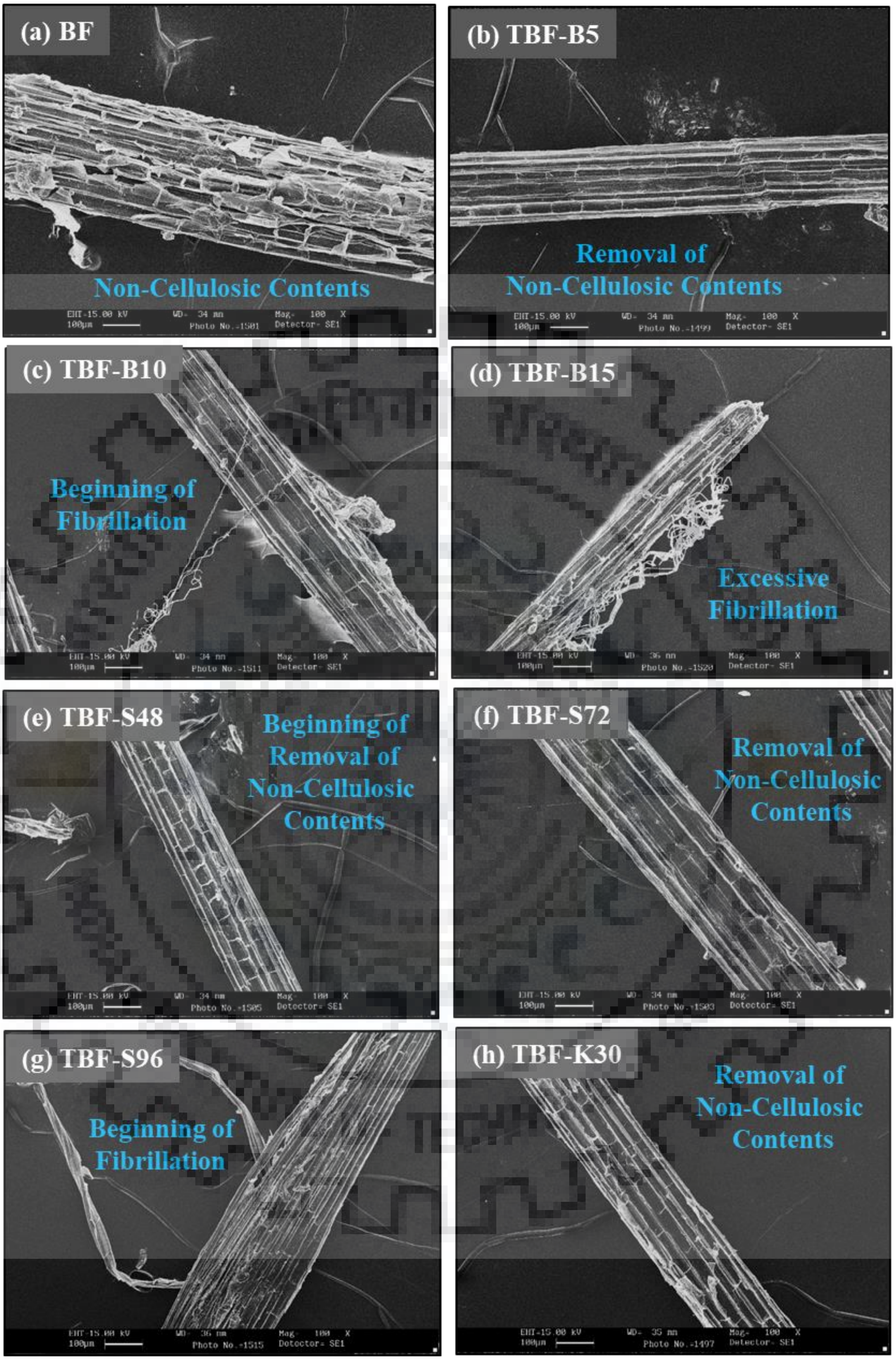


Fig. 4. 24 SEM micrographs of the untreated and treated banana fibers

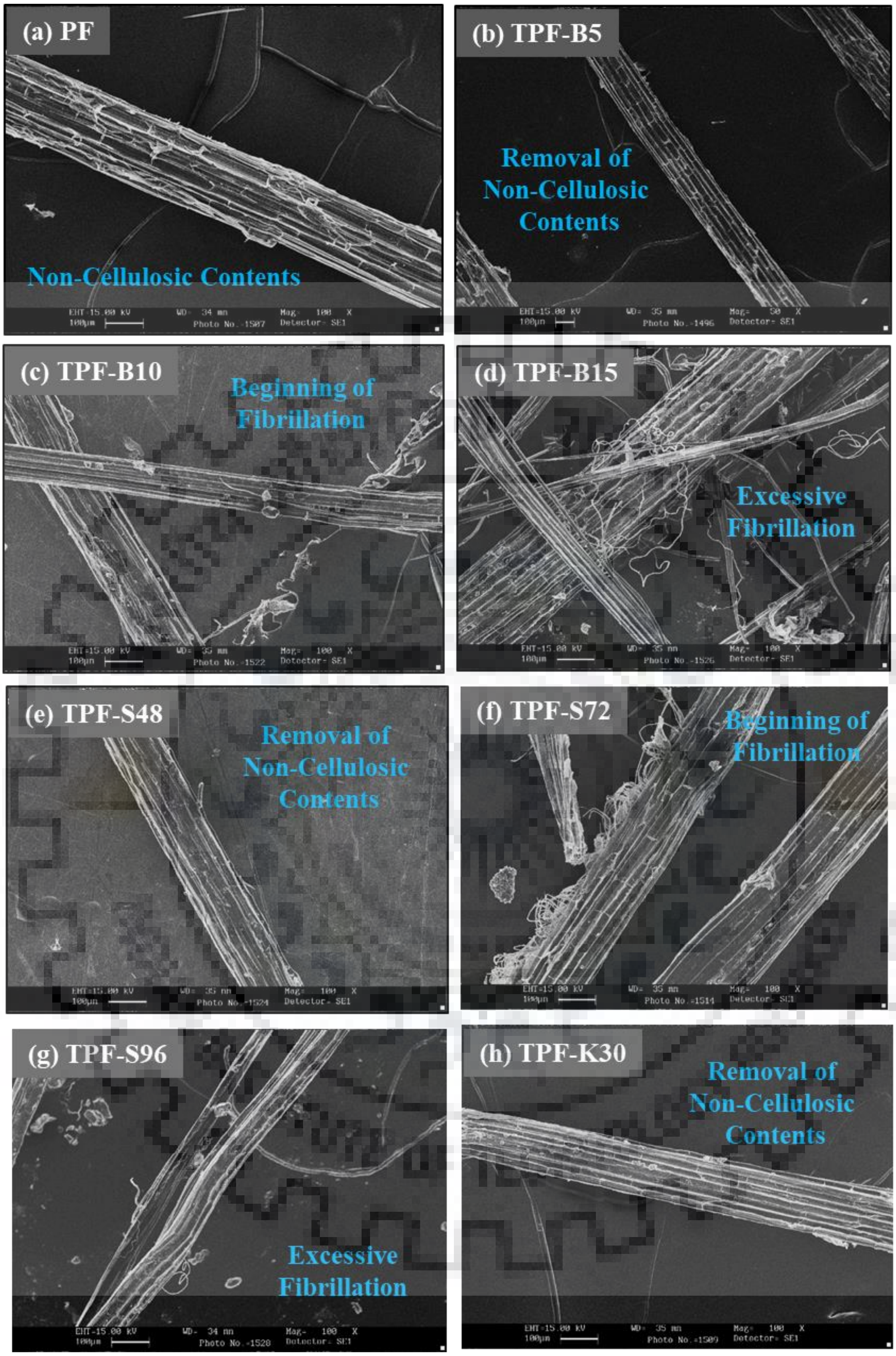


Fig. 4. 25 SEM micrographs of the untreated and treated pineapple fibers

4.2.3.1.2 Thermal Behavior

TGA and DTG curves of untreated and treated banana and pineapple fibers are shown in Fig. 4.26 and Fig. 4.27, respectively. The degradation profile of these fibers can be characterized by different stages. The first stage of loss in weight at a temperature range of 50-150°C is attributed to the evaporation of moisture absorbed by the fibers [66]. This is followed by the second stage of degradation observed at a temperature range of 200-300°C depicting the degradation of hemicellulose, waxes, and other non-cellulosic substances present in the fiber. The next sharp peak was observed in the temperature range of 300-375°C, which corresponds to the degradation of cellulose present within the fiber [143]. Furthermore, the last stage of degradation was observed between 400°C and 500°C, this can be attributed to the pyrolysis of lignin present in the fibers [137].

Thermal behavior of fibers was also characterized by extracting the data from TGA thermographs. The four levels (5%, 25%, 50%, and 75%) of weight loss and corresponding degradation temperatures were selected and compared (Table 4.4).

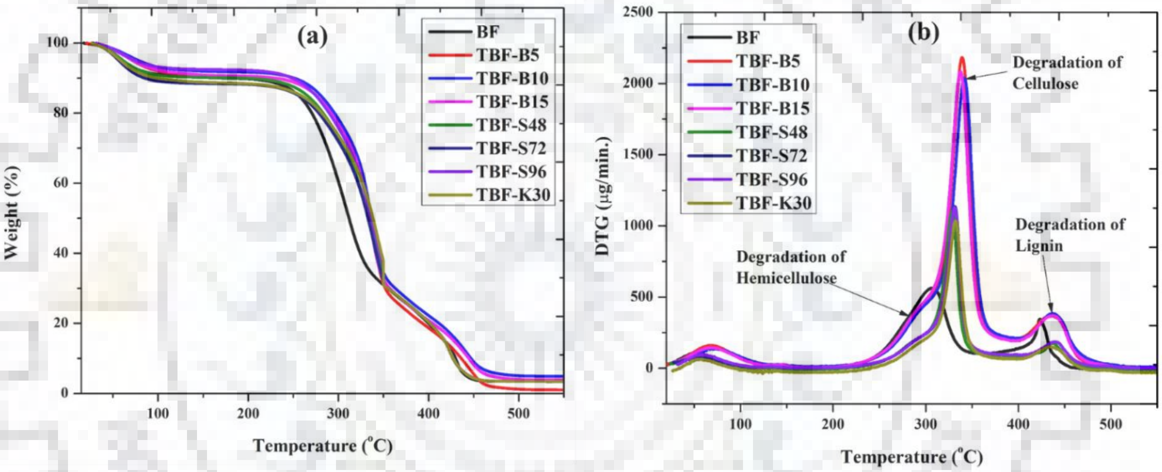


Fig. 4. 26 TGA and DTG curves of untreated and treated banana fibers

It can be observed that the degradation temperature of treated fibers is higher than the untreated fibers at all the selected levels. This depicts the enhancement in thermal stability of fibers post chemical treatment. It is attributed to the effective removal of hemicellulose and other non-cellulosic content from the surface of fibers. It can also be observed that the thermal stability of the fiber increases with an increase in the chemical concentration (in case of borax treatment) and treatment time (in case of sodium bicarbonate treatment).

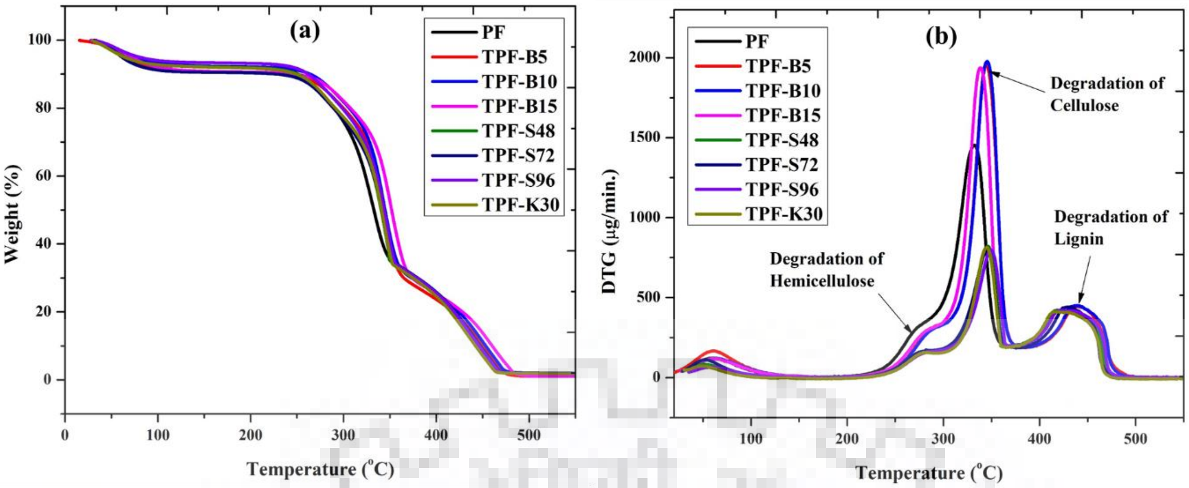


Fig. 4. 27 TGA and DTG curves of untreated and treated pineapple fibers

Table 4. 4 TGA results of untreated and treated banana and pineapple fibers

Sample Name		**Degradation Temperature (^{o}C)**			
		T_5	**T_{25}**	**T_{50}**	**T_{75}**
Banana Fiber	**BF**	60.35	280.05	311.73	378.35
	TBF-B5	71.73	304.53	335.22	380.24
	TBF-B10	78.17	307.8	336.59	385.82
	TBF-B15	79.23	309.56	338.56	387.25
	TBF-S48	61.29	295.92	333.07	379.22
	TBF-S72	68.36	298.65	334.57	382.96
	TBF-S96	74.67	301.9	336.58	385.63
	TBF-K30	62.35	296.45	338.26	379.76
Pineapple Fiber	**PF**	73.13	302.29	332.8	401.26
	TPF-B5	74.85	314.96	343.18	402.05
	TPF-B10	76.77	319.52	344.78	403.56
	TPF-B15	78.69	322.85	351.79	405.75
	TPF-S48	73.56	307.98	341.99	401.68
	TPF-S72	76.58	310.84	342.15	402.31
	TPF-S96	78.75	311.6	342.8	406.78
	TPF-K30	75.68	310.3	343.95	402.48

4.2.3.1.3 Tensile Behavior of Fibers

The tensile behavior in context of strength and modulus of the untreated and treated banana and pineapple fibers are depicted in Fig. 4.28 and Fig. 4.29, respectively. In the case of borax treatment, an increment in the strength and modulus of TBF-B5 and TPF-B5 was observed. It is attributed to the removal of hemicellulose and other non-cellulosic content as well as the surface defect present on the surface of fibers, these defects may act as a potential source of stress concentration during loading. It has been reported that the removal of hemicellulose improves the strength of the fiber as it promotes the formation of hydrogen bond between the cellulosic fibrils resulting in the improvement in close packing of fibrils. This improvement in the formation of hydrogen bond between the cellulosic fibrils increases the homogeneity of the fibers and improves the load-bearing capability between the interfibrillar regions [137].

Moreover, the removal of hemicellulose, waxes, and other non-cellulosic substances from the surface of the fiber leading to increased aspect ratio resulting in the improvement in tensile properties of the fibers. As the concentration of borax increases, excessive removal of hemicellulose was observed (Fig. 4. 24 and Fig. 4.25) that lead to the detachment of fibrils resulting in a reduction of tensile properties of the fibers.

In the case of sodium bicarbonate treatment, a gradual increase in tensile properties of fibers was observed when the fibers were treated up to 72 h. It is attributed to the effective removal of non-cellulosic content from the surface of the fibers. Sodium bicarbonate takes longer time to remove the desired amount of the hemicellulose from the surface of the fibers. It has already been discussed that the sodium bicarbonate behaves like mild NaOH, which react with the hydroxyl group of the lignocellulosic contents of the fiber. As the treatment was conducted at room temperature and being a mild alkaline in nature, it takes a longer time to get the desired results. However, after 72 h, as the treatment time increases, excessive removal of hemicellulose from the surface of the fiber causes the weakening of the fiber and further reduces the tensile properties. As compared to borax and sodium bicarbonate treatment, the tensile properties of the fibers treated with potassium permanganate were found to be lower. It may be attributed to the weakening of fibers due to higher concentration of KMnO4 and treatment time, that causes the excessive removal of cementing substances within the cellulose which leads to the reduction in the tensile properties of the fibers [135], [142].

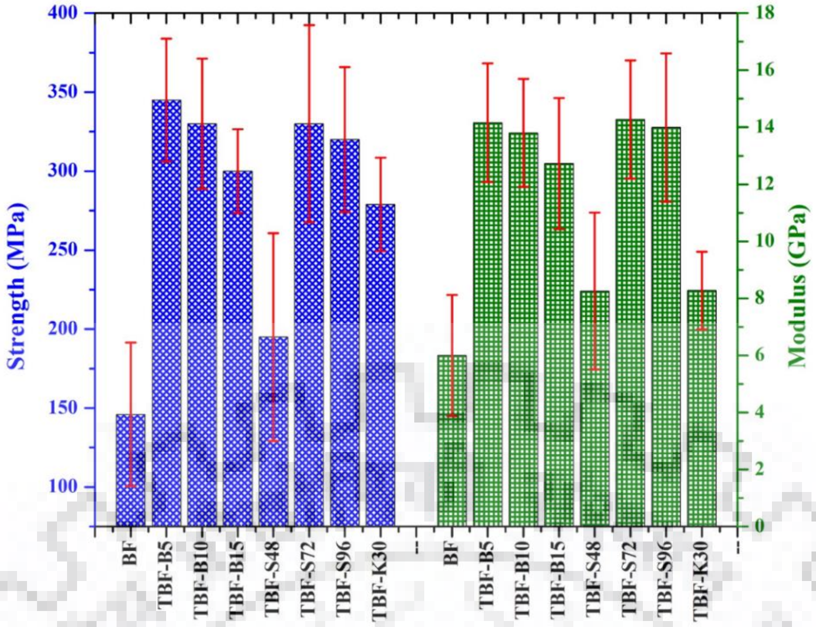


Fig. 4. 28 Tensile properties of untreated and treated banana fiber

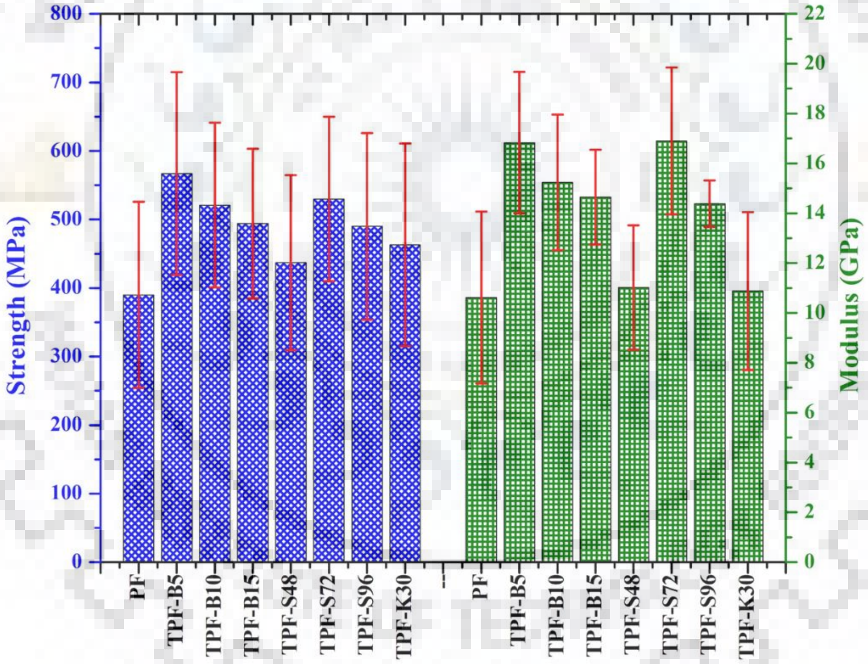


Fig. 4. 29 Tensile properties of untreated and treated pineapple fiber

4.2.3.2 Mechanical Behavior of the Composites

Comparative graphs showing the mechanical properties (tensile, flexural and impact) of untreated and treated banana and pineapple fiber reinforced PLA based composites are represented in Fig. 4.30, Fig. 4.31 and Fig 4.32. It can be seen that the incorporation of treated fiber into PLA matrix exhibit the significant improvement in the mechanical properties (tensile, flexural and impact) compared to the untreated fiber-reinforced composites. The mechanical properties of the composites incorporating fibers treated with 5% borax solution were found to be higher as compared to all other developed composites. As the concentration of borax increases beyond 5%, a significant reduction in mechanical properties was observed and found to be minimum at 15%. In the case of sodium bicarbonate treatment, the mechanical properties of the composite increase gradually with the treatment time and were found to be maximum at 72 h. After 72 h, the mechanical properties of the composites start decreasing

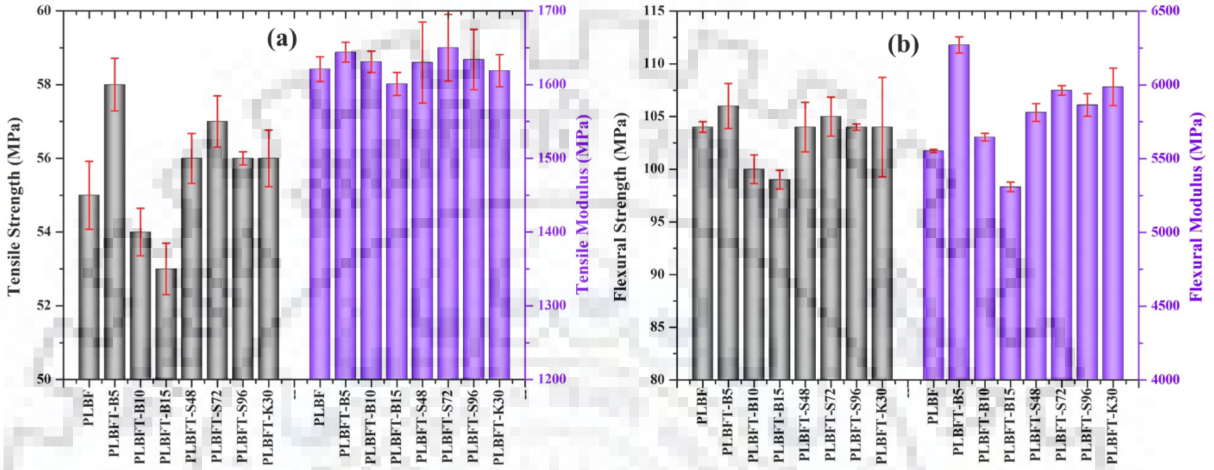


Fig. 4. 30 Tensile and flexural properties of the banana fiber based PLA composites

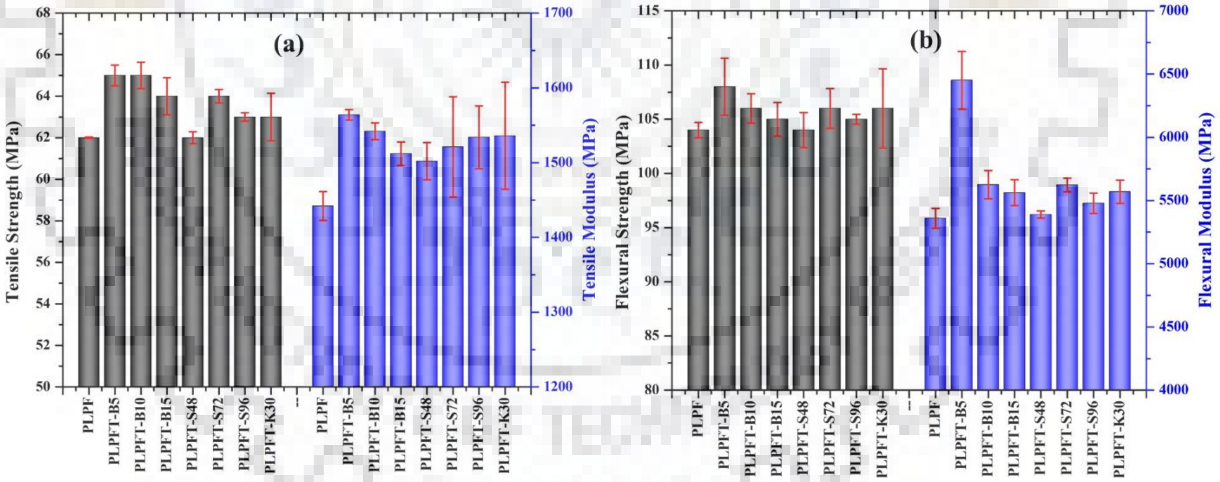


Fig. 4. 31 Tensile and flexural properties of the pineapple fiber-based PLA composites

The improvement in mechanical properties (tensile, flexural and impact) at 5% (in case of borax treatment) and at 72h (in case of sodium bicarbonate treatment) is attributed to the improvement in interfacial interaction between the fibers and matrix. The chemical treatment removes the hemicellulose, waxes, and other non-cellulosic substances from the surface of the fiber leading to increased aspect ratio and surface area which ensures better wettability with the matrix resulting in improved interfacial interaction between the fibers and matrix [144],

[145]. This improvement leads to better load carrying capacity of the composites incorporating treated fibers. Moreover, the improvement in interfacial interaction increases the orientation of fibers and molecular orientation of polymers during injection molding which further results in the improvement in mechanical properties of the composites. Moreover, the increase in tensile properties of the fibers (as discussed in section 4.2.3.1.3) further contributes to enhancing the mechanical properties of the composites.

The decline in mechanical properties of the composites after 5% (in case of borax treatment) and post 72 h (in case of sodium bicarbonate treatment) is attributed to the weakening of fibers due to excessive removal of hemicellulose lead to the detachment of fibrils which reduces the tensile strength of the fibers resulting in the decrease in the mechanical properties of the composites. Moreover, the increase in fibrillation means an increased number of fibers for the same weight fraction, within the developed composites. This facilitates the propagation of crack through the inter-fiber gaps during loading. Moreover, the increased number of fiber ends sometimes act as a stress concertation zone which further facilitates the propagation of crack leading to a decrease in mechanical properties of the composites.

The mechanical properties of the PLBF-K30 and PLPF-K30 composites was found to be lower as compared to PLBF-B5 and PLPF-B5 composites, respectively. It can be due to a reduction in properties of the fibers due to excessive removal of hemicellulose which may lead to the fibrillation of fibers resulting in the reduction of mechanical properties of the composites. However, the mechanical properties of PLBF-K30 and PLPF-K30 composites was found to higher as compared to PLBF and PLPF composites, respectively.

The mechanical properties (tensile, flexural and impact) of untreated and treated banana and pineapple fiber based PP composites depicted the similar trend of variation as PLA based composites. Similar to PLA based composites, the mechanical properties of the PPBF-B5 (in case of banana fiber-based composites) and PPPF-B5 (in case of pineapple fiber-based composites) composites was found to be higher as compared to other developed composites.

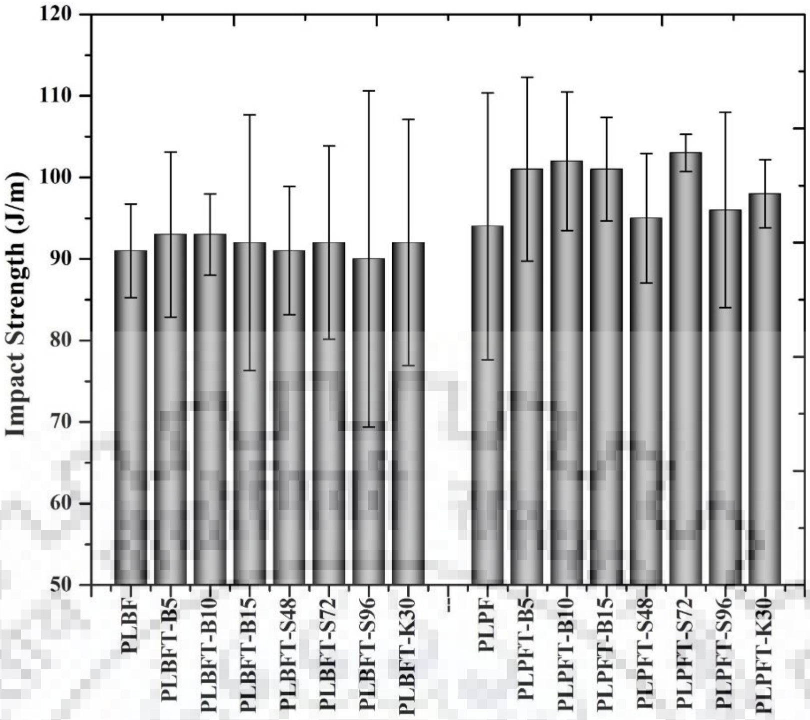


Fig. 4. 32 Impact strength of banana and pineapple fiber-based PLA composites

In the case of borax treatment, the properties of the composites were found to be maximum when the fibers were treated with an aqueous solution containing 5% borax. However, a gradual reduction in mechanical properties was observed as the concertation of borax increases.

Similar to PLA based composites, when the fibers were treated in sodium bicarbonate solution. A gradual improvement in mechanical properties was observed up to 72 h, beyond 72 h a significant reduction in mechanical properties was observed.

When the fibers were treated with potassium permanganate solution, as compared to PPBF-B5 and PPPF-B5 composites, the mechanical properties of the PPBF-K30 and PPPF-K30 composites, respectively were found to be lower while it was found to be higher as compared to PLBF and PLPF composites, respectively. The similar trend of variation in mechanical properties was also observed for the PLA based composites.

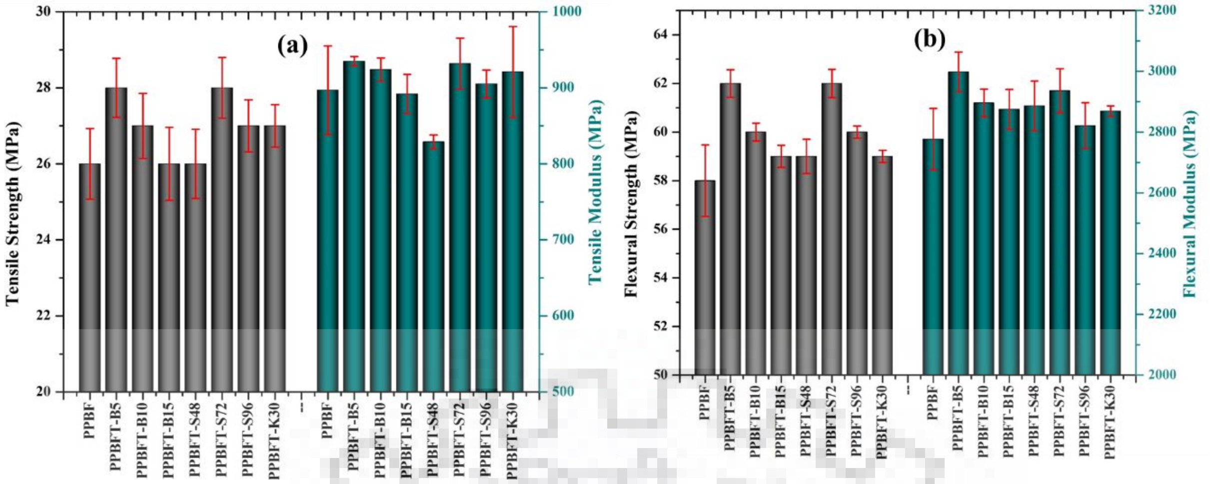


Fig. 4. 33 Tensile and flexural properties of the banana fiber-based PP composites

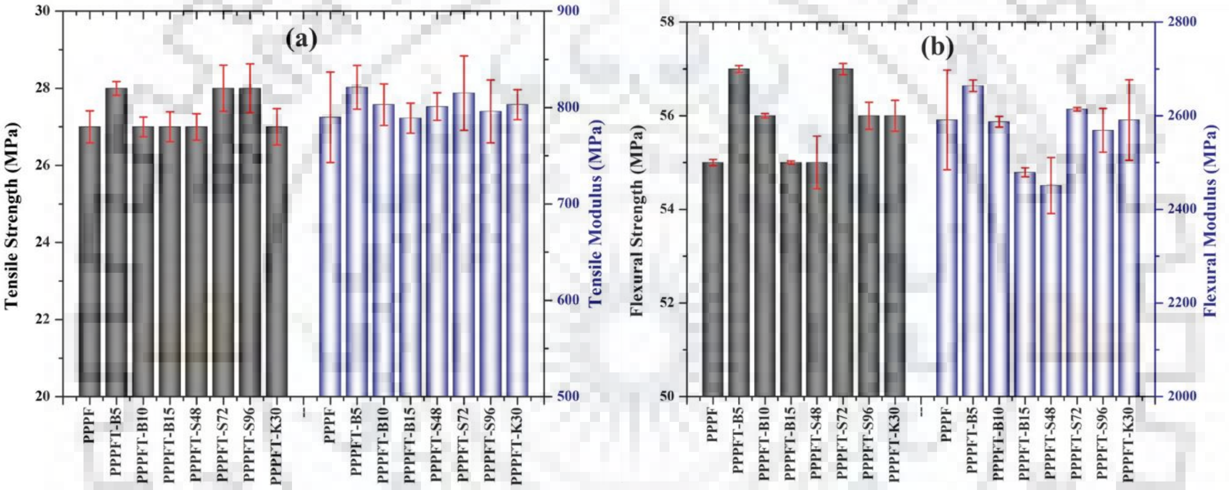


Fig. 4. 34 Tensile and flexural properties of the pineapple fiber-based PP composites

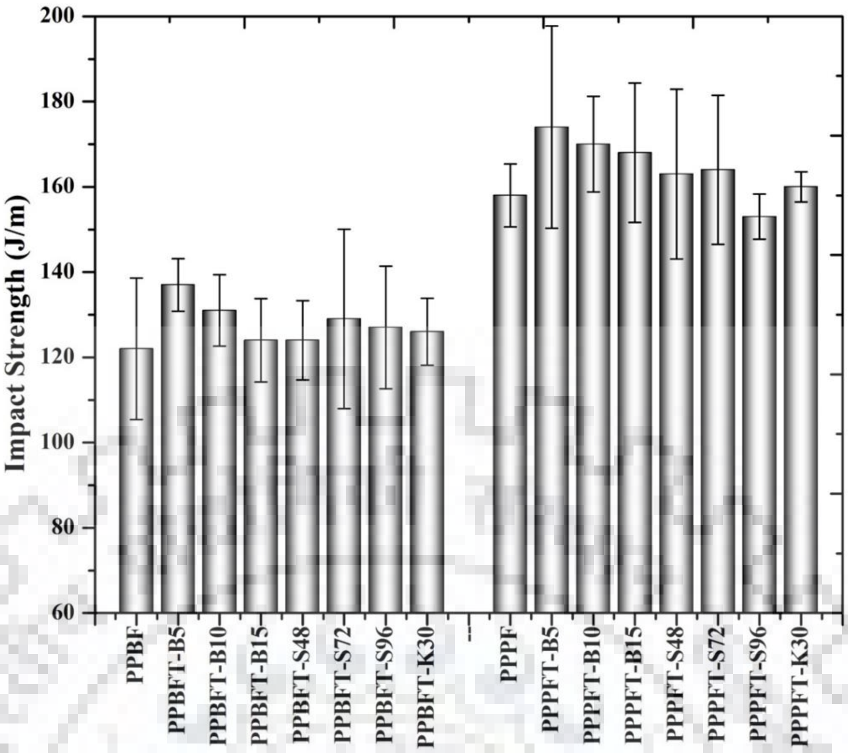


Fig. 4. 35 Impact strength of banana and pineapple fiber-based PP composites

4.2.3.3 Morphological Analysis

The claims made in support of the variation in mechanical properties of the developed composites are validated by observing the fracture surface of the failed tensile test specimens. The fractography of the specimens and mode of fracture was analyzed using SEM micrographs (Fig. 4.36 and 4.37). In Fig. 4.36 (a, e) and Fig. 4.37 (a, e), the fiber pull-out, fiber-matrix debonding can be seen as the foremost cause for the rupture of composites. It can be due to the poor interfacial interaction between the constituents. Fig. 4.36 (b-d) and Fig. 4.37 (b-d) depicts the improvement in interfacial adhesion between the fibers and matrix as the concentration of borax increase, this can be confirmed with the presence of increased number of fibers breaking instead of pull out. The enhancement in adhesion between the constituents is attributed to the removal of hemicellulose, waxes and other non-cellulosic substances from the surface of the fibers.

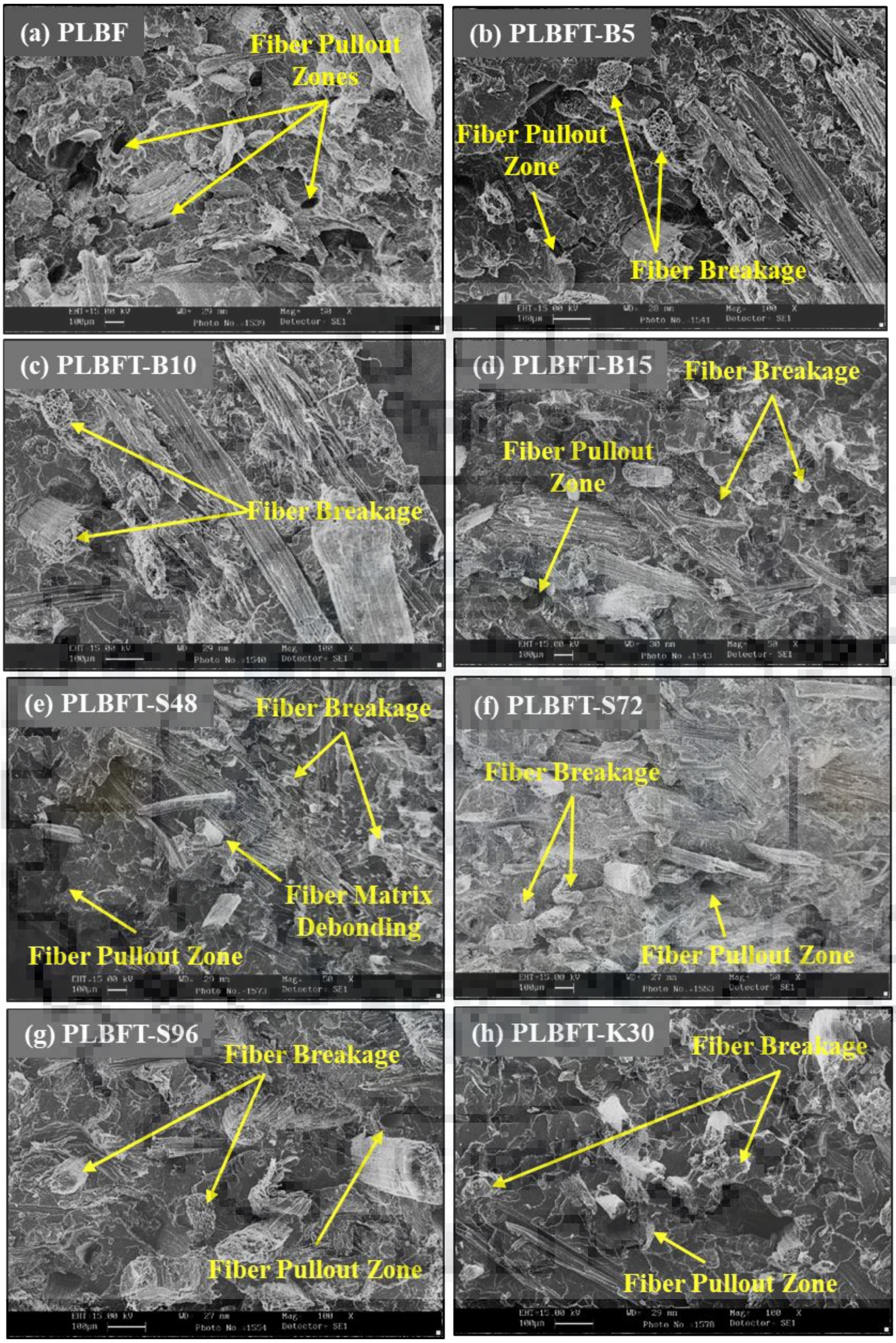


Fig. 4. 36 Fractographs of untreated and treated banana fiber reinforced PLA composites

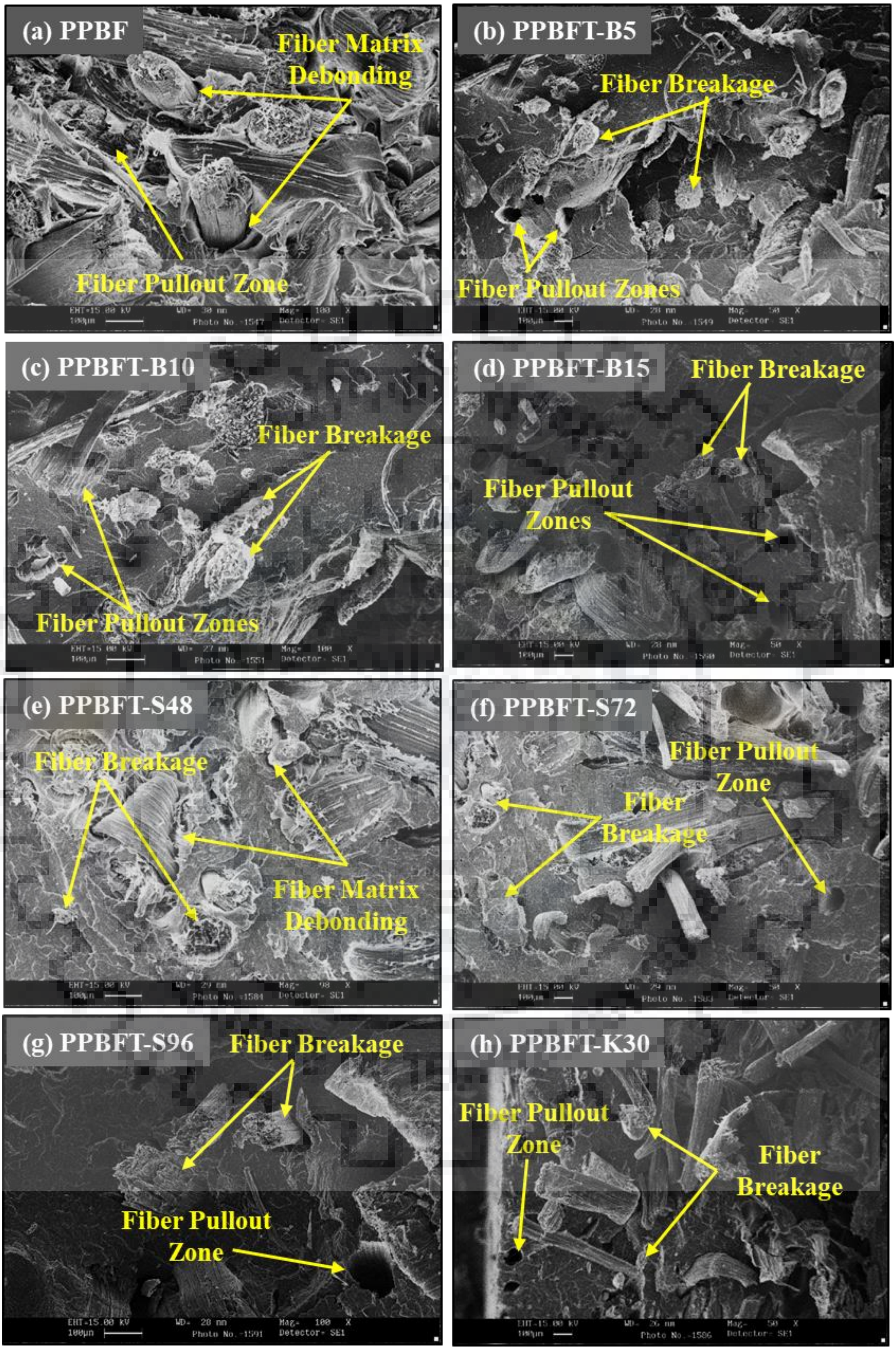


Fig. 4. 37 Fractographs of untreated and treated banana fiber reinforced PP composites

This reduces the hydrophilicity and increases the strength of the fibers as well as the wettability of fibers during processing. The similar trend of variation in interfacial interaction was observed when the fibers were treated with sodium bicarbonate solution (Fig. 4.36 (e-g) and Fig. 4.37 (e-g)). An improvement in interfacial interaction between the fibers and matrices was observed with treatment time. This can be confirmed with the presence of reduced number of fiber pull-outs and increased number of fiber breakage. In Fig. 4.36 (h) and Fig. 4.37 (h), an improvement in interfacial interaction was observed as compared to Fig. 4.36 (a) and Fig. 4.37 (a), respectively. It can be attributed to the removal of hemicellulose and other non-cellulosic substances from the surface of the fibers when the fibers were treated with potassium permanganate solution.

The current experimental investigation reveals that the mechanical properties (tensile, flexural and impact) of the composites incorporating fibers treated with borax is superior as compared to the composites incorporating fibers treated with sodium bicarbonate and potassium permanganate, respectively. Therefore, the borax treatment has been identified as the superior chemical treatment route for the treatment of banana and pineapple fibers.

The mechanical properties of the composites incorporating fibers treated with 5% borax solution were found to be maximum as compared to all other developed composites. Hence, the composites incorporating fibers treated with 5 % borax solution were found to be optimum and selected for further investigations.

CHAPTER SUMMARY

This chapter has provided the following information:

- The effect of three processing techniques on the distribution and orientation of fibers within the developed composites.
- The understanding of the effect of processing routes on the crystallinity, dynamic mechanical behavior and mechanical behavior of the developed composites.
- The effect of three types of chemical treatments on the morphology, thermal behavior and tensile properties of the fibers.
- The influence of chemical treatments on the mechanical behavior of the developed composites.
- The optimum treatment conditions such as; concentration and treatment time for the effective removal of hemicellulose, waxes and other non-cellulosic content from the surface of banana and pineapple fibers.

The next chapter presents the recyclability assessment of the banana and pineapple fiber reinforced PP and PLA based composites.

CHAPTER 5

RECYCLABILITY ASSESMENT OF THE BANANA AND PINEAPPLE FIBER REINFORCED PP AND PLA BASED COMPOSITES

The current investigation explores the recyclability assessment of banana and pineapple fiber reinforced PP and PLA based composites. The performance of the recycled composites was investigated in terms of fiber aspect ratio, mechanical, thermal and dynamic mechanical behavior as well as the crystallinity.

5.1 INTRODUCTION

5.2 EXPERIMENTAL DETAILS

The recyclability assessment of the developed composites has been experimentally investigated as depicted in Fig. 5.1

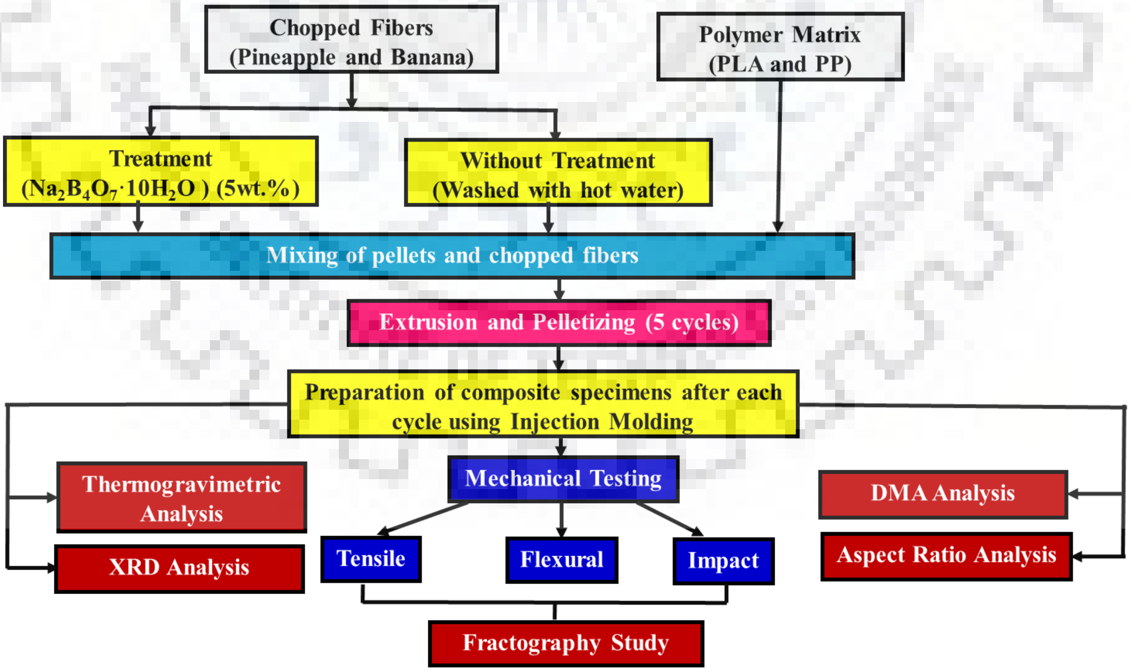


Fig. 5. 1 Flow diagram of the work plan

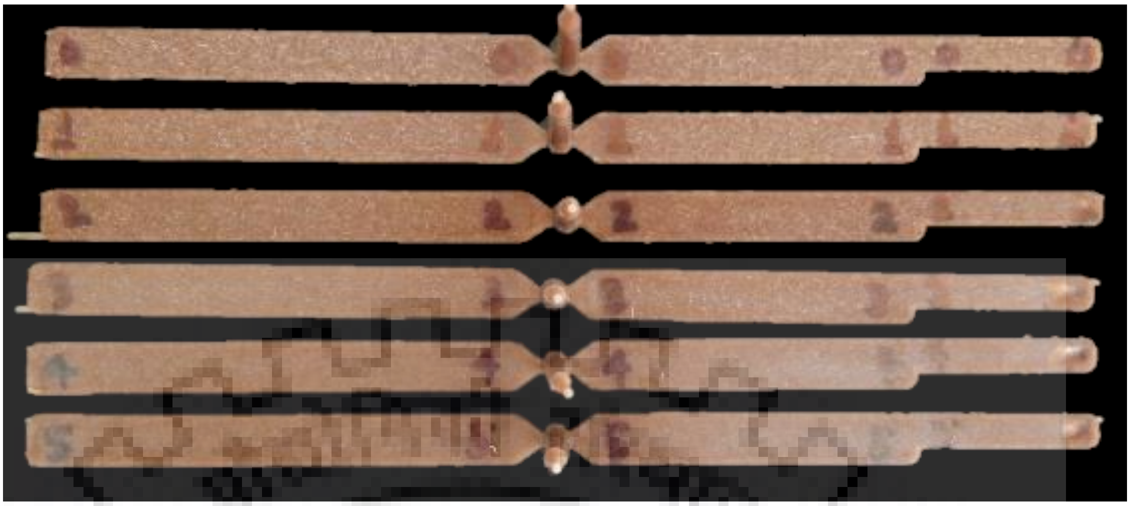


Fig. 5. 2   PLA based recycled composite specimens

Table 5. 1 Designation of the recycled composites

Cycle No	**PLA Based Composites**				**PP Based Composites**			
	Banana Fiber		**Pineapple Fiber**		**Banana Fiber**		**Pineapple Fiber**	
	Untreated	**Treated**	**Untreated**	**Treated**	**Untreated**	**Treated**	**Untreated**	**Treated**
Cycle 0	PLB	PLBT	PLP	PLPT	PPB	PPBT	PPP	PPPT
Cycle 1	PLB-1	PLBT-1	PLP-1	PLPT-1	PPB-1	PPBT-1	PPP-1	PPPT-1
Cycle 2	PLB-2	PLBT-2	PLP-2	PLPT-2	PPB-2	PPBT-2	PPP-2	PPPT-2
Cycle 3	PLB-3	PLBT-3	PLP-3	PLPT-3	PPB-3	PPBT-3	PPP-3	PPPT-3
Cycle 4	PLB-4	PLBT-4	PLP-4	PLPT-4	PPB-4	PPBT-4	PPP-4	PPPT-4
Cycle 5	PLB-5	PLBT-5	PLP-5	PLPT-5	PPB-5	PPBT-5	PPP-5	PPPT-5

5.3 RESULTS AND DISCUSSION

5.3.1 Thermal Behavior

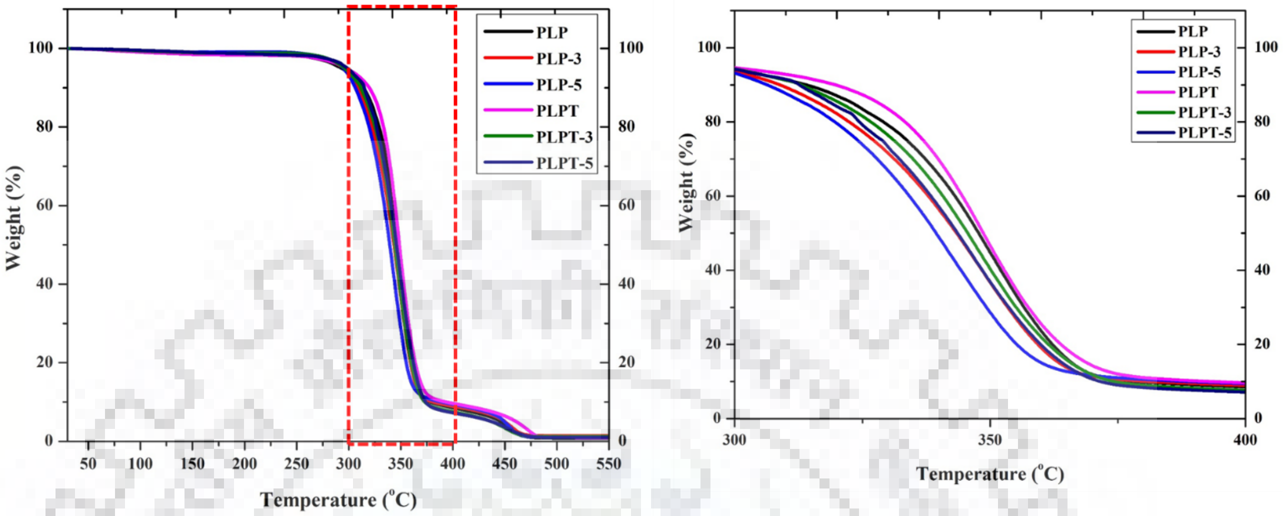


Fig. 5. 3 TGA curves of the PLA based recycled composites

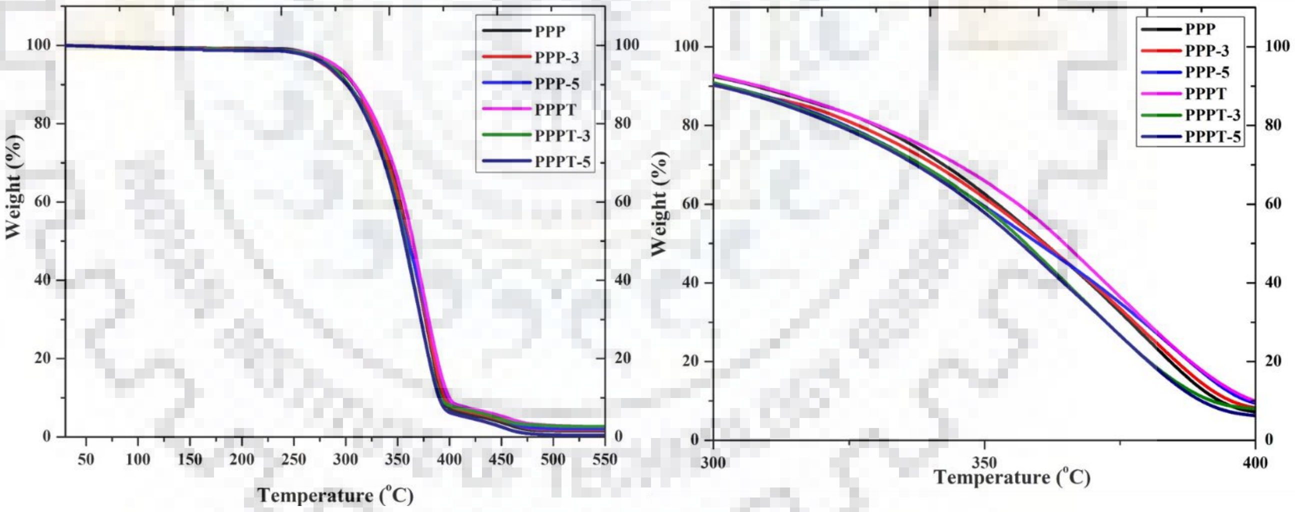


Fig. 5. 4 TGA curves of the PP based recycled composites

5.3.2 Mechanical and Morphological Behavior

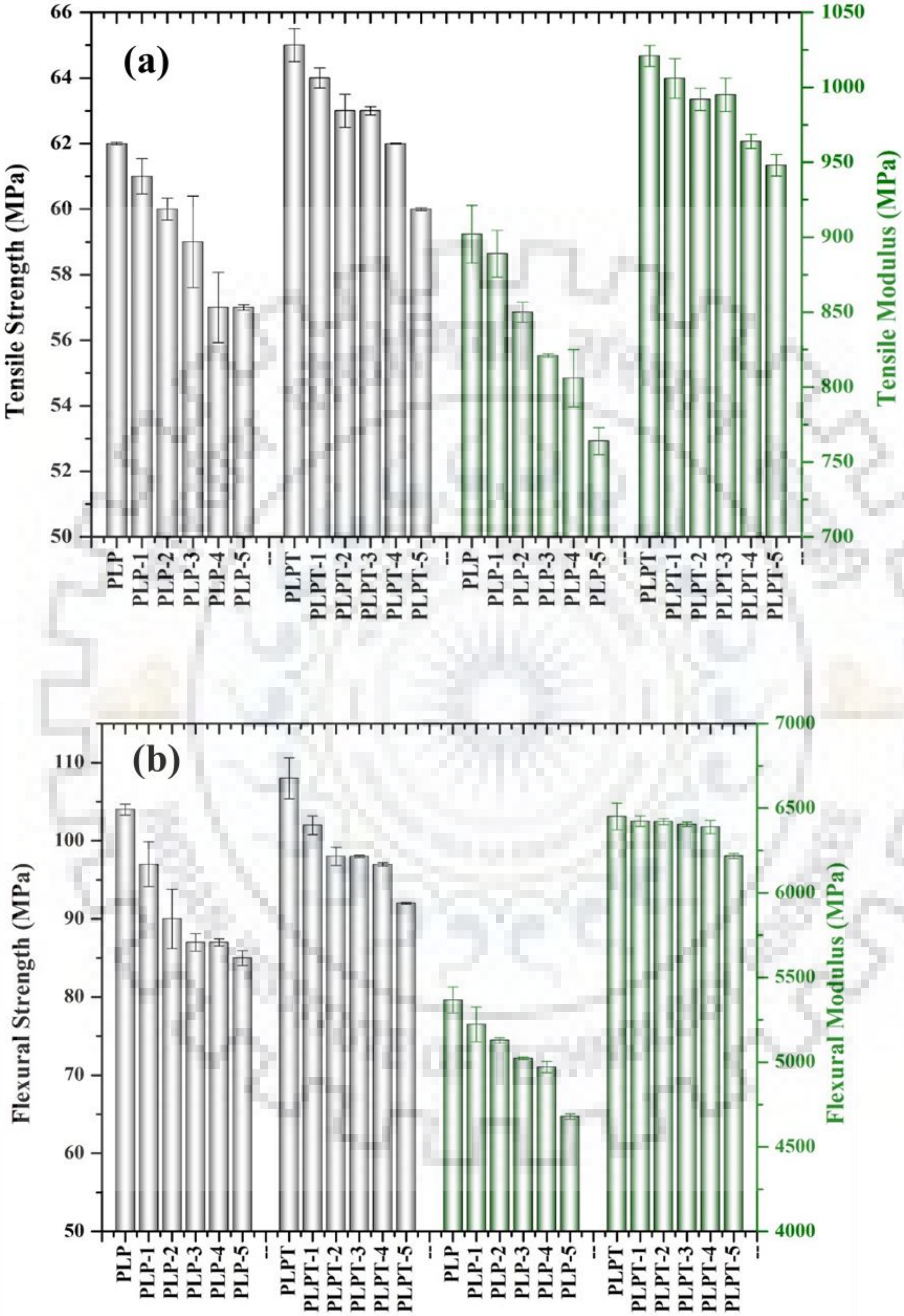


Fig. 5. 5 (a) Tensile and (b) flexural properties of the PLA based recycled composites

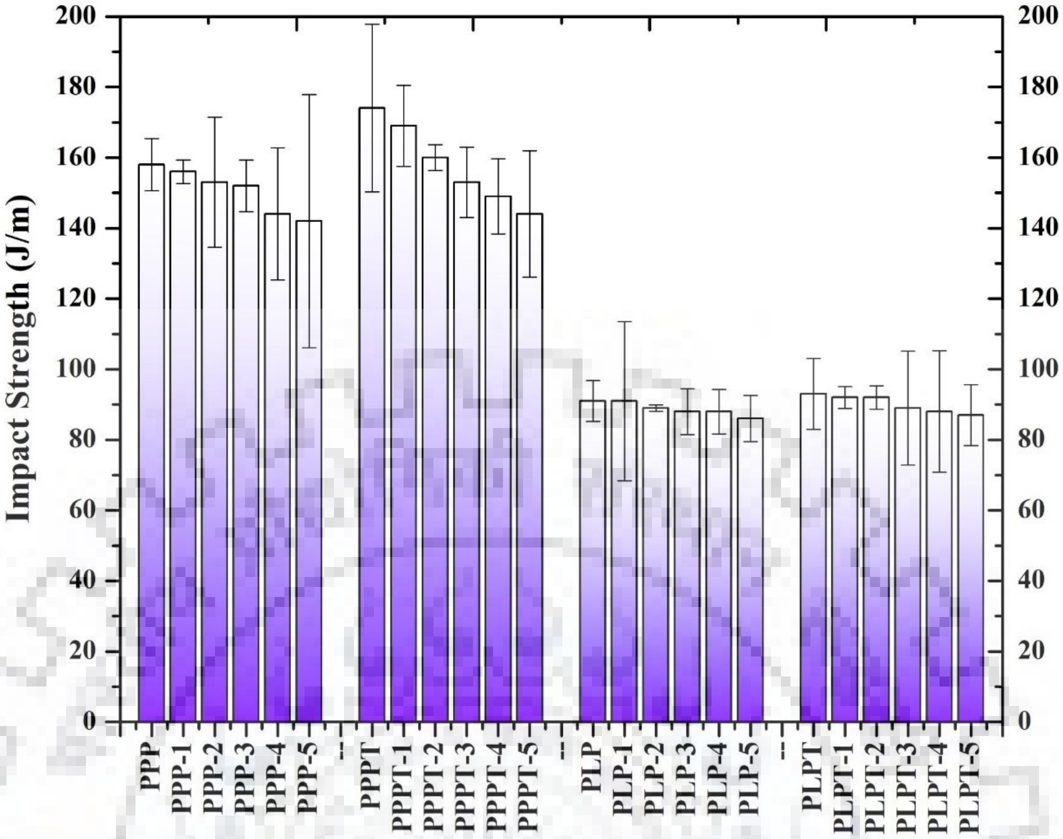


Fig. 5. 6 Impact strength of PP and PLA based recycled composites

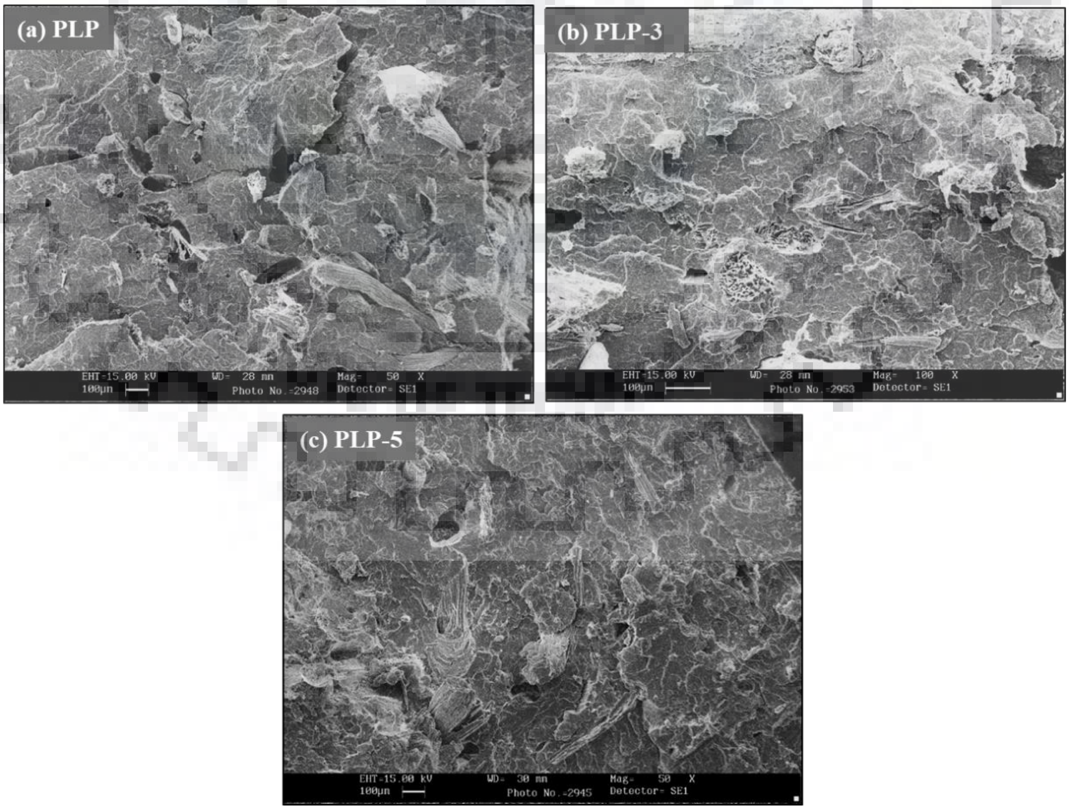


Fig. 5. 7 Fractographs of the tensile tested PLA based recycled composites

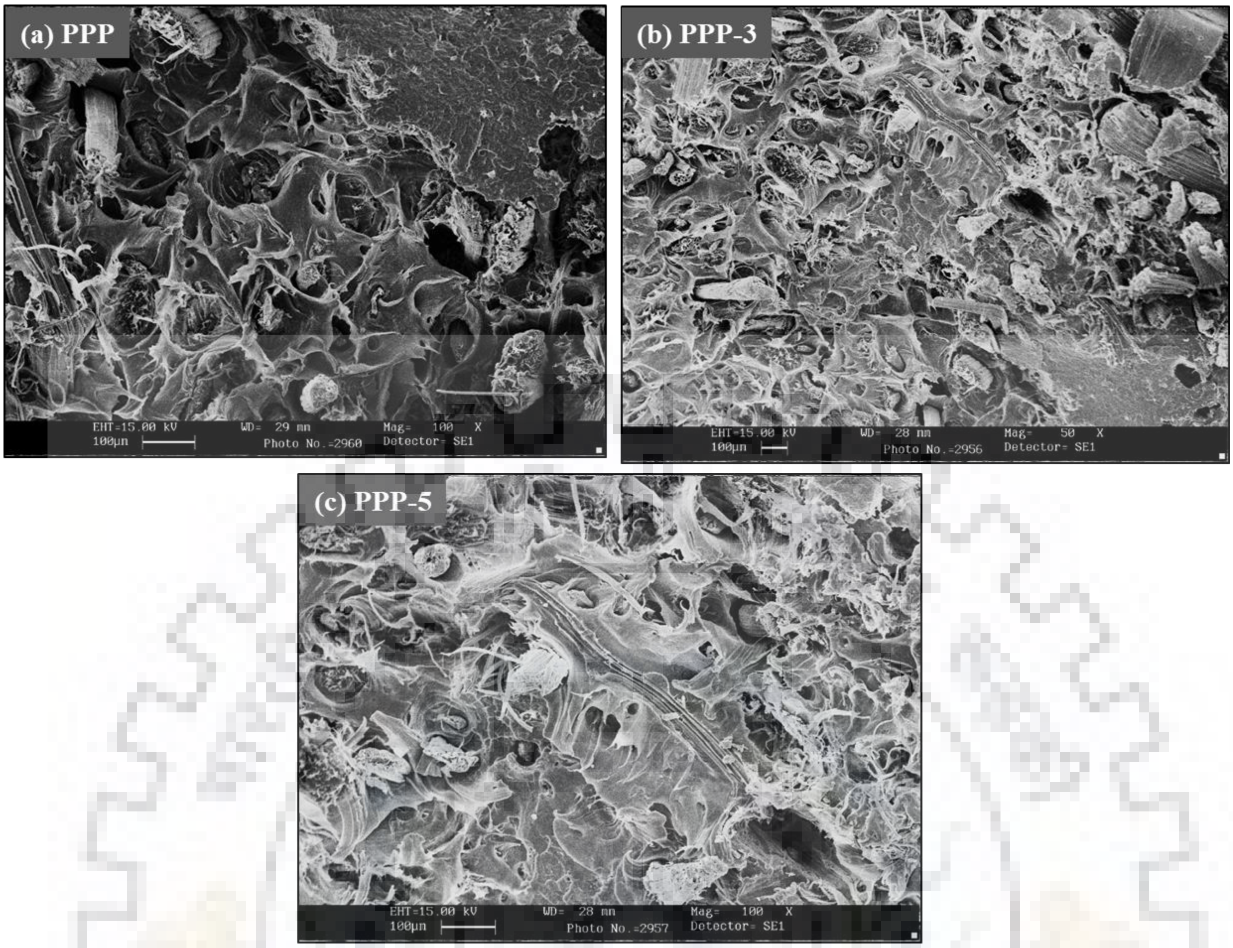
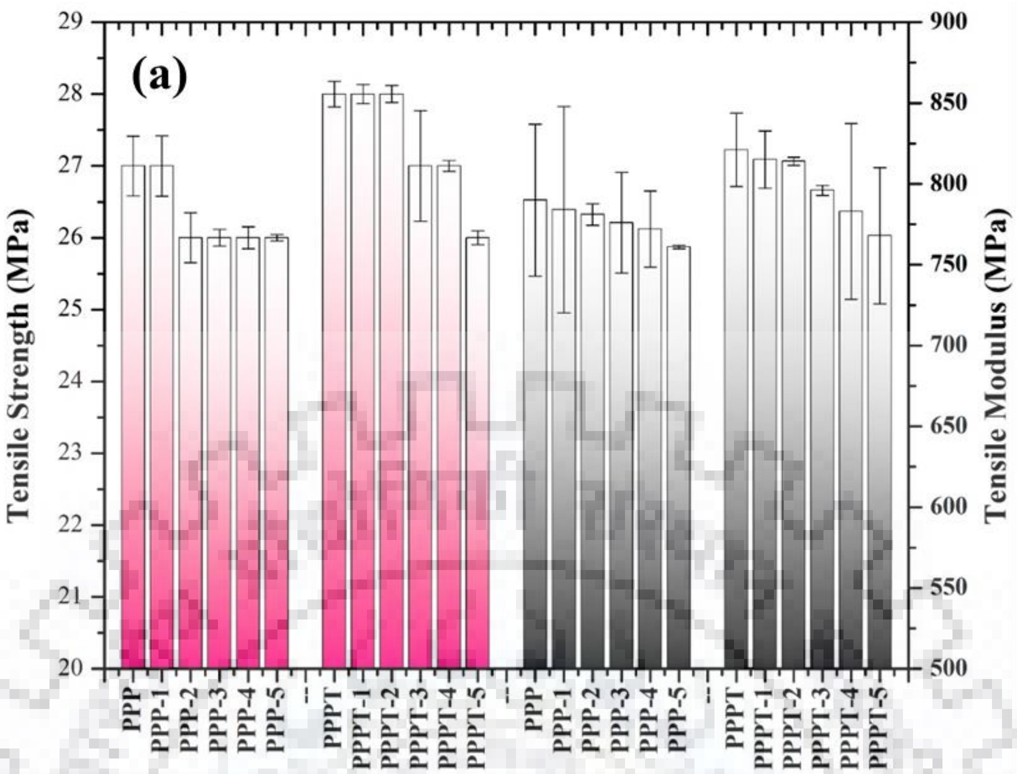


Fig. 5. 8 Fractographs of the tensile tested PP based recycled composites



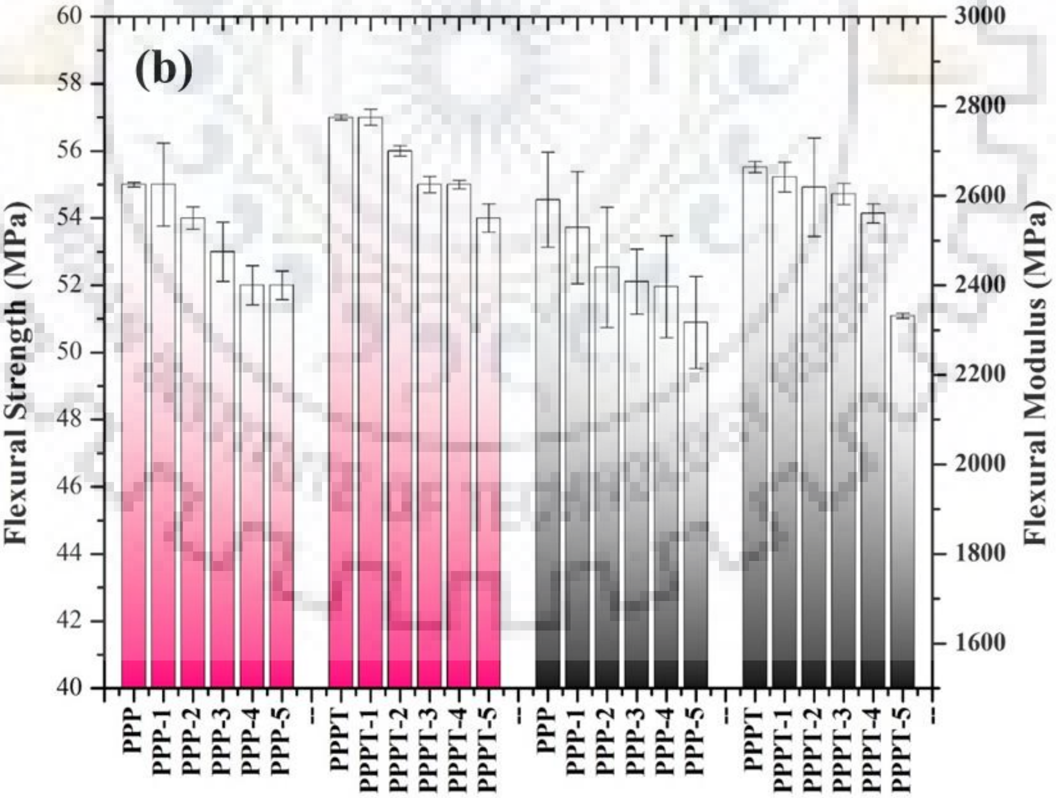


Fig. 5. 9 (a) Tensile and (b) flexural properties of the PP based recycled composites

5.3.3 Dynamic Mechanical Analysis

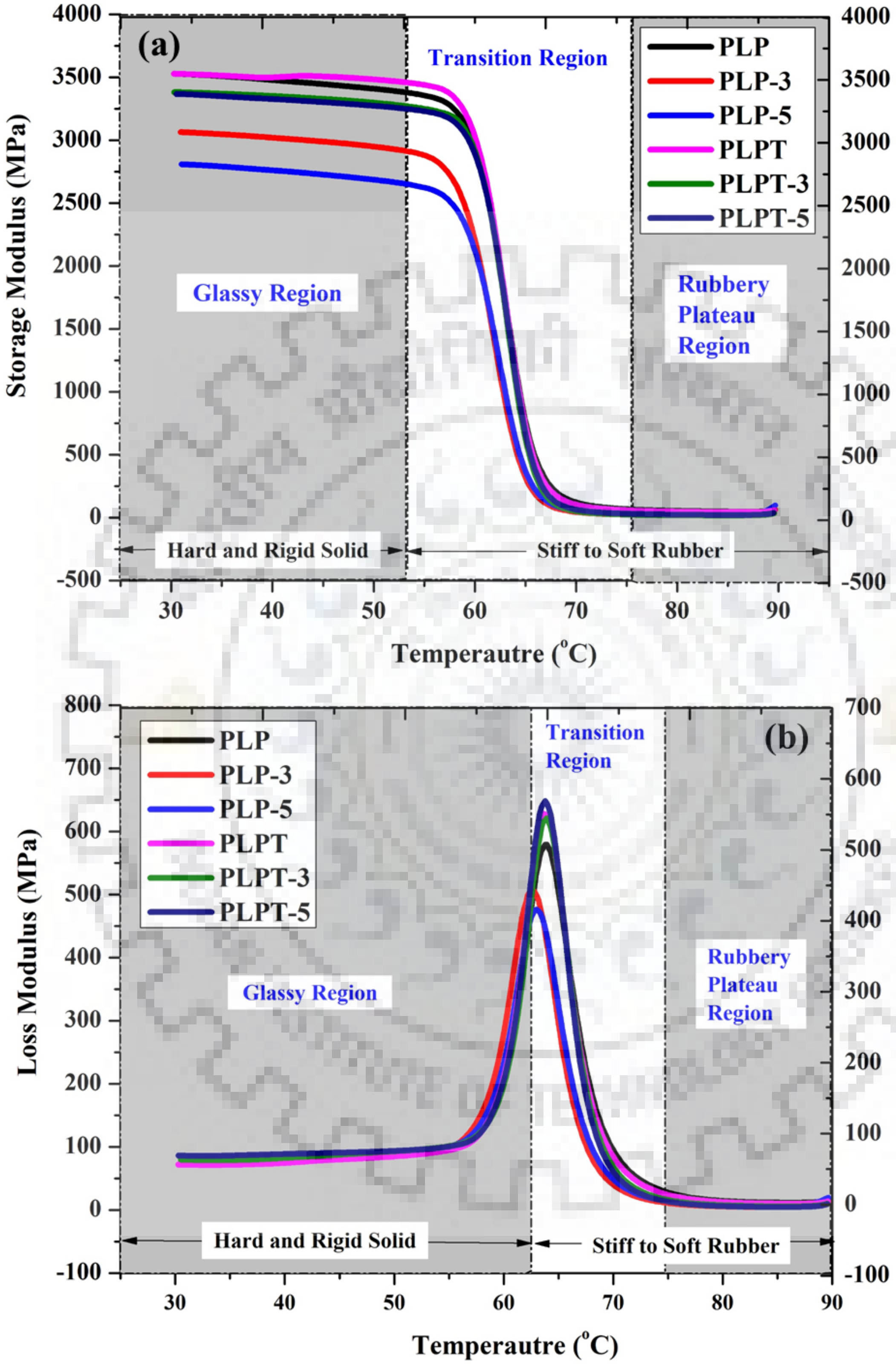


Fig. 5. 10 (a) Storage and loss modulus of the PLA based recycled composites

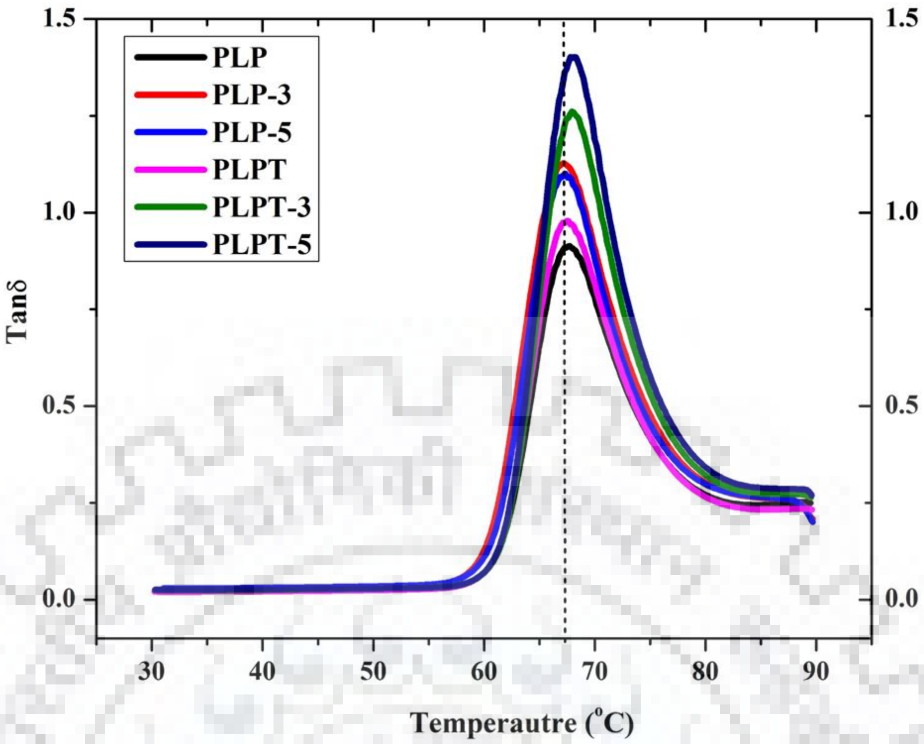


Fig. 5. 11 Tan delta of the PLA based recycled composites

5.3.4 XRD Analysis

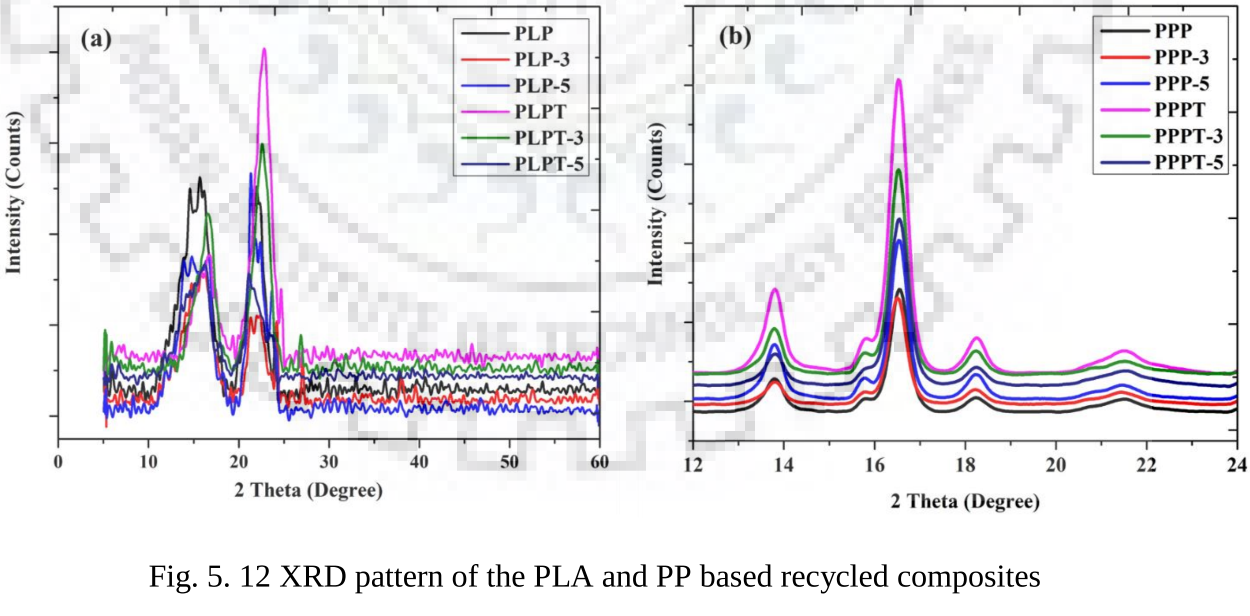


Fig. 5. 12 XRD pattern of the PLA and PP based recycled composites

5.3.5 Aspect Ratio Analysis

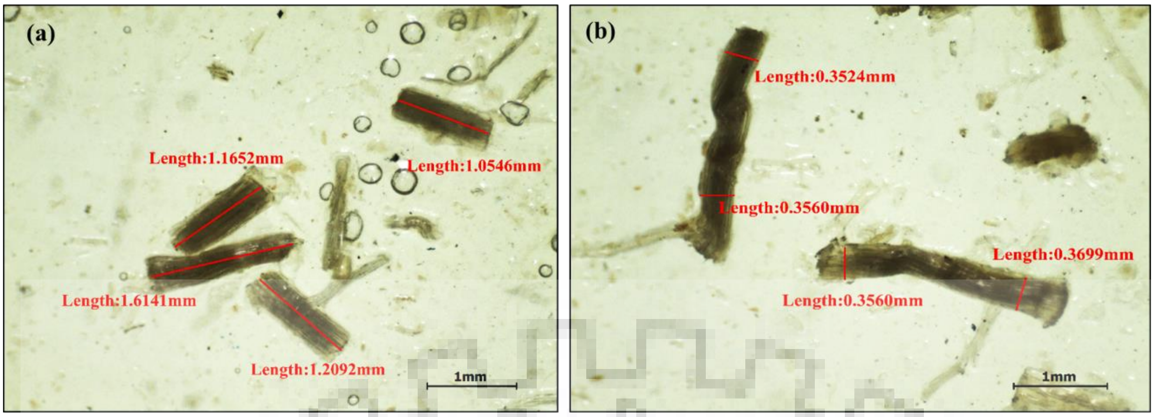


Fig. 5. 13 Aspect ratio measurement using stereo microscope

Table 5. 2 Effect of recycling on the variation of aspect ratio of untreated banana fiber based PLA composite

Recycling No.	Fiber Length (mm)	Fiber Diameter (mm)	Aspect Ratio
0	2.570	0.436	5.896
1	2.313	0.351	6.576
2	1.828	0.344	5.311
3	1.451	0.317	4.572
4	1.431	0.294	4.865
5	1.182	0.223	5.286

CHAPTER SUMMARY

- The recyclability assessment of banana and pineapple fiber reinforced PP and PLA based composites was investigated.
- The performance of the recycled composites was investigated in terms of fiber aspect ratio, mechanical, thermal and dynamic mechanical behavior.
- The effect of recycling on the crystallinity of the developed composites has been explored.
- The effect of chemical treatment on the recycling behavior of the developed composites has also been investigated.
- The attrition of fibers in terms of reduction in length and diameter was measured by examining the fiber using stereo microscope.

- The SEM examination was conducted to investigate the mode of fracture of the tensile tested recycled composite specimens.

The next chapter presents the environmental aging of the natural fiber reinforced PP and PLA based composites.

CHAPTER 6

ENVIRONMENTAL AGING OF THE NATURAL FIBER REINFORCED PP AND PLA BASED COMPOSITES

In the current chpater, the environmental aging behavior of the developed composites has been performed in various environments (tap water, 5% NaOH solution, 5% H_2SO_4 solution, 5% NaCl solution and outdoor weather). The composite specimens were exposed to these environments for a period of 6 months with an analysis interval of 2 months. The effect of environmental aging on the behavior of the developed composites has been assessed in terms of variation in weight, mechanical properties and crystallinity as well as the change in morphology.

6.1 INTRODUCTION

6.2 EXPERIMENTAL DETAILS

The environmental aging behavior of the developed composites has been experimentally investigated as depicted in Fig. 6.1.

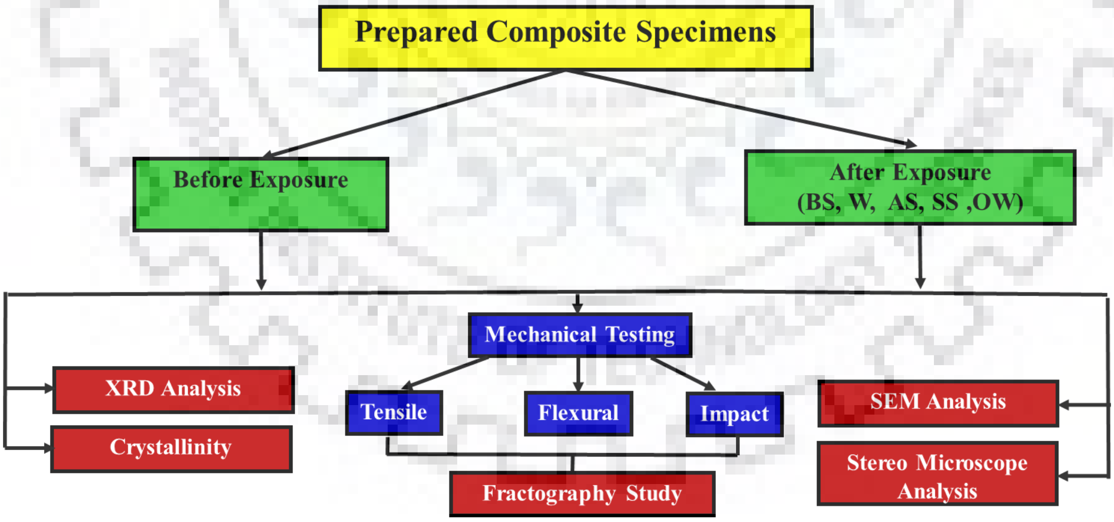
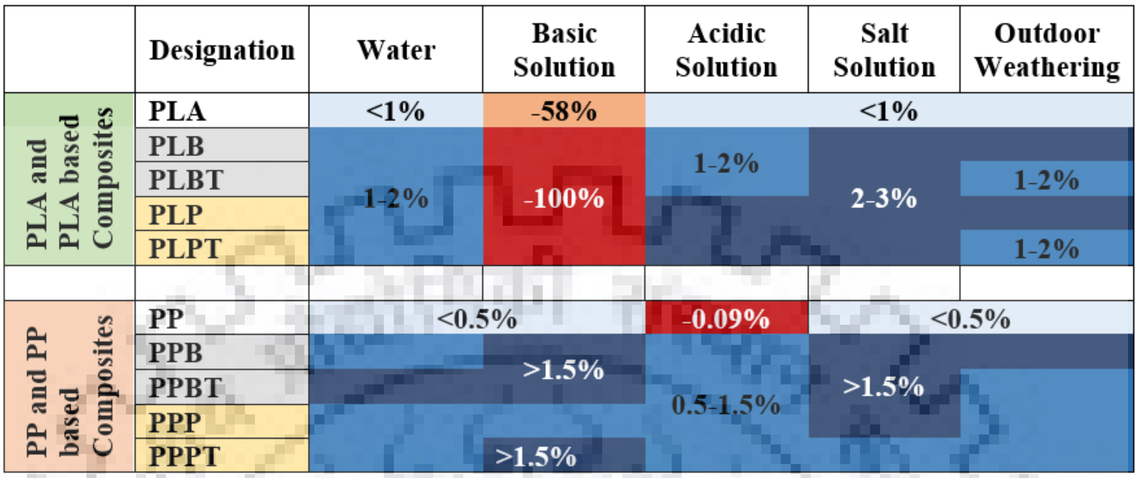


Fig. 6. 1 Flow diagram of the work plan

6.3 RESULTS AND DISCUSSION

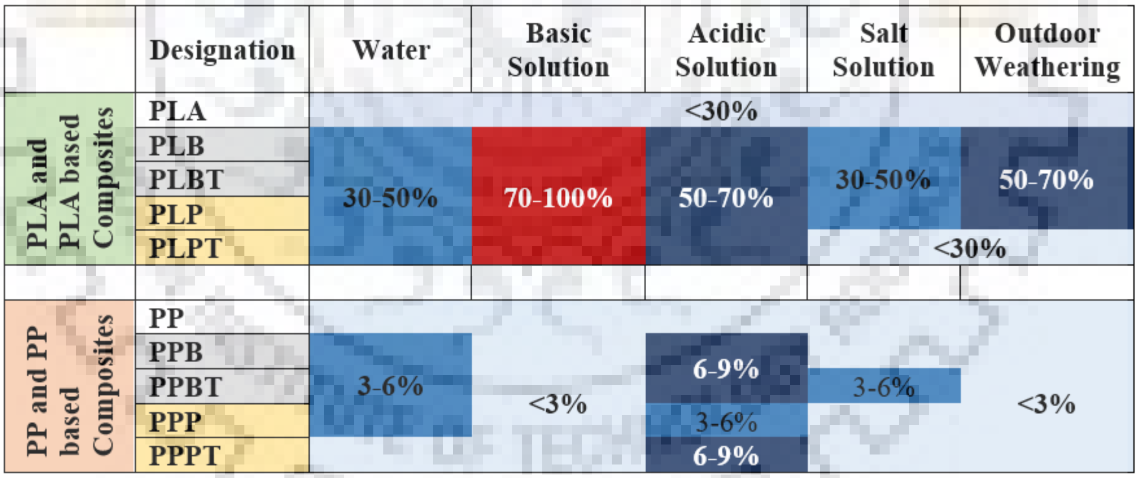
6.3.1 Variation in Weight



	Designation	Water	Basic Solution	Acidic Solution	Salt Solution	Outdoor Weathering
PLA and PLA based Composites	PLA	<1%	-58%	<1%		
	PLB	1-2%	-100%	1-2%	2-3%	
	PLBT					1-2%
	PLP					
	PLPT					1-2%
PP and PP based Composites	PP	<0.5%		-0.09%	<0.5%	
	PPB		>1.5%	0.5-1.5%	>1.5%	
	PPBT					
	PPP					
	PPPT		>1.5%			

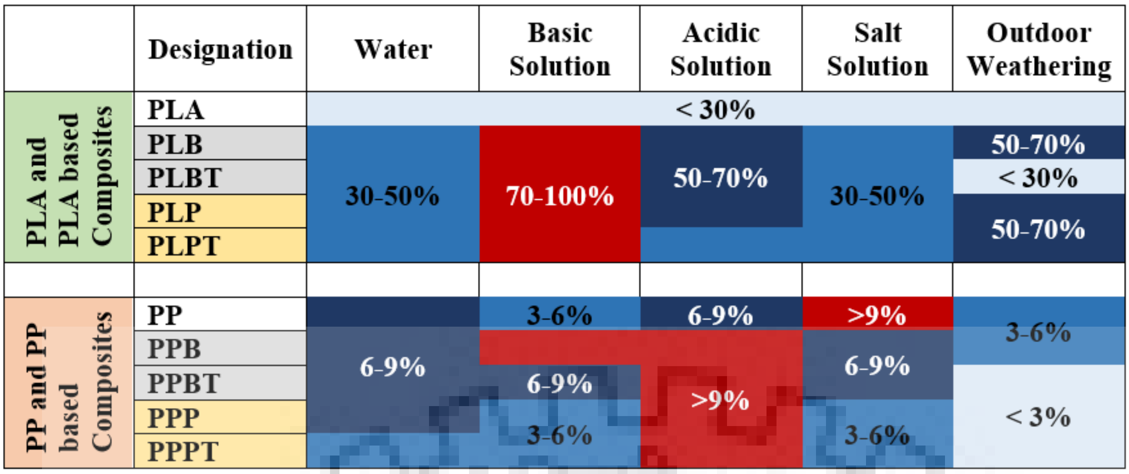
Fig. 6. 2 Variation in weight of the neat polymers and developed composites

6.3.2 Variation in Mechanical Properties



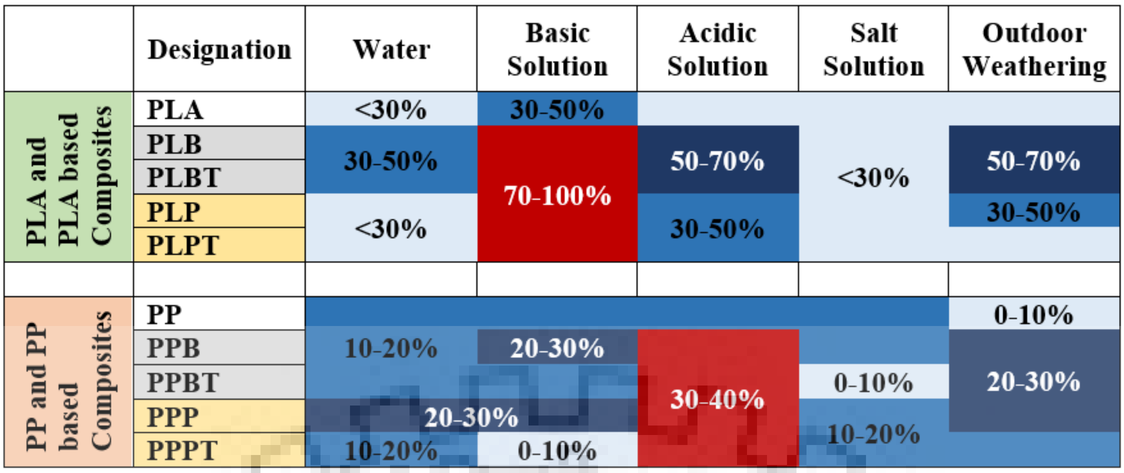
	Designation	Water	Basic Solution	Acidic Solution	Salt Solution	Outdoor Weathering
PLA and PLA based Composites	PLA	<30%				
	PLB	30-50%	70-100%	50-70%	30-50%	50-70%
	PLBT					
	PLP					
	PLPT				<30%	
PP and PP based Composites	PP		<3%			<3%
	PPB	3-6%		6-9%		
	PPBT				3-6%	
	PPP			3-6%		
	PPPT			6-9%		

Fig. 6. 3 Reduction in tensile strength of the neat polymers and developed composites



	Designation	Water	Basic Solution	Acidic Solution	Salt Solution	Outdoor Weathering
PLA and PLA based Composites	**PLA**	< 30%				
	PLB	30-50%	70-100%	50-70%	30-50%	50-70%
	PLBT					< 30%
	PLP					50-70%
	PLPT					
PP and PP based Composites	**PP**	6-9%	3-6%	6-9%	>9%	3-6%
	PPB			>9%	6-9%	
	PPBT		6-9%			< 3%
	PPP		3-6%		3-6%	
	PPPT					

Fig. 6. 4 Reduction in flexural strength of the neat polymers and developed composites



	Designation	Water	Basic Solution	Acidic Solution	Salt Solution	Outdoor Weathering
PLA and PLA based Composites	PLA	<30%	30-50%		<30%	
	PLB	30-50%	70-100%	50-70%		50-70%
	PLBT					
	PLP	<30%		30-50%		30-50%
	PLPT					
PP and PP based Composites	PP					0-10%
	PPB	10-20%	20-30%	30-40%		20-30%
	PPBT				0-10%	
	PPP	20-30%			10-20%	
	PPPT	10-20%	0-10%			

Fig. 6. 5 Reduction in impact strength of the neat polymers and developed composites

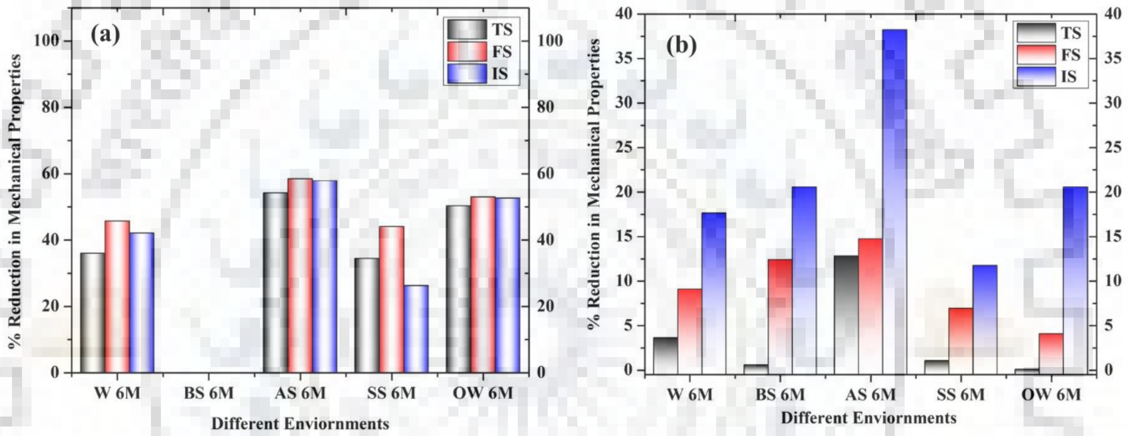


Fig. 6. 6 Trend of reduction in mechanical properties of untreated banana fiber reinforced (a) PLA and (b) PP based composites

6.3.3 XRD Analysis

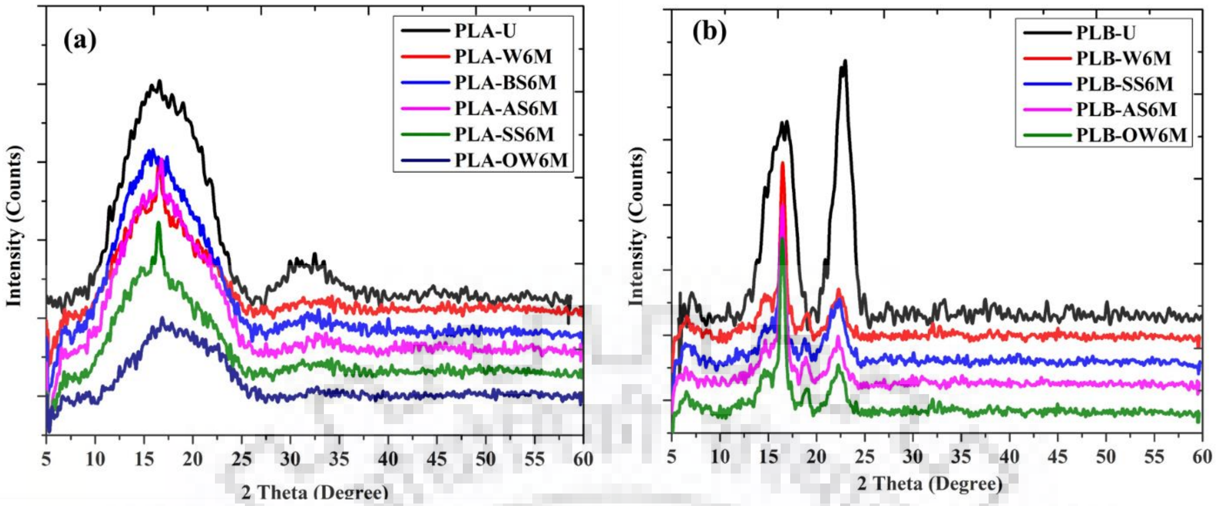


Fig. 6. 7 XRD pattern of the (a) neat PLA and (b) PLB composites before and after 6 months of exposure

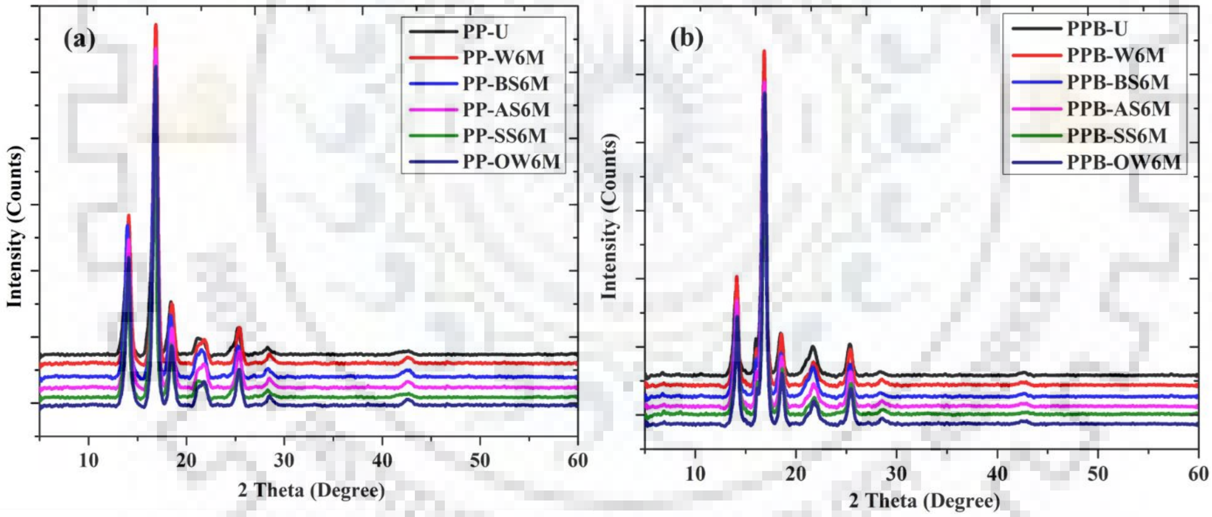


Fig. 6. 8 XRD pattern of the (a) neat PP and (b) PPB composites before and after 6 months of exposure

6.3.4 Morphological Examination

6.3.4.1 Scanning Electron Microscope Examination

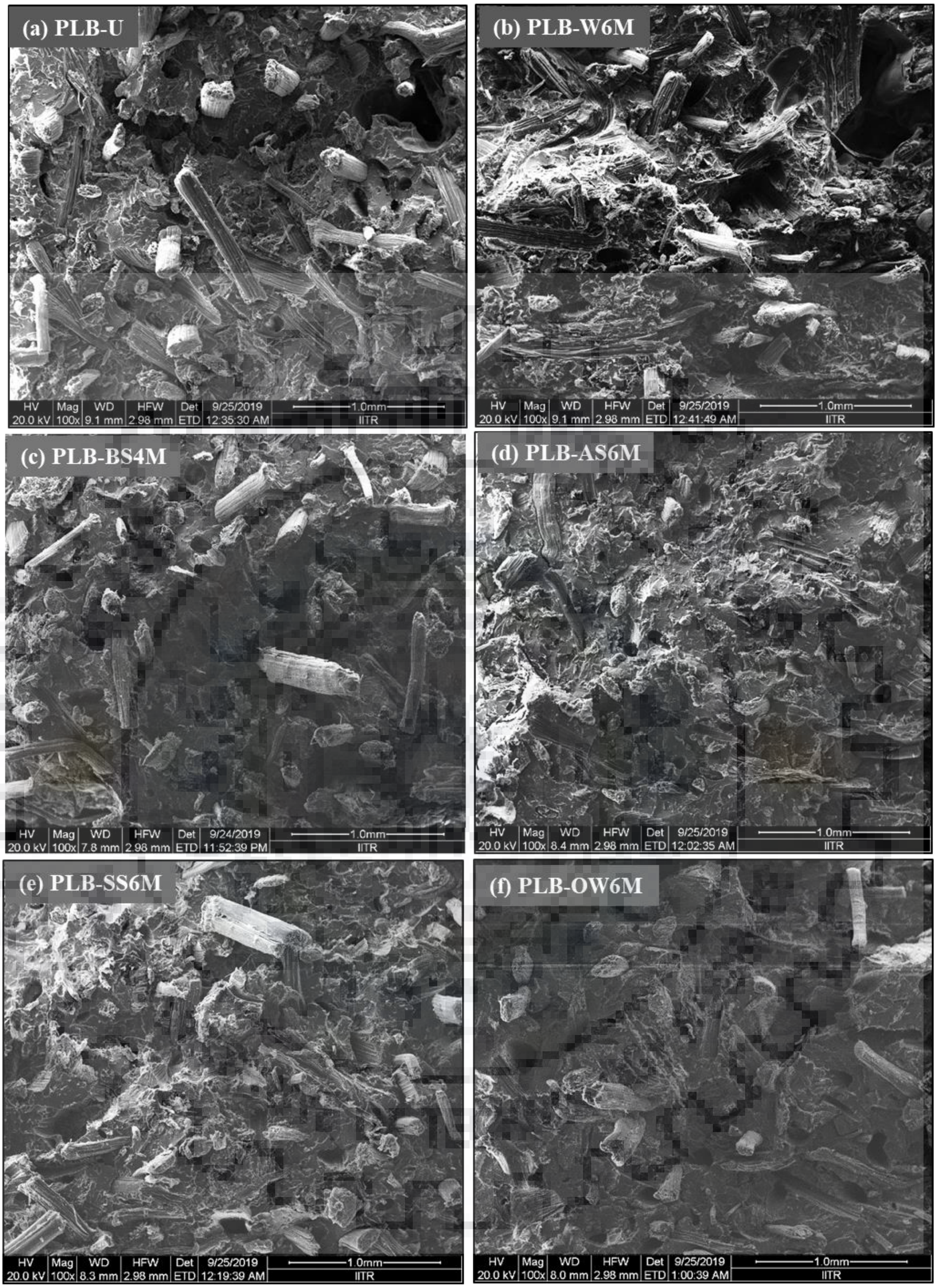


Fig. 6. 9 Fractograph of PLB composites before and after 6 months (4 months in case of basic solution) of exposure

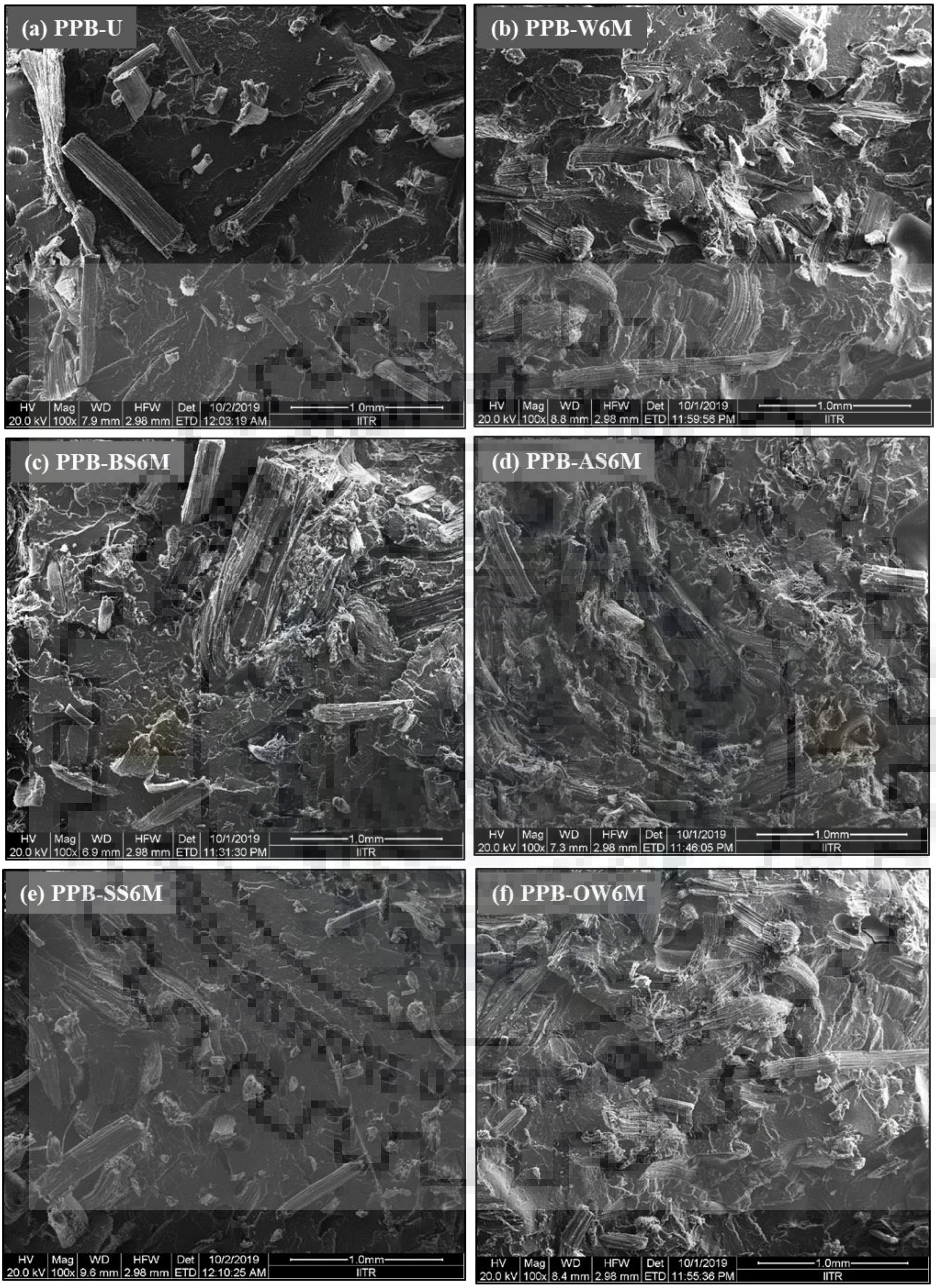


Fig. 6. 10 Fractograph of PPB composites before and after 6 months of exposure

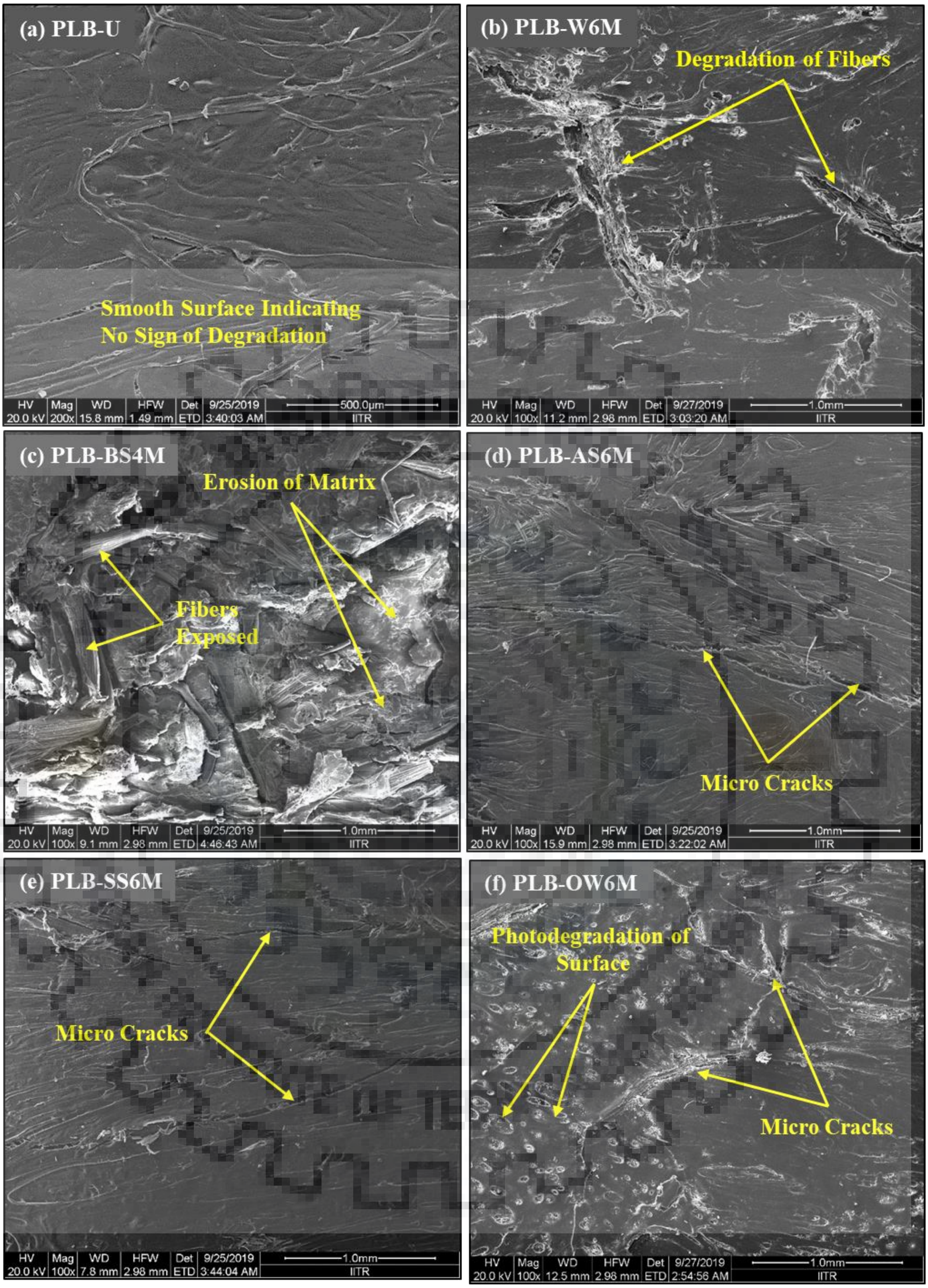


Fig. 6. 11 SEM images of surface of PLB composites before and after 6 months (4 months in case of basic solution) of exposure

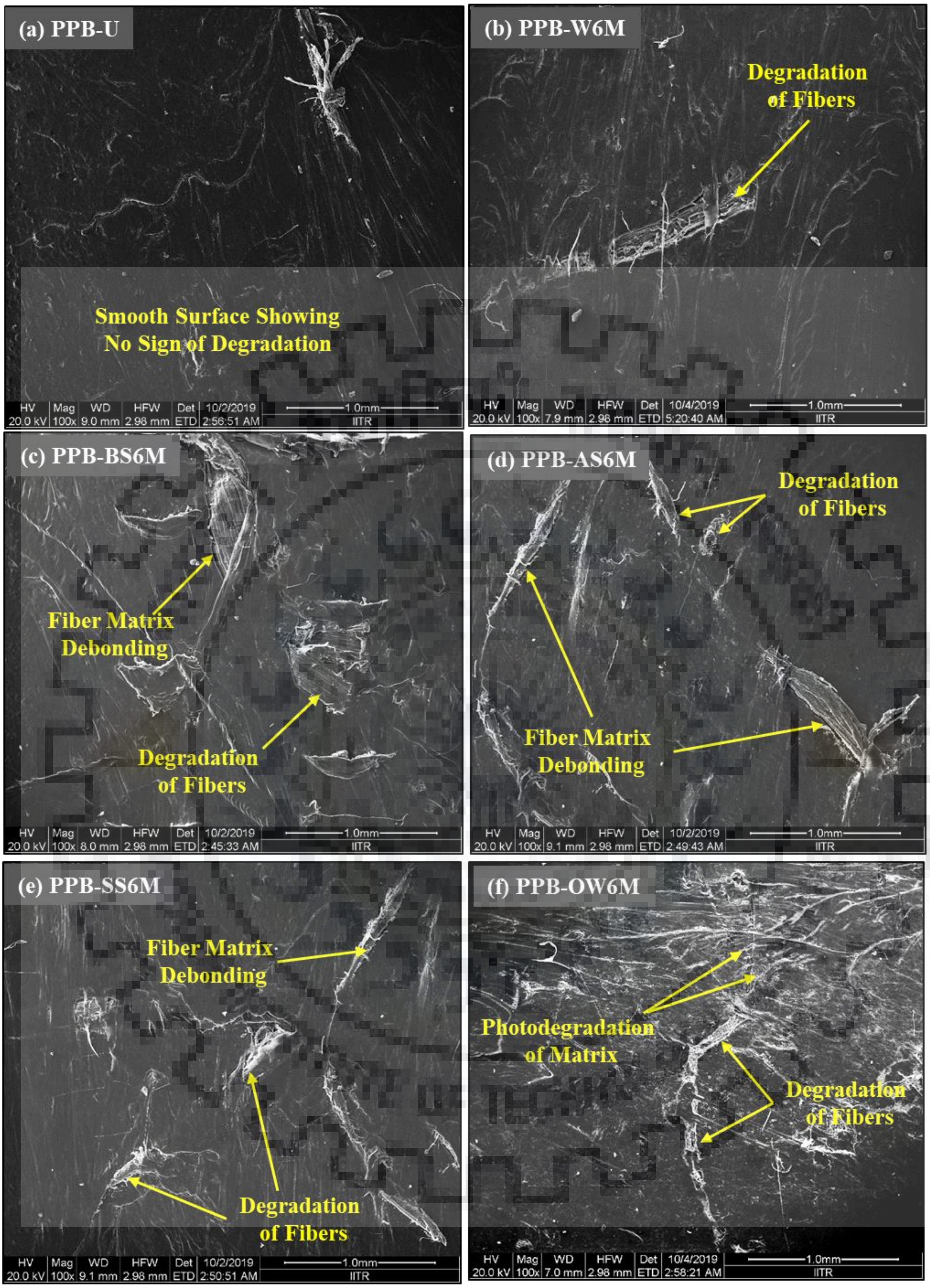


Fig. 6. 12 SEM images of surface of PPB composites before and after 6 months of exposure

6.3.4.2 Stereo Microscope Examination

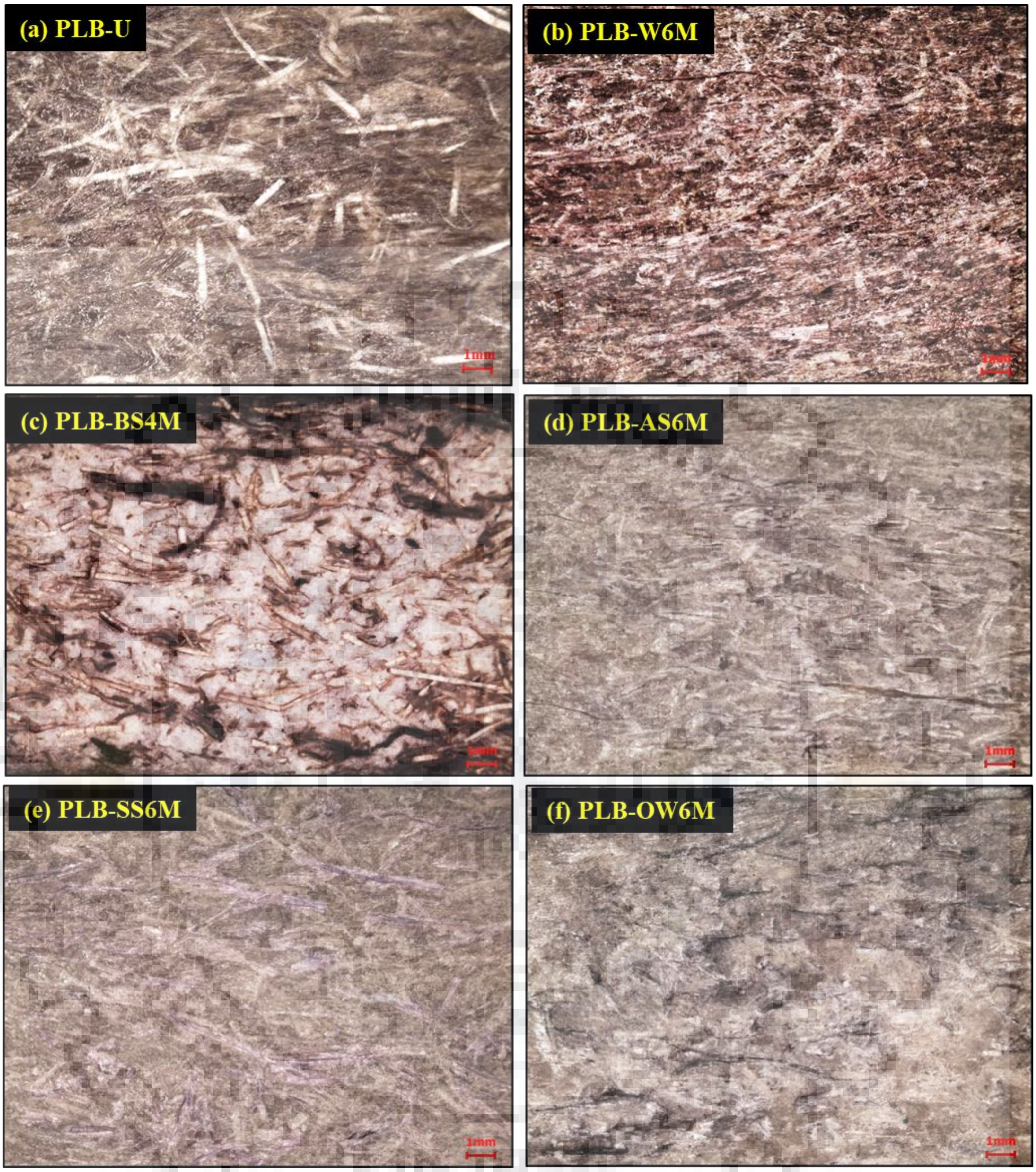


Fig. 6. 13 SM images of surface of PLB composites before and after 6 months (4 months in case of basic solution) of exposure

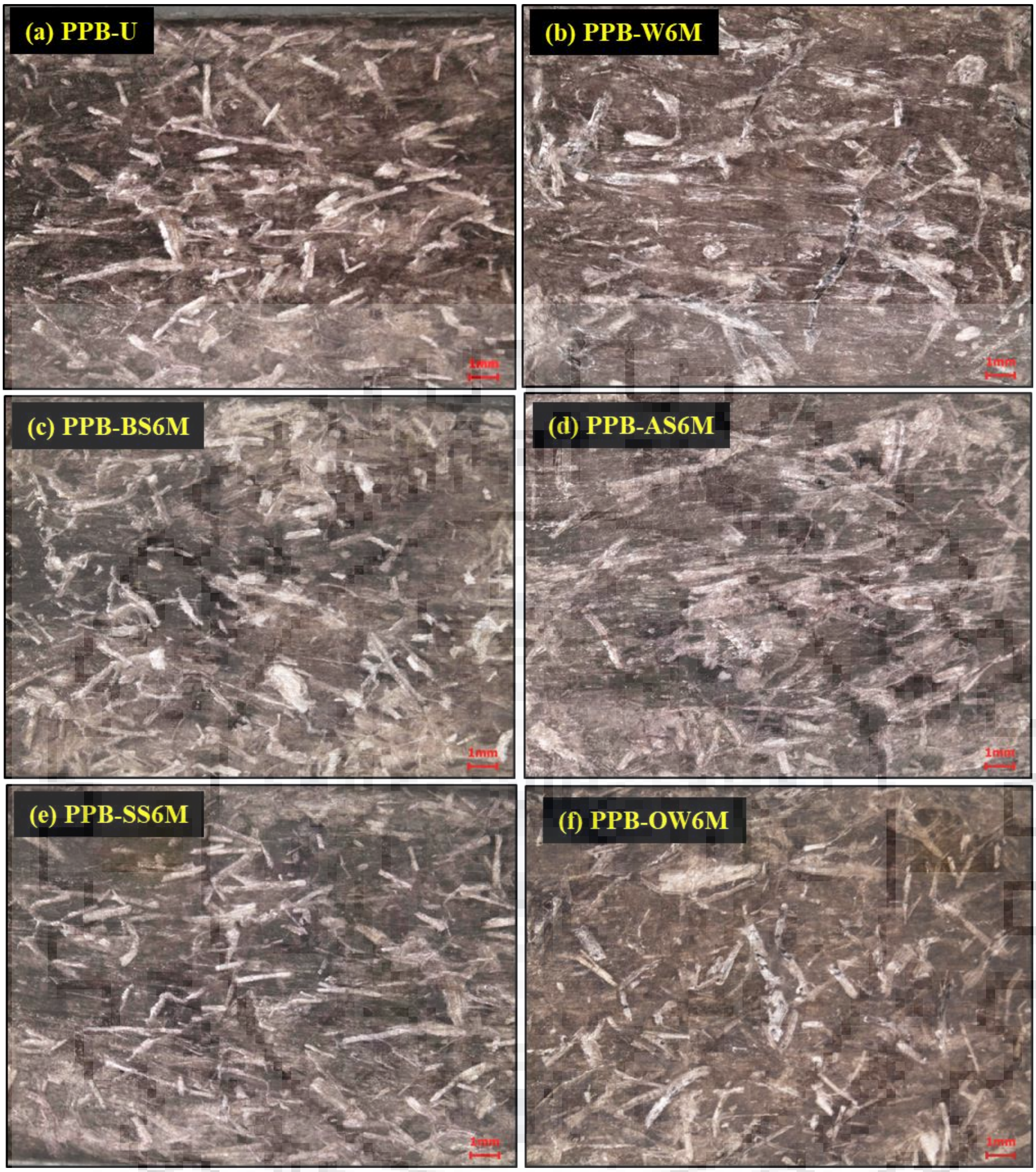


Fig. 6. 14 SM images of surface of PPB composites before and after 6 months of exposure

CHAPTER SUMMARY

- The environmental aging behavior of the developed composites has been performed in various environments (tap water, 5% NaOH solution, 5% H_2SO_4 solution, 5% NaCl solution and outdoor weather).
- The composite specimens were exposed to these environments for a period of 6 months with an analysis interval of 2 months.

- The effect of environmental aging on the behavior of the developed composites has been assessed in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.
- The effect of chemical treatment on the environmental aging of the composites has also been investigated.
- The SEM and SM examination was conducted to examine the change in variation of surface morphology of the composites.
- The SEM examination was also conducted to investigate the mode of fracture of the tensile tested specimens.

The next chapter presents degradation behavior of the natural fiber reinforced PP and PLA based composites

CHAPTER 7

DEGRADATION BEHAVIOR OF THE NATURAL FIBER REINFORCED PP AND PLA BASED COMPOSITES

In the current experimental investigation, the degradation behavior of the neat polymers and developed composites was analyzed in different mediums (cow manure, organic compost and farmland soil) for a period of 6 months with an analysis interval of 2 months. The degradation behavior was investigated in terms of variation in weight, mechanical properties and crystallinity as well as the change in morphology

7.1 INTRODUCTION

7.2 EXPERIMENTAL DETAILS

The degradation behavior of the developed composites has been experimentally investigated as depicted in Fig. 7.1.

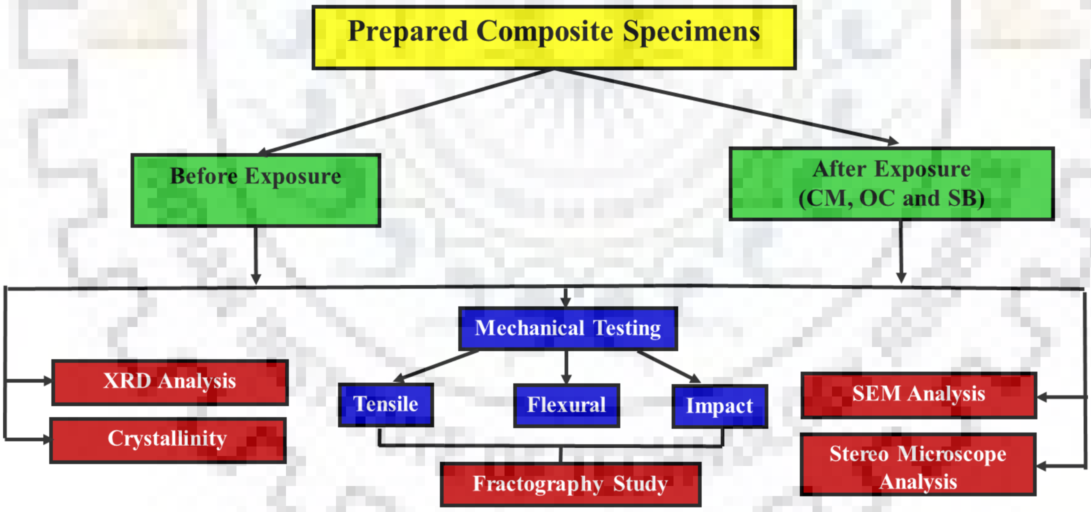
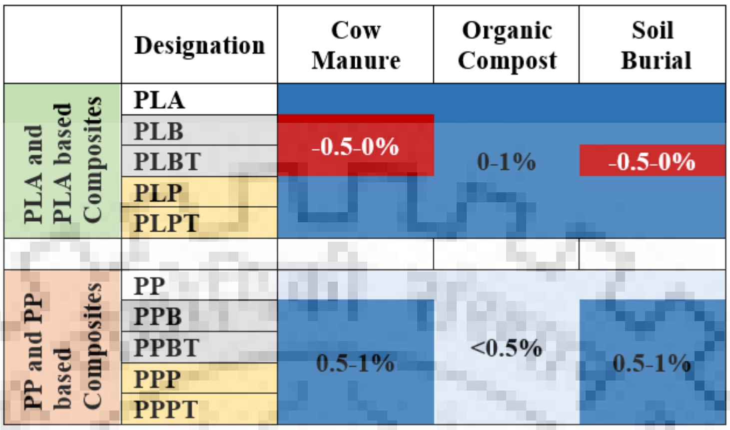


Fig. 7. 1 Flow diagram of the work plan

7.3 RESULTS AND DISCUSSION

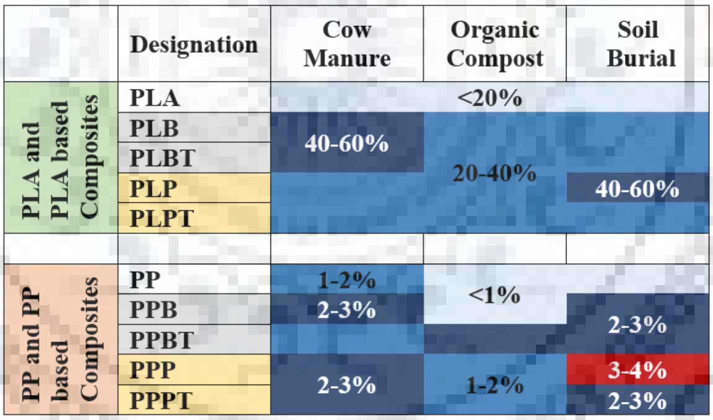
7.3.1 Variation in Weight



	Designation	Cow Manure	Organic Compost	Soil Burial
PLA and PLA based Composites	PLA			
	PLB	-0.5-0%	0-1%	
	PLBT			-0.5-0%
	PLP			
	PLPT			
PP and PP based Composites	PP		<0.5%	
	PPB	0.5-1%		0.5-1%
	PPBT			
	PPP			
	PPPT			

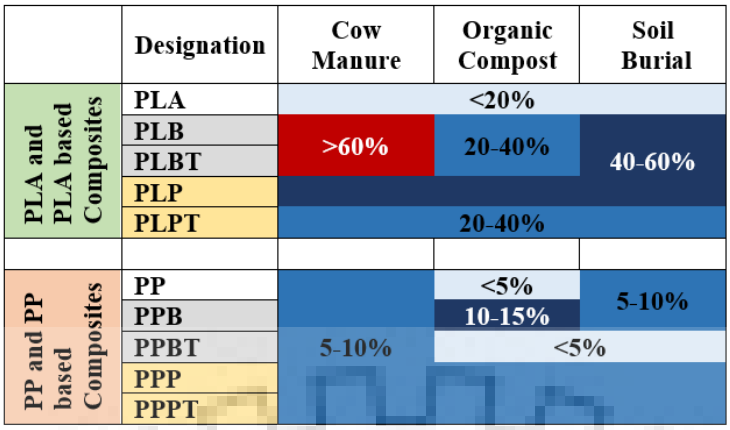
Fig. 7. 2 Variation in weight of the neat polymers and developed composites

7.3.2 Variation in Mechanical Properties



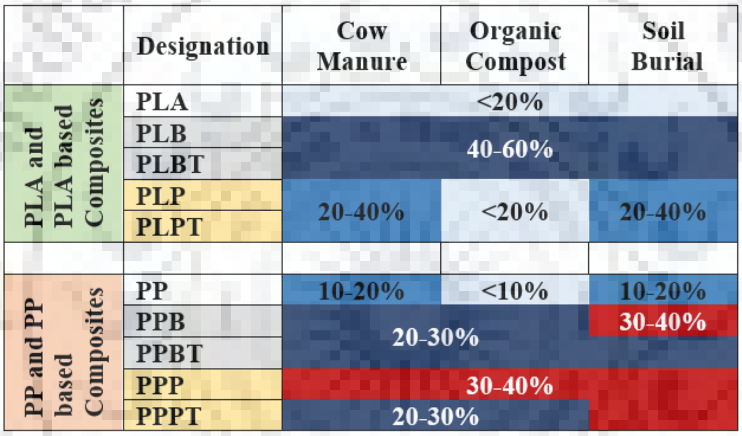
	Designation	Cow Manure	Organic Compost	Soil Burial
PLA and PLA based Composites	PLA	<20%	<20%	<20%
	PLB	40-60%	20-40%	
	PLBT			
	PLP			40-60%
	PLPT			
PP and PP based Composites	PP	1-2%	<1%	
	PPB	2-3%		2-3%
	PPBT			
	PPP	2-3%	1-2%	3-4%
	PPPT			2-3%

Fig. 7. 3 Reduction in tensile strength of the neat polymers and developed composites



	Designation	Cow Manure	Organic Compost	Soil Burial
PLA and PLA based Composites	PLA	<20%		
	PLB	>60%	20-40%	40-60%
	PLBT			
	PLP			
	PLPT	20-40%		
PP and PP based Composites	PP	5-10%	<5%	5-10%
	PPB		10-15%	
	PPBT		<5%	
	PPP			
	PPPT			

Fig. 7. 4 Reduction in flexural strength of the neat polymers and developed composites



	Designation	Cow Manure	Organic Compost	Soil Burial
PLA and PLA based Composites	PLA	<20%		
	PLB	40-60%		
	PLBT			
	PLP	20-40%	<20%	20-40%
	PLPT			
PP and PP based Composites	PP	10-20%	<10%	10-20%
	PPB	20-30%		30-40%
	PPBT			
	PPP	30-40%		
	PPPT	20-30%		

Fig. 7. 5 Reduction in impact strength of the neat polymers and developed composites

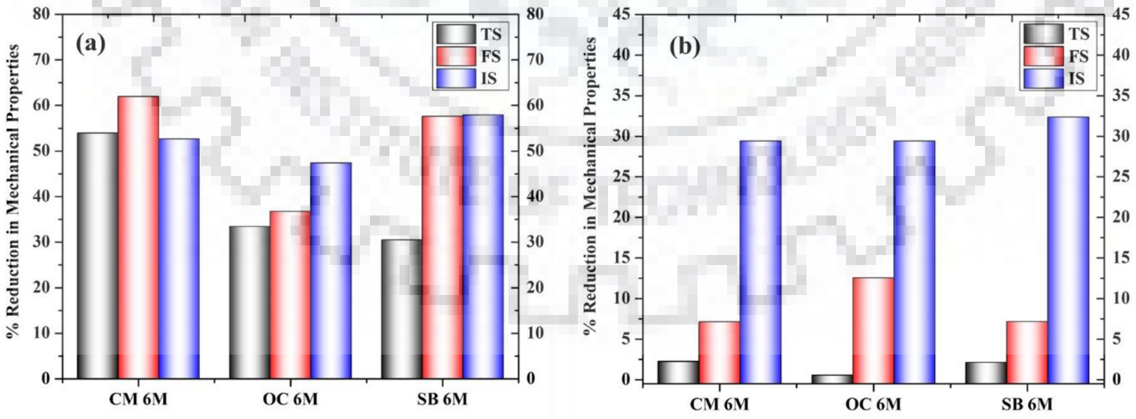


Fig. 7. 6 Trend of reduction in mechanical properties of untreated banana fiber reinforced (a) PLA and (b) PP based composites

7.3.3 XRD Analysis

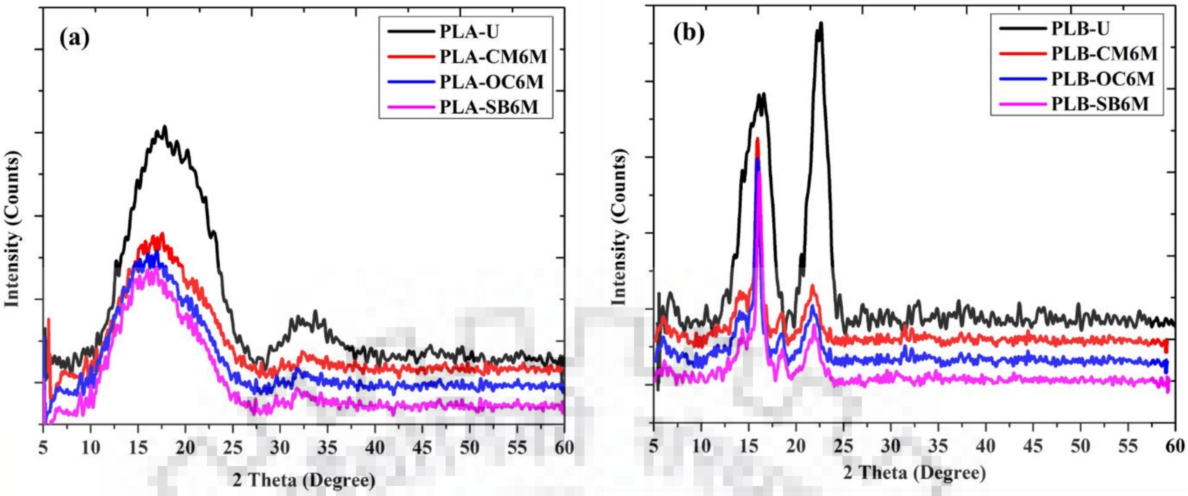


Fig. 7. 7 XRD pattern of the (a) neat PLA and (b) PLB composites before and after 6 months of exposure

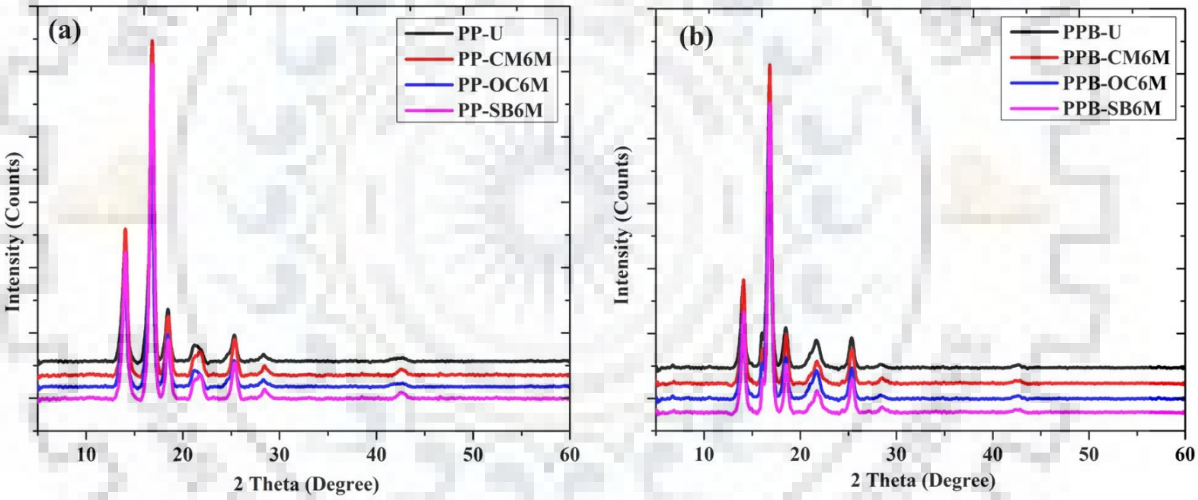


Fig. 7. 8 XRD pattern of the (a) neat PP and (b) PPB composites before and after 6 months of exposure

7.3.4 Morphological Examination

7.3.4.1 Scanning Electron Microscope Examination

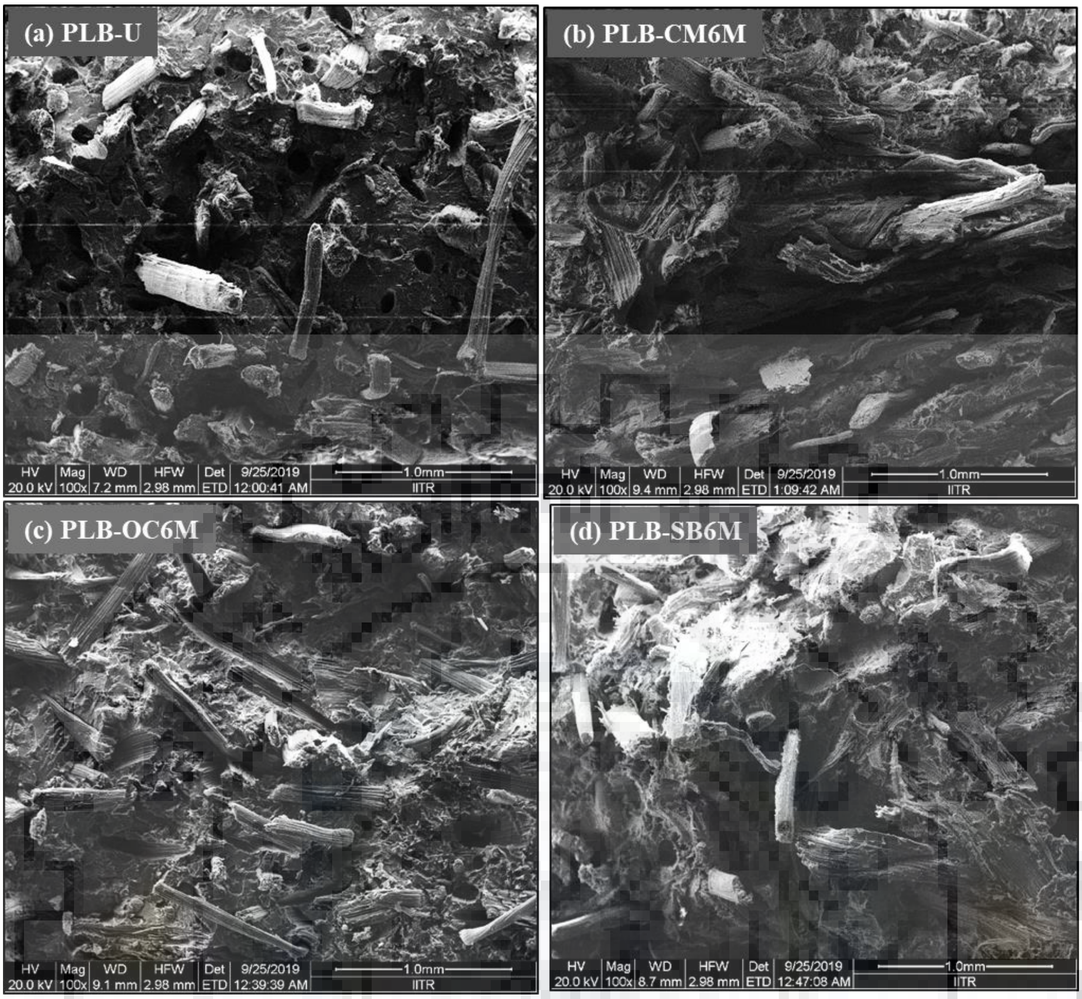


Fig. 7. 9 Fractograph of PLB composites before and after 6 months of exposure

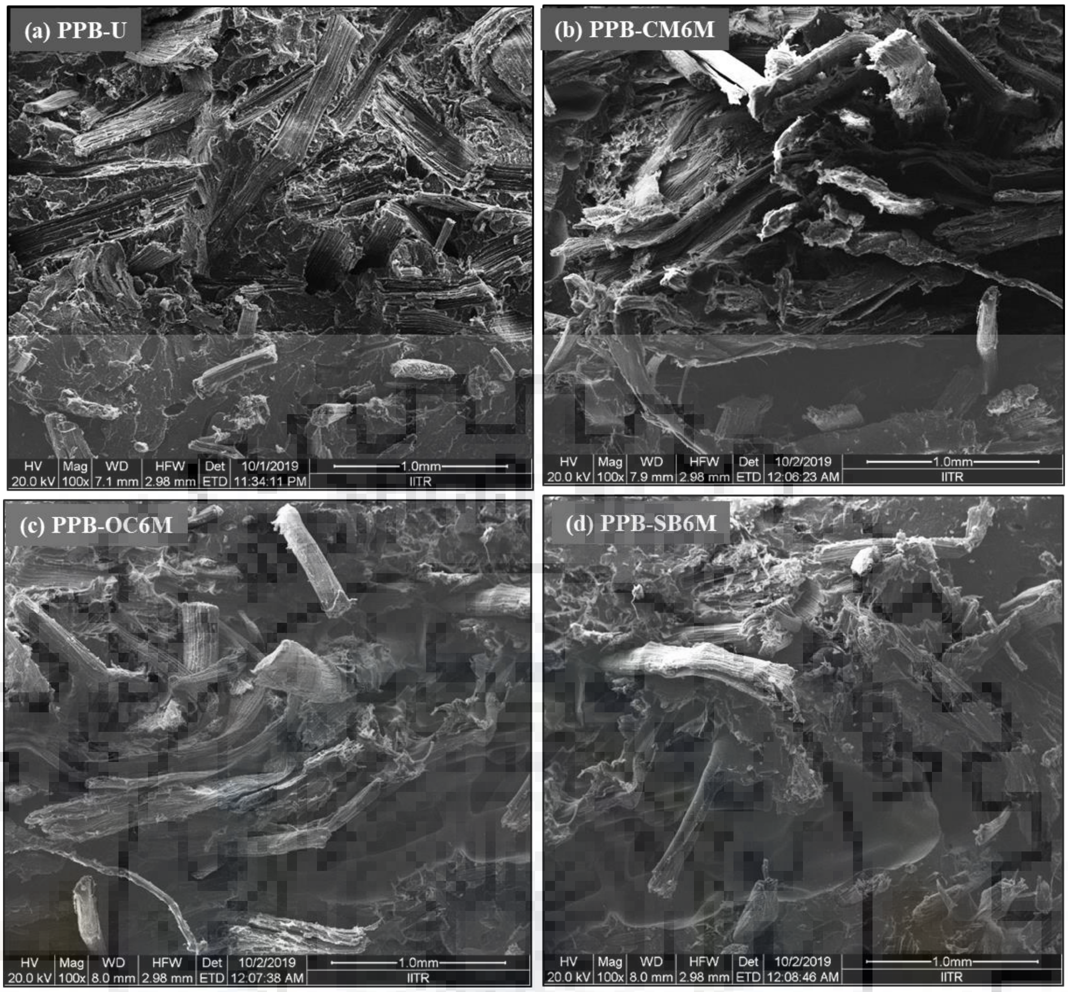


Fig. 7. 10 Fractograph of PPB composites before and after 6 months of exposure

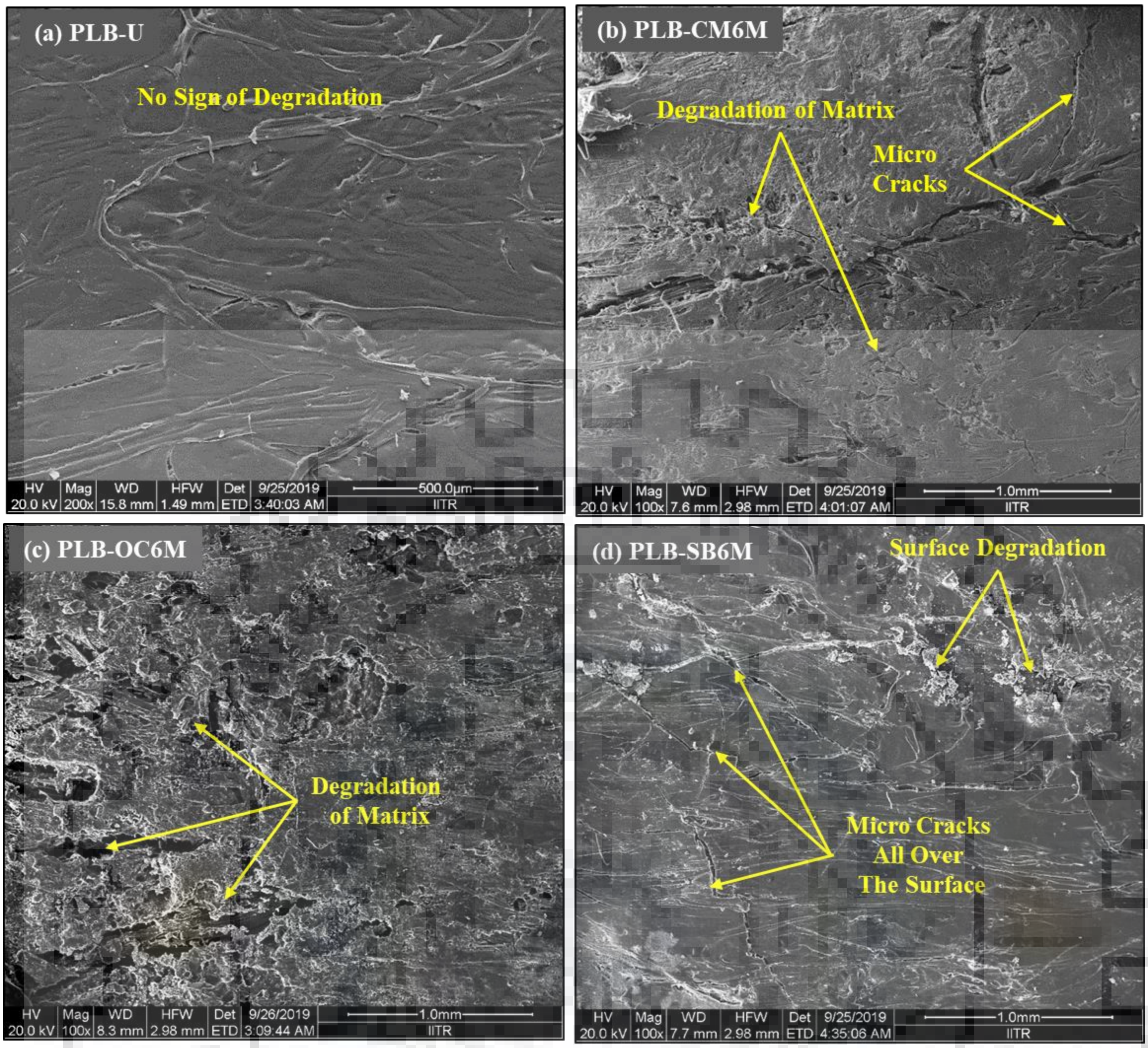


Fig. 7. 11 SEM images of surface of PLB composites before and after 6 months of exposure

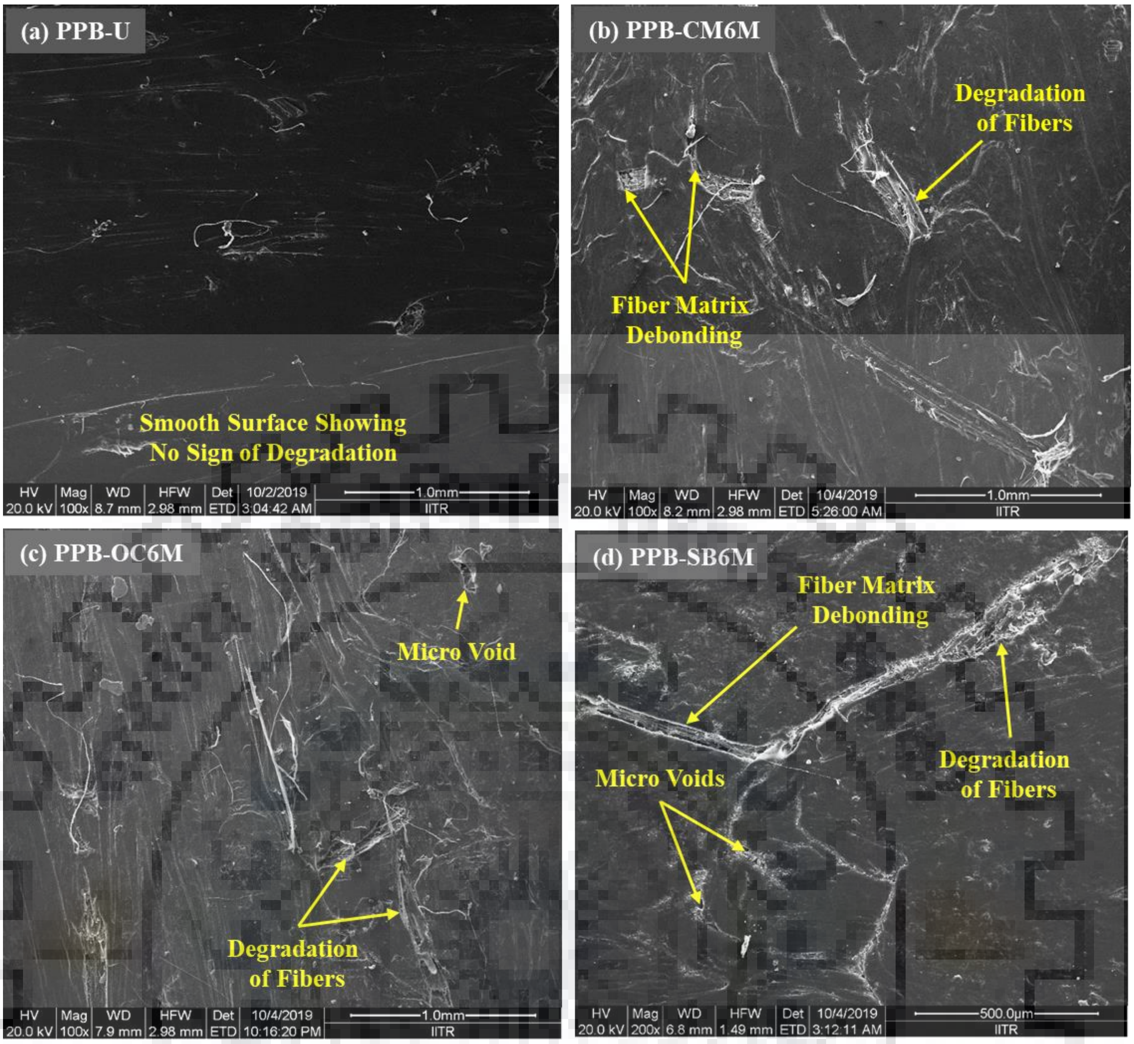


Fig. 7. 12 SEM images of surface of PPB composites before and after 6 months of exposure

7.3.4.2 Stereo Microscope Examination

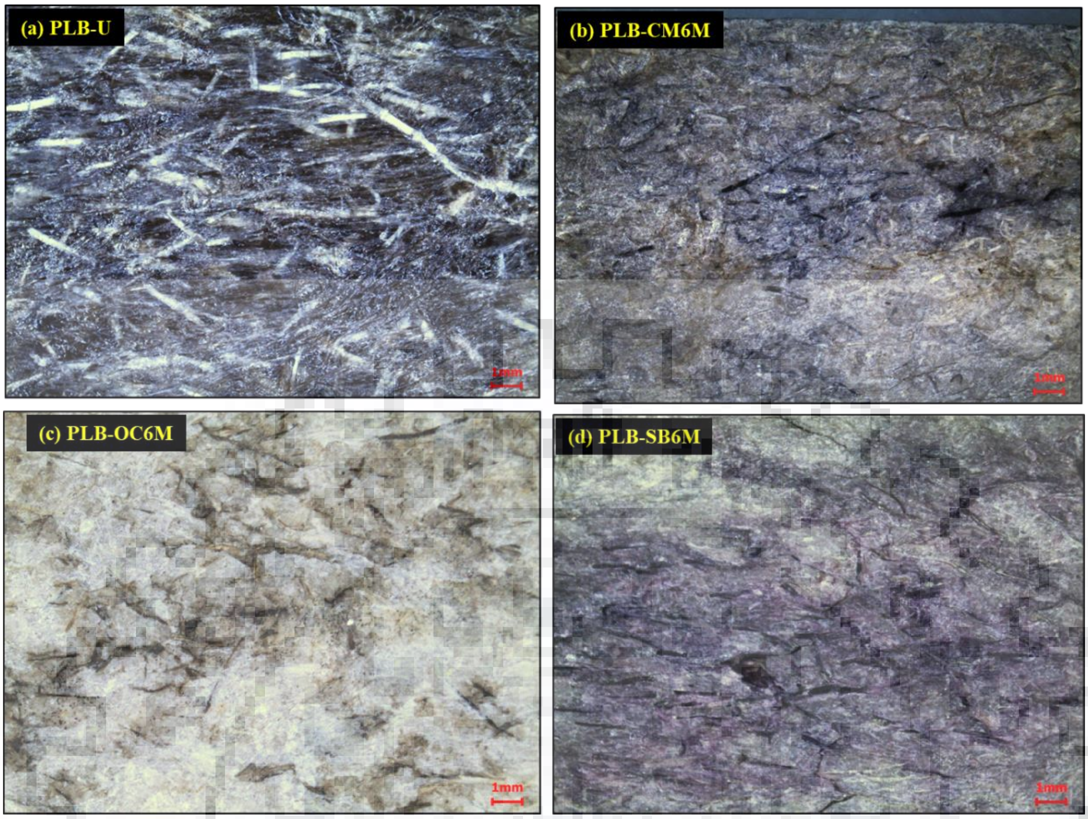


Fig. 7. 13 SM images of surface of PLB composites before and after 6 months of exposure

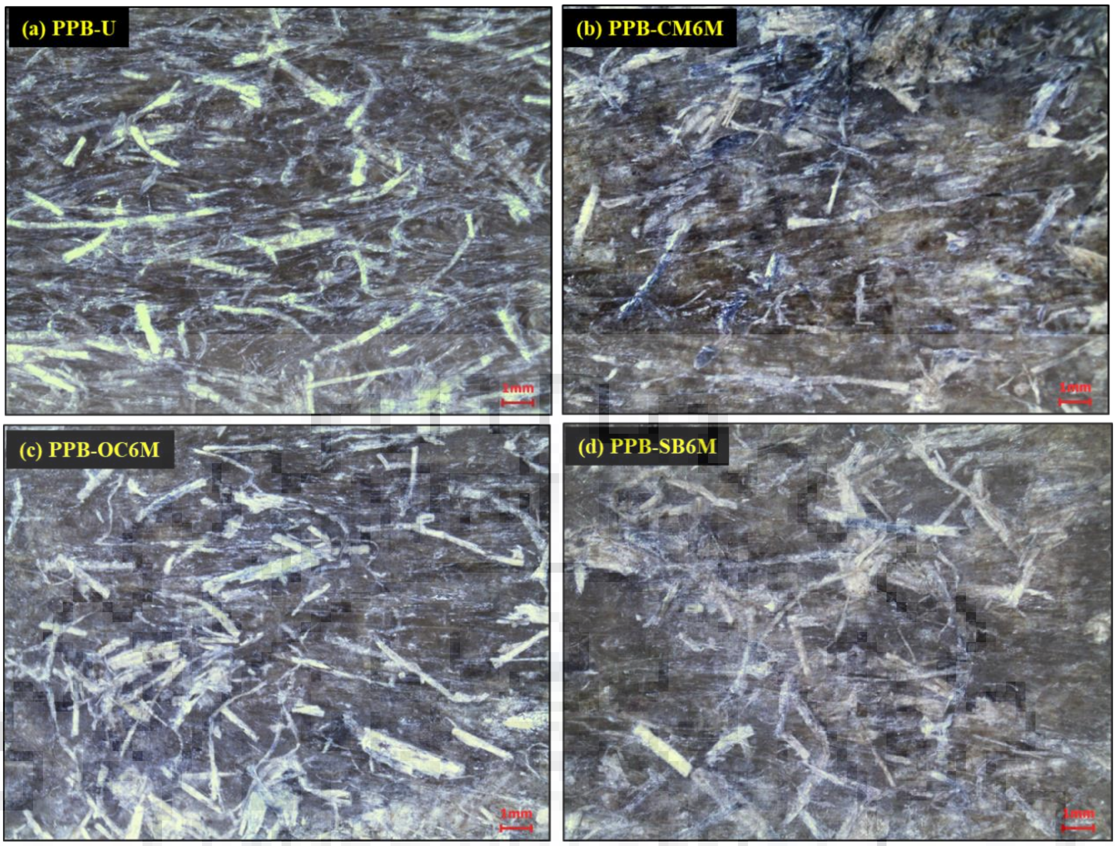


Fig. 7. 14 SM images of surface of PPB composites before and after 6 months of exposure

CHAPTER SUMMARY

- The degradation behavior of the neat polymer and developed composites was analyzed in different mediums (cow manure, organic compost and farmland soil) for a period of 6 months with an analysis interval of 2 months.
- The degradation behavior was investigated in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.
- The effect of chemical treatment on the degradation behavior of the composites has also been investigated.
- The SEM and SM examination was conducted to examine the change in variation of surface morphology of the composites.
- The SEM examination was also conducted to investigate the mode of fracture of the tensile tested specimens.

The next chapter concludes the findings of the research work. The future direction of the current research endeavor has also been outlined.

CHAPTER 8

SUMMARY AND CONCLUSIONS

This chapter concludes the findings of the research work. The future direction of the current research endeavor has also been outlined.

8.1 SUMMARY OF THE RESERCH FINDINGS

The current research endeavor gives an insight into the development and degradation behavior of the partially and fully biodegradable composites. The current research endeavor broadly comprises of four studies:

Study I: Development of Polymer Matrix Composites

- The polymer composites based on two types of natural fibers (banana and pineapple fibers) and two types of matrices (PLA and PP) were fabricated using three different processing techniques, namely direct injection molding (DIM), extrusion injection molding (EIM) and extrusion compression molding (ECM).
- The thermal and mechanical characterization as well as dynamic mechanical analysis has been performed to understand and compare the performance of the developed composites.
- The behavior of the composites has been analyzed in context of extracted fiber morphology as well as the distribution and orientation of fibers within the developed composites.
- The current investigation focuses on the feasibility of using sodium bicarbonate and borax for the treatment of banana and pineapple fibers prior to their incorporation in PP and PLA matrices. The potassium permanganate treatment was also conducted for the reference.
- The effect of varying treatment time (in case of sodium bicarbonate) and varying chemical concentration (in case of borax) on the behavior of the fibers as well the composites has been investigated.
- The effect of chemical treatments on the behavior of the fibers was investigated in terms of morphology, thermal and tensile properties of the fiber. The effect of chemical treatment on the mechanical behavior of the composites has also been investigated.

Study II: Recyclability Assessment of the Banana and Pineapple Fiber Reinforced PP and PLA based Composites

- The recyclability assessment of banana and pineapple fiber reinforced PP and PLA based composites was investigated.
- The performance of the recycled composites was investigated in terms of fiber aspect ratio, mechanical, thermal and dynamic mechanical behavior.
- The effect of recycling on the crystallinity of the developed composites has been explored.
- The effect of chemical treatment on the recycling behavior of the developed composites has also been investigated.
- The attrition of fibers in terms of reduction in length and diameter was measured by examining the fiber using stereo microscope.
- The SEM examination was conducted to investigate the mode of fracture of the tensile tested recycled composite specimens.

Study III: Environmental Aging of the Natural Fiber Reinforced PP and PLA based Composites

- The environmental aging behavior of the developed composites has been performed in various environments (tap water, 5% NaOH solution, 5% H_2SO_4 solution, 5% NaCl solution and outdoor weather).
- The composite specimens were exposed to these environments for a period of 6 months with an analysis interval of 2 months.
- The effect of environmental aging on the behavior of the developed composites has been assessed in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.
- The effect of chemical treatment on the environmental aging of the composites has also been investigated.
- The SEM and SM examination was conducted to examine the change in variation of surface morphology of the composites.
- The SEM examination was also conducted to investigate the mode of fracture of the tensile tested specimens.

Study IV: Degradation Behavior of the Natural Fiber Reinforced PP and PLA based Composites

- The degradation behavior of the neat polymer and developed composites was analyzed in different mediums (cow manure, organic compost and farmland soil) for a period of 6 months with an analysis interval of 2 months.
- The degradation behavior was investigated in terms of change in color, variation in weight, mechanical properties and crystallinity as well as the change in morphology.
- The effect of chemical treatment on the degradation behavior of the composites has also been investigated.
- The SEM and SM examination was conducted to examine the change in variation of surface morphology of the composites.
- The SEM examination was also conducted to investigate the mode of fracture of the tensile tested specimens.

8.2 CONCLUSIONS

The key conclusions that can be drawn from the current research endeavor are:

8.2.1 Development of Polymer Matrix Composites

- The processing routes have a substantial influence on the distribution, orientation and attrition of fibers as well as the crystallinity, mechanical properties and dynamic mechanical properties of the developed composites.
- Stereo microscope analysis revealed an improvement in the distribution and orientation of fibers during EIM. It also revealed that the fibers near the surface of the mold, aligned in the flow direction whereas aligned randomly at the core region.
- It also exhibited that the orientation of fibers in the flow direction increases with an increase in the viscosity of the melt.
- As compared to DIM and ECM, the crystallinity, as well as the tensile and flexural properties of composites fabricated by EIM were found to be superior. The storage and loss modulus of composites fabricated by EIM was found to be maximum.
- The thermal stability of the fiber improved after chemical treatment. The thermal stability of the fibers increases with an increase in the chemical concentration (in case of borax treatment) up to 15% and treatment time (in case of sodium bicarbonate treatment) up to 96 h.
- In the case of borax treatment, an increment in the strength and modulus of the fiber treated with 5wt.% borax solution (TPF-B5) was observed.

- In the case of sodium bicarbonate treatment, the tensile properties of the fiber treated for the period of 72h (TPF-72) were found to be maximum.
- The mechanical properties of the composites incorporating fibers treated with 5% borax solution were found to be higher as compared to all other developed composites and selected for further investigation.

8.2.2 Recyclability Assessment of the Banana and Pineapple Fiber Reinforced PP and PLA based Composites

- The tensile and flexural properties of the recycled composites was observed to decline with every subsequent recycling stage. However, the reduction in tensile properties is marginal.
- The reduction in mechanical properties is attributed to the degradation of polymers (in case of PLA) due to chain scission and degradation of fibers due to fiber attrition.
- The crystallinity of the composites was found to increase up to 3 cycles and decrease subsequently.
- The storage and loss modulus of the composites was found to decline with every subsequent recycling stage.
- The thermal stability of the composites decreases with every subsequent recycling stages.
- The length and diameter of the fiber decreases with recycling stages.
- The fractographs of the tensile tested specimens confirmed the improvement in interfacial bonding between the fibers and matrices.

8.2.3 Environmental Aging of the Natural Fiber Reinforced PP and PLA based Composites

- The degradation of the PLA based composites was found to be maximum in basic solution. The exposed specimens dissolve completely after 6m in basic solution (i.e. 5% NaOH solution) due to hydrolysis of the PLA in alkaline medium.
- A significant reduction in tensile, flexural and impact strength of all the composites was observed in outdoor weather.
- The crystallinity of the neat PLA and PLA based composites was found to increase after exposure whereas no significant change in crystallinity of neat PP and PP based composites was observed.

- As compared to untreated fiber based composites, the degradation of the treated fiber based composites was found to be lower.
- An increase in weight of all the composite specimens (except PLA and PLA based in basic solution) was observed.

8.2.4 Degradation Behavior of the Natural Fiber Reinforced PP and PLA based Composites

- As compared to organic compost, the reduction in terms of tensile, flexural and impact strength of all the composites was found to be higher in the case of cow manure and farmland soil.
- In case of PP based composites, the maximum reduction in tensile strength even after 6 months of exposure is only 3-4% indicating the non-biodegradability of the PP.
- The crystallinity of the neat PLA and PLA based composites was found to increase after exposure whereas no significant change in crystallinity of neat PP and PP based composites was observed.
- As compared to untreated fiber based composites, the degradation of the treated fiber based composites was found to be lower.
- Marginal variation in weight of the composite specimens was observed in all the mediums.

8.3 SCOPE FOR FUTURE WORK

The current research endeavor leaves a wide scope for future investigators to explore several other aspects related to the development, recycling and degradation behavior of natural fiber based partially and fully biodegradable polymer composites. Some recommendations for future research include:

- In the present investigation, the fiber of average length 5mm was used for the development of the composites. Further studies can be performed to investigate the effect of varying fiber length on the performance of composites.
- The relationship between the distribution and orientation of fiber with the properties of the developed composites may be simulated using finite element based tools.
- The ecofriendly treatment using borax and sodium bicarbonate (in accelerated condition) can be further explored for other lignocellulosic fibers as well.

- The recycling behavior of the natural fiber based composites at the end of service life can also be explored.
- The degradation (thermal and environmental) retardant materials can be included during processing and effect of these materials can be investigated on the environmental aging behavior of the natural fiber based composites in other environmental conditions.
- The degradation behavior of the natural fiber based composites can be investigated in the industrial composting conditions.
- The effect of temperature (above glass transition) on the degradation behavior of the natural fiber based composites can also be explored.
- The commercial viability of the PLA based composites can be explored.

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LIST OF PUBLICATIONS

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[1] **U. K. Komal,** M. K. Lila and I. Singh “PLA/Banana Fiber Based Sustainable Biocomposites: A Manufacturing Perspective” *Composites Part B: Engineering* **(Accepted). (IF: 6.864)**

[2] **U. K. Komal**, V. Verma, T. Ashwani, N. Verma and I. Singh “Effect of Chemical Treatment on Thermal, Mechanical and Degradation Behavior of Banana Fiber Reinforced Polymer Composites” *Journal of Natural Fibers*, DOI: 10.1080/15440478.2018.1550461. **(IF: 1.252)**

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[5] M. K. Lila, **U. K. Komal** and I. Singh "Extraction and Characterization of Munja Fibers and Its Reinforcement Potential in Biocomposites".

[6] M. K. Lila, **U. K. Komal** and I. Singh "Effect of Thermal Post Processing on Bagasse Fiber reinforced PP Composites".

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