

**DEVELOPMENT AND CHARACTERIZATION
OF COMPRESSION MOLDED
FLAX FIBER-REINFORCED
BIOCOMPOSITES**

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By

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ABSTRACT

Flax fibers are often used as reinforcement for thermoset and thermoplastic to produce biocomposite products. These products exhibit numerous advantages such as good mechanical properties, low density, and biodegradability. Thermoplastics are usually reinforced with flax fiber using injection molding technology and limited research has been done on compression molded thermoplastic biocomposite. Therefore, commercial thermoplastic high density polyethylene (HDPE) and polypropylene (PP) were selected for developing compression molded flax reinforced biocomposites in this research project. The main goal of this research was to develop compression molded biocomposite board using Saskatchewan flax fiber and investigate the effect of flax fiber and processing parameters (molding temperature and molding pressure) on the properties of biocomposite.

The fiber was cleaned and chemically treated with alkaline and silane solution that modified the fiber surface. Chemical treatments significantly increased the mechanical properties due to better fiber-polymer interfacial adhesion and also reduced the water absorption characteristics. The silane treatment showed better results than alkaline treatment. Differential scanning calorimetry (DSC) test and scanning electron microscopy (SEM) test were performed to study the thermal and morphological properties of the untreated and chemically treated flax fiber. Flax fiber and thermoplastic resin was mixed using a single-screw extruder to ensure homogenous mixing. HDPE- and PP-

based biocomposites were developed through compression molding with three different pretreated flax fiber (untreated, alkaline, silane treated fiber), three levels of fiber content (10%, 20%, and 30% by wt), two levels of molding temperature (150°C, 175°C for HDPE and 175°C, 195°C for PP) and two levels of molding pressure (6.89 and 10.34 MPa for both HDPE and PP).

Increase in fiber content increased composite color index, density, water absorption, tensile strength, Young's modulus, bending strength, and flexural modulus. However for the HDPE composites, tensile and bending strength decreased after 20% flax fiber loading. For the PP composites the, tensile and bending strength decreased after 10% flax fiber loading. Analysis of variance (ANOVA) was performed to quantitatively show the significant effects of the process variables (molding temperature, pressure, and fiber content) and their interactions on the response variables (physical and mechanical properties of biocomposites). The duncan multiple range test (DMRT) was also performed to compare the treatment means. Superposition surface methodology was adapted for both HDPE and PP composites to determine the following optimum values of process variables: for HDPE biocomposites, fiber content = 13%, molding temperature = 155°C, molding pressure = 8.62 MPa; for PP biocomposites, fiber content = 11%, molding temperature= 184°C and molding pressure = 8.27 MPa.

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DEDICATION

*I dedicate this thesis to my loving family who encouraged me
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1. INTRODUCTION

In today's world energy scenario, petroleum resources are becoming depleted and demand is increasing along with increase in their hazardous effect on the environment. Therefore, there is a growing awareness for an integrated approach considering global environmental factors, sustainability, industrial ecology, and engineering for developing alternative materials and products. Biocomposites are one of the new alternative structural materials that are developed by combining natural fiber and petrochemical based polymers. The more usage of natural fiber makes the product less hazardous and reduces usage of petroleum-based polymers.

Natural fibers are gaining importance in the manufacture of biocomposites for various applications due to their desirable properties (Bledski et al. 1999). Currently the major thrust of on-going research in the development of biocomposite is on flax, hemp, jute, coir, palm, and other natural fibers. The properties of natural fiber depend on factors like fiber length, maturity as well as processing methods adopted for the extraction of fibers. Properties such as density, electrical resistivity, ultimate tensile strength, Young's modulus, and many others, are related to the internal structure and chemical composition of fibers (Mohanty et al. 2001; Reddy and Yan 2005). Flax is considered to be one of the strongest and widely available bast fibers in Canada. In recent years, considerable interest has been developed in natural fiber for reinforcing different thermoplastics. A major portion of the biocomposite market is dominated by

automotive industry for making interior parts and bumpers in Europe. It is also now being used in food packaging materials and pharmaceutical products (Bledski et al. 1999). Flax has lower density than the glass fiber and has comparable tensile strength, therefore it has the potential to replace synthetic fiber (Joffe et al. 2003).

Since 1994, Canada has been the world's leading producer and exporter of oilseed flax (Prairie flax products Inc. 2007). The total acreage under flax production was 805,000 hectares across Canada in 2006-07 which reduced to 528,000 hectares in 2007-2008 (Agriculture and agri-food Canada 2008). This decrease in flax production was due to the increase in canola acreage because of increasing price and strong future prices of canola whereas flax price has been flat. To enhance the value of the flax crop, efforts are needed to develop value-added products from flax crop residues/ flax straw and fiber. More than half of all Canadian flax is produced in Saskatchewan, with the remainder grown in Manitoba and Alberta. Overall in the Canadian prairie provinces, the amount of potential salvageable oilseed flax straw is 500,000 to 1,000,000 tonnes annually (Flax council of Canada 2008). Saskatchewan has largest area planted to oilseed flax, regularly exceeding 400,000 hectares. But there are only three fiber processing plants in Saskatchewan and Manitoba which process only part of the available straw and not a single industry is engaged in processing high quality flax-based commercial products. Thus, flax straw has been burned by most of the farmers across the prairies because it does not decompose easily. Hence,

there is research needed for developing value-added flax fiber and straw biocomposites.

Since the last decade, thermoplastics and thermosets have been used to develop natural-fiber based composites for the European automotive industry in products such as door panels, seat backs, headliners, package trays, dashboards, and trunk liners. This trend has now reached North America. Among the different molding techniques, compression molding is one of the most widely used simple process for composite manufacturing. Some of the advantages of compression molding are there is very little throw away material, simple mold required, and best suitable for large parts. However, mostly thermoset materials are being used to develop biocomposite by compression molding technique and little work has been done with thermoplastics with natural fiber. Due to dwindling petroleum resources and problem of their recyclability, the emphasis is more on thermoplastic instead of thermoset material. There is no detailed analysis available on development of compression molded flax-reinforced thermoplastic biocomposite and the effect of compression molding parameters on the mechanical properties of flax fiber-based thermoplastic composites.

In this research, Saskatchewan-grown flax fiber and basic molding technology compression molding is used to develop a value-added product. For developing high quality flax fiber biocomposite, fiber percentage for reinforcing the thermoplastic polymer resins (high density polyethylene and polypropylene) would be optimized along with processing conditions. The compression molded green board developed at optimal or best condition and material could be used

for automotive parts, construction industries and other commercial applications. This will help in developing new industries and provide some direction for value-added utilization and further research on Saskatchewan flax/ Canadian flax.

1.1 Objectives

The overall goal of this research is to develop compression molded green board using Saskatchewan flax fiber and streamline the manufacturing process with optimal processing condition and fiber percentage. To achieve the main goal the following specific objectives were set for the research:

1. to determine the influence of two different chemical treatments (alkaline & silane) on fiber morphology and the final compression molded biocomposites product;
2. to choose appropriate polymer (HDPE and PP) as matrix and processing parameters (molding temperature, pressure and residence time) for developing the flax fiber reinforced biocomposites;
3. to investigate the effect of flax fiber loading on different physical and mechanical properties of compression molded biocomposites;
4. to investigate the effect of operating parameters (molding temperature and pressure) during compression molding on different physical and mechanical properties of the biocomposites;
5. to determine the optimal fiber loading, molding temperature and pressure; and

6. to characterize and compare the two different polymer resins (HDPE & PP) based flax reinforced compression molded biocomposites.

In this research, a compression molded flax fiber reinforced green board was developed and physical properties, thermal properties, and mechanical properties were determined. Literature review of flax fiber, surface modification, thermoplastic polymer and processing techniques is given in Chapter two. Chapters three presents the material used, chemical treatment, experimental design, processing techniques, and characterization tests performed to achieve the above mentioned specific objectives. Results of different physical (SEM, color, density, water absorption), thermal (DSC) and mechanical (tensile, flexural, hardness) tests are presented and discussed in Chapter four. Based on the set response variable, optimal fiber content and processing parameters (molding temperature, molding pressure) for both HDPE-and PP-based composites are also enlisted in chapter four. Chapter five concludes the thesis by summarizing the main observations based on the results discussed in preceding chapters. Some important recommendations for future studies and commercial development of the product are given in chapter six.

2. LITERATURE REVIEW

The literature on flax fiber, chemical treatments, thermoplastics, compounding and processing techniques required for understanding prior to developing a compression molded flax fiber reinforced biocomposites are reviewed and presented in this chapter.

2.1 Flax Fiber

Flax (*Linum usitatissimum*) is one of the oldest fiber grown in North America. Flax is a dicotyledon which belongs to the linacea family. This plant is mainly used for textiles, paper, composite products, and omega-3 fatty acid. It is used in the manufacture of fine linens (Edwards et al. 1997). The by-product after extracting oil from seed is used as animal feed. The principal constituent of flax fibers is cellulose, with smaller amounts of hemicellulose, lignin, pectins, oils, and waxes. The cellulose, hemicellulose, and pectins are found in the cell walls. The proportion of these components in a fiber depends on the age, source of the fiber, and the extraction conditions (Hearle et al. 1963). Flax is a plant with a single stem nearly one meter in height and its diameter at the base varies between 1 to 2 mm. Flax and other natural fibers exhibit considerable variation in diameter along with the length of individual filaments (Franck 2005).

The individual (i.e., ultimate) fibers are formed in bundles that encircle the core tissue. Flax, like other bast fiber plants, also needs to undergo the process

of retting to separate the fiber from the woody cells, which is termed shive, and constitutes the major trash component of flax fibers. The word "bast" refers to the outer portion of the stem of these plants. This stringy, vascular portion comprises 10 to 40% of the mass of the stem depending upon the species of bast plant, as well as the particular variety, or cultivar, within a bast plant.

The structural components of the fibers, i.e. cellulose, hemicellulose, and lignin, influence the mechanical properties and durability of fibers. Additional characteristics include fiber strength, fiber fineness, the polymerization of the cellulose, cleanness or purity, and homogeneity of the sample also effect the mechanical properties. Plant fiber properties directly influence the physical parameters of the fiber-reinforced composites (Jahn et al. 2002).

Natural fibers have an advantage over glass fibers in that they are less expensive, abundantly available from renewable resources, and have high specific strength. Flax fiber has great potential to replace glass fiber for developing high performance composites (Joffe et al. 2003).

2.1.1 Fiber structure

In plant science, the term 'fiber' is referred to as a single cell. Fiber cells consist of primary cell wall, middle lamella, and secondary cell walls. The dimension and arrangement of unit cells in a fiber determine the structure and also influence the properties of the fibers. The dimensions of individual fiber in natural fibers are dependent on the species, maturity, and location of the fibers in the plant and also on the fiber extraction conditions (Franck 2005).

When used for applications such as textiles and paper, the length to diameter ratio (l/d) of individual cells in a fiber affects the flexibility and resistance to rupture of the fibers and products made from them (Reddy et al. 2005). Transversally, unit cells in all of the natural-fibers (bio-fibers) have a central hollow cavity called the lumen. The shape (round, polygonal or elliptical) and size of the lumen depends on the source of the fiber and thickness of the cell wall. The presence of the hollow lumen decreases the bulk density of the fiber and acts as an acoustic and thermal insulator. These properties make bio-fibers preferable for lightweight composites used as noise and thermal insulators in automobiles (Netravali et al. 2003). All synthetic fiber consists of long chain molecules and all fibers are oriented in varied degrees. The orientation means the alignment of long chain molecules relative to fiber axis. The degree of orientation of the fiber can be controlled (Mauer and Wechsler 1953).

2.1.2 Composition of flax fiber

Plant fibers mainly consist of cellulose, hemicelluloses, and lignin. Though apart from these, the plant fibers also consist of pectin, water solubles, moisture, fat, protein, ash, and wax. The proportion of these components in a fiber depends on the age, source of the fiber, and the extraction conditions used to obtain the fibers (Hearle et al. 1963). Table 2.1 shows the chemical composition of different plant fibers.

Cellulose is a hydrophilic glucan polymer consisting of a linear chain of 1, 4- β -bonded anhydroglucose units that contain alcoholic hydroxyl groups (Bledski

and Gassan 1999). These hydroxyl groups form intramolecular hydrogen bonds inside the macromolecule itself and among other cellulose macromolecules as well as with hydroxyl groups from the air. Therefore, all of the natural fibers are hydrophilic in nature. The chemical structure of cellulose from different natural fibers remains the same but the degree of polymerization (DP) differs. DP affects the mechanical properties of fiber significantly (Mohanty et al. 2000). Solid cellulose forms a microcrystalline structure with crystalline regions, i.e. regions of high order, and amorphous regions, i.e., regions of low order (Bledski and Gassan 1999).

Table 2.1 Chemical composition of plant fibers (Franck 2005).

	Cellulose (%)	Hemi-Cellulose (%)	Pectin (%)	Lignin (%)	Water Solubles (%)	Fat and wax (%)	Moisture (%)
Cotton	82.70	5.70	-	-	1.00	0.60	10.00
Jute	64.40	12.00	0.20	11.90	1.10	0.50	10.00
Flax	64.10	16.70	1.80	2.00	3.90	1.50	10.00
Ramie	68.60	13.10	1.90	0.60	5.50	0.30	10.00
Hemp	67.00	16.10	0.80	3.30	2.10	0.70	10.00
Sunn fiber	67.80	16.60	0.30	3.50	1.40	0.40	10.00
Sisal	65.80	12.00	0.80	9.90	1.20	0.30	10.00
Abaca	63.20	19.60	0.50	5.10	1.40	0.20	10.00

Hemicellulose comprises a group of polysaccharides that remains associated with the cellulose after lignin has been removed. Hemicellulose differs from cellulose in three important aspects. In the first place, it contains several different sugar units, whereas cellulose contains only 1, 4- β -D-glucopyranose units. Secondly, it exhibits a considerable degree of chain branching, whereas

cellulose is strictly a linear polymer. Thirdly, the degree of polymerization of hemicellulose is ten to one hundred times smaller than that of native cellulose (Bledski and Gassan 1999).

Lignins can be defined as complex hydrocarbon polymer with both aliphatic and aromatic constituents (Bledski and Gassan 1999). Before chemical extraction, in their natural state fiber surfaces have waxes, and other encrusting substances such as hemicellulose, lignin, and pectin that form a thick outer layer to protect the cellulose inside. During fiber extraction, most of the surface waxes and other non-cellulosic substances are removed.

When these fibers are used as reinforcement for composites, the removal of surface waxes and encrusting substances makes the fiber surface rough and improves the adhesion of fibers and polymer matrix. The presence of impurities on the surface of the fibers affects the appearance and processability of the fibers. Chemical, biological, and physical treatments are used to improve the morphological features, processability, and utility of the fiber.

2.1.3 Properties of flax fiber

The amount of cellulose and noncellulosic constituents in a fiber determines its structure and properties and influences its crystallinity and moisture absorption properties. Flax fiber properties are controlled by the molecular fine structure of the fibers that is affected by growing conditions and the processing technique used. One of the outstanding properties of flax fiber is that it can withstand processing temperatures up to 250°C (Sreekala et al. 2000)

and is therefore quite suitable for making biocomposites with polymers. Filament and individual fiber properties can vary widely depending on the source, age, separating technique, moisture content, speed of testing, and history of fiber. The lignin content of the fibers influences its structure, properties, and morphology. The waxy substances of natural fibers generally influence the fiber's adhesion and wettability characteristics (Mohanty et al. 2000). Flax fiber has low density compared to synthetic glass fiber with comparable tensile strength and modulus. The strength characteristics of fiber depend on various factors like the properties of the individual constituents, the fibrillar structure, and the lamellae matrix (Joseph et al. 2000).

Properties such as density, electrical resistivity, ultimate tensile strength, and initial modulus depend upon the internal structure and chemical composition of fibers (Mohanty et al. 2001; Reddy and Yan 2005). Quality and other properties of fibers depend on factors such as size, maturity, and processing methods adopted for the extraction of fiber. Desirable properties for fibers include excellent tensile strength and modulus, high durability, low bulk density, good moldability, and biodegradability. A comparison of properties of some natural fibers with conventional manmade fibers is given below in Table 2.2. The high tensile strength of flax may be attributed to its high cellulose content and comparatively low microfibrillar angle (Reddy and Yan 2005). However, it is not possible to correlate the fiber strength exactly with cellulose content and microfibrillar angle because of the very complex structure of natural fibers.

Table 2.2 Comparative properties of some natural fibers with conventional manmade fibers (Mohanty et al. 2000).

Fiber	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break %
Cotton	1.5-1.6	287-800	5.5-12.6	7.0-8.0
Jute	1.3-1.45	393-773	13-26.5	1.16-1.5
Flax	1.50	345-1100	27.6	2.7-3.2
Hemp	-	690	-	1.6
Ramie	1.50	400-938	61.4-128	1.2-3.8
Sisal	1.45	468-640	9.4-22.01	3-7
Coir	1.15	131-175	4-6	15-40
E-glass	2.5	2000-3500	70	2.5
S-glass	2.5	4570	86	2.8
Aramid	1.4	3000-3150	63-67	3.3-3.7
Carbon	1.7	4000	230-240	1.4-1.8

Natural fibers also undergo various degradations such as biological degradation, moisture sorption, ultra violet degradation, thermal degradation, and strength reduction (Mohanty et al. 2000). Therefore, during processing and biocomposite manufacturing fiber treatment and surface modification is important.

2.2 Flax Fiber Surface Modification

Flax is widely preferred because of its higher strength over other natural fibers and hemp can be preferred based on its high yield of straw and fibers. Suitable matrix materials can be resin systems, thermoplastic starch, and polyolefins such as polyethylene and polypropylene. Polypropylene is more preferable because of higher economic, recycling, and technical characteristics.

The homogeneity of the fiber and matrix compound, the degree of elementarization and degumming, and good adhesion between the fiber and matrix are important for selection of natural fiber and polymer resin. The degree of polymerization and crystallization, the moisture absorption and retention properties of the individual components and the compound itself, and the fire retardant properties of the resulting compound should also be taken into consideration while choosing flax and hemp fibers for reinforcement/filler purposes in virgin/recycled polymer matrices. All these properties may depend, to some significant extent, upon the interfacial compatibility. The presence of hydroxyl groups makes flax and hemp fibers incompatible with polymer matrices such as polyethylene.

It was reported that flax and hemp fibers are more hydrophilic in nature than other green fibers, and that the applied separation methods affect fiber surface morphology and consequently the surface area. However, the hydrophilic character of flax or any other natural fibers leads to poor compatibility with hydrophobic polymer matrices and also to a poor dimensional stability as water uptake makes the fibers swell. Swelling of fibers can lead to micro-cracking of the composite resulting in the degradation of mechanical properties. This problem can be overcome by treating fibers with suitable chemicals to decrease the hydroxyl group from the fibers. The moisture absorption and swelling of treated flax fiber composites is approximately 30% lower than that of composites based on untreated flax fibers (Stamboulis et al. 2000). Strong intermolecular fiber-matrix bonding decreases the rate of moisture absorption in biocomposite.

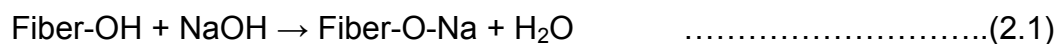
Therefore, inherent lack of compatibility between lignocellulosic fibers and polymeric matrices such as polypropylene (PP) / polyethylene (PE) leads to poor dispersion of the cellulosic material in the thermoplastic melt and also to poor adhesion between fibers and matrices, both factors determining to a large extent the final performance of the composites. In order to improve adhesion between polymer matrix and fiber, some of the fiber surface modifications are carried out.

Before chemical extraction, in their natural state, fiber surfaces have waxes and other encrusting substances such as hemicellulose, lignin, and pectin that form a thick outer layer to protect the cellulose inside. During chemical treatment, most of the surface waxes and other non-cellulosic substances are removed (Li et al. 2007). When these fibers are used as reinforcement for composites, the removal of surface waxes and encrusting substances makes the fiber surface rough and improves the adhesion of fibers and polymer matrix. The presence of impurities on the surface of the fibers affects the appearance and processability of the fibers. Chemical, biological, and physical treatments are used to improve the morphological features, processability, and utility of the fiber.

The hydroxyl group in flax fibers contributes to a poor interface when combined with hydrophobic matrices. Physical and chemical methods can be used to improve this interface. These modification methods are of different efficiency for the adhesion between the matrix and fiber (Cappelletto et al. 2000). Different treatments of flax fibers aimed at improving the adhesion with a polymer matrix may alter not only the fiber surface properties but also fiber strength (Joffe et al. 2003). Physical methods, such as stretching, calendering, thermal

treatment, and the production of hybrid yarns do not change the chemical composition of the fibers (Bledzki and Gassan 1999). But fibers change structural and surface properties and thereby influence the mechanical bonding to polymers. The different surface chemical modifications of natural fibers aimed at improving the adhesion with a polymer matrix were performed by a number of researchers described in following paragraphs.

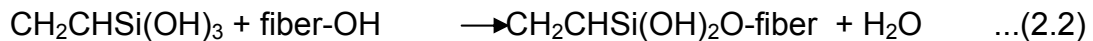
Alkaline treatment is one of the most common treatments adopted to modify fiber before reinforcing any thermoplastic or thermoset polymer (Ray et al. 2000). In this treatment, removal of hydrogen bonding in the network structure is most important modification which increases the surface roughness. This treatment also removes certain amount of lignin, wax, and oils covering the external surface of the fiber cell wall, depolymerize the native cellulose structure, and expose the short length crystallites (Mohanty et al. 2001). This treatment directly influences cellulosic structure of plant fibers, degree of polymerization, and removal of lignin and hemicellulosic compounds may lead to change in molecular orientation of the cellulose crystallites. The reaction of sodium hydroxide with natural fiber is given by the following equations (Agrawal et al. 2000):



Researchers varied the concentration and time of treatment. Sodium hydroxide (NaOH) (5%) solution was used for time varied from 8 to 72 h by Ray and co-workers. (2001). Morrison and co-workers (2000) and Jacob and co-

workers (2004) used different concentrations (0.5, 1, 2, 4, and 10%). Weyenberg and co-workers (2005) soaked flax fiber in the alkaline solution (1%, 2%, and 3%) for 20 min at room temperature. Jähn (2002) reported that this treatment has a lasting effect on the mechanical behavior of flax fibers, especially on fiber strength and stiffness. This treatment results in a better mechanical interlocking by increasing the surface roughness, as well as the amount of cellulose exposed on the fiber surface and thus, increasing the number of possible reaction sites (Valadez et al. 1999). This treatment along with silane treatment also improves the mechanical, impact, fatigue, and dynamic mechanical behavior of fiber-reinforced composite (Mohanty et al. 2001).

Silane treatment mainly involves three processes namely, hydrolysis, condensation, and bond formation. In this treatment, in the presence of moisture, hydrolyzable alkoxy group leads to the formation of silanols. The silanol then reacts with the OH⁻ group of the fiber, forming stable covalent bonds to the cell wall that are chemisorbed onto the fiber surface (Agrawal et al. 2000). The reaction schemes are given as follows:



Agrawal and co-workers (2000) treated oil palm fiber with 1% silane solution in a water-ethanol mixture (40:60) for about 3 h and observed that the treatment improved the thermal stability of the composites. Valadez and co-workers (1999) treated henequén fibers with a 0.033% w/w aqueous silane

solution and tested their adsorption isotherms and tensile strength. They found that the effect of the silane treatment was higher than alkaline treatment.

Acetylation is a well-known esterification method to introduce plasticization to cellulosic fibers. In this method the fiber is treated with pre-heated acetic anhydride and then with acetone (Hill et. al. 1998). In this process, the ester bond between the plant cell wall polymeric material and the acetyl group is subject to hydrolysis with simultaneous loss of modifying agent as acetic acid. Hill and co-workers (1998) reported that development in resistance to microbial degradation was observed.

In acrylation treatment, acrylic acid is also used in graft polymerization to modify fiber surface (Xu et al. 2002; Karlsson and Gatenholm 1999). This reaction is initiated by free radicals of the cellulose molecule. Cellulose is treated with an aqueous solution with selected ions and exposed to high energy radiation. Then, the cellulose molecule cracks and radicals are formed (Bledzki et al. 1999). Sreekala and co-workers (2002) reported that fibers were mixed with 10% NaOH for about 30 min and then treated with solution containing different concentrations of acrylic acid at 50°C for 1h. The fibers were washed with water/alcohol mixture and dried.

Several researchers investigated potassium permanganate (KMnO_4) solution (in acetone) with different concentrations to treat fiber for 1 to 3 min (Joseph et al. 1996; Paul et al. 1997; Joseph et al. 1999). This treatment leads to the formation of cellulose radical through Mn^{3+} ion formation. Paul and co-

workers (1997) reported that the highly reactive Mn^{3+} ions are responsible for initiating graft copolymerization.

Christophe and co-workers (2005) reported that classical sodium hydroxyl plus acetic anhydride based treatments with formic acid treatment significantly improves the flax fiber-polyester adhesion. Some other processes like bleaching, grafting of monomer on cellulose macromolecule, and coupling have been reported.

The chemical coupling method is one of the important chemical method, which improves interfacial adhesion. In this method, the fiber surface is treated with a compound that forms a bridge of chemical bonds between fiber and matrix (Bledski and Gassan 1999). The chemical composition of coupling agents allows them to react with the fiber surface forming a bridge of chemical bonds between the fiber and matrix. The development of a definitive theory for the mechanism of bonding by coupling agents in composites is a complex problem. Generally, coupling agents are molecules possessing two functions. The first function is to react with OH^- groups of cellulose and the second is to react with functional groups of the matrix. Bledzki and Gassan (1999) outlined several mechanisms of coupling in materials. Most researchers found these treatments were effective and showed better interfacial bonding. Some of the coupling agents like benzoyl peroxide (Joseph et al. 1996; Sreekala et al. 2000), acetic anhydride (Hill et al. 1998; Sreekala et al. 2003; Nair et al. 2001), maleic acid anhydride (Gassan and Bledski 1997; Van de Oever and Perjs 1998; Joseph et al. 2003), isocyanates (George et al. 1996; Maldas et al. 1989), sodium chlorite (Mishra et al. 2002;

Mustata 1997), and stearic acid (Paul et al. 1997; Zafeiropoulos et al. 2002) were also studied and used to modify the surface between fiber and matrix. Presently in industry, the most common process of bleaching the cellulose/jute uses oxidizing agents such as sodium hypochlorite, calcium hypochlorite, or hydrogen peroxide. It was also reported that nascent oxygen is involved in the reaction process.

2.3 Thermoplastic Matrices for Biocomposite

Though flax fiber pre-treatment is important, properties of polymers also play vital role in biocomposite formulation. Lignocellulosic fibers like flax fiber are prone to decomposition after 184°C, therefore, low processing temperature is applicable. Thermoplastic like Polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS) are the most common thermoplastic workable in the low processing temperature (Schartel et al. 2003). Most of the thermoplastic are amorphous and semi-crystalline. Thermoplastics can be used for manufacturing a wide range of products depending upon the properties of the particular polymer.

Polyethylene (PE) is a thermoplastic commodity used extensively in consumer products (over 60 million tonnes are produced worldwide every year) (Wikipedia 2007). Based on its density and branching, PE is classified into several different categories. The mechanical properties of PE also depend significantly on variables such as the extent and type of branching, the crystal structure, and the molecular weight. Low density polyethylene (LDPE) has good

electrical properties including low power factor and it is resistant to moisture and most chemicals other than oxidizers (Beadle 1971). LDPE is used to manufacture bottles and other containers, toys, kitchenware, water tanks, packaging film, coated materials for packaging, water and chemical pipe, wire insulation and sheathing, and film for agricultural and building applications (Beadle 1971). Linear low density polyethylene (LLDPE) has same density and melt index with conventional LDPE and is used for manufacturing films or flexible model products. It is claimed to have better impact, tear, or puncture properties (Charrier 1991). High-density polyethylene (HDPE) is harder and more brittle than LDPE and resistant to some of solvents that attack the low-density product (Beadle 1971). HDPE can be used for various high quality product because of its greater tensile strength due to less branching. Most of the HDPEs are formulated for extrusion and blow molding applications. HDPE is used widely in wood plastic composite (Wikipedia 2007).

Polypropylene (PP) has several outstanding properties like lightweight, heat resistance, hardness, surface gloss, stain resistance, stiffness, chemical resistance, stress-crack resistance, and dimensional stability. This make polypropylene and propylene copolymers excellent choices for molding items such as house wares, appliance parts, automobile parts and accessories, closures, laboratory ware, hospital ware, toys, sporting goods, and miscellaneous items for home and industry (Beadle 1971). A comparison of HDPE and PP with other thermoplastic polymers is given in Table 2.3. Most of the properties of PP and HDPE are comparable. However, PP is less tough than HDPE and less

flexible than LDPE. Some of the expensive thermoplastics like polyether ether ketone (PEEK), polyphenylene sulfide (PPS) are semi-crystalline in nature with higher glass transition temperature and better mechanical properties than conventional thermoplastics like PP and PE (Campbell 2004).

Table 2.3 Physical and Mechanical properties of various polymers (Van Velde and Kickens 2001).

Properties	Limit	PP	LDPE	HDPE	PA-6	PC	PBT	PET	PEEK	PPS
ρ (g/cm ³)	Upper	0.920	0.925	1.000	1.14	1.24	1.35	1.40	1.32	1.40
	Lower	0.899	0.910	0.941	1.09	1.19	1.23	1.30	1.264	1.30
W _{24h} (%)	Upper	0.02	<0.015	0.2	1.8	1.19	0.10	0.07		0.05
	Lower	<0.01		<0.01	1.3	0.12	0.08			0.03
σ_{\max} (MPa)	Upper	41.4	78.36	38	79	72	55.9	70	103.5	90
	Lower	26	4	14.5	43	53	51.8	50	70	65.6
E (GPa)	Upper	1.776	0.38	1.49	2.9	3	2.37	4.0	3.8	3.9
	Lower	0.95	0.055	0.413		2.3		2.7	3.1	2.6
σ_f (MPa)	Upper	55.2			117.3	93.2	96	112.3	110.4	151
	Lower				69	81.4	82.8	110.4	110	96
E _f (GPa)	Upper	1.73		1.07	2.8	2.38	2.6	2.8	3.9	4.1
	Lower	0.83		0.41	1.9	2.14	1.9		2.8	3.4
PP: Polypropylene LDPE: Low-density polyethylene HDPE: High-density polyethylene PA-6: Polyamide 6 PC: Polycarbonate				PBT: Polybutylene Terephthalate PET: Polyethylene Terephthalate PEEK: Polyether Ether Ketone PPS: Polyphenylene Sulfide						

There are many aspects and properties to consider when choosing a thermoplastic resin for a product. Some of the properties that are generally considered in manufacturing a biocomposite are tensile strength, flexibility, color (transparent vs. opaque), chemical resistance, and fatigue resistance. But the most important aspect of thermoplastics is its ease of bonding with natural or synthetic fiber and cost.

Glass transition temperature (T_g) of the polymer is an important factor in processing and desired mechanical properties of thermoplastic composite. It was reported that amorphous thermoplastic performs well below T_g and the flexibility of amorphous polymers is reduced drastically when they are cooled below the T_g . At temperatures below T_g , there is no segmental motion and any dimensional changes in the polymer because of the temporary distortions of the primary valence bonds. For example, polyvinyl chloride has T_g of 81°C and is therefore unsuitable for applications where the operating temperature is close to boiling point of water (Mascia 1982). As flax is susceptible to degradation when exposed to elevated temperatures for prolonged period of time, especially in the case of a flax-reinforced plastic, the application temperature of the eventual product should remain relatively low (e.g. maximum 100°C). Some polymers may surpass their T_g at processing temperature but this is not necessarily a problem since the major part of the composite strength (unidirectional reinforced composite) is determined by its fibers (Van Velde and Kiekens 2001).

Other than T_g , the melting point (T_m), is a more important parameter because above this temperature, the whole polymer chain is mobile and the mechanical properties are virtually reduced to zero. Process temperature (T_p) should be higher than the T_m because the viscosity of the polymer reduces drastically and the polymer is easy to process. However, sometimes degradation of polymer can occur, therefore, additives are necessary to prevent thermal degradation of the polymer at these elevated temperatures. Therefore, low

process temperature (and melt point) may be advantageous as it reduces the energy cost of the production process and prevents the degradation of polymer.

In North America, some of the industries have already started using natural fiber in automotive body parts. Findlay Industries (Troy, MI) makes interior trim panels from long-fiber jute, coated with resin, called Findlay-Form using injection molding technology (ILSR Report 1996). Natural Fiber Composite (NFC) in Baraboo, WI is marketing recycled wood based composites in which wood and plastic are compounded using extrusion and injection molding to manufacture automotive parts and window frames. Apart from these industries, another industry uses flax for automotive body parts. Cambridge Industries (Madison Heights, MI) manufactures natural fiber-reinforced polypropylene material called EmpeFlex™. EmpeFlex™ mats use flax as the natural fiber source (ILSR Report 1996). Injection molded polypropylene with 25% flax straw fiber (% by weight) caused significant increase in tensile modulus (Hornsby et al. 1997). In jute fiber reinforced HDPE composites, the mechanical properties are enhanced at fiber loading of 10% to 30% and starts deteriorating at more than 30% fiber (Mohanty et al. 2006). Major work has been done on flax fiber using injection molding technique. There is no work done on flax-reinforced HDPE composites developed by compression molding technique and limited work has been done on compression molded flax reinforced PP composites. There are not many details available about the flax composition, properties, and cost effectiveness. In Canada, no industry is involved in manufacturing flax- reinforced

biocomposite by compression molding technique for automotive or structural applications.

2.4 Processing Techniques of Biocomposite

Thermoplastic fiber-reinforced composites can be processed by a wide variety of distinct methods or techniques. Some of the techniques to process thermoplastic involved in the continuous manufacture of a product having a uniform cross-section are extrusion, extrusion covering, film blowing and calendaring, sheet thermoforming, blow molding, rotational molding, compression molding, transfer molding, injection molding, and reaction injection molding casting (Charrier 1991).

2.4.1 Extrusion compounding process

Extrusion is an important process which is used to manufacture products of good dimensional uniformity and quality at economic rates. It basically involves continuously melting and mixing of polymer, shaping a fluid polymer through the orifice of a suitable tool (die), and subsequently solidifying into a product (Strong 2006). In the case of thermoplastics, the feed material in powder or pellet form, is heated to a fluid state and pumped into the die through a screw extruder and then while exiting from the die, solidified by cooling.

In order for the emerging extrudates to maintain their shape until they solidify, extrusion grades tend to have relatively high molecular weights associated with high viscosity and melt strength (Charrier 1991). Oladipo and

Wichman (1999) investigated aspen wood fiber/HDPE composite and the components were fed at pre-determined mass flow rates, based on the desired wood fiber mass fraction in the composite, into an extruder having a 28 mm co-rotating twin screws operating at temperature of 150°C and a screw rotational speed of 100 rpm. This temperature ensured that while the polymer was fully melted (melting point is 120-135°C), the wood fibers were not burned. Short flax fiber-reinforced compounds can be made by mixing flax fibers with a thermoplastic matrix at elevated temperature in an extruder or a kneader (Harriette et. al. 2005). It was reported that keratin feather fiber and HDPE are compounded best at 205°C at 75 rpm in a Brabender mixing head (Barone et al. 2005). Siaotong (2006) investigated the extrusion parameters, their effect on biocomposite properties, and determined optimum extrusion parameters (temperature = 75-118.1-128.1-138.1-148.1°C and screw speed = 125.56 rpm). It was also reported temperature and screw speed affect the fiber degradation.

2.4.2 Compression molding

Compression molding is the oldest plastic molding method. A compression mold consists of two halves into which are machined the mold cavities. The mold temperature is maintained using electric heaters, and the mold is held shut with a hydraulic cylinder, or toggle clamp. Material is placed in the mold, and it is closed under high pressure and high temperature of molding area (Strong, 2006). Contact with the heated mold surface softens the material, allowing it to fill in the entire cavity and initiating a chemical reaction, which cures the part. Cure time is

determined by the thickest cross section, mold temperature, material type, and grade. After curing, the mold opens and the part is ejected. Hydraulic press is the common type of compression molding machine. Compression molding is mostly used for thermoset material and for some limited thermoplastics.

Compression molded composite such as sheet-molded compound (SMC) is mainly used for preparing thin structural parts (Dumont et al. 2006). In glass fiber-based compressed molded composite, decreasing the molding temperature and mold-closing speed increases tensile modulus (Kim et al. 1997). For manufacturing large, thin, strong, stiff, and lightweight fiber reinforced composite, compression molding process can be effectively used (Park et al. 2001). It was found that during injection molding and extrusion process, sometimes the properties of fiber is damaged due to the rotating screw (Carneiro and Maia 2000). However during compression molding no damage has been reported to the fibers which preserves the isotropic properties of the composites and reduces the changes in physical properties. Molding temperature and pressure plays an important role in physical and mechanical properties of bicomposites. Higher temperature reduces the viscosity of the thermoplastic and provides better wetting of fibers, but at the same time higher temperature can damage the natural fiber. Molding pressure is important in compressing the material and removal of the air trapped inside which is responsible for voids in composites (Barboza 1994).

Khondker and co-workers (2006) investigated manufacturing of compression molded unidirectional PP composites reinforced with jute yarns and

reported that composites with 20% jute fiber content showed significant increase in tensile and bending properties. Zampaloni and co-researchers (2007) reported that compression molded kenaf-reinforced PP composites have higher tensile and flexural strength compared to sisal and coir reinforced thermoplastic. There are only few studies conducted on compression molded wood-PP composites. Properties of compression molded PP wood composites are significantly affected by processing conditions (Geimer et al. 1993; Danyadi et al. 2007).

2.5 Summary

Overall, the potential salvageable oilseed flax straw is 500,000 to 1,000,000 tonnes annually in the prairie provinces of Canada. Flax fiber are hydrophilic in nature and different physical and chemical surface modification techniques can be used to improve fiber-polymer adhesion. Among thermoplastics, HDPE and PP are the most widely used. Biocomposite of high quality can be developed by reinforcing these thermoplastic with flax fiber. Compression molding is one of the simple and basic technologies to develop composites at predefined pressure and temperature. Parameters like, molding temperature, pressure, and cooling time have significant effect on the properties of the product. But this technique may produce products which are less consistent due to poor dispersion. Extrusion can be used for compounding fiber and polymer which will improve the fiber dispersion. There has been no research done on compression molded flax-reinforced HDPE biocomposite and limited work has been done on compression molding natural fiber-reinforced PP

biocomposite. Major work has been done on injection molding and rotational molding using flax fiber with HDPE and PP. Value-added research on flax fiber and HDPE using basic techniques like compression molding to develop high quality biocomposites would be a vital step toward developing new industries and alternative for PP based composites.

3. MATERIALS AND METHOD

This chapter illustrates and explains the materials used, chemical treatments, processing techniques, and experimental design adopted in the present study to develop a compression molded flax reinforced green board. To characterize the developed biocomposite product, specimens were cut out of the molded biocomposite board to determine various physical and mechanical properties following ASTM standards. The different tests performed according to ASTM standards are also outlined in this chapter.

3.1 Materials

Oilseed flax fiber obtained from Biofibre Ltd. (Canora, SK) was used for developing biocomposite in this research. The flax fiber was cleaned, treated, and dried. Dried fiber was ground to 2 mm using a grinding mill (Thomas Wiley Laboratory Mill, Thomas Scientific, Swedesboro, NJ). The size reduction of flax fiber was done to ensure homogeneous mixing of fiber and polymer resin. The cleaned and treated flax fiber was used to reinforce two thermoplastic resins, HDPE and PP to develop compression molded green board or biocomposite and compare their properties. The grade and properties of HDPE and PP used in this research is given below in Table 3.1.

Table 3.1 Typical Properties of HDPE and PP

Polymer	High Density Polyethylene (HDPE)	Polypropylene (PP)
Grade	Exxon Mobil HDPE – HD 8760.29 supplied by Exxon Mobil	PRO-FAX 7823 supplied by Ashland Chemicals
Form	35 US Mesh Powder	Pellets
Melt Flow Index (MFI) (g/10 min)	5.0 (ASTM D 1238, 190°C)	0.25 (ASTM D 1238, 230°C)
Density (g/cm ³)	0.948	0.904
Melting Point (°C)	131	164
Tensile Strength (MPa)	23.4	26.8
Flexural Modulus (MPa)	1060	1100

3.2 Cleaning and Treatment of Flax Fiber

The flax fiber was cleaned with 2% regular detergent and hot water. This flax fiber was termed as untreated flax fiber. Further, two portions of cleaned flax fiber were subjected to two different chemical treatments.

The first chemical treatment of the flax fiber was alkaline treatment. This treatment is one of the most commonly adopted to treat fiber before use as reinforcement in any thermoplastic or thermoset polymer (Ray et al. 2000). In this treatment, flax fiber was immersed in 5% NaOH solution for 3 h and then was washed thoroughly with reverse osmosis (RO) water.

The second chemical treatment adapted was silane treatment. Under this treatment, the flax fibers were immersed in 5% NaOH solution for 30 min. During this treatment, the OH⁻ group of the cellulose and lignin of the fiber becomes activated. Then flax fiber was thoroughly cleaned with RO water. The pre-treated flax fiber was submerged in an alcohol water mixture (60:40) containing 2.5%

triethoxyvinylsilane coupling agent for 1 h. Finally the flax fibers were again washed thoroughly with reverse osmosis (RO) water.

After cleaning and chemical treatment, there were three different types of fiber viz., untreated flax fiber, alkaline treated flax fiber, and silane treated flax fiber ready for drying and biocomposite preparation.

3.3 Drying and Size Reduction of Flax Fiber

The re-circulating cabinet type heat pump dryer was used to dry the flax fiber after cleaning and chemical treatment. The dryer has two small household type dehumidifiers and air was re-circulated through the fiber from the bottom to top. Each unit has condenser and evaporator coils, which provides the heating and dehumidification for the process air of the dryer. The flax fiber was dried in the dryer for 24 h at 50°C to reduce the moisture content to 2% wet basis (wb).

Dried fiber was ground to 2 mm using the grinding mill (Thomas Wiley Laboratory Mill, Thomas Scientific, Swedesboro, NJ). The particle size distribution of ground fibers was determined following ASAE S319.3 (ASAE, 1997) using a Ro-Tap testing sieve shaker (Tyler Industrial Products, Mentor, OH). Sieve numbers and nominal openings (in parenthesis) used for the ground fibers were US sieve nos. 12 (1.680 mm), 16 (1.190 mm), 20 (0.841 mm), 30 (0.595 mm), 40 (0.420 mm), and 50 (0.297 mm). The results are presented in Table 3.2.

Table 3.2 Particle size distribution of ground flax fibers.

Type of Fiber	d_{gw}^* (mm)	s_{gw}^{**} (mm)
Untreated flax fiber	0.649	0.59
Alkaline treated flax fiber	0.710	0.67
Silane treated flax fiber	0.665	0.64

* d_{gw} = geometric mean length/diameter or median size of particles by mass, mm

* s_{gw} = geometric standard deviation of particle length/diameter by mass, mm

3.4 Experimental Design

The composite board were developed using three types of flax fiber (untreated fiber, alkaline treated fiber, and silane treated fiber) with two thermoplastic resins (HDPE and PP). Previous studies indicate that fiber content, molding temperature, and molding pressure play important role in physical and mechanical properties of the natural fiber-reinforced biocomposites. The percentage of fiber loading, temperature, and pressure during compression molding were the experimental process variables.

3.4.1 Fiber content

To reinforce the thermoplastic, three percentages of flax fiber loading were used along with control sample (virgin polymer) with 0% fiber content. Fiber loading used were 10%, 20%, and 30% fiber content by mass to reinforce the thermoplastic biocomposite.

3.4.2 Molding temperature

Two molding temperatures were selected for compression molding based on some preliminary experiments for manufacturing the biocomposites for each

thermoplastic, respectively. The results of preliminary experiments are given and discussed in results and discussion chapter. The molding temperatures selected and used for developing HDPE and PP biocomposites are given in Table 3.3.

Table 3.3 Molding temperatures selected for HDPE and PP biocomposites.

Polymer	Temperature 1	Temperature 2
HDPE	150°C	170°C
PP	175°C	195°C

3.4.3 Molding pressure

Two molding pressure levels were selected for compression molding based on some preliminary experiments for manufacturing the biocomposites for each thermoplastic respectively. The results of preliminary experiments are given and discussed in results and discussion chapter. The molding pressures selected and used for developing HDPE and PP biocomposites are given in Table 3.4.

Table 3.4 Molding pressure levels selected for HDPE and PP biocomposites.

Polymer	Pressure 1	Pressure 2
HDPE	6.89 MPa	10.34 MPa
PP	6.89 MPa	10.34 MPa

The residence time and cooling time were selected based on preliminary experiments. The residence time selected for all biocomposite samples was 10 min. All biocomposite samples were water cooled and the cooling time used was 10 min. Based on the aforementioned process variables (3 levels of fiber content, 2 levels of molding temperature, 2 levels of molding pressure) along with three type of flax fiber, the experiment was a 3 x 3 x 2 x 2 full factorial design. Table 3.5 summarizes the complete experimental design.

Table 3.5 Experimental design for the three different flax fiber and two thermoplastic resins.

Fiber Type	Fiber Content (%)	Temperature (°C)	Pressure (MPa)	Polymer	Sample
Control Sample	0	150	6.89	HDPE	1
Control Sample	0	150	10.34	HDPE	1
Control Sample	0	170	6.89	HDPE	1
Control Sample	0	170	10.34	HDPE	1
Untreated Fiber	10	150	6.89	HDPE	1
Untreated Fiber	10	150	10.34	HDPE	1
Untreated Fiber	10	170	6.89	HDPE	1
Untreated Fiber	10	170	10.34	HDPE	1
Untreated Fiber	20	150	6.89	HDPE	1
Untreated Fiber	20	150	10.34	HDPE	1
Untreated Fiber	20	170	6.89	HDPE	1
Untreated Fiber	20	170	10.34	HDPE	1
Untreated Fiber	30	150	6.89	HDPE	1
Untreated Fiber	30	150	10.34	HDPE	1
Untreated Fiber	30	170	6.89	HDPE	1
Untreated Fiber	30	170	10.34	HDPE	1
Alkaline Treated Fiber	10	150	6.89	HDPE	1
Alkaline Treated Fiber	10	150	10.34	HDPE	1
Alkaline Treated Fiber	10	170	6.89	HDPE	1
Alkaline Treated Fiber	10	170	10.34	HDPE	1
Alkaline Treated Fiber	20	150	6.89	HDPE	1
Alkaline Treated Fiber	20	150	10.34	HDPE	1
Alkaline Treated Fiber	20	170	6.89	HDPE	1
Alkaline Treated Fiber	20	170	10.34	HDPE	1
Alkaline Treated Fiber	30	150	6.89	HDPE	1
Alkaline Treated Fiber	30	150	10.34	HDPE	1
Alkaline Treated Fiber	30	170	6.89	HDPE	1
Alkaline Treated Fiber	30	170	10.34	HDPE	1
Silane Treated Fiber	10	150	6.89	HDPE	1
Silane Treated Fiber	10	150	10.34	HDPE	1
Silane Treated Fiber	10	170	6.89	HDPE	1
Silane Treated Fiber	10	170	10.34	HDPE	1
Silane Treated Fiber	20	150	6.89	HDPE	1
Silane Treated Fiber	20	150	10.34	HDPE	1
Silane Treated Fiber	20	170	6.89	HDPE	1
Silane Treated Fiber	20	170	10.34	HDPE	1
Silane Treated Fiber	30	150	6.89	HDPE	1
Silane Treated Fiber	30	150	10.34	HDPE	1
Silane Treated Fiber	30	170	6.89	HDPE	1
Silane Treated Fiber	30	170	10.34	HDPE	1
Sub-Total (HDPE based samples)					40

Table 3.5 continued.

Fiber Type	Fiber Content (%)	Temperature (°C)	Pressure (MPa)	Polymer	Sample
Control Sample	0	175	6.89	PP	1
Control Sample	0	175	10.34	PP	1
Control Sample	0	195	6.89	PP	1
Control Sample	0	195	10.34	PP	1
Untreated Fiber	10	175	6.89	PP	1
Untreated Fiber	10	175	10.34	PP	1
Untreated Fiber	10	195	6.89	PP	1
Untreated Fiber	10	195	10.34	PP	1
Untreated Fiber	20	175	6.89	PP	1
Untreated Fiber	20	175	10.34	PP	1
Untreated Fiber	20	195	6.89	PP	1
Untreated Fiber	20	195	10.34	PP	1
Untreated Fiber	30	175	6.89	PP	1
Untreated Fiber	30	175	10.34	PP	1
Untreated Fiber	30	195	6.89	PP	1
Untreated Fiber	30	195	10.34	PP	1
Alkaline Treated Fiber	10	175	6.89	PP	1
Alkaline Treated Fiber	10	175	10.34	PP	1
Alkaline Treated Fiber	10	195	6.89	PP	1
Alkaline Treated Fiber	10	195	10.34	PP	1
Alkaline Treated Fiber	20	175	6.89	PP	1
Alkaline Treated Fiber	20	175	10.34	PP	1
Alkaline Treated Fiber	20	195	6.89	PP	1
Alkaline Treated Fiber	20	195	10.34	PP	1
Alkaline Treated Fiber	30	175	6.89	PP	1
Alkaline Treated Fiber	30	175	10.34	PP	1
Alkaline Treated Fiber	30	195	6.89	PP	1
Alkaline Treated Fiber	30	195	10.34	PP	1
Silane Treated Fiber	10	175	6.89	PP	1
Silane Treated Fiber	10	175	10.34	PP	1
Silane Treated Fiber	10	195	6.89	PP	1
Silane Treated Fiber	10	195	10.34	PP	1
Silane Treated Fiber	20	175	6.89	PP	1
Silane Treated Fiber	20	175	10.34	PP	1
Silane Treated Fiber	20	195	6.89	PP	1
Silane Treated Fiber	20	195	10.34	PP	1
Silane Treated Fiber	30	175	6.89	PP	1
Silane Treated Fiber	30	175	10.34	PP	1
Silane Treated Fiber	30	195	6.89	PP	1
Silane Treated Fiber	30	195	10.34	PP	1
Sub-Total (Polypropylene based samples)					40
Total Samples					80

3.5 Sample preparation and Biocomposite Board Development

The PP pellets were ground by the grinding mill (Thomas Wiley laboratory mill, Thomas Scientific, Swedesboro, NJ)(Figure 3.1). The flax fiber and polymer resin was weighed as per proportion mentioned before and mixed using a rotating type mixer (National Hardware, Dresden, ON).



Figure 3.1 Thomas Wiley laboratory mill.

The mixture of HDPE/ PP and flax fiber was fed into the single screw extruder (Akron Inc., Batavia, OH) (Figure 3.2) at temperature of up to 190°C with a screw speed of 60 rpm. The extruded strands were air cooled and pelletized and these pellets were further ground to 2 mm size using the grinding mill (Thomas Wiley laboratory mill, Thomas Scientific, Swedesboro, NJ). Preliminary experiments were conducted to find the best residence time and curing time. The details of experimental results are given in the results and discussion chapter.



Figure 3.2 Single screw extruder.

A rectangular mold (Figure 3.3) was designed to mold a rectangular sample of 200 mm x 200 mm size. The mold was made up of construction grade steel. Two temperatures and pressures were identified based on some preliminary experiments and differential scanning calorimetry (DSC) results.



Figure 3.3 Rectangular mold used in the experiments.

The ground samples were then fed into the designed mold and the mold was subjected to selected temperature and pressure by compression molding machine (Miller Machine Tools, J.B. Miller Machinery & Supply Co. Ltd, Toronto,

ON)(Figure 3.4). The residence time for biocomposite preparation during compression molding was 10 min. The boards developed were cured by the water-cooling system of the compression molding system. Pressure was maintained during the curing process to develop green boards with better dimension stability and mechanical properties.



Figure 3.4 The compression molding machine used in the experiments.

3.6 Characterization of Flax Fiber and Compression Molded Biocomposite

To study the morphology and thermal behavior of the untreated and chemically treated flax fiber, scanning electron microscopy (SEM) and DSC tests were performed. The various ASTM tests adopted for testing the various physical and mechanical properties of the specimens cut out of the molded biocomposite are given below.

3.6.1 Scanning electron microscope image analysis

The morphology of the fiber after chemical treatment and fiber orientation/dispersion in the compression molded biocomposite can be studied by images

captured by scanning electron microscope (SEM 505, Philips, Holland) (Figure 3.5). The fiber/composites samples surface was vacuum coated with a thin layer of gold to provide electrical conductivity. The layer of gold coating was thin and did not affect the resolution significantly. Two set of samples from each type of fibers/composite was examined. All SEM tests were conducted at Department of Biology, University of Saskatchewan.



Figure 3.5 Scanning electron microscope.

3.6.2 Differential scanning calorimetry

Thermal analysis on flax fiber, pure polymer resin and biocomposites was performed using DSC Model Q2000 (TA Instruments, New Castle, DE) (Figure 3.6). DSC is a thermo-analytical technique in which heat flow is measured as a function of temperature or time. The thermograms were then analyzed for any changes in the thermal behavior of the fibers/composites. Sample weighing between 5 to 10 mg were placed in an aluminum pan and sealed with the crucible sealing press. The DSC system was operated in a dynamic mode with a

heating scheme of 40 to 300°C, heating rate of 10°C/min and a chart of heat flow versus temperature was produced.



Figure 3.6 Differential scanning calorimeter.

3.6.3 Melt flow index (ASTM D1238)

Melt flow index (MFI) is an assessment of average molecular mass and is an inverse measure of the melt viscosity. MFI of the ground extruded samples was measured by the melt indexer (Tinius Olsen Testing Machine Company, Hallikainen Instruments, Richmond, CA) (Figure 3.7). Approximately 10 g of the ground extruded material was loaded into the barrel of the melt flow apparatus. The barrel was heated to a temperature 190°C and 230°C for HDPE- and PP-based material, respectively. A weight specified for the material is applied to a plunger and the molten material is forced through the die. Samples were

collected for 1 min and 6 min time interval following ASTM procedure D1238 (ASTM 2003) and weighed. Melt flow index values are expressed in g/10 min.



Figure 3.7 Melt flow indexer.

3.6.4 Color analysis

To analyze the degree of degradation of the biocomposite material due to temperature and pressure during compression molding, the color index was measured and compared using the HunterLab Spectrocolorimeter (Hunter Associates Laboratory Inc., Reston, VA)(Figure 3.8). Color was analyzed in terms of L (0=black to 100=white), a (-a=green to +a=red) and b (-b=blue to +b=yellow) values. Rectangular samples of 25.4 mm by 76.2 mm cut from compression molded board were used for color measurement. For the color test, viewing area of 12.77mm (0.50 in.) and port size of 25.4mm (1 in.) were used. The total color difference index (ΔE) which represents the deviation from the reference stage was used as an indicator of degree of degradation. The index ΔE

was determined by equation 3.1 (Chen and Rawaswamy 2002; Methakhup et.al. 2005).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (3.1)$$

Where,

$$\Delta L = L - L_{\text{ref}}, \Delta a = a - a_{\text{ref}}, \Delta b = b - b_{\text{ref}}$$

L, a, b = color coordinates of the samples

$L_{\text{ref}}, a_{\text{ref}}, b_{\text{ref}}$ = color coordinates of the control sample (0% fiber) of HDPE and PP boards.



Figure 3.8 HunterLab spectrophotometer.

HunterLab values L, a, and b are averages of three replications with three readings for each replication.

3.6.5 Density test

Density test was conducted to investigate and compare the actual density with the ideal density. The density test was also used to study the effect of process variables (fiber content, molding temperature, molding pressure) on the mechanical properties of the biocomposite boards. The density of biocomposite

samples is determined as the mass per unit volume and is expressed in grams per cubic centimeter. Ideal density was computed using the following equation (Stroshine 2000):

$$\rho_{ideal} = \frac{1}{\frac{m_{plastic}}{\rho_{plastic}} + \frac{m_{fiber}}{\rho_{fiber}}} \dots\dots\dots (3.2)$$

where,

ρ_{ideal} = ideal density (g/cm³)

$m_{plastic}$ = mass fraction of plastic (decimal)

m_{fiber} = mass fraction of fiber (decimal)

$\rho_{plastic}$ = density of plastic (g/cm³)

ρ_{fiber} = density of fiber (g/cm³)

The actual density was measured by dividing the mass of biocomposite samples by the volume. Rectangular specimens were cut from each sample with dimensions of 25.4 mm x 76.2 mm. The mass of the samples was measured at room temperature using a Galaxy 160D weighing scale (OHAUS Scale Corporation, Pine Brook, NJ). The volume of the biocomposite samples was measured using a gas-operated pycnometer (Quantachrome Corporation, Boynton Beach, FL)(Figure 3.9) using nitrogen gas. Density of three replications was measured for each sample and average was reported as actual density. For each HDPE- and PP-based samples, the actual density was compared with the ideal density.



Figure 3.9 Gas-operated pycnometer for measuring volume of biocomposite sample.

The deviation of actual density of HDPE and PP composite from the ideal density is computed using equation given below.

$$\rho_{\text{deviation}} = \frac{\rho_{\text{actual}} - \rho_{\text{ideal}}}{\rho_{\text{ideal}}} \times 100 \quad \dots\dots\dots (3.3)$$

where,

$\rho_{\text{deviation}}$ = density deviation (%)

ρ_{actual} = actual density (g/cm³)

ρ_{ideal} = ideal density (g/cm³)

3.6.6 Water absorption test (ASTM D570)

Water absorption characteristics of composites are altered by the addition of flax fibers because these fibers have a greater affinity to water. According to ASTM standard D570 (ASTM 2003c), rectangular specimens were cut from each

sample with dimensions of 25.4 mm x 76.2 mm. The samples were dried in an oven at 50°C for 24 h, cooled in a desiccator, and immediately weighed to the nearest 0.001 g. In order to measure the water absorption of biocomposite, all samples were immersed in water for about 24 h at room temperature (ca. 21°C) as described in ASTM D570 procedure. Three replicate specimens were tested. At the end of soaking, excess water on the surface of the samples was removed before weighing. The percentage increase in mass during immersion was calculated to the nearest 0.01% as follows:

$$\text{Water absorption} = \frac{(\text{Conditioned mass} - \text{Dry mass})}{\text{Dry mass}} \times 100 \quad \dots\dots\dots (3.3)$$

3.6.7 Tensile strength test (ASTM 638)

Tensile property data are more useful in preferential selection of a particular type of plastic from large group of plastic materials. The familiar dog-bone shape sample was utilized in the testing procedure. This type specimen is the preferred specimen and was used with sufficient material having a thickness of 3.2 mm. These were conditioned at 24°C and 50% relative humidity for 72 h. An Instron Universal testing machine (Model 1011, Instron Corp., Canton, MA) shown in Figure 3.10 was used to perform the tensile strength test at a crosshead speed of 5 mm/min as described in ASTM D638-02a (ASTM 2003b) and each test was performed until tensile failure occurred.

The maximum load value F_{max} was recorded by the instrument, which can be recalled after the completion of the test. The tensile strength (σ_t) is calculated from the following equation:

$$\sigma_t = \frac{F_{\max}}{A} \dots\dots\dots (3.4)$$

Where,

A is the cross sectional area (mm^2)

F_{\max} = maximum load value (N)

Young's Modulus (E) was also determined using the following equation:

$$E = \frac{\Delta\sigma}{\Delta\varepsilon} \dots\dots\dots (3.5)$$

Where,

$\Delta\sigma$ = the change in tensile stress before the material yields

$\Delta\varepsilon$ = the change in tensile strain before the material yields



Figure 3.10 Instron Model 1011 universal testing machine.

3.6.8 Three point bending test (ASTM 790)

This test helps in characterizing the thermomechanical behavior of plastic materials. A specimen of rectangular cross section which behaves as a beam is tested in flexure. The bar rests on two supports and is loaded by means of loading nose midway between the supports. The test specimen of known geometry was placed in mechanical linear displacement at fixed frequencies at isothermal conditions. The flexural modulus of the biopolymeric material was measured by three point bending. The size of test specimen was according to ASTM 790-02 specifications (ASTM, 2003). This test can be used to assess modulus as a function of temperature, effect of fiber loading and dispersion, and effect and role of curing.

3.6.9 Hardness test (ASTM D2240)

This test helps in characterizing viscoelastic behavior of the material. This test method is based on the penetration of a specific type of indenter when forced into the material under specified conditions. The hardness of biocomposite boards was measured by following ASTM D2240 specification (ASTM 2003), using a Shore D type durometer (Shore Instrument and MFG Co., Freeport, NY). The hardness of each sample was calculated as average of ten readings.

3.7 Statistical Analysis and Optimization

The effect of fiber treatment, fiber content, molding temperature, and molding pressure on density, color, water absorption, tensile strength, Young's

modulus, flexural strength, flexural modulus, and hardness of biocomposite boards were analyzed and studied. The experimental design for this research was 3 x 3 x 2 x 2 full factorial design having 3 types of treated fiber, 3 levels of fiber content, 2 levels of molding temperature and 2 levels of molding pressure.

Univariate analysis of variance (ANOVA) was used to analyze the treatment means and Duncan's multiple range test (DMRT) was used to compare the treatment means. SPSS 14.0 (SPSS 2005) for windows software was used to perform ANOVA and DMRT test. Response surface plots were generated using Tecplot 9.2 software (Tecplot 2001) to show the effect of the three process variables (fiber content, molding temperature, molding pressure) on the response variables.

The optimum processing temperature and pressure along with optimal fiber content was determined by following conventional graphical method (Siaotong 2006; Carrillo et al. 2004; Carrillo et al. 2002; Guillow and Floros 1993). Tecplot 9.2 software (Tecplot 2001) was used to generate contour plots of response variables and these plots were used to determine the optimal value of process variables (for each HDPE and PP composites) by applying superposition surface methodology.

3.8 Summary

This chapter presented and discussed the materials and methods used to achieve the specific objectives mentioned in first chapter. Two type of chemically treated (alkaline and silane) and untreated flax fiber was used as reinforcement

in HDPE- and PP-based composites. To ensure homogeneous mixing, fiber and thermoplastic resin was compounded by single screw extruder. Extruded strand were pelletize, ground, and fed into compression molding machine to develop biocomposite boards. Forty different bicomposite samples with 3 types of flax fiber, 3 levels of fiber content, 2 levels of molding temperature, and 2 levels of molding pressure were developed for each HDPE and PP resin, respectively. Thermal characterization of flax fiber and biocomposite samples was done by DSC tests. SEM test was performed to study the morphological characteristics of different type of treated fiber and bicomposite samples. Density deviation, water absorption, and color test was done to determine the physical characteristics of the biocomposite samples. Tensile, flexural, and hardness tests were performed to determine the mechanical characteristics of the biocomposite samples. All tests were performed following ASTM standard procedures. Eight response variables was used to determine optimum fiber loading and processing parameters (molding temperature and molding pressure) by following conventional graphical method (CGM).

4. RESULTS AND DISCUSSIONS

This chapter discusses the effect of two chemical treatments (alkaline and silane), different fiber percentages, molding temperature and molding pressure on the final compression molded biocomposite product. The results of tests conducted to characterize the biocomposites developed with different combination of fiber type, fiber percentage loading and processing parameters are discussed in this chapter.

4.1 Selection of Molding Temperature and Pressure

To determine and select two levels of temperature and pressure some preliminary experiments were conducted. Based on DSC results of the ground extruded biocomposite samples, initial levels of temperature and pressure were selected, and biocomposite were developed.

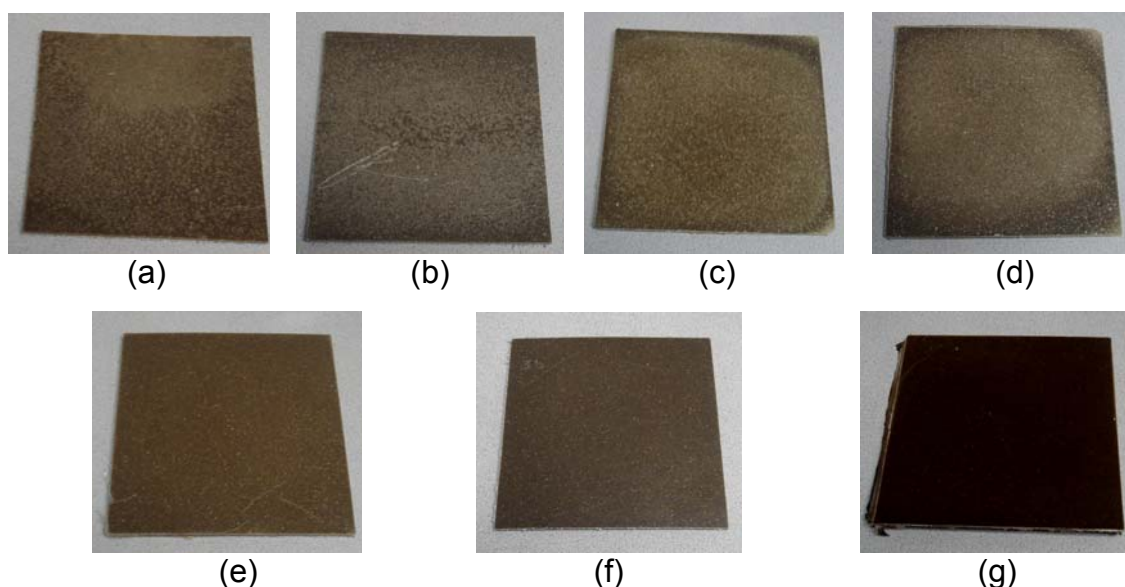


Figure 4.1 HDPE Biocomposite prepared at a) 135°C & 3.45 MPa, b) 140°C & 3.45 MPa, c) 135°C & 6.89 MPa, d) 140°C & 6.89 MPa, e) 150°C at 6.89 MPa, f) 170°C at 10.34 MPa, g) 180°C at 10.34 MPa.

HDPE-based biocomposites were molded at temperatures of 135°C, 140°C, 150°C, 170°C, 180°C, and pressure of 3.45 MPa, 6.89MPa, 10.34MPa. The biocomposites were reinforced with 20% flax fiber by mass (Figure 4.1).

The board prepared at pressure of 3.45 MPa had pores on both the surfaces due to inadequate pressure. At both 135°C and 140°C temperature, the polymer was not properly melted. Temperatures 150 °C and 170°C were found suitable at 6.89 MPa and 10.34 MPa. However, above 10.34 MPa of pressure, there was problem of splashing and material coming out of the mold which led to boards of variable thickness. The board color and odor indicates that at 180°C, the fibers in the board were burnt. Table 4.1 shows the final selected levels of temperatures and pressure for compression molding of HDPE composites.

Table 4.1 Molding temperature and pressure levels selected for HDPE Biocomposites.

Polymer	Temperature (°C)	Pressure (MPa)
HDPE	150	6.89, 10.34
	170	6.89, 10.34

Same pressure levels of 6.89 and 10.34 MPa were selected for PP-based biocomposites. The PP-based biocomposites were developed at temperature levels of 160°C, 165°C, 170°C, 175°C, 195°C, and 200°C (Figure 4.2).

The temperatures 160°C, 165°C, and 170°C were found not able to completely melt the polymer resin and develop uniform board. Temperatures 175°C and 195°C were found suitable at 6.89 and 10.34 MPa pressure levels to develop uniform and strong biocomposite board. Above 195°C, burnt spots were

found on the surface of biocomposite. Table 4.2 shows the final selected levels of temperatures and pressure for compression molding of PP composites.

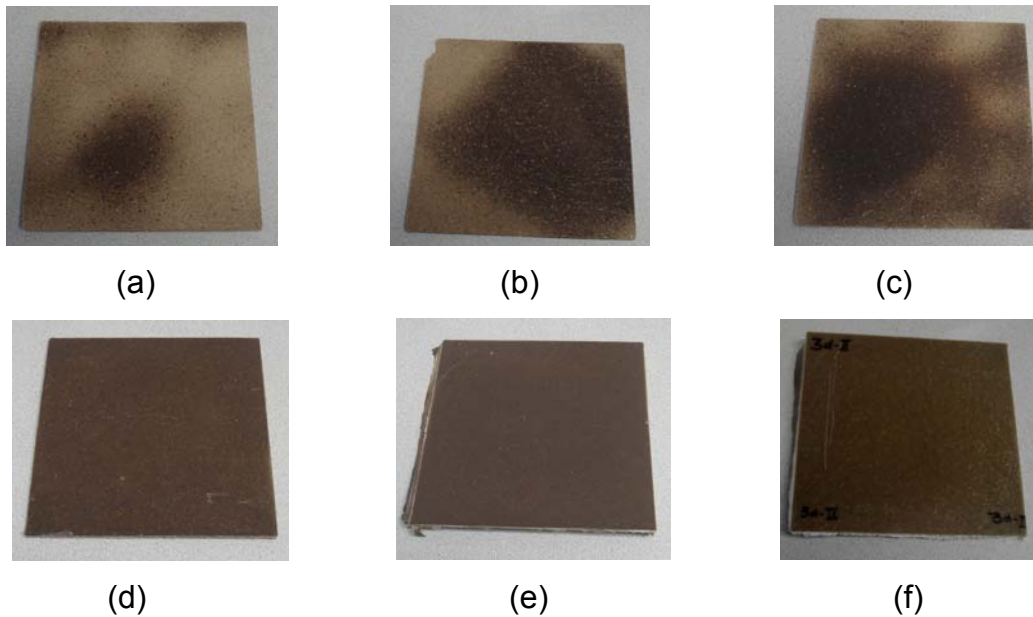


Figure 4.2 PP Biocomposite prepared at a) 160°C & 6.89 MPa, b) 165°C & 6.89 MPa, c) 170°C & 6.89 MPa, d) 175°C & 6.89 MPa, e) 195°C & 6.89 MPa, f) 200°C at 6.89 MPa.

Table 4.2 Molding temperature and pressure levels selected for PP Biocomposites.

Polymer	Temperature (°C)	Pressure (MPa)
PP	175	6.89, 10.34
	195	6.89, 10.34

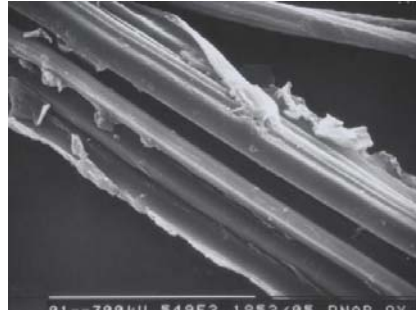
4.2 Morphological Characterization

SEM analysis of flax fiber and the cross section of several HDPE and PP composites were performed to examine the effect of chemical treatment and dispersion of fiber in the polymer resin.

4.2.1 Flax fiber

Flax fiber morphology plays important role in flax-polymer adhesion and physical and mechanical properties of biocomposite. The SEM images were

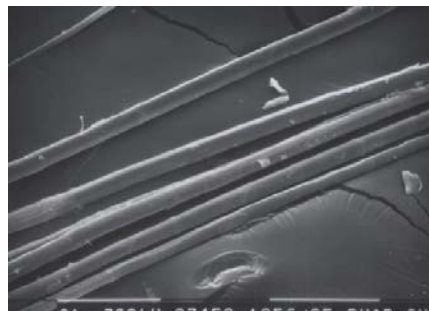
taken to study the effect of different chemical treatment. SEM images in Figure 4.3 below, clearly shows that substantial amount of waxy substances are stuck to the untreated individual fiber.



a) Untreated flax fibers



b) Alkaline treated flax fibers



c) Silane treated flax fibers

Figure 4.3 SEM images of untreated and chemically treated flax fiber.

In alkaline and silane treatment, most of the waxy substances encrusting the flax fibers were successfully removed. The flax fiber surface became rough after both chemical treatment and small cracks were observed on fiber surface

which may result in better bonding with polymer resin. The change in morphology of flax fiber and removal of lignin, pectin, and waxy substances improved the fiber-polymer adhesion and enhanced the mechanical properties of the final product. After silane treatment, a surface coating was formed on the fiber. This can be explained by the fact that the flax fiber has micropores on the surface and coupling agent penetrates into the pores and forms coating on the surface (Wang et al. 2007).

4.2.2 Biocomposite boards

Biocomposite boards prepared with different percentages and types of flax fiber vary in mechanical and physical properties. The dispersion of fiber in the polymer is also attributed to the variation in mechanical and physical properties of biocomposites. SEM images were captured to study the effect of fiber pretreatment and loading on the fiber dispersion in the polymer matrices. Figure 4.4 shows the SEM images of HDPE- and PP-based biocomposites with different level of flax fiber and different treated flax fiber.

For both HDPE- and PP-based biocomposites, those with untreated flax fiber were more porous compared to treated fiber. Untreated flax fiber based biocomposites contained non-uniform air voids which later resulted into poor mechanical properties. The alkaline and silane treated fiber have better dispersion throughout the biocomposite boards which enhanced their mechanical properties. The composites became more porous with increase in flax fiber content. Chemically treated fiber reinforced composites have efficient fiber-matrix adhesion (Mohanty et al. 2006).

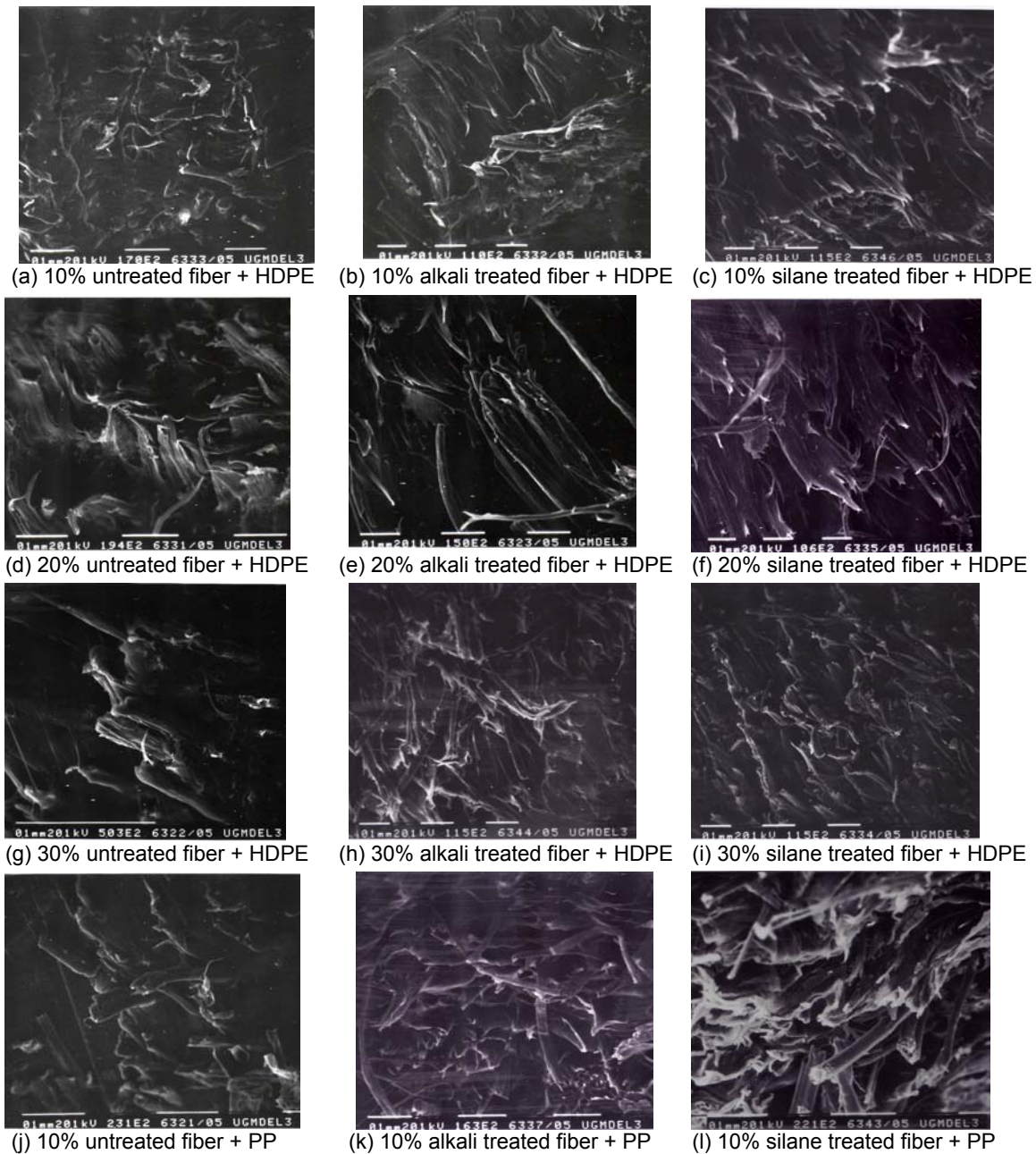


Figure 4.4 SEM images of untreated and treated flax fiber reinforced biocomposite samples.

4.3 Thermal Characterization

All processing of the flax fiber and polymer resins (HDPE-PP) was performed under 200°C. DSC thermograms were analyzed for melting point and

degradation temperature in the temperature range of 40 to 300°C. DSC was used to determine not only the melting point (T_m) but also the melting range of the polymer.

4.3.1 Flax fiber

DSC analysis enables the identification of thermochemical activity occurring in the fiber as heat is applied. The endothermic peak shown in Figures 4.5 to 4.7 represents the absorbance of heat due to moisture content in untreated and treated flax fiber. In natural fiber, the degradation is different at temperature below 300°C and temperature above 300°C (Van de Velde and Kiekens, 2002). In this research, all the processing was done below 300°C and below this temperature degradation may have occurred due to the thermal depolymerisation of hemicellulose and decomposition of the α -cellulose (Manfredi et al. 2006).

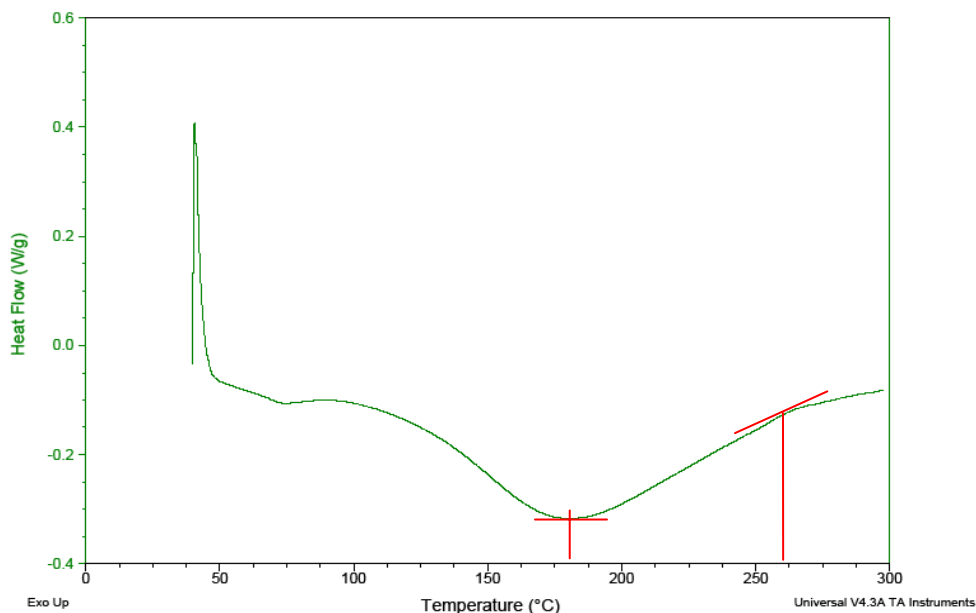


Figure 4.5 DSC thermogram of untreated treated flax fiber.

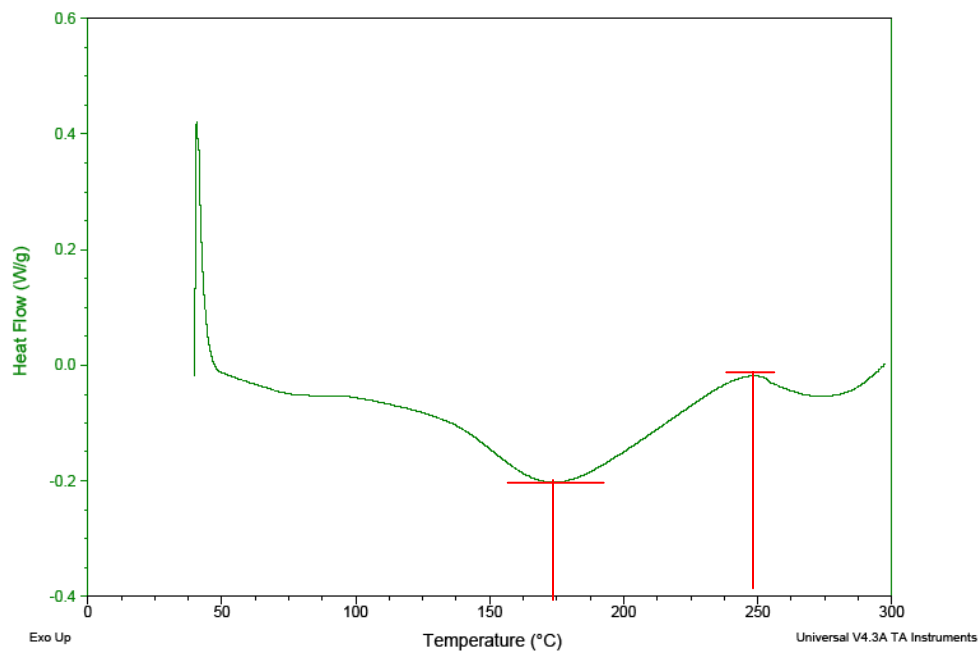


Figure 4.6 DSC thermogram of alkaline treated flax fiber.

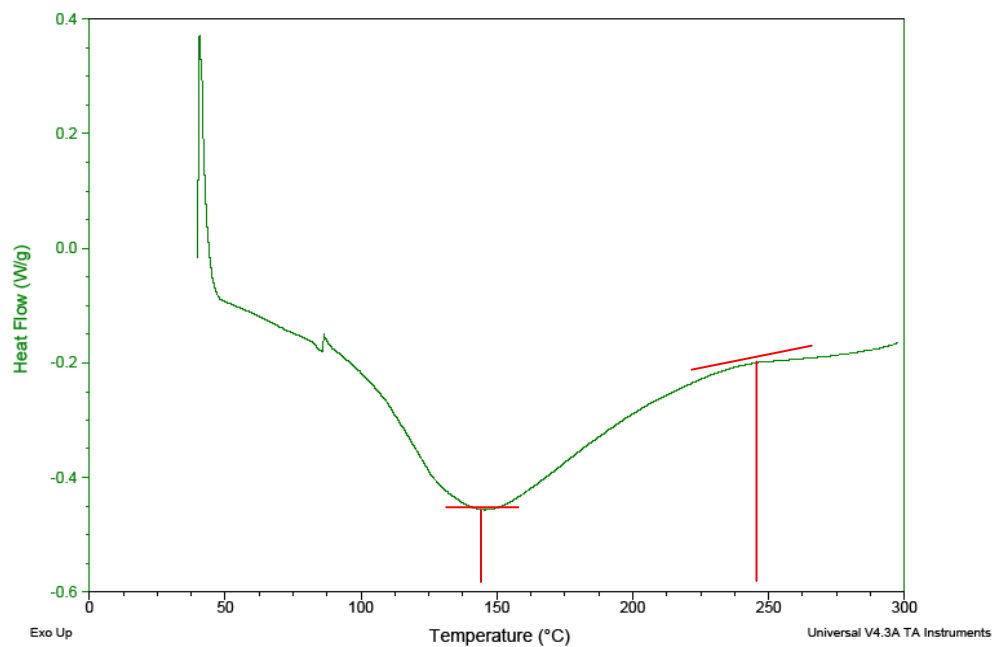


Figure 4.7 DSC thermogram of silane treated flax fiber

All the composite boards were prepared below 200°C and there were no exothermic reactions in the region below 200°C, which suggest that there was no

fiber degradation due the processing of composite boards. The DSC heating curve of untreated and treated flax fiber is shown in Figures 4.5 to 4.7. Figure 4.5 shows a broad endotherm in the untreated flax DSC curve indicating the presence of water. This endotherm becomes narrower in DSC curves for alkaline and silane treated fiber shown in Figures 4.6 and 4.7, respectively. The untreated flax fiber adsorbed more amount of moisture and therefore, it took longer time and higher temperature for removal of the bound water. In all the three DSC curves, a slight exothermic peak was found around 250°C, which indicates the first decomposition temperature of flax fiber that could be due to the lignin or hemicellulose degradation.

4.3.2 Ground extruded samples

The glass transition temperature (T_g) of ground extruded biocomposite samples could not be observed between 40-300°C. The T_g of pure polyethylene and polypropylene is usually below -100°C and -10°C (Van Velde and Kiekens 2001), respectively. Tables 4.3 and 4.4 show the melting points of all the extruded samples prepared for compression molding. A small change in the T_m (melting point temperature) of the polymers due to fiber incorporation was observed. The increase of T_m may be attributed to the plasticization effect of the fiber that diffuses into the polymer. The incorporation of 10, 20, and 30% of flax fiber in HDPE and PP-based composites increases the T_m of fiber composites. The increased melting point of composites meant that thermal resistance increased due to flax fiber addition. The chemical treatment of flax fiber did not

have any significant effect on the melting point of the HDPE and PP composites. Wang (2004) reported that there was less than 1°C difference in melting point of HDPE-based biocomposites reinforced with 10% of different chemically treated fiber.

Table 4.3 Melting points of HDPE-based biocomposite samples.

Sample ID	Sample	Melting Point (°C)
1a	HDPE + 10% untreated flax fiber	130
1b	HDPE + 20% untreated flax fiber	130
1c	HDPE + 30% untreated flax fiber	131
2a	HDPE + 10% alkaline treated flax fiber	131
2b	HDPE + 20% alkaline treated flax fiber	131
2c	HDPE + 30% alkaline treated flax fiber	131
3a	HDPE + 10% silane treated flax fiber	130
3b	HDPE + 20% silane treated flax fiber	130
3c	HDPE + 30% silane treated flax fiber	130
HDPE	HDPE + 0 % flax fiber (control sample)	129

Table 4.4 Melting points of PP-based biocomposite samples.

Sample ID	Sample	Melting Point (°C)
1d	PP + 10% untreated flax fiber	164
1e	PP + 20% untreated flax fiber	164
1f	PP + 30% untreated flax fiber	163
2d	PP + 10% alkaline treated flax fiber	164
2e	PP + 20% alkaline treated flax fiber	164
2f	PP + 30% alkaline treated flax fiber	164
3d	PP + 10% silane treated flax fiber	164
3e	PP + 20% silane treated flax fiber	164
3f	PP + 30% silane treated flax fiber	164
PP	PP + 0 % flax fiber (control sample)	163

These sample identifications will also be used in further tests and the sample ingredients remain the same.

4.4 Melt Flow Index of Ground Extruded Samples

Melt flow index (MFI) as an indicator for viscosity of the extrudates made from HDPE and PP with different percentages of flax fiber is shown in Figures 4.8 and 4.9, respectively. The results indicate that both factors, namely, fiber type and fiber content, significantly affected the MFI of the product.

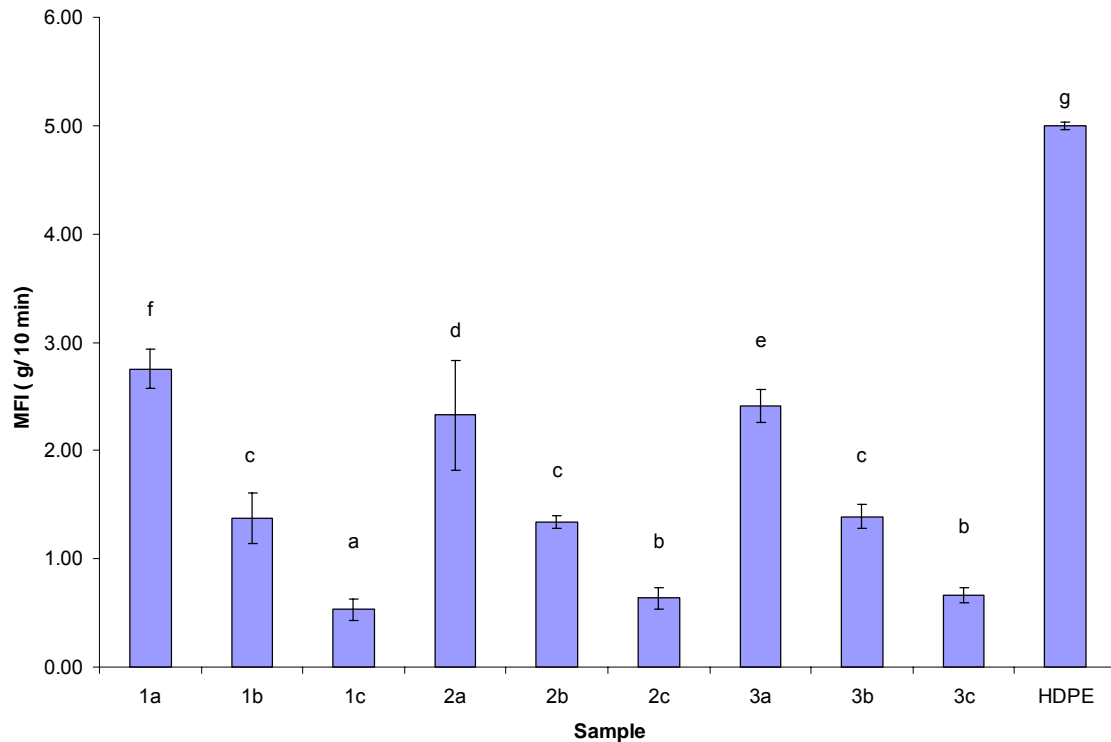


Figure 4.8 Melt flow index of HDPE extrudates;
a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The ANOVA (refer to Appendix A.5) revealed that both the fiber content and fiber type along with interaction of fiber content*fiber type had a significant effect on

the MFI of HDPE-based biocomposite extrudates ($P < 0.05$). For HDPE extrudates, the MFI varied from 0.53 g/10 min (at 30% untreated fiber content) to 5.0 g/10 min (at 0% fiber content). Flax fiber reinforcement hinders the polymer movement during the melting and therefore reduces the MFI. Siaotong (2006) also reported similar results that MFI of HDPE-based extrudates varied from 0.56 g/10 min (at 25% flax fiber) to 5.02 g/10 min (at 0% flax fiber).

For PP-based biocomposite extrudates, the MFI varied from 0.06 g/10 min (at 30% untreated fiber content) to 0.23 g/10 min (at 0% fiber content). The MFI for all PP extrudates was low, therefore, 5% paraffin wax added as processing aid.

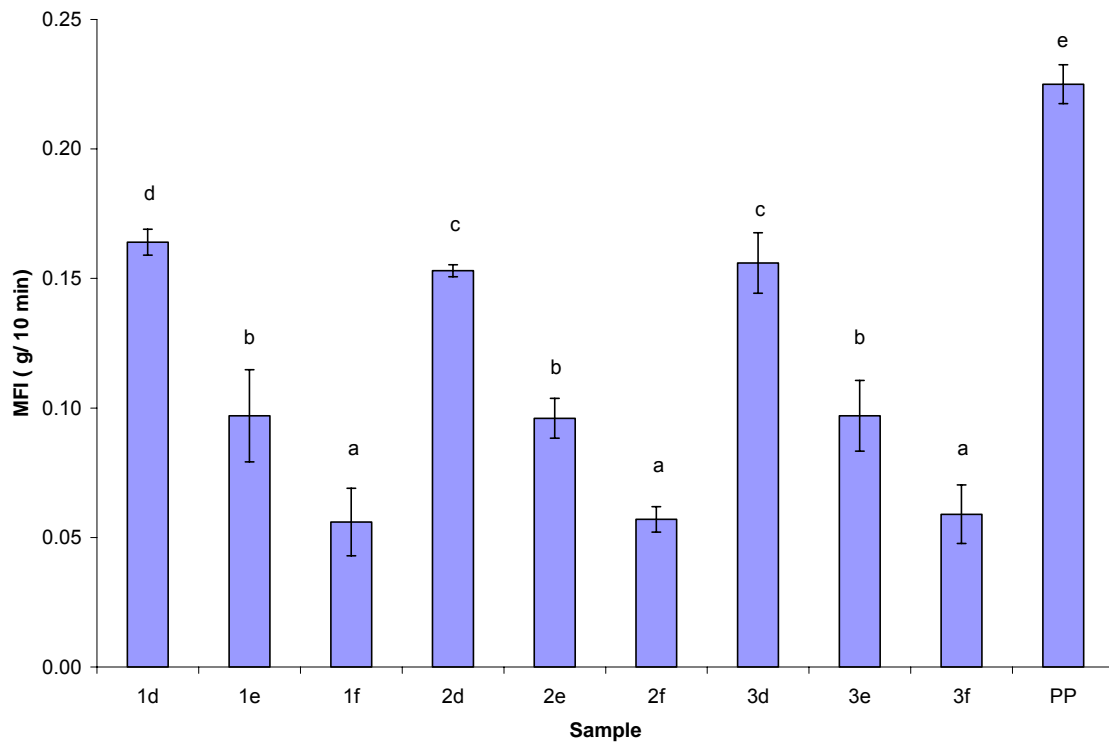


Figure 4.9 Melt flow index of PP extrudates;
a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The ANOVA (refer to Appendix A.14) revealed that both the fiber content and fiber type along with interaction of fiber content*fiber type had significant effect on the MFI of PP based composites ($P < 0.05$). The effect of fiber loading on PP based composites was similar to HDPE based composites.

4.5 Physical Properties

Experimental results of color, density, and water absorption tests are discussed in this section to characterize the physical properties of different biocomposite board developed with 3 levels of fiber loading and 3 types of treated fiber at 4 different processing conditions with 2 levels each of molding temperature and molding pressure. The sample IDs with details for HDPE- and PP-based biocomposites mentioned in Tables 4.3 and 4.4 are used in all the figures illustrating different physical properties. The IDs C-I, C-II, C-III and C-IV represent the four processing conditions. Details of the processing conditions are given in Tables 4.5 and 4.6.

Table 4.5 Processing conditions for HDPE based biocomposites.

Condition	Temperature (°C)	Pressure (MPa)
C-I	150	6.89
C-II	150	10.34
C-III	170	6.89
C-IV	170	10.34

Table 4.6 Processing conditions for PP based biocomposites.

Condition	Temperature (°C)	Pressure (MPa)
C-I	175	6.89
C-II	175	10.34
C-III	195	6.89
C-IV	195	10.34

Surface response plots were generated for silane treated flax fiber-reinforced biocomposites data only to study the effect of fiber content, molding temperature and molding pressure on the response variable due to the fact that silane treated fiber reinforced composites provided best results for all the variables.

4.5.1 Biocomposite boards color analysis

The color index (ΔE) of biocomposite boards was determined to study the effect of fiber loading, fiber type, and processing condition on the physical appearance of the biocomposite boards. Experimental results of color index (ΔE) are presented in Figure 4.10 for HDPE-based biocomposite boards and in Figure 4.11 for PP-based biocomposite boards.

The color index (ΔE) of HDPE-based biocomposite boards varied from 0 to 55. The ANOVA (refer to Appendix A.2) showed that ΔE of HDPE biocomposites was significantly dependent on fiber type, fiber content, temperature, pressure, and all the interactions between fiber content, fiber type, temperature, and pressure ($P < 0.05$). The ΔE was higher for biocomposites with untreated flax fiber. Lignin content imparts brown color to the flax fiber. Hence, the untreated flax fibers were darker in color compared to chemically treated fiber. The ΔE increased with increase in the fiber content, temperature and pressure. Higher fiber content gave darker color to the composite boards prepared. Biocomposite boards prepared at higher temperature and pressure were darker in color and resulted in higher ΔE . The same effect of fiber content,

temperature, and pressure on ΔE is illustrated by the response surface plots (refer to Appendix C.1-C.2).

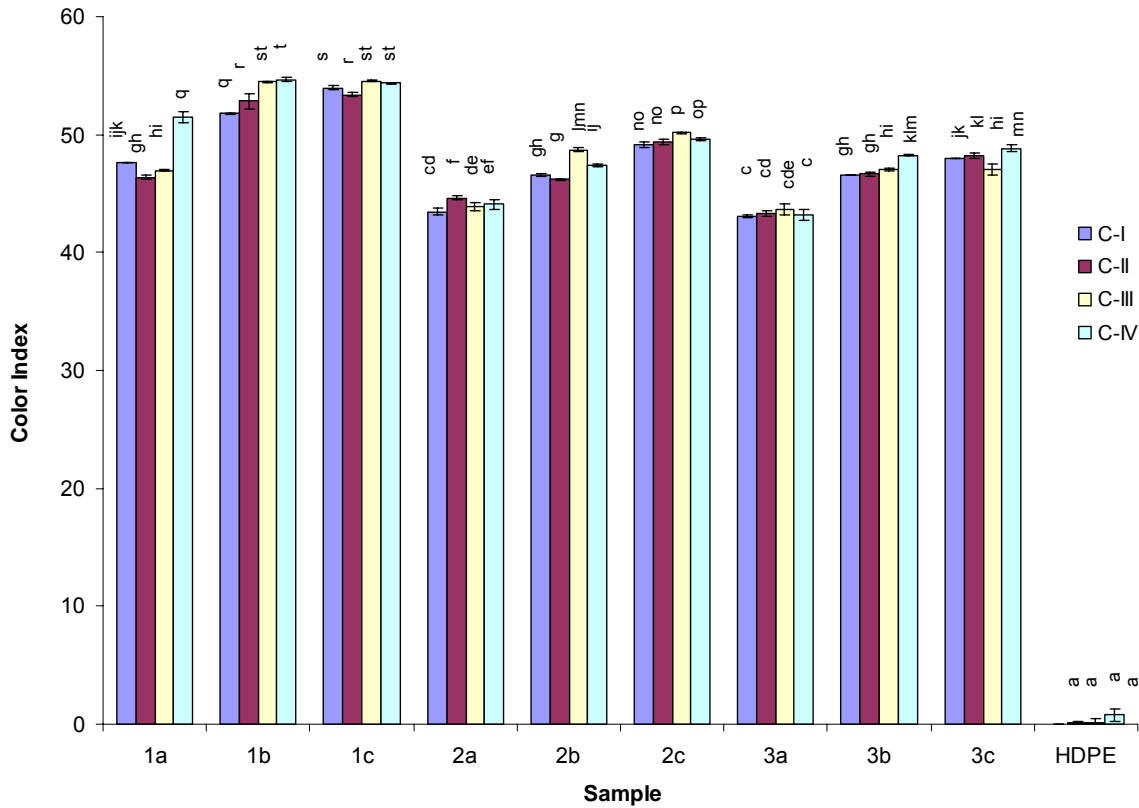


Figure 4.10 Color index of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The color index (ΔE) of PP biocomposite boards varied from 0 to 54. The pressure did not have any significant effect on the color index ΔE . The ANOVA (refer to Appendix A.11) showed that ΔE of PP biocomposites was significantly dependent on fiber type, fiber content, temperature, and all the interactions between fiber content, fiber type, temperature, and pressure ($P < 0.05$). The color index behavior of PP-based biocomposite was found similar to that of

HDPE composites. The effect of fiber content, temperature, and pressure on ΔE is illustrated by the response surface plots (refer to Appendix C.17-C.18).

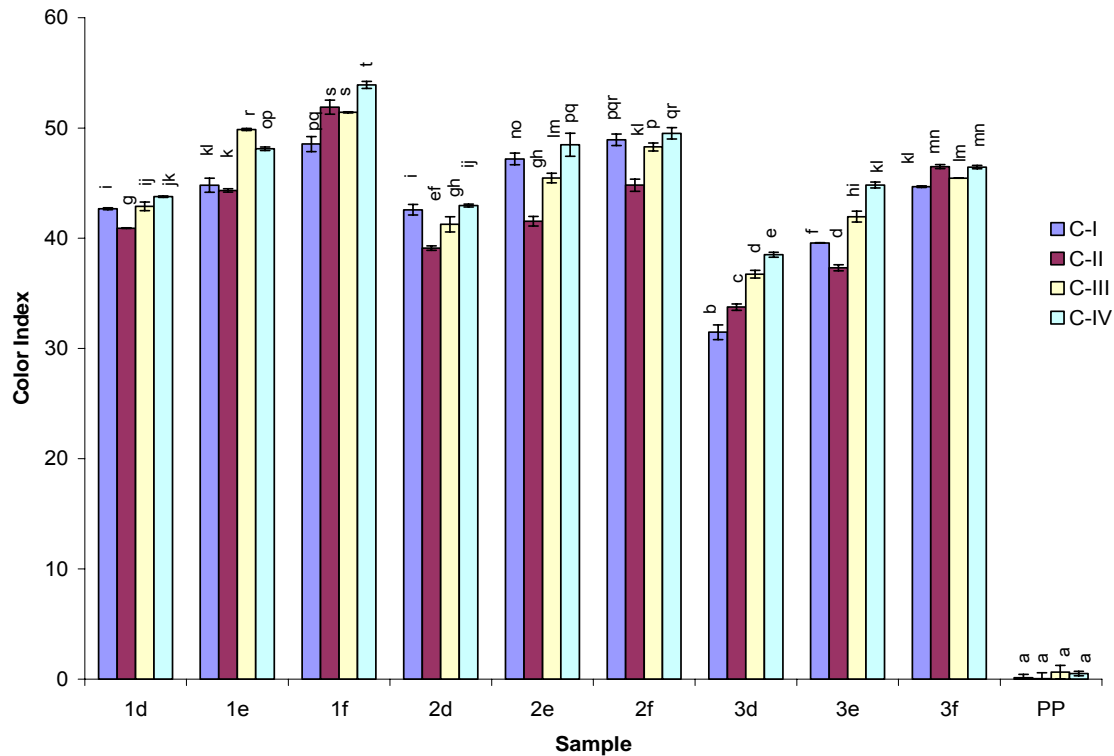


Figure 4.11 Color index of PP-based biocomposites;
a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The effect of fiber loading and molding temperature on PP based biocomposites was found similar to HDPE-based biocomposites.

4.5.2 Biocomposite boards density

The effect of fiber type, fiber content, molding temperature, and pressure on the density of HDPE and PP composites is presented in Figures 4.12 and 4.13 respectively. For HDPE composites, the density varied from 0.946 g/cm^3 to 1.072 g/cm^3 . The ANOVA (refer to Appendix A.1) showed that density of HDPE-based biocomposites was significantly dependent on fiber content, temperature,

and all the interactions between fiber content, fiber type, temperature, and pressure except fiber type*temperature ($P < 0.05$). The chemical treatment and pressure does not have significant effect on the density of HDPE biocomposites. Figure 4.12 indicates that the increase in fiber content increases the composite density. This can be explained by the fact that the density of flax fiber is higher than that of HDPE. The effect of fiber content, temperature, and pressure on HDPE-based biocomposites density is illustrated by the response surface plots (refer to Appendix C.3-C.4).

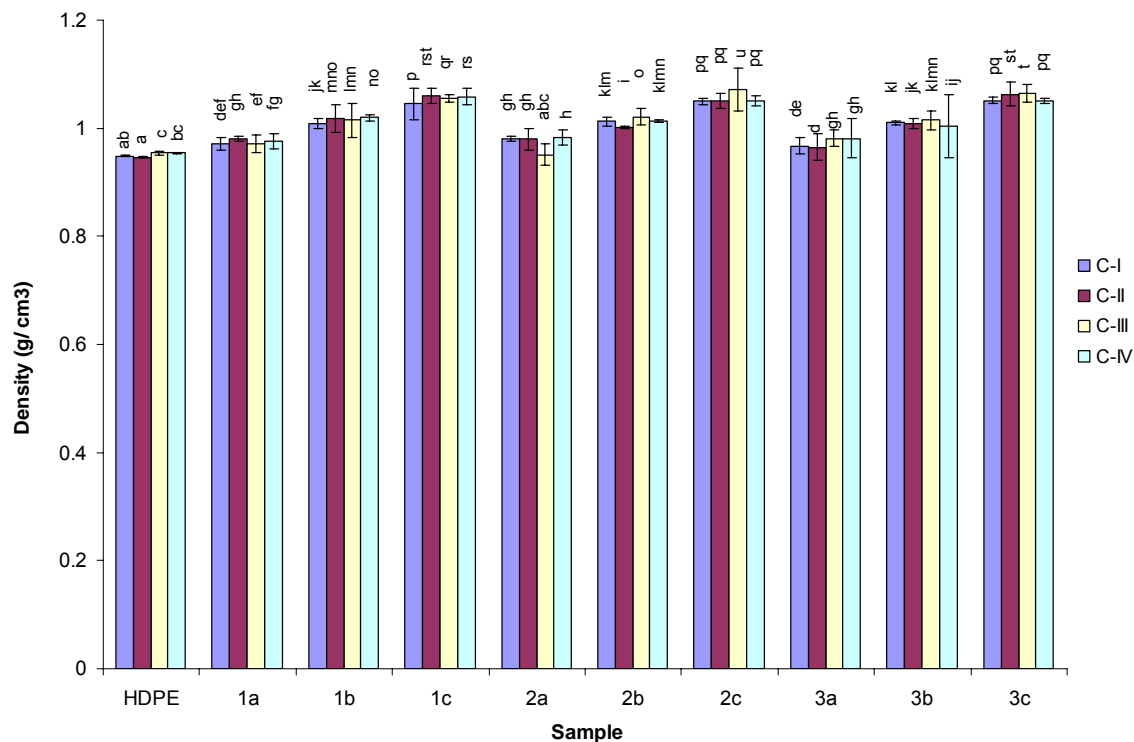


Figure 4.12 Actual density of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

Table 4.7 presents the density deviation of actual density of HDPE-based biocomposites developed at four different processing conditions from the ideal

density. It indicates that the actual density was found less than the ideal density in most of cases which explain the fact that there were some air voids present in the biocomposite developed. The biocomposite boards with 30% flax fiber contains the maximum number of voids because of higher negative density deviation from the ideal density. Siaotong (2006) reported that the density of HDPE biocomposite prepared by extrusion process is higher than ideal density because higher barrel temperature enables the polymer resin to melt more consistently and thorough mixing with the fiber without introducing much air.

Table 4.7 Density and density deviation (%) of HDPE-based biocomposites.

Sample ID	Ideal Density (g/cm ³)	Condition I (T=150, P=6.89)		Condition II (T=150, P=10.34)		Condition III (T=170, P=6.89)		Condition IV (T=150, P=10.34)	
		Actual Density	Density Deviation	Actual Density	Density Deviation	Actual Density	Density Deviation	Actual Density	Density Deviation
		(g/cm ³)	(%)	(g/cm ³)	(%)	(g/cm ³)	(%)	(g/cm ³)	(%)
HDPE	0.948	0.948	0.04%	0.947	-0.14%	0.955	0.70%	0.954	0.61%
1a	0.977	0.970	-0.71%	0.980	0.32%	0.972	-0.56%	0.976	-0.15%
1b	1.007	1.009	0.20%	1.018	1.16%	1.015	0.83%	1.019	1.26%
1c	1.096	1.045	-4.67%	1.060	-3.26%	1.055	-3.77%	1.059	-3.42%
2a	0.981	0.981	-0.02%	0.980	-0.06%	0.951	-3.04%	0.983	0.25%
2b	1.022	1.012	-0.93%	1.002	-1.97%	1.021	-0.06%	1.013	-0.82%
2c	1.078	1.050	-2.67%	1.050	-2.61%	1.072	-0.56%	1.051	-2.59%
3a	0.976	0.967	-0.92%	0.965	-1.15%	0.981	0.53%	0.981	0.53%
3b	1.025	1.011	-1.37%	1.009	-1.57%	1.015	-0.98%	1.004	-2.05%
3c	1.083	1.051	-2.93%	1.063	-1.88%	1.065	-1.63%	1.050	-3.07%

For PP-based biocomposites, the density varied from 0.904 g/cm³ to 1.040 g/cm³. The ANOVA (refer to Appendix A.10) showed that density of PP biocomposites was significantly dependent on fiber type, fiber content, pressure, and all the interactions between fiber content, fiber type, temperature, and pressure ($P < 0.05$). The molding temperature did not have a significant effect on

the PP composites. Figure 4.13 indicates that the increase in fiber content increased the composite density. This can be explained by the fact the density of flax fiber is higher than that of PP. The effect of fiber content, temperature, and pressure on PP-based biocomposites density is illustrated by the response surface plots (refer to Appendix C.19-C.20).

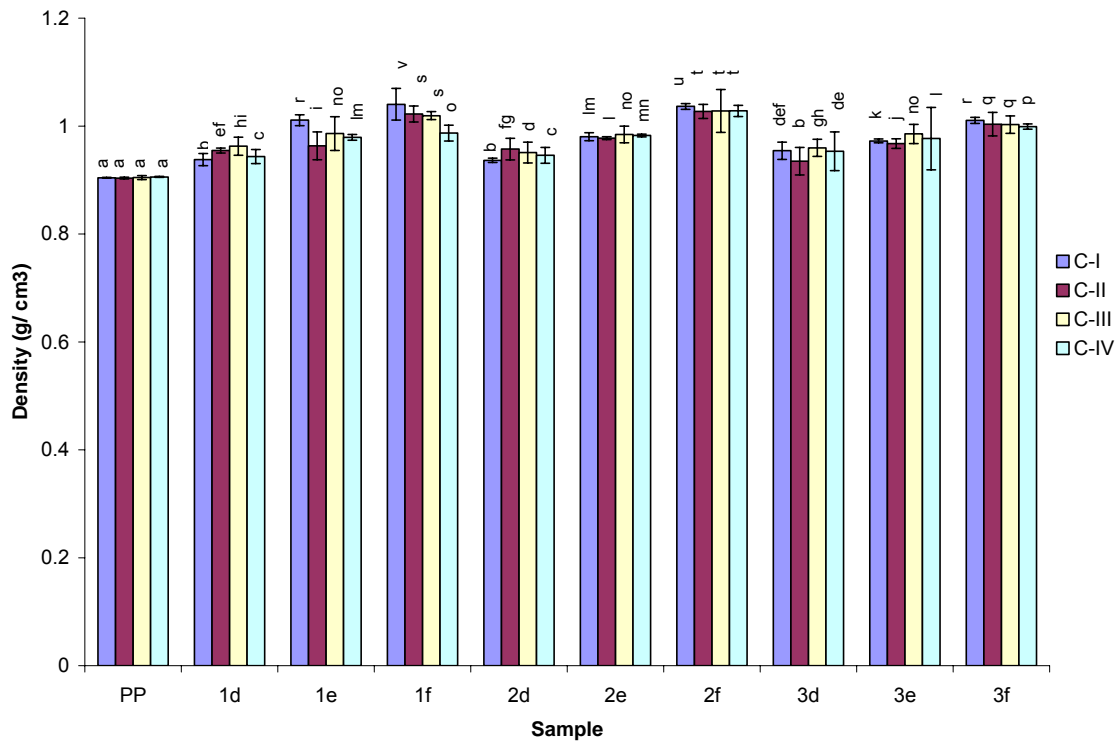


Figure 4.13 Actual density of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

Table 4.8 presents the density deviation of actual density of PP biocomposites developed at four different processing conditions from the ideal density. The results indicate the density deviation was higher for PP-based biocomposites reinforced with untreated flax fiber. The presence of air voids explains the reason for lower actual density of PP-based biocomposite.

Table 4.8 Density and density deviation (%) of PP-based biocomposites.

Sample ID	Ideal Density (g/cm ³)	Condition I (T=175, P=6.89)		Condition II (T=175, P=10.34)		Condition III (T=195, P=6.89)		Condition IV (T=195, P=10.89)	
		Actual Density (g/cm ³)	Density Deviation (%)	Actual Density (g/cm ³)	Density Deviation (%)	Actual Density (g/cm ³)	Density Deviation (%)	Actual Density (g/cm ³)	Density Deviation (%)
PP	0.904	0.904	0.04%	0.904	-0.04%	0.905	0.07%	0.906	0.21%
1d	0.957	0.938	-1.97%	0.955	-0.21%	0.963	0.62%	0.944	-1.36%
1e	1.009	1.011	0.15%	0.964	-4.55%	0.986	-2.30%	0.979	-3.01%
1f	1.072	1.040	-2.96%	1.022	-4.63%	1.019	-4.92%	0.987	-7.94%
2d	0.955	0.937	-1.95%	0.957	0.22%	0.951	-0.44%	0.946	-0.97%
2e	1.006	0.980	-2.59%	0.978	-2.84%	0.984	-2.18%	0.983	-2.35%
2f	1.058	1.036	-2.01%	1.027	-2.87%	1.028	-2.81%	1.028	-2.78%
3d	0.958	0.954	-0.36%	0.935	-2.37%	0.960	0.20%	0.953	-0.47%
3e	0.992	0.973	-1.90%	0.968	-2.41%	0.985	-0.61%	0.977	-1.48%
3f	1.015	1.011	-0.45%	1.004	-1.15%	1.003	-1.24%	0.999	-1.60%

PP based composites have higher density deviation than HDPE composites. HDPE have higher MFI which explains the fact that flax fiber wetting is better in HDPE composites and thus have less air voids.

4.5.3 Water absorption characteristics of biocomposite boards

Water absorption is one of the important properties considered for different commercial application of biocomposite. Higher water absorption leads to poor dimensional stability and hence is not recommended. The water absorption characteristics of HDPE- and PP-based biocomposites are presented in Figures 4.14 and 4.15, respectively. For HDPE-based biocomposites, the mass increase varied from 0% to 2.7%. The ANOVA (refer to Appendix A.3) showed that water absorption characteristics of HDPE biocomposites was significantly dependent on fiber type, fiber content, temperature, and all the interactions between fiber content, fiber type, and temperature ($P < 0.05$). The molding pressure and all the interactions with pressure did not have significant

effect on the HDPE composites except the interaction of fiber type*fiber content*temperature*pressure. Figure 4.14 indicates that increase in fiber content increased the water absorption. This can be explained by the fact the flax fiber is hydrophilic in nature and have greater affinity for water than the HDPE.

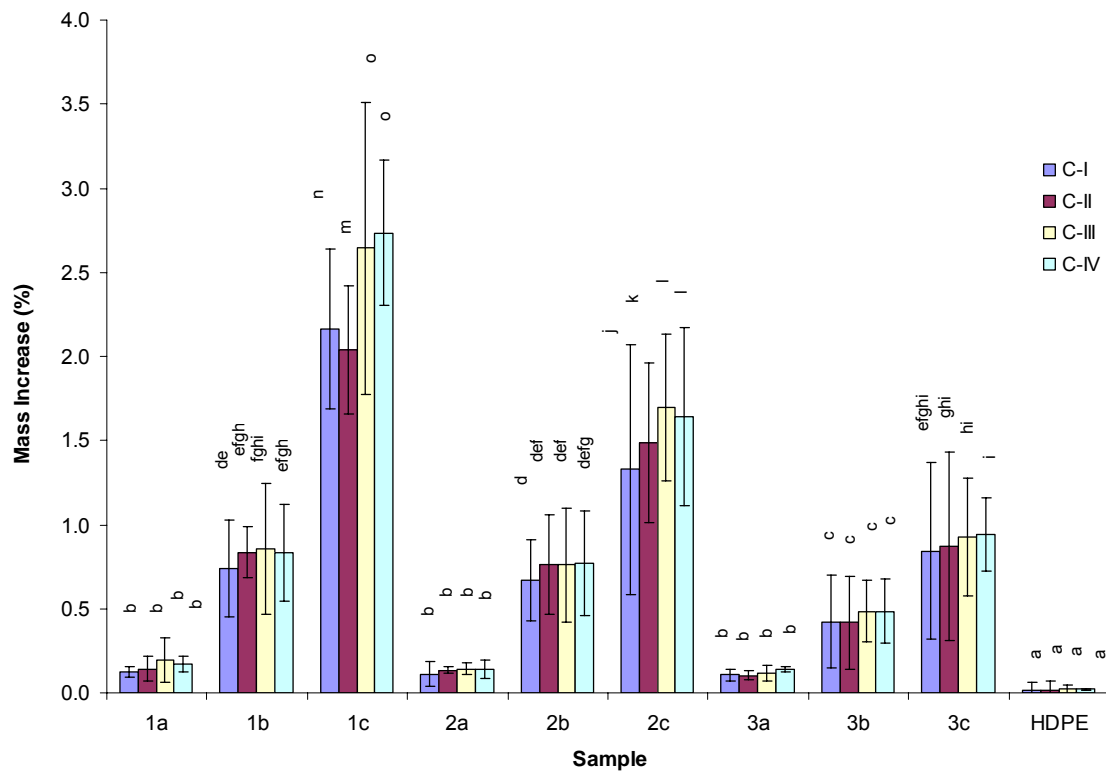


Figure 4.14 Water absorption characteristics of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The chemical treatments have significantly reduced the water absorption. Silane treatment showed better results and reduced the mass increase of 30% flax fiber reinforced HDPE composites to less than 1%. The maximum water absorption and change in dimension was observed for 30% untreated flax fiber reinforced HDPE composites. The maximum change in thickness and width of the HDPE biocomposites (30% untreated fiber content) was 2.7% and 2.4%, respectively (refer to Appendix E.1). The effect of fiber content, temperature, and

pressure on water absorption characteristics of HDPE-based biocomposites is illustrated by the response surface plots (refer to Appendix C.5-C.6).

For PP-based biocomposites, the mass increase varied from 0% to 6%. The ANOVA (refer to Appendix A.12) showed that water absorption characteristics of PP-based biocomposites was significantly affected by fiber type, fiber content, temperature, pressure, and all the interactions between fiber content, fiber type, pressure, and temperature except the interaction of fiber content *temperature*pressure ($P < 0.05$). Figure 4.15 indicates that increase in fiber content increased the water absorption. The reason is same as explained for HDPE composites that the flax fibers have greater affinity to water than PP.

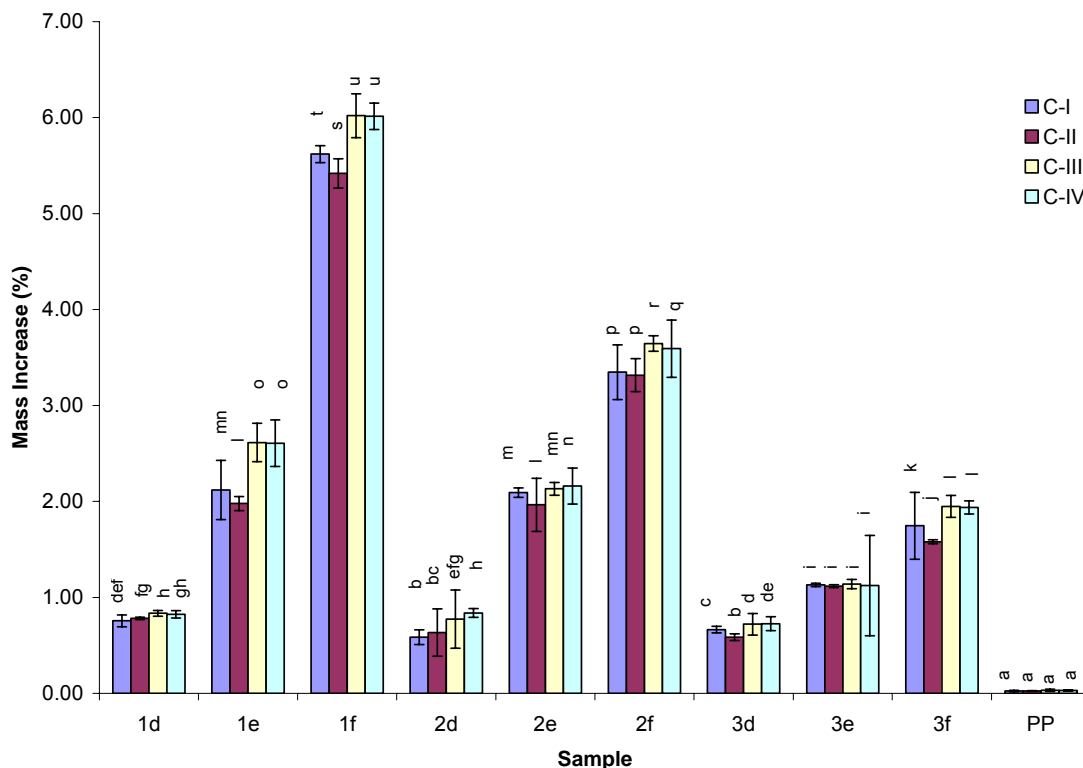


Figure 4.15 Water absorption characteristics of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The chemical treatments did significantly reduce the water absorption of natural fiber-reinforced composites (Bledzki and Gassan 1999; Mohanty et al. 2001; Wang 2004; Siaotong 2006). Silane treatment has also showed better results for PP-based biocomposites and reduces the mass increase of 30% flax fiber reinforced PP composites to less than 2%. The untreated flax fiber reinforced PP composites absorb more water due to higher density deviation from the ideal density as mentioned previously. The maximum increase in thickness and width of the PP biocomposites (30% untreated fiber content) was 3.95% and 1.59%, respectively (refer to Appendix E.2). The dimensional changes of PP-based biocomposites were higher than HDPE-based biocomposites which explain the polymer-fiber adhesion was better for HDPE-based biocomposites. This can be attributed to the fact that the selected grade of HDPE has higher MFI than PP which provided better wetting of flax fiber for better polymer-fiber adhesion. The effect of fiber content, temperature, and pressure on water absorption characteristics of PP-based biocomposites is illustrated by the response surface plots (refer to Appendix C.21-C.22).

4.6 Mechanical Properties

The mechanical properties of HDPE and PP composites were characterized by the tensile strength, Young's modulus, flexural strength, flexural modulus, and hardness number. The sample IDs with details for HDPE- and PP-based biocomposites mentioned in Tables 4.3 and 4.4 are used in the all the figures illustrating different mechanical properties. C-I, C-II, C-III, and C-IV

represent the four processing conditions. The details are given in Tables 4.5 and 4.6. Surface response plots were generated for silane treated reinforced composites data only to study the effect of fiber content, molding temperature, and molding pressure on the response variable due to the fact that silane treated fiber reinforced composites provided best results for all the variables.

4.6.1 Tensile strength of biocomposite boards

The tensile strength of HDPE- and PP-based biocomposites is presented in Figures 4.16 and 4.17, respectively. For HDPE-based biocomposites, the tensile strength varied from 15 MPa to 18 MPa.

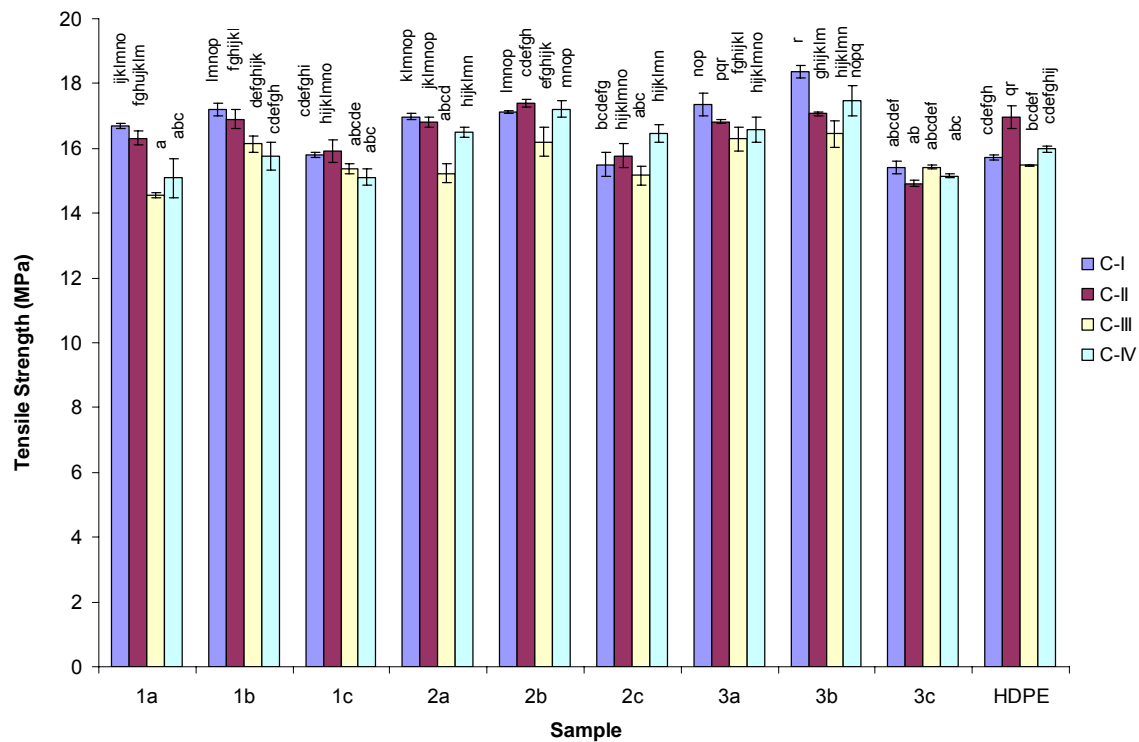


Figure 4.16 Tensile strength of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The ANOVA (refer to Appendix A.6) showed that tensile strength of HDPE-based biocomposites was significantly dependent on fiber type, fiber content, temperature, and all the interactions between fiber content, fiber type, temperature, and pressure except for interaction of fiber content*fiber type*temperature and fiber content*fiber type*pressure ($P < 0.05$). Figure 4.16 shows that tensile strength increased with increase in fiber content, but above 20% fiber content the tensile strength started decreasing. For all the combination of fiber fiber and HDPE, tensile strength was found higher at low molding temperature. Similar results were reported for glass fiber-reinforced compression molded composite (Kim et al. 1997). Removal of lignin and extractibles and with a small increase in cellulose content can also lead to increase in tensile strength (Bledzki et al.2008). The effect of fiber content, temperature, and pressure on tensile strength of HDPE-based biocomposites is illustrated by the response surface plots (refer to Appendix C.7-C.8).

For PP-based biocomposites, the tensile strength varied from 15 MPa to 20 MPa. The ANOVA (refer to Appendix A.15) showed that tensile strength of PP-based biocomposites was significantly dependent on fiber type, fiber content, pressure, and all the interactions between fiber content, fiber type, temperature, and pressure except for interaction of fiber content*pressure, fiber type*pressure, and fiber content*fiber type*temperature* pressure ($P < 0.05$). The tensile strength was found highest for 10% silane treated flax fiber reinforced PP biocomposites. The tensile strength started decreases above 10% flax fiber. The effect of temperature on PP-based biocomposites was found similar to HDPE-

based biocomposites as discussed earlier. The effect of fiber content, temperature, and pressure on tensile strength of PP-based biocomposites is illustrated by the response surface plots (refer to Appendix C.23-C.24).

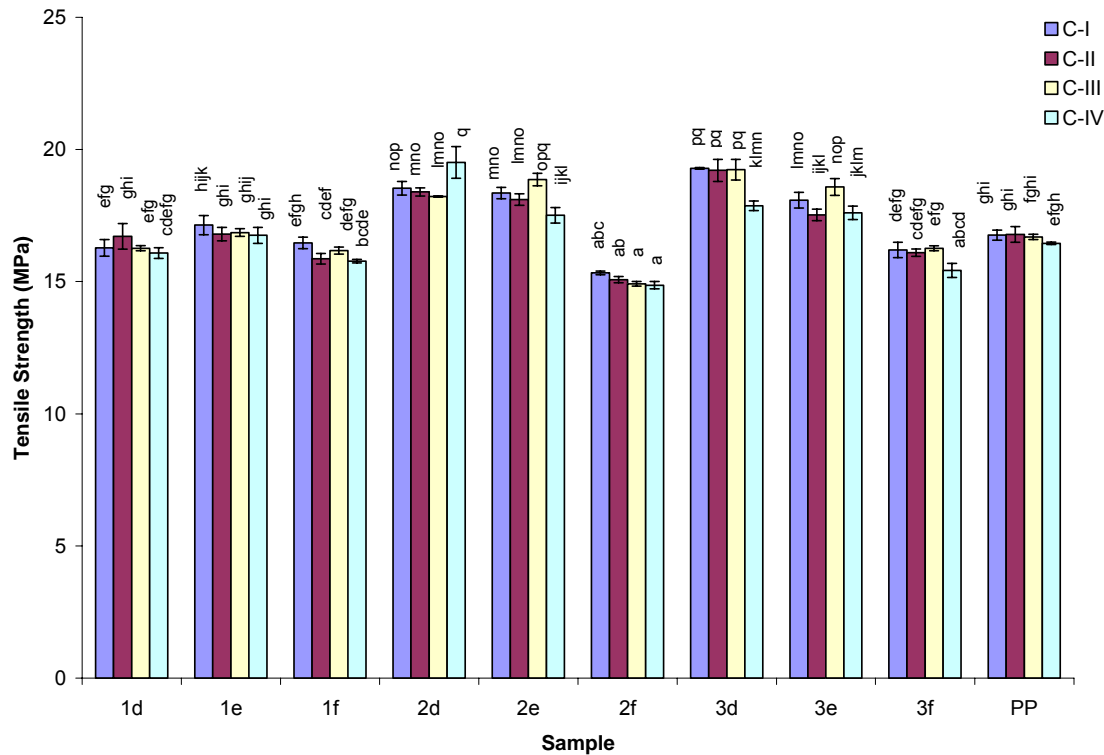


Figure 4.17 Tensile strength of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

Silane treated flax fiber reinforced HDPE- and PP-based biocomposites showed better tensile strength compared to alkaline treated and untreated flax fiber reinforced biocomposites due better interfacial adhesion. The interfacial adhesion can be enhanced by better fiber wettability. Wettability of flax fiber can be improved by chemical treatment due to reduction of the polar components of their surface energies (Cantero et al. 2003).

4.6.2 Young's modulus of biocomposite boards

Young's modulus is a measure of the stiffness of a material and is one of the primary properties considered when selecting a material in many engineering applications. The young's modulus of HDPE- and PP-based biocomposites is presented in Figures 4.18 and 4.19, respectively. For HDPE-based biocomposites, the modulus varied from 275 MPa to 662 MPa. Flax fiber reinforcement contributed an increase of 142% in Young's modulus of HDPE-based biocomposites (30% flax fiber). The ANOVA (refer to Appendix A.7) showed that Young's modulus of HDPE-based biocomposites was significantly dependent on fiber type, fiber content, temperature, and the interactions of fiber type*pressure and fiber content*temperature*pressure ($P < 0.05$).

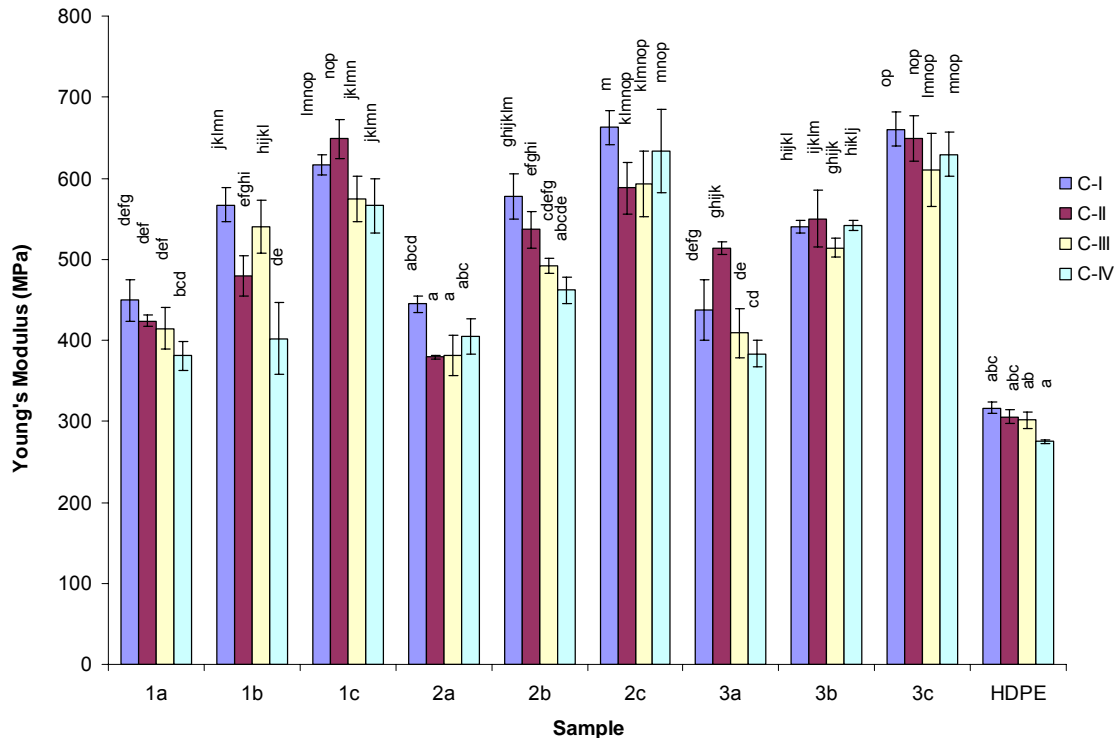


Figure 4.18 Young's modulus of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

Figure 4.18 shows that the Young's modulus increased with increase in fiber content. For all the combination of flax fiber and HDPE, Young's modulus was found higher at low molding temperature. Both silane and alkaline treatment of flax fiber improved the Young's modulus of HDPE-based biocomposites. The effect of fiber content, temperature, and pressure on Young's modulus of HDPE-based biocomposites is illustrated by the response surface plots (refer to Appendix C.9-C.10).

For PP-based composites, the modulus varied from 427 MPa to 656 MPa. Flax fiber reinforcement exhibits an increase of 54% in Young's modulus of PP-based biocomposites (30% flax fiber).

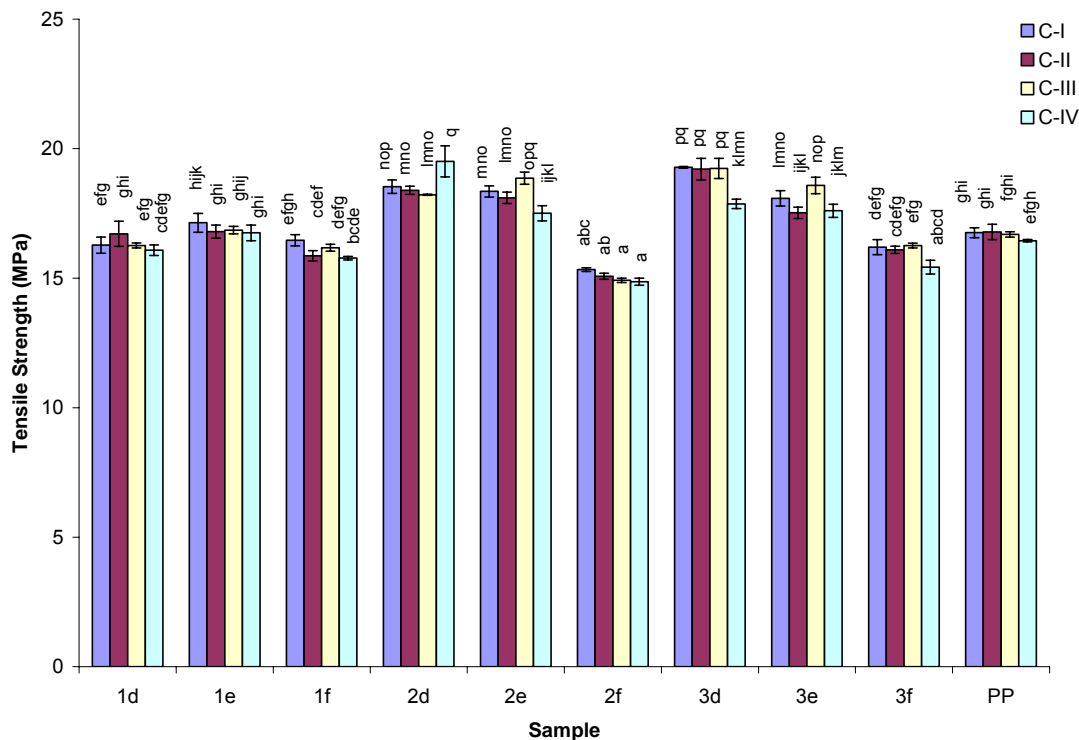


Figure 4.19 Young's modulus of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The ANOVA (refer to Appendix A.16) showed that Young's modulus of PP-based biocomposites was significantly dependent on fiber type, fiber content, pressure, and the interactions of fiber type*fiber content, fiber type*temperature, and fiber content*fiber content*temperature ($P < 0.05$). The stiffness of PP-based biocomposites also increased with increase in fiber content (Figure 4.19). For all the combination of fiber and PP, Young's modulus was found higher at low molding temperature. The effect of fiber content, temperature, and pressure on Young's modulus of PP-based biocomposites is illustrated by the response surface plots (refer to Appendix C.25-C.26).

The increase in Young's modulus was found higher for HDPE-based composites compared to PP-based composites due to better fiber dispersion in HDPE matrix and lower density deviation in HDPE biocomposites. The increase in Young's modulus of these compression molded PP-based biocomposites was lower than the earlier reported injection molded Eucalyptus wood fiber-reinforced PP which exhibited an increase of 200% in Young's modulus (Karmarkar et al 2007).

4.6.3 Flexural strength of biocomposite boards

The flexural strength of HDPE- and PP-based biocomposites is presented in Figures 4.20 and 4.21, respectively. For HDPE-based biocomposites, the flexural strength varied from 24 MPa to 31 MPa. The ANOVA (refer to Appendix A.8) showed that flexural/bending strength of HDPE-based biocomposites was significantly dependent on fiber type, fiber content, temperature, pressure, and the interactions of fiber type*fiber content, fiber type*temperature, fiber

type*pressure, fiber type*fiber content*pressure, temperature*pressure, and fiber type*fiber content*temperature*pressure($P < 0.05$).

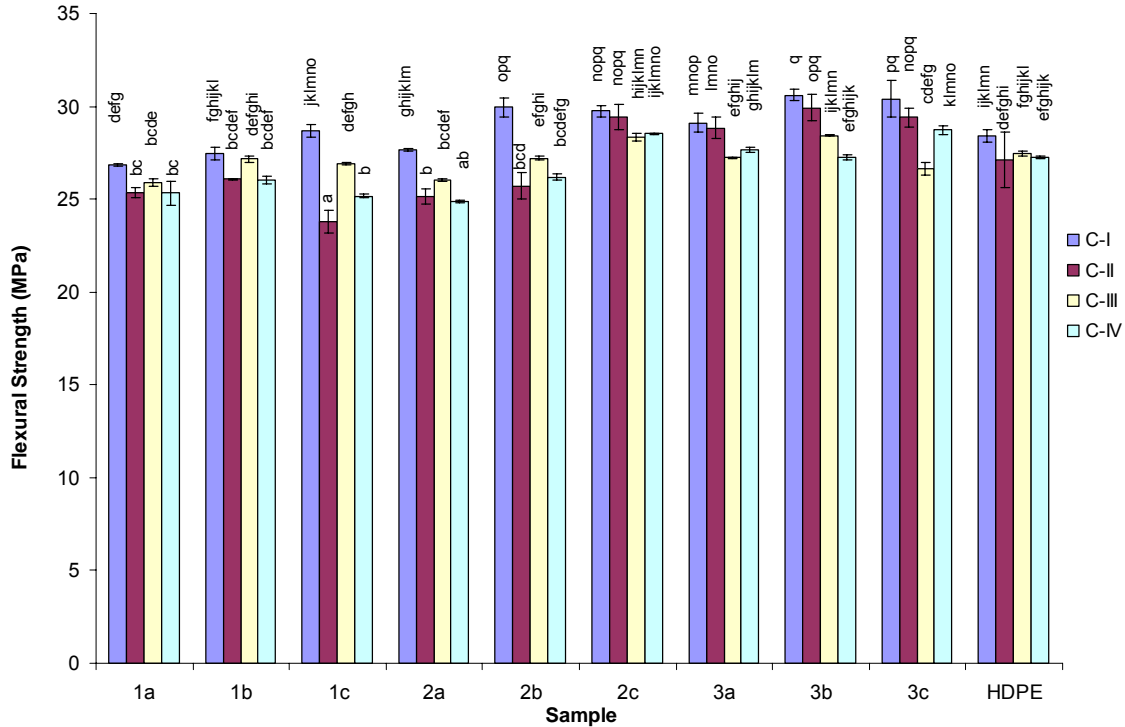


Figure 4.20 Flexural strength of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The flexural load induces both compressive and tensile stresses during flexural test (Bledzki et al. 2008). Figure 4.20 shows that the flexural strength increased with increase in fiber content. Flax fiber possesses higher strength and fiber-polymer bonding increases the flexural strength of the biocomposite. For all the combination of fiber fiber and HDPE, flexural strength was found higher at processing condition 1 having low molding temperature (150°C) and low pressure (6.89 MPa). Chemically treated flax fiber gave superior flexural strength because it improves the fiber-polymer interfacial adhesion. Similar observation

was reported by other researchers (Bledzki et al. 2008; Khanam et al. 2007; Sain et al. 2005) for other natural fiber based composites. The effect of fiber content, temperature, and pressure on flexural strength of HDPE composites is illustrated by the response surface plots (refer to Appendix C.11-C.12).

For PP-based biocomposites, the flexural strength showed the same trend and varied from 28 MPa to 37 MPa (Figure 4.21). However, flexural strength of PP-based composites was higher than HDPE biocomposites. This was due to the fact that PP has higher strength than HDPE.

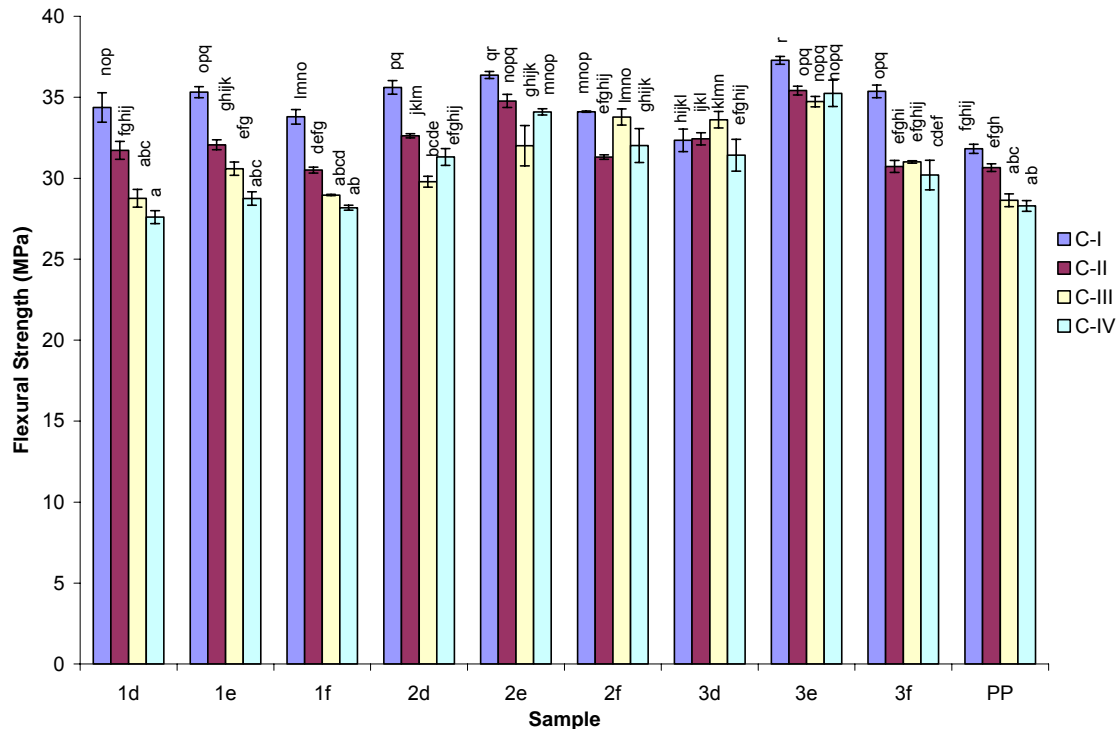


Figure 4.21 Flexural strength of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The quantitative analyses by ANOVA (refer to Appendix A.17) showed that flexural strength of PP biocomposites was significantly dependent on fiber type, fiber content, temperature, pressure, and all the interactions between fiber

type, fiber content, temperature, and pressure except fiber content*temperature, fiber type*fiber content*pressure, fiber content*temperature*pressure, and fiber type*temperature*pressure ($P < 0.05$).

The effect of fiber content, temperature, and pressure on flexural strength of PP-based biocomposites is illustrated by the response surface plots (refer to Appendix C.27-C.28).

4.6.4 Flexural modulus of biocomposite boards

The flexural modulus of HDPE- and PP-based biocomposites is presented in Figures 4.22 and 4.23, respectively. For both HDPE and PP-based biocomposites there was significant increase in flexural modulus with increase in fiber content. For HDPE-based biocomposites, the flexural modulus was doubled from 512 MPa to 1161 MPa. The ANOVA (refer to Appendix A.9) showed that flexural modulus of HDPE-based biocomposites was significantly dependent on fiber type, fiber content, temperature, pressure, and all the interactions between fiber type, fiber content, temperature, and pressure except the interaction of fiber type*temperature, fiber type*pressure, fiber content*pressure, and fiber content*temperature*pressure ($P < 0.05$). Flexural modulus was found higher at low molding temperature (150°C) and low pressure (6.89 MPa) condition. Chemical treatment provides better bonding with flax fiber and enhanced the flexural modulus. Flexural modulus was found highest for silane treated flax fiber reinforced HDPE composites (30% fiber). The effect of fiber content, temperature, and pressure on flexural modulus of HDPE

composites is illustrated by the response surface plots (refer to Appendix C.13-C.14).

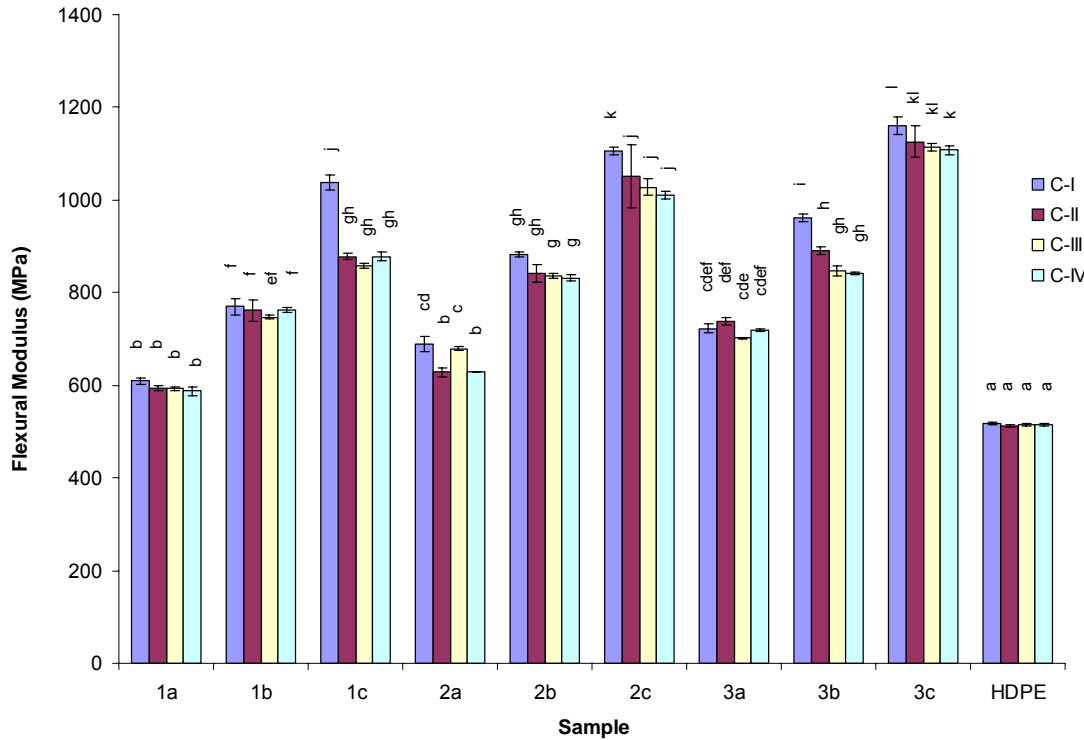


Figure 4.22 Flexural modulus of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

For PP-based biocomposites, the flexural modulus also increased significantly from 640 MPa to 1174 MPa. The effect of fiber loading and processing condition was found similar to HDPE biocomposites. The ANOVA (refer to Appendix A.18) showed that flexural modulus of PP-based biocomposites was significantly dependent on fiber type, fiber content, pressure, and all the interactions between fiber type, fiber content, temperature, and pressure except the interaction of temperature*pressure ($P < 0.05$). The flexural modulus of both HDPE and PP was found comparable with each other.

Response surface plots (refer to Appendix C.29-C.30) illustrates the effect of fiber content, temperature, and pressure on flexural modulus of PP-based biocomposites.

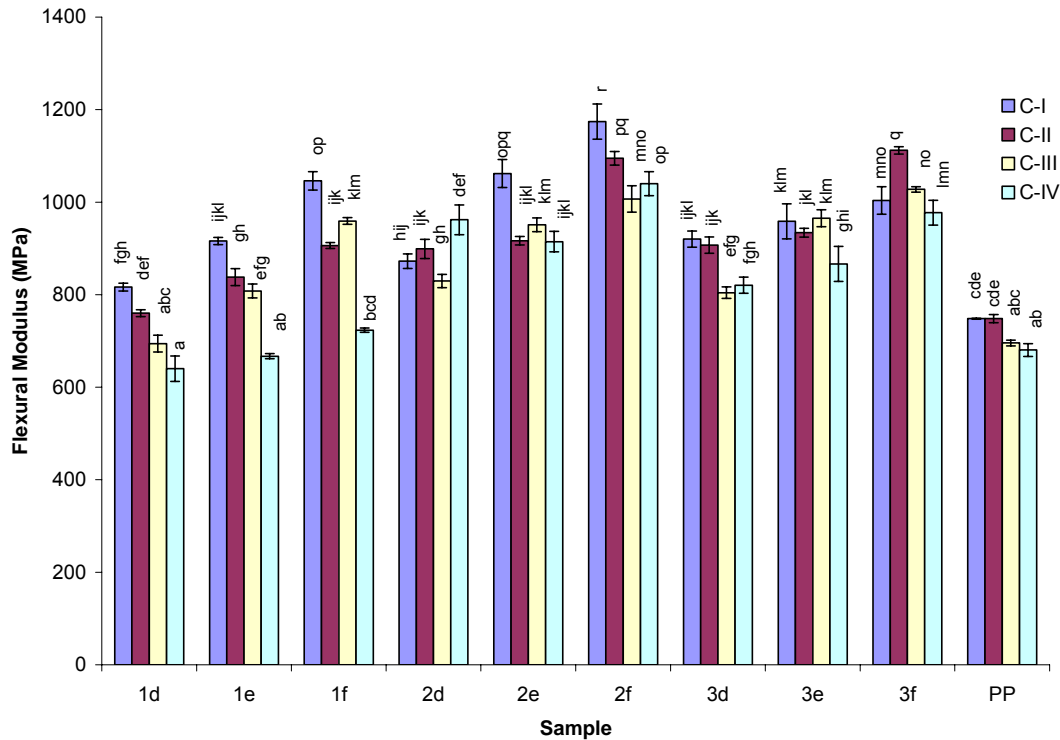


Figure 4.23 Flexural modulus of PP-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

4.6.5 Hardness of biocomposite boards

The effect of fiber type, fiber content, molding temperature, and pressure on the hardness of HDPE- and PP-based biocomposites is presented in Figures 4.24 and 4.25, respectively. The hardness number was determined as average of 10 readings of shore durometer. This method of measurement provides an empirical hardness value that does not correlate well to other properties.

For HDPE-based biocomposites, the durometer hardness number varied from 63 to 65. Statistical analyses ANOVA (refer to Appendix A.4) showed that hardness of HDPE-based biocomposites was significantly affected by only fiber content and the interactions between fiber type*pressure and temperature*pressure ($P < 0.05$). Figure 4.24 shows that the hardness decreased with increase in fiber content. Chemical treatment did not have any significant effect on the hardness of HDPE-based biocomposites.

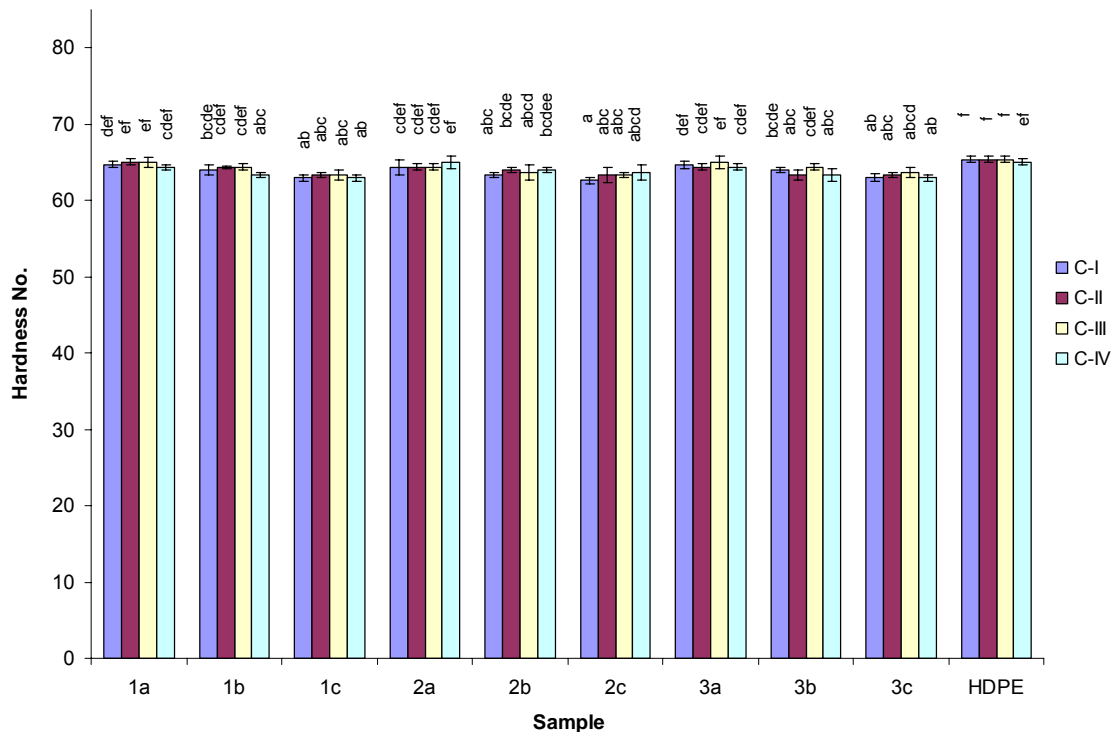


Figure 4.24 Hardness No. of HDPE-based biocomposites; a, b, c: means that same letter designation are not statistically different ($P = 0.05$) by Duncan's multiple range test.

The effect of fiber content, temperature, and pressure on hardness of HDPE-based biocomposites is also illustrated by the response surface plots (refer to Appendix C.15-C.16).

For PP-based biocomposites, the durometer hardness no. was higher than HDPE biocomposites and varied from 65 to 69 (Figure 4.25). PP biocomposites was also only affected by fiber loading. Figure 4.25 shows that the hardness decreased with increase in fiber content. Chemical treatment did not have any significant effect on the hardness of PP-based biocomposites. The ANOVA (refer to Appendix A.13) showed that hardness of PP biocomposites was significantly dependent on fiber content and the interactions between temperature*pressure ($P < 0.05$).

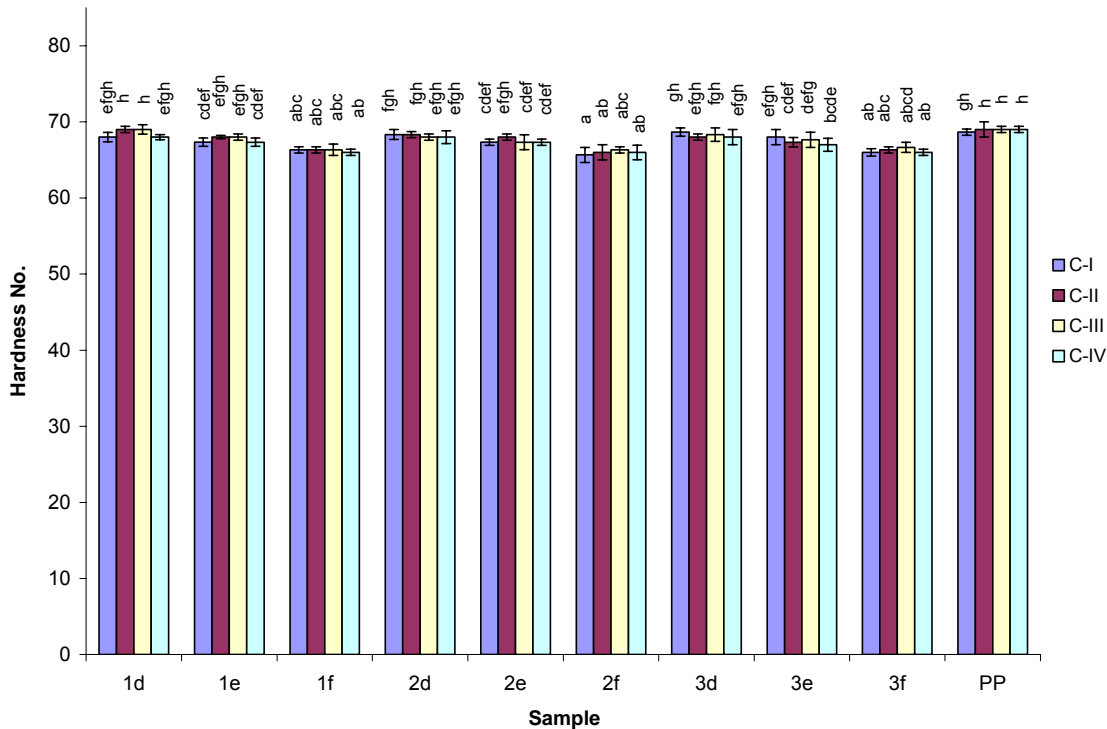


Figure 4.25 Hardness No. of PP-based biocomposites;
a, b, c: means that same letter designation are not statistically different ($P = 0.05$)
by Duncan's multiple range test.

The effect of fiber content, temperature, and pressure on hardness of PP-based composites is also illustrated by the response surface plots (refer to Appendix C.31-C.32).

4.7 Optimization of Fiber Content and Processing Parameters

Experimental results indicated that silane treated flax fiber reinforced HDPE- and PP-based biocomposite board have better physical and mechanical properties. Therefore, the optimal values of fiber content, molding temperature, and molding pressure was determined by utilizing and generating surface response plots and contour plot for silane treated reinforced HDPE- and PP-based biocomposites data.

Conventional graphical method (CGM) was applied as optimization technique (Siaotong 2006; Carrillo et al. 2004; Carrillo et al. 2002; Guillou and Floros 1993) to obtain optimal values of fiber content, molding temperature, molding pressure using 8 response variables. For both HDPE and PP composites, contour plots of the response variables (refer to Appendix D) were generated, analyzed, and superimposed applying superposition surface methodology to generate three contour plots for observation and selection of superior (optimum) combination of fiber content, molding temperature, and molding pressure for the production of optimized flax fiber reinforced HDPE/PP – based biocomposite boards by compression molding process.

For HDPE-based biocomposites, 4 contour plots were generated by tecplot 9.2 software for each response variables. Superposition of the 4 contours plots for each response was carried out to obtain the best (optimum) values of fiber content, temperature, and pressure. Table 4.9 lists the optimum values of fiber content, temperature, and pressure for each response variables.

Table 4.9 Optimum values of fiber content, temperature, and pressure for each response variables of HDPE-based biocomposites.

Response Variable	Optimum Fiber Content (%)	Optimum Temperature (°C)	Optimum Pressure (MPa)
Density	0	150, 170	6.89, 10.34
Color	0	150	6.89, 10.34
Water absorption	0	150	10.34
Tensile Strength	20	150, 170	6.89, 10.34
Young's Modulus	30	150	6.89, 10.34
Bending Strength	20	150	6.89
Flexural Strength	30	150	6.89, 10.34
Hardness	0	150, 170	6.89, 10.34

However, for specific application relevant weight can be added to the response variable to determine the final best (optimum) values of fiber content, temperature, and pressure. In this research equal weight was assigned to all eight response variables and the values of fiber content, temperature, and pressure were averaged to determine the final best (optimum) values for the production of optimized flax fiber reinforced HDPE composite board by compression molding process.

$$\text{Fiber content} = \frac{0\%(4) + 20(2) + 30(2)}{8} = 13 \%$$

$$\text{Temperature} = \frac{150(8) + 170(3)}{11} = 155^{\circ}\text{C}$$

$$\text{Pressure} = \frac{6.89(7) + 10.34(7)}{14} = 8.62 \text{ MPa}$$

For PP-based biocomposites, same procedure was followed to generate and superposition of 4 contour plots for each response variables. Table 4.10 lists

the optimum values of fiber content, temperature, and pressure for each response variables.

Table 4.10 Optimum values of fiber content, temperature, and pressure for each response variables of PP-based biocomposites.

Response Variable	Optimum Fiber Content (%)	Optimum Temperature (°C)	Optimum Pressure (MPa)
Density	0	175, 195	6.89
Color	0	175, 195	10.34
Water absorption	0	175, 195	10.34
Tensile Strength	10	175	6.89
Young's Modulus	30	195	6.89, 10.34
Bending Strength	20	175	6.89
Flexural Strength	30	175, 195	6.89
Hardness	0	175, 195	6.89, 10.34

Similar to HDPE composites, equal weight was assigned to all eight response variables of PP composites and the values of fiber content, temperature, and pressure were also averaged to determine the final best (optimum) values for the production of optimized flax fiber reinforced PP composite board by compression molding process.

$$\text{Fiber content} = \frac{0\%(4) + 10(1) + 20(1) + 30(2)}{8} = 11 \%$$

$$\text{Temperature} = \frac{175(7) + 195(6)}{13} = 184^{\circ}\text{C}$$

$$\text{Pressure} = \frac{6.89(6) + 10.34(4)}{10} = 8.27 \text{ MPa}$$

Table 4.11 lists the optimum values of fiber content, temperature, and pressure for each HDPE-and PP-based biocomposites, respectively. Optimal

values were determined by assigning equal weights to all eight response variables. However, for different applications different weights can be added to each response variables to determine optimal values.

Table 4.11 Optimum values of fiber content, temperature, and pressure for HDPE- and PP-Based Composites.

Process Variable	Optimum Fiber Content	Optimum Temperature	Optimum Pressure
HDPE	13 %	155 °C	8.62 MPa
PP	11 %	184 °C	8.27 MPa

These results compared with that of roto-molded biocomposite by Siaotong (2006) indicates that compression molded biocomposite can be reinforced with higher fiber content than roto-molded composites.

4.8 Summary

This chapter presented and discussed the results of preliminary experiments, different physical, thermal, and mechanical tests performed to study the effect of fiber loading and processing parameters (molding temperature, molding pressure) on developed biocomposite samples. In general, chemical treatments have significant effect on physical and mechanical properties of both HDPE- and PP-based biocomposites. Silane treatment showed better results compared to alkaline treatment. Therefore, optimum fiber loading, molding temperature, and molding pressure was determined using silane treated flax fiber reinforced biocomposites data only. Fiber loading played a significant role in physical and mechanical properties of both HDPE- and PP-based biocomposites.

Effect of molding temperature was found more significant compared to effect of molding pressure on properties of developed biocomposites. PP-based biocomposites showed higher density deviation and water absorption characteristics than HDPE-based biocomposites. Mechanical properties of both HDPE- and PP-based biocomposites were found comparable. Further, a detailed summary of the observed results and conclusions is presented in the next chapter.

5. SUMMARY AND CONCLUSIONS

The use of flax fiber for reinforcing thermoplastic resin has been investigated by several researchers and flax fiber has shown promising results as reinforcement for thermoplastic based products. However, major work has been done with injection molding and rotational molding. Most of the research reviewed indicated that only a limited work had been done on using flax fiber with thermoplastics to develop compression-molded biocomposites. Thus, the overall goal of this research was to develop compression molded green board using Saskatchewan flax fiber and to characterize the board to streamline the manufacturing process with optimal processing condition and fiber percentage to achieve biocomposites with desired properties.

The conclusions that were drawn from the experimental results to achieve the final goal have been subdivided and listed according to specific objectives set for the research.

5.1 Influence of two chemical treatments (alkaline and silane) on fiber morphology and the final compression molded biocomposite product:

- Both treatments removed the waxy encrusting substance from the surface of the flax fiber. The silane treatment provided a surface coating on the fiber
- Both chemical treatments provided better dispersion of flax fiber with the polymer resin. The silane treatment was more effective than the alkaline treatment in reducing the water absorption of 30% (wt %) flax fiber-

reinforced HDPE composites to less than 1%, and the water absorption of 30% flax fiber reinforced PP composites to less than 2%.

- The alkaline treatment enhanced the mechanical properties of HDPE and PP composites for all percentages of flax fiber compared to untreated flax fiber reinforced composites. The silane treatment further improved some of the mechanical properties compared to alkali treated flax fiber reinforced HDPE and PP composites.
- Chemical treatment did not have any significant effect on the hardness of the HDPE and PP composites.

5.2 Selection of processing parameters for HDPE and PP composites:

- Two levels of molding temperature (150°C, 170°C) and molding pressure (6.89 MPa, 10.34 MPa) were selected for processing the HDPE biocomposites based on some preliminary experiments.
- Two levels of molding temperature (175°C, 195°C) and molding pressure (6.89 MPa, 10.34 MPa) were selected for processing the PP biocomposites based on some preliminary experiments.

5.3 Effect of flax fiber loading on compression molded biocomposites:

- Increase in fiber loading increased the composite color index, density, water absorption, tensile strength, Young's modulus, bending strength, and flexural modulus. However, for HDPE composites, tensile and bending strength started decreasing beyond 20% (wt %) of flax fiber. For PP composites, the tensile and bending strength started decreasing beyond 10% (wt %) of flax fiber.

5.4 Effect of molding temperature and pressure on different physical and mechanical biocomposite of the biocomposites:

- Both HDPE and PP composites have better mechanical properties (tensile strength, Young's modulus, and bending strength) at lower molding temperature.
- The effect of pressure did not have any regular pattern.
- ANOVA was performed to quantitatively show the significant effects of the process variables (molding temperature, pressure, and fiber content) on the response variables (physical and mechanical properties).

5.5 Determine the optimal fiber loading, molding temperature, and pressure

- CGM was adopted to determine the optimum fiber loading, molding temperature, and pressure by superposition surface methodology.
- For HDPE biocomposites, the optimum values were 13% (wt %) flax fiber content, 155°C, and 8.62 MPa.
- For PP biocomposites, the optimum values were 11% (wt %) flax fiber content, 184°C, and 8.27 MPa.

5.6 Characterization and comparison of the two different polymer resins (HDPE & PP) based flax reinforced compression molded biocomposite:

- Three physical and five mechanical properties were measured to characterize the HDPE and PP composites
- The water absorption of PP composites was higher than that of HDPE composites. The dispersion of flax fiber was more uniform in HDPE composites. This can be explained by the fact that MFI of HDPE

composites was higher which provided better wetting of fiber, improving the fiber-polymer adhesion. The density deviation of actual density from ideal density was higher for PP composites resulting in more air voids in PP composites.

- Mechanical properties of HDPE and PP composites were found comparable. However, PP was found harder than the HDPE composites.

In this study, it was found that flax fiber served as reinforcement for both HDPE and PP resins. PP is largest commodity plastic presently used for various biocomposite application. The result of HDPE based composites were found promising and HDPE can be used as replacement of PP for compression molded products for commercial purposes.

6. RECOMMENDATIONS

Flax fiber reinforced thermoplastic biocomposites can be successfully manufactured by compression molding process. Extrusion process with combination of compression molding technology can be used to develop uniformly distributed flax fiber reinforced HDPE/PP biocomposites. Based on this study, several recommendations are made for further studies.

- Only two levels of temperature and pressure were selected for study. In future studies, a broader temperature and pressure profile should be studied to have better understanding of the effect of temperature and pressure.
- The role of twin-screw extruder can be investigated for compounding process for better fiber-polymer mixing for compression molded products
- Some additional thermal properties studies (thermal conductivity) are suggested for further characterizing the compression molded product.
- Studies on additional mechanical properties like impact strength are recommendation for future.
- The effect of residence time and cooling time could be investigated in future studies to understand the physical and mechanical properties of composite.
- Only one size of flax fiber was used in this study, in future, effect of fiber size can be investigated to determine optimum flax fiber length for compression molding.

- Flow enhancer is recommendation for low MFI thermoplastics to improve fiber –polymer adhesion.
- Comparison studies for cost effectiveness and performance are recommended for future to evaluate the commercialization and market possibilities of the developed product.

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APPENDICES

APPENDIX A

Analyses of Variance (ANOVA)

Table A.1 Analysis of variance of actual density for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	0.127 ^a	35	0.004	317.388	0.000
Error	0.001	72	0.000		
Total	111.179	108			
Corrected Total	0.128	107			
Fiber Type	0.000	2	0.000	1.929	0.153
Fiber Content	0.121	2	0.060	5279.929	0.000
Temperature	0.000	1	0.000	25.409	0.000
Pressure	0.000	1	0.000	2.635	0.109
Fiber Type * Fiber content	0.000	4	0.000	4.830	0.002
Fiber Type * Temperature	0.000	2	0.000	2.197	0.119
Fiber Content * Temperature	0.000	2	0.000	6.032	0.004
Fiber Type * Fiber Content * Temperature	0.002	4	0.000	33.769	0.000
Fiber Type * Pressure	0.001	2	0.000	27.462	0.000
Fiber Content * Pressure	0.001	2	0.000	23.886	0.000
Fiber Type * Fiber Content * Pressure	0.001	4	0.000	19.603	0.000
Temperature * Pressure	0.000	1	0.000	13.496	0.000
Fiber Content * Temperature * Pressure	0.000	2	0.000	12.557	0.000
Fiber Type * Temperature * Pressure	0.001	2	0.000	43.302	0.000
Fiber Content * Fiber Type * Temperature * Pressure	0.000	4	0.000	9.910	0.000

^aR Squared = .994 (Adjusted R Squared = .990)

Table A.2 Analysis of variance of color index for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1383.87 ^a	35	39.539	301.062	0.000
Error	9.46	72	0.131		
Total	253525.64	108			
Corrected Total	1393.3309	107			
Fiber Type	697.03	2	348.516	2653.683	0.000
Fiber Content	573.67	2	286.837	2184.043	0.000
Temperature	25.03	1	25.032	190.601	0.000
Pressure	3.35	1	3.353	25.529	0.000
Fiber Type * Fiber content	19.54	4	4.885	37.195	0.000
Fiber Type * Temperature	9.18	2	4.591	34.958	0.000
Fiber Content * Temperature	7.28	2	3.640	27.712	0.000
Fiber Type * Fiber Content * Temperature	3.88	4	0.971	7.390	0.000
Fiber Type * Pressure	2.69	2	1.343	10.229	0.000
Fiber Content * Pressure	2.12	2	1.059	8.064	0.001
Fiber Type * Fiber Content * Pressure	9.73	4	2.432	18.514	0.000
Temperature * Pressure	1.75	1	1.746	13.293	0.001
Fiber Content * Temperature * Pressure	7.95	2	3.976	30.277	0.000
Fiber Type * Temperature * Pressure	2.86	2	1.432	10.903	0.000
Fiber Content * Fiber Type * Temperature * Pressure	17.81	4	4.452	33.899	0.000

^aR Squared = .993 (Adjusted R Squared = .990)

Table A.3 Analysis of variance of water absorption for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	55.958 ^a	35	1.599	450.343	0.000
Error	0.256	72	0.004		
Total	126.249	108			
Corrected Total	56.214	107			
Fiber Type	7.237	2	3.618	1019.219	0.000
Fiber Content	40.093	2	20.046	5646.577	0.000
Temperature	0.474	1	0.474	133.560	0.000
Pressure	0.008	1	0.008	2.308	0.133
Fiber Type * Fiber content	7.218	4	1.804	508.248	0.000
Fiber Type * Temperature	0.146	2	0.073	20.513	0.000
Fiber Content * Temperature	0.427	2	0.213	60.120	0.000
Fiber Type * Fiber Content * Temperature	0.255	4	0.064	17.928	0.000
Fiber Type * Pressure	0.006	2	0.003	0.800	0.453
Fiber Content * Pressure	0.002	2	0.001	0.309	0.735
Fiber Type * Fiber Content * Pressure	0.006	4	0.002	0.439	0.780
Temperature * Pressure	0.005	1	0.005	1.465	0.230
Fiber Content * Temperature * Pressure	0.021	2	0.011	3.011	0.055
Fiber Type * Temperature * Pressure	0.005	2	0.003	0.708	0.496
Fiber Content * Fiber Type * Temperature * Pressure	0.056	4	0.014	3.922	0.006

^aR Squared = .995 (Adjusted R Squared = .993)

Table A.4 Analysis of variance of hardness for HDPE-based biocomposites.

Source	Type III Sum of Squares	Df	Mean Square	F	Sig.
Corrected Model	46.667 ^a	35	1.333	4.364	0.000
Error	22.000	72	0.306		
Total	952102.000	108			
Corrected Total	68.667	107			
Fiber Type	0.389	2	0.194	0.636	0.532
Fiber Content	34.889	2	17.444	57.091	0.000
Temperature	0.333	1	0.333	1.091	0.300
Pressure	0.148	1	0.148	0.485	0.488
Fiber Type * Fiber content	0.556	4	0.139	0.455	0.769
Fiber Type * Temperature	1.167	2	0.583	1.909	0.156
Fiber Content * Temperature	0.222	2	0.111	0.364	0.696
Fiber Type * Fiber Content * Temperature	0.111	4	0.028	0.091	0.985
Fiber Type * Pressure	4.130	2	2.065	6.758	0.002
Fiber Content * Pressure	0.519	2	0.259	0.848	0.432
Fiber Type * Fiber Content * Pressure	0.370	4	0.093	0.303	0.875
Temperature * Pressure	1.815	1	1.815	5.939	0.017
Fiber Content * Temperature * Pressure	1.130	2	0.565	1.848	0.165
Fiber Type * Temperature * Pressure	0.296	2	0.148	0.485	0.618
Fiber Content * Fiber Type * Temperature * Pressure	0.593	4	0.148	0.485	0.747

^aR Squared = .680 (Adjusted R Squared = .524)

Table A.5 Analysis of variance of melt flow index (MFI) for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	16.526919 ^a	8	2.0658648	1690.253	0.000
Error	0.022	18	0.0012222		
Total	76.7004	27			
Corrected Total	16.548919	26			
Fiber Type	0.0649852	2	0.0324926	26.584848	0.000
Fiber Content	16.186674	2	8.093337	6621.8212	0.000
Fiber Type * Fiber content	0.2752593	4	0.0688148	56.30303	0.000

^aR Squared = .999 (Adjusted R Squared = .998)

Table A.6 Analysis of variance of tensile strength for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	84.571 ^a	35	2.416	10.442	0.000
Error	16.660	72	0.231		
Total	28473.919	108			
Corrected Total	101.232	107			
Fiber Type	5.140	2	2.570	11.106	0.000
Fiber Content	22.193	2	11.096	47.954	0.000
Temperature	10.641	1	10.641	45.986	0.000
Pressure	0.088	1	0.088	0.380	0.540
Fiber Type * Fiber content	13.242	4	3.311	14.307	0.000
Fiber Type * Temperature	3.825	2	1.913	8.265	0.001
Fiber Content * Temperature	5.180	2	2.590	11.193	0.000
Fiber Type * Fiber Content * Temperature	1.188	4	0.297	1.284	0.284
Fiber Type * Pressure	2.936	2	1.468	6.344	0.003
Fiber Content * Pressure	3.324	2	1.662	7.182	0.001
Fiber Type * Fiber Content * Pressure	2.205	4	0.551	2.382	0.059
Temperature * Pressure	5.333	1	5.333	23.049	0.000
Fiber Content * Temperature * Pressure	1.966	2	0.983	4.248	0.018
Fiber Type * Temperature * Pressure	4.979	2	2.490	10.760	0.000
Fiber Content * Fiber Type * Temperature * Pressure	2.332	4	0.583	2.519	0.049

^aR Squared = .835 (Adjusted R Squared = .755)

Table A.7 Analysis of variance of young's modulus for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	895937.85 ^a	35	25598.224	12.207	0.000
Error	150985.93	72	2097.027		
Total	30045395.86	108			
Corrected Total	1046923.79	107			
Fiber Type	19226.09	2	9613.047	4.584	0.013
Fiber Content	725972.65	2	362986.323	173.096	0.000
Temperature	51973.23	1	51973.228	24.784	0.000
Pressure	8209.36	1	8209.357	3.915	0.052
Fiber Type * Fiber content	4504.09	4	1126.023	0.537	0.709
Fiber Type * Temperature	854.53	2	427.267	0.204	0.816
Fiber Content * Temperature	869.73	2	434.867	0.207	0.813
Fiber Type * Fiber Content * Temperature	14464.34	4	3616.086	1.724	0.154
Fiber Type * Pressure	16680.84	2	8340.420	3.977	0.023
Fiber Content * Pressure	9359.40	2	4679.698	2.232	0.115
Fiber Type * Fiber Content * Pressure	16252.25	4	4063.063	1.938	0.113
Temperature * Pressure	321.71	1	321.713	0.153	0.696
Fiber Content * Temperature * Pressure	14221.77	2	7110.885	3.391	0.039
Fiber Type * Temperature * Pressure	2641.41	2	1320.705	0.630	0.536
Fiber Content * Fiber Type * Temperature * Pressure	10386.44	4	2596.610	1.238	0.302

^aR Squared = .856 (Adjusted R Squared = .786)

Table A.8 Analysis of variance of flexural strength for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	327.20 ^a	35	9.349	20.995	0.000
Error	32.06	72	0.445		
Total	81646.97	108			
Corrected Model	359.266	107			
Fiber Type	109.57	2	54.788	123.040	0.000
Fiber Content	34.15	2	17.076	38.347	0.000
Temperature	35.26	1	35.260	79.186	0.000
Pressure	36.27	1	36.273	81.460	0.000
Fiber Type * Fiber content	32.25	4	8.063	18.108	0.000
Fiber Type * Temperature	14.09	2	7.050	15.832	0.000
Fiber Content * Temperature	0.31	2	0.157	0.353	0.704
Fiber Type * Fiber Content * Temperature	1.21	4	0.304	0.684	0.606
Fiber Type * Pressure	15.66	2	7.830	17.584	0.000
Fiber Content * Pressure	2.74	2	1.370	3.076	0.052
Fiber Type * Fiber Content * Pressure	20.36	4	5.091	11.434	0.000
Temperature * Pressure	13.45	1	13.448	30.200	0.000
Fiber Content * Temperature * Pressure	0.42	2	0.212	0.476	0.623
Fiber Type * Temperature * Pressure	2.30	2	1.152	2.588	0.082
Fiber Content * Fiber Type * Temperature * Pressure	9.12	4	2.280	5.120	0.001

^aR Squared = .911 (Adjusted R Squared = .867)

Table A.9 Analysis of variance of flexural modulus for HDPE-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3098146.05 ^a	35	88518.46	111.191	0.0000
Error	57318.53	72	796.09		
Total	79233897.01	108			
Corrected Total	3155464.58	107			
Fiber Type	434773.89	2	217386.94	273.068	0.0000
Fiber Content	2497443.11	2	1248721.55	1568.567	0.0000
Temperature	38060.68	1	38060.68	47.809	0.0000
Pressure	18440.99	1	18440.99	23.164	0.0000
Fiber Type * Fiber content	36545.60	4	9136.40	11.477	0.0000
Fiber Type * Temperature	911.15	2	455.58	0.572	0.5668
Fiber Content * Temperature	10753.96	2	5376.98	6.754	0.0020
Fiber Type * Fiber Content * Temperature	12708.80	4	3177.20	3.991	0.0056
Fiber Type * Pressure	2535.90	2	1267.95	1.593	0.2105
Fiber Content * Pressure	3677.52	2	1838.76	2.310	0.1066
Fiber Type * Fiber Content * Pressure	11878.97	4	2969.74	3.730	0.0082
Temperature * Pressure	12869.66	1	12869.66	16.166	0.0001
Fiber Content * Temperature * Pressure	2525.43	2	1262.72	1.586	0.2118
Fiber Type * Temperature * Pressure	6226.41	2	3113.20	3.911	0.0244
Fiber Content * Fiber Type * Temperature * Pressure	8794.00	4	2198.50	2.762	0.0340

^aR Squared = .982 (Adjusted R Squared = .973)

Table A.10 Analysis of variance of actual density for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	0.099	35	0.003	506.242	0.000
Error	0.000	72	0.000		
Total	104.323	108			
Corrected Total	0.099	107			
Fiber Type	0.002	2	0.001	162.065	0.000
Fiber Content	0.083	2	0.041	7394.921	0.000
Temperature	0.000	1	0.000	3.353	0.071
Pressure	0.002	1	0.002	357.988	0.000
Fiber Type * Fiber content	0.003	4	0.001	126.174	0.000
Fiber Type * Temperature	0.001	2	0.000	83.876	0.000
Fiber Content * Temperature	0.002	2	0.001	174.219	0.000
Fiber Type * Fiber Content * Temperature	0.001	4	0.000	30.070	0.000
Fiber Type * Pressure	0.002	2	0.001	134.439	0.000
Fiber Content * Pressure	0.001	2	0.000	51.993	0.000
Fiber Type * Fiber Content * Pressure	0.001	4	0.000	46.977	0.000
Temperature * Pressure	0.000	1	0.000	2.783	0.100
Fiber Content * Temperature * Pressure	0.000	2	0.000	9.469	0.000
Fiber Type * Temperature * Pressure	0.001	2	0.000	82.934	0.000
Fiber Content * Fiber Type * Temperature * Pressure	0.002	4	0.000	88.412	0.000

^aR Squared = .996 (Adjusted R Squared = .994)

Table A.11 Analysis of variance of color index for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2626.462	35	75.042	195.840	0.000
Error	27.589	72	0.383		
Total	213410.325	108			
Corrected Total	2654.050	107			
Fiber Type	757.412	2	378.706	988.325	0.000
Fiber Content	1350.570	2	675.285	1762.320	0.000
Temperature	202.158	1	202.158	527.579	0.000
Pressure	0.717	1	0.717	1.871	0.176
Fiber Type * Fiber content	60.560	4	15.140	39.512	0.000
Fiber Type * Temperature	9.783	2	4.892	12.766	0.000
Fiber Content * Temperature	25.689	2	12.844	33.521	0.000
Fiber Type * Fiber Content * Temperature	32.660	4	8.165	21.309	0.000
Fiber Type * Pressure	28.298	2	14.149	36.925	0.000
Fiber Content * Pressure	12.663	2	6.331	16.523	0.000
Fiber Type * Fiber Content * Pressure	20.495	4	5.124	13.372	0.000
Temperature * Pressure	46.099	1	46.099	120.307	0.000
Fiber Content * Temperature * Pressure	49.880	2	24.940	65.086	0.000
Fiber Type * Temperature * Pressure	9.845	2	4.923	12.847	0.000
Fiber Content * Fiber Type * Temperature * Pressure	19.632	4	4.908	12.809	0.000

^aR Squared = .990 (Adjusted R Squared = .985)

Table A.12 Analysis of variance of water absorption for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	267.628	35	7.647	7454.272	0.000
Error	0.074	72	0.001		
Total	737.571	108			
Corrected Total	267.702	107			
Fiber Type	55.996	2	27.998	27293.939	0.000
Fiber Content	160.194	2	80.097	78082.971	0.000
Temperature	1.479	1	1.479	1441.333	0.000
Pressure	0.040	1	0.040	38.962	0.000
Fiber Type * Fiber content	48.885	4	12.221	11914.006	0.000
Fiber Type * Temperature	0.285	2	0.143	138.958	0.000
Fiber Content * Temperature	0.252	2	0.126	123.067	0.000
Fiber Type * Fiber Content * Temperature	0.353	4	0.088	85.987	0.000
Fiber Type * Pressure	0.010	2	0.005	4.856	0.011
Fiber Content * Pressure	0.035	2	0.017	17.031	0.000
Fiber Type * Fiber Content * Pressure	0.015	4	0.004	3.585	0.010
Temperature * Pressure	0.038	1	0.038	37.359	0.000
Fiber Content * Temperature * Pressure	0.003	2	0.001	1.297	0.280
Fiber Type * Temperature * Pressure	0.010	2	0.005	5.062	0.009
Fiber Content * Fiber Type * Temperature * Pressure	0.034	4	0.009	8.298	0.000

^aR Squared = 1.000 (Adjusted R Squared = 1.000)

Table A.13 Analysis of variance of hardness for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	96.324	35	2.752	7.077	0.000
Error	28.000	72	0.389		
Total	1023487.000	108			
Corrected Total	124.324	107			
Fiber Type	1.130	2	0.565	1.452	0.241
Fiber Content	84.796	2	42.398	109.024	0.000
Temperature	0.231	1	0.231	0.595	0.443
Pressure	0.454	1	0.454	1.167	0.284
Fiber Type * Fiber content	0.315	4	0.079	0.202	0.936
Fiber Type * Temperature	0.019	2	0.009	0.024	0.976
Fiber Content * Temperature	0.574	2	0.287	0.738	0.482
Fiber Type * Fiber Content * Temperature	0.759	4	0.190	0.488	0.744
Fiber Type * Pressure	1.463	2	0.731	1.881	0.160
Fiber Content * Pressure	0.019	2	0.009	0.024	0.976
Fiber Type * Fiber Content * Pressure	0.648	4	0.162	0.417	0.796
Temperature * Pressure	2.676	1	2.676	6.881	0.011
Fiber Content * Temperature * Pressure	1.241	2	0.620	1.595	0.210
Fiber Type * Temperature * Pressure	0.019	2	0.009	0.024	0.976
Fiber Content * Fiber Type * Temperature * Pressure	1.981	4	0.495	1.274	0.288

^aR Squared = .775 (Adjusted R Squared = .665)

Table A.14 Analysis of variance of melt flow index for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	0.046	8	0.006	2696.74	0.000
Error	0.000	18	0.000		
Total	0.339	27			
Corrected Total	0.046	26			
Fiber Type	0.000	2	0.000	15.10	0.000
Fiber Content	0.046	2	0.023	10746.83	0.000
Fiber Type * Fiber content	0.000	4	0.000	12.52	0.000

^aR Squared = .999 (Adjusted R Squared = .999)

Table A.15 Analysis of variance of tensile strength for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	192.928	35	5.512	27.869	0.000
Error	14.241	72	0.198		
Total	31846.643	108			
Corrected Total	207.169	107			
Fiber Type	27.174	2	13.587	68.695	0.000
Fiber Content	109.237	2	54.619	276.147	0.000
Temperature	0.597	1	0.597	3.019	0.087
Pressure	2.884	1	2.884	14.584	0.000
Fiber Type * Fiber content	40.675	4	10.169	51.412	0.000
Fiber Type * Temperature	0.367	2	0.184	0.929	0.400
Fiber Content * Temperature	0.434	2	0.217	1.098	0.339
Fiber Type * Fiber Content * Temperature	1.855	4	0.464	2.345	0.063
Fiber Type * Pressure	1.457	2	0.728	3.683	0.030
Fiber Content * Pressure	1.613	2	0.807	4.078	0.021
Fiber Type * Fiber Content * Pressure	1.981	4	0.495	2.504	0.050
Temperature * Pressure	0.376	1	0.376	1.900	0.172
Fiber Content * Temperature * Pressure	1.211	2	0.605	3.060	0.053
Fiber Type * Temperature * Pressure	0.132	2	0.066	0.333	0.718
Fiber Content * Fiber Type * Temperature * Pressure	2.934	4	0.733	3.708	0.008

^aR Squared = .931 (Adjusted R Squared = .898)

Table A.16 Analysis of variance of young's modulus for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	355626.442	35	10160.755	30.528	0.000
Error	23964.231	72	332.837		
Total	29415165.507	108			
Corrected Total	379590.673	107			
Fiber Type	2520.691	2	1260.346	3.787	0.027
Fiber Content	283487.106	2	141743.553	425.865	0.000
Temperature	435.166	1	435.166	1.307	0.257
Pressure	1513.280	1	1513.280	4.547	0.036
Fiber Type * Fiber content	41944.853	4	10486.213	31.506	0.000
Fiber Type * Temperature	5838.775	2	2919.388	8.771	0.000
Fiber Content * Temperature	1841.355	2	920.678	2.766	0.070
Fiber Type * Fiber Content * Temperature	14749.166	4	3687.292	11.078	0.000
Fiber Type * Pressure	480.354	2	240.177	0.722	0.489
Fiber Content * Pressure	564.002	2	282.001	0.847	0.433
Fiber Type * Fiber Content * Pressure	1186.860	4	296.715	0.891	0.474
Temperature * Pressure	3.827	1	3.827	0.011	0.915
Fiber Content * Temperature * Pressure	647.527	2	323.763	0.973	0.383
Fiber Type * Temperature * Pressure	89.214	2	44.607	0.134	0.875
Fiber Content * Fiber Type * Temperature * Pressure	324.267	4	81.067	0.244	0.913

^aR Squared = .937 (Adjusted R Squared = .906)

Table A.17 Analysis of variance of flexural strength for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	651.471 ^a	35	18.613	22.279	0.000
Error	60.153	72	0.835		
Total	114415.127	108			
Corrected Total	711.624	107			
Fiber Type	132.989	2	66.494	79.591	0.000
Fiber Content	111.822	2	55.911	66.922	0.000
Temperature	161.529	1	161.529	193.342	0.000
Pressure	62.655	1	62.655	74.995	0.000
Fiber Type * Fiber content	27.643	4	6.911	8.272	0.000
Fiber Type * Temperature	41.915	2	20.958	25.085	0.000
Fiber Content * Temperature	3.530	2	1.765	2.113	0.128
Fiber Type * Fiber Content * Temperature	31.630	4	7.908	9.465	0.000
Fiber Type * Pressure	6.983	2	3.491	4.179	0.019
Fiber Content * Pressure	9.432	2	4.716	5.645	0.005
Fiber Type * Fiber Content * Pressure	8.115	4	2.029	2.428	0.055
Temperature * Pressure	28.686	1	28.686	34.335	0.000
Fiber Content * Temperature * Pressure	3.799	2	1.900	2.274	0.110
Fiber Type * Temperature * Pressure	2.285	2	1.142	1.367	0.261
Fiber Content * Fiber Type * Temperature * Pressure	18.459	4	4.615	5.524	0.001

^aR Squared = .915 (Adjusted R Squared = .874)

Table A.18 Analysis of variance of flexural modulus for PP-based biocomposites.

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1680899.04 ^a	35	48025.687	37.885	0.000
Error	91271.71	72	1267.663		
Total	90323007.85	108			
Corrected Total	711.624	107			
Fiber Type	452662.03	2	226331.014	178.542	0.000
Fiber Content	688889.63	2	344444.814	271.716	0.000
Temperature	234948.07	1	234948.068	185.340	0.000
Pressure	89263.00	1	89263.000	70.415	0.000
Fiber Type * Fiber content	18179.71	4	4544.926	3.585	0.010
Fiber Type * Temperature	22511.33	2	11255.666	8.879	0.000
Fiber Content * Temperature	4337.11	2	2168.554	1.711	0.188
Fiber Type * Fiber Content * Temperature	8518.35	4	2129.589	1.680	0.164
Fiber Type * Pressure	53919.52	2	26959.762	21.267	0.000
Fiber Content * Pressure	17824.92	2	8912.458	7.031	0.002
Fiber Type * Fiber Content * Pressure	31379.71	4	7844.928	6.188	0.000
Temperature * Pressure	4517.61	1	4517.613	3.564	0.063
Fiber Content * Temperature * Pressure	16095.21	2	8047.603	6.348	0.003
Fiber Type * Temperature * Pressure	1731.85	2	865.927	0.683	0.508
Fiber Content * Fiber Type * Temperature * Pressure	36120.99	4	9030.246	7.124	0.000

^aR Squared = .915 (Adjusted R Squared = .874)

APPENDIX B

DSC Thermograms of HDPE and PP Extrudates Samples

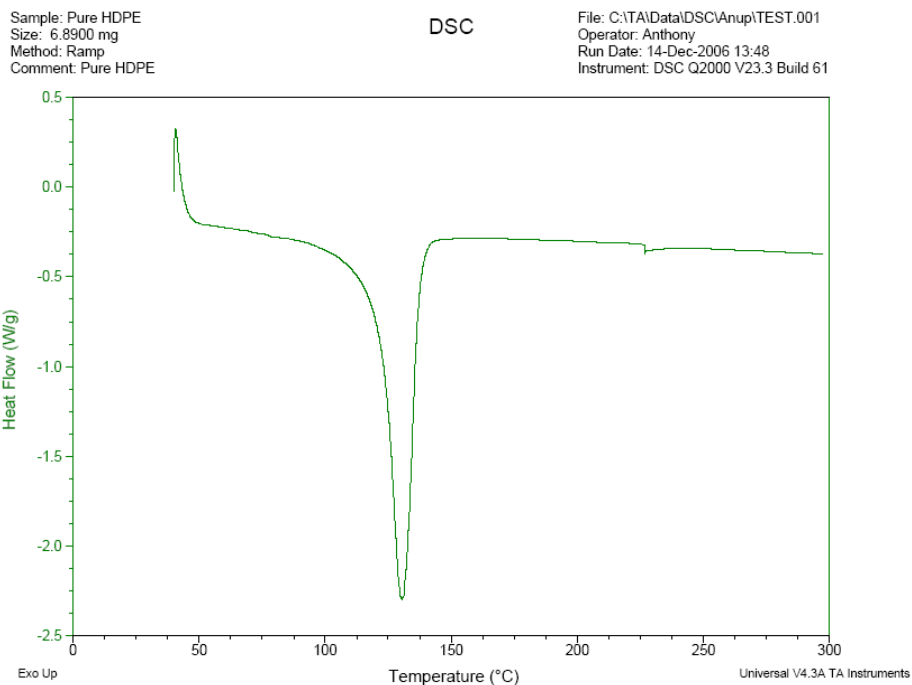


Figure B.1 DSC thermogram of HDPE.

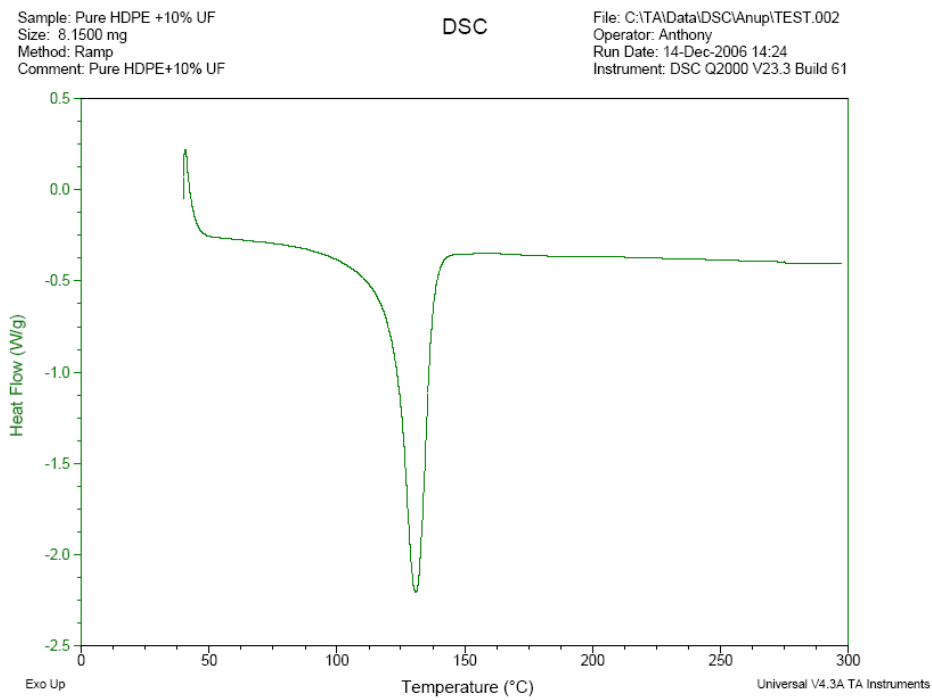


Figure B.2 DSC thermogram of HDPE with 10% untreated flax fiber.

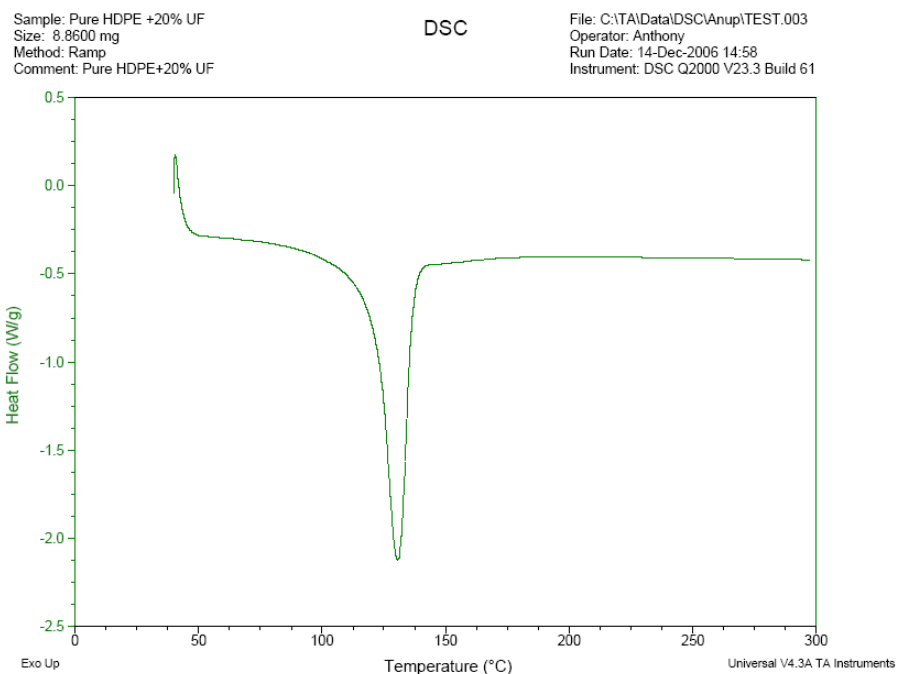


Figure B.3 DSC thermogram of HDPE with 20% untreated flax fiber.

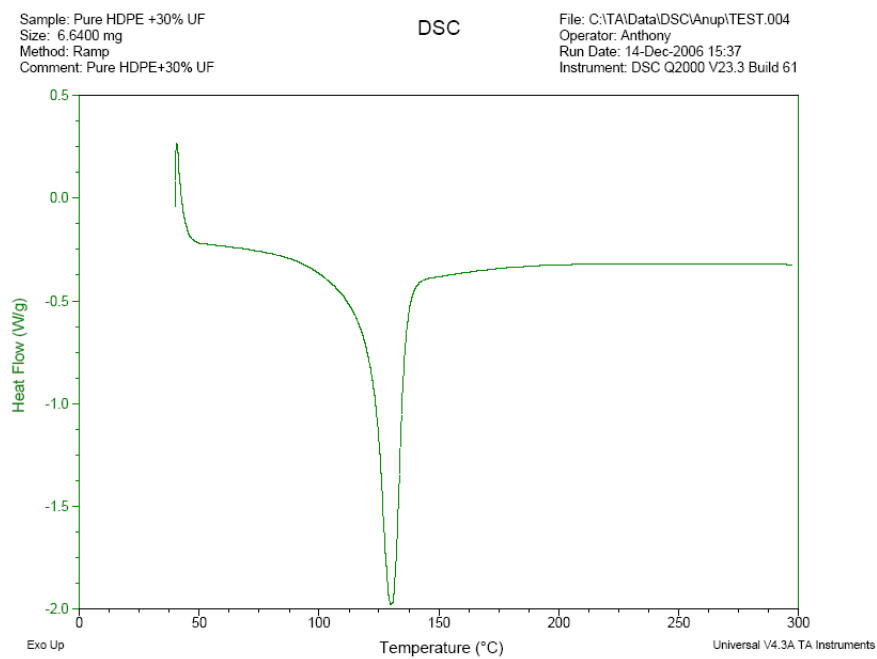


Figure B.4 DSC thermogram of HDPE with 30% untreated flax fiber.

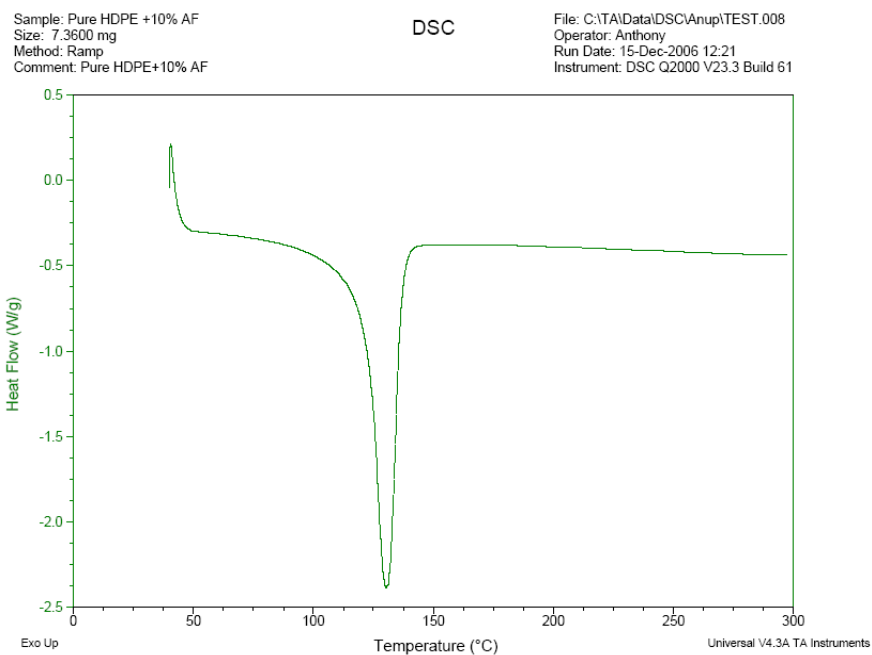


Figure B.5 DSC thermogram of HDPE with 10% alkaline treated flax fiber.

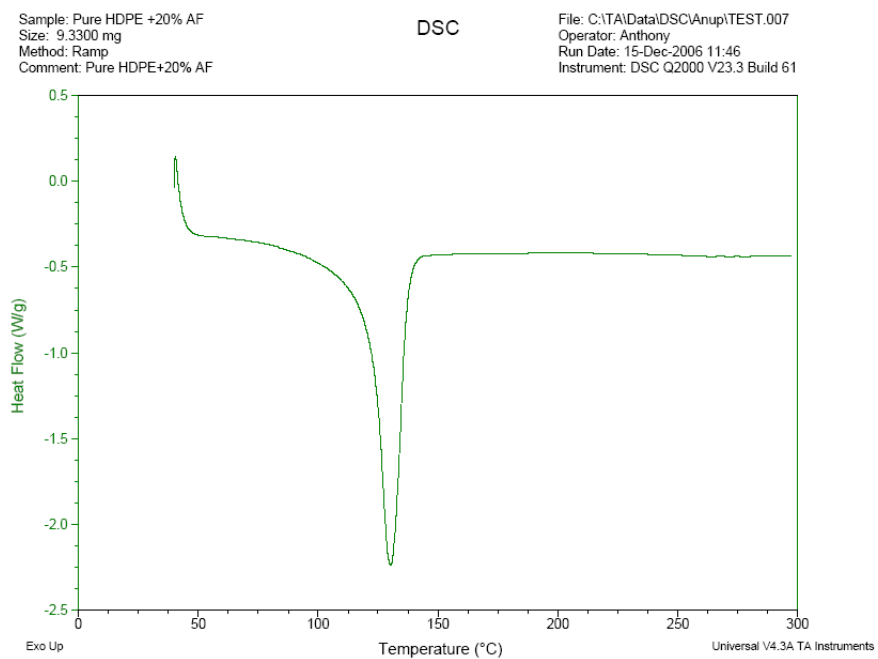


Figure B.6 DSC thermogram of HDPE with 20% alkaline treated flax fiber.

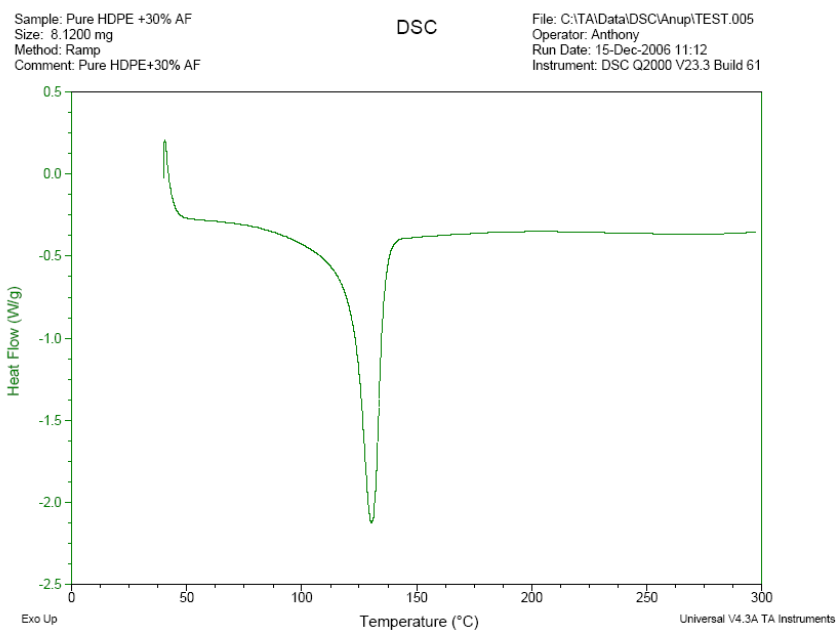


Figure B.7 DSC thermogram of HDPE with 30% alkaline treated flax fiber.

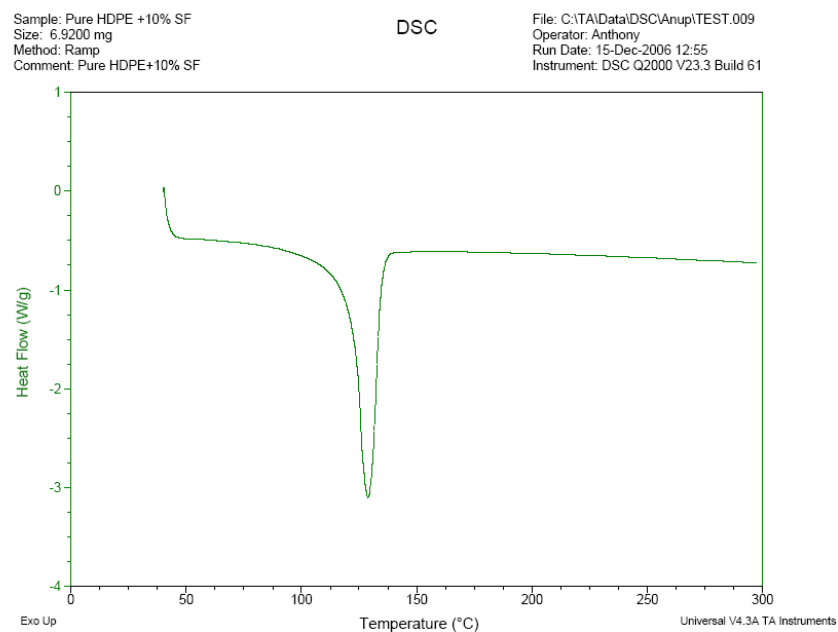


Figure B.8 DSC thermogram of HDPE with 10% silane treated flax fiber.

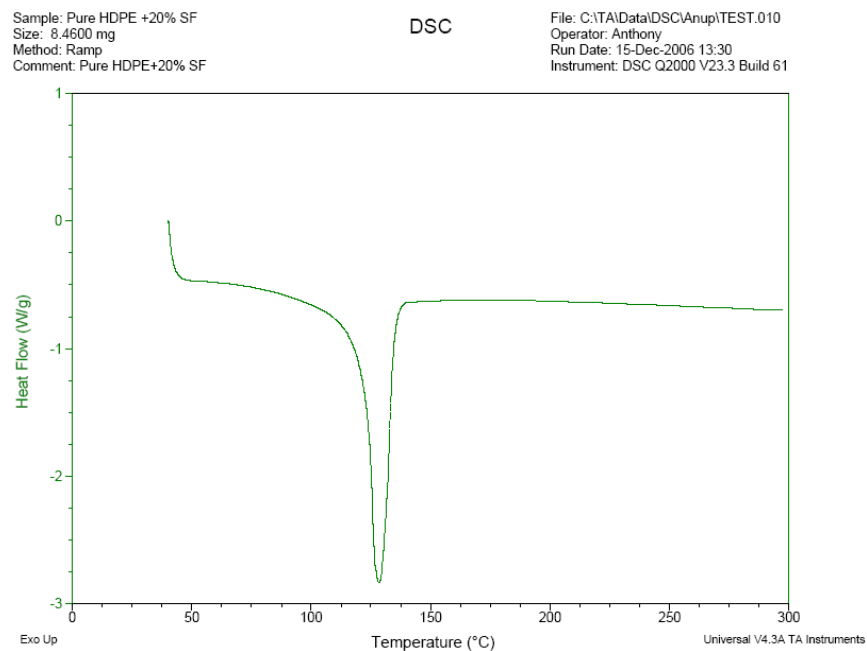


Figure B.9 DSC thermogram of HDPE with 20% silane treated flax fiber.

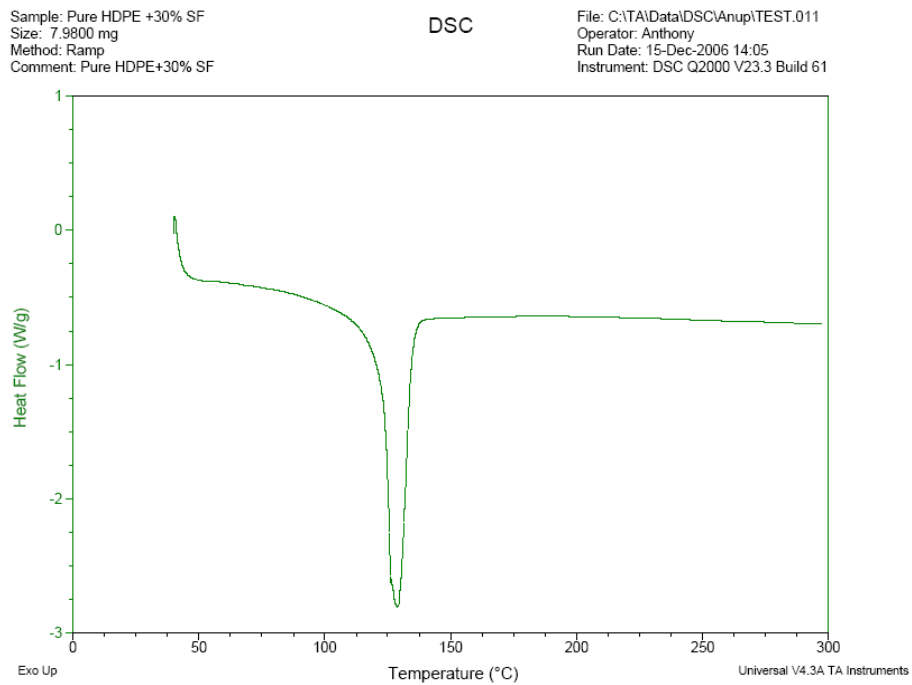


Figure B.10 DSC thermogram of HDPE with 30% silane treated flax fiber.

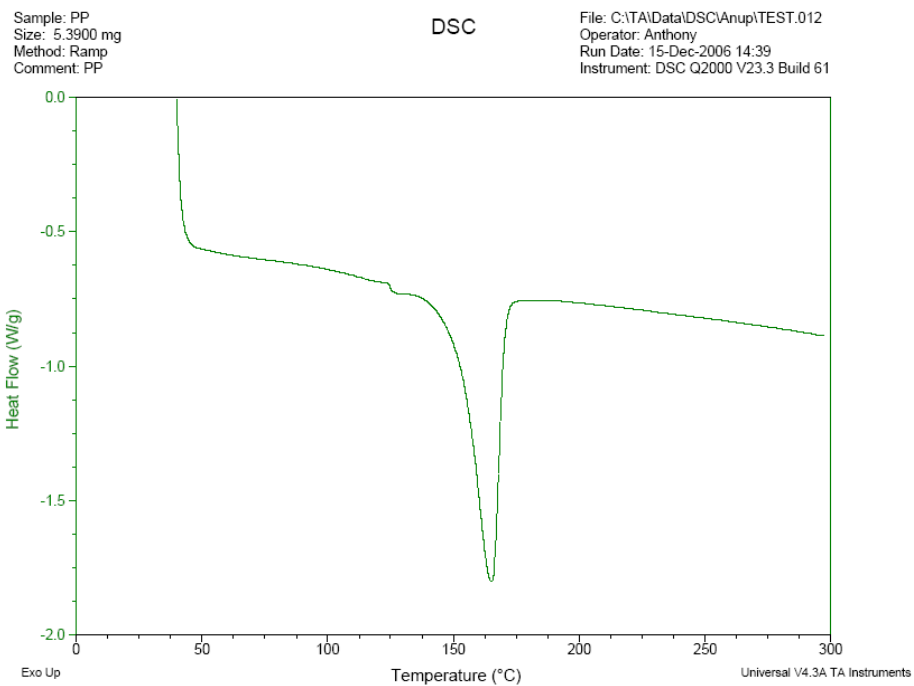


Figure B.11 DSC thermogram of PP.

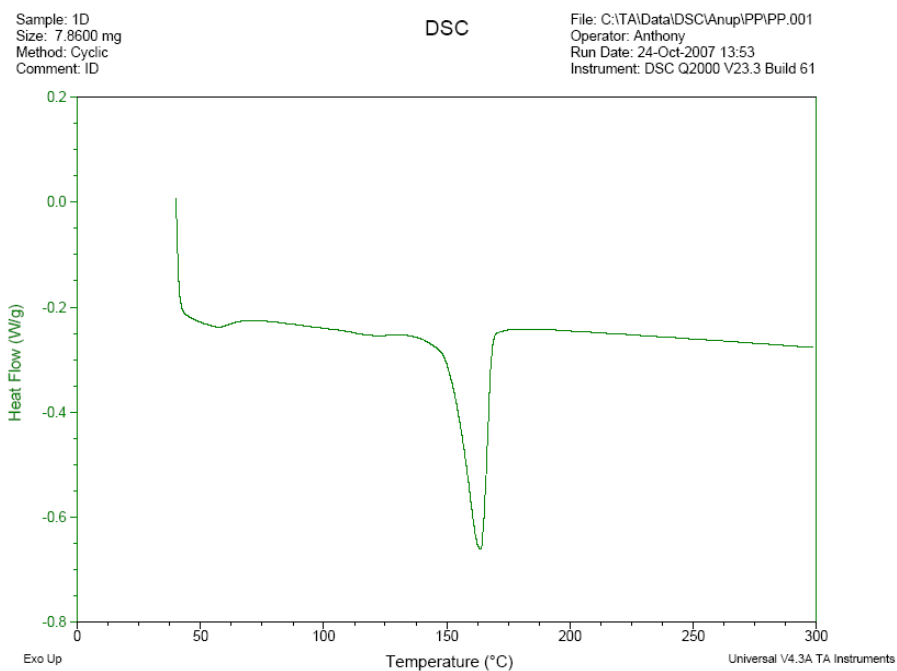


Figure B.12 DSC thermogram of PP with 10% untreated flax fiber.

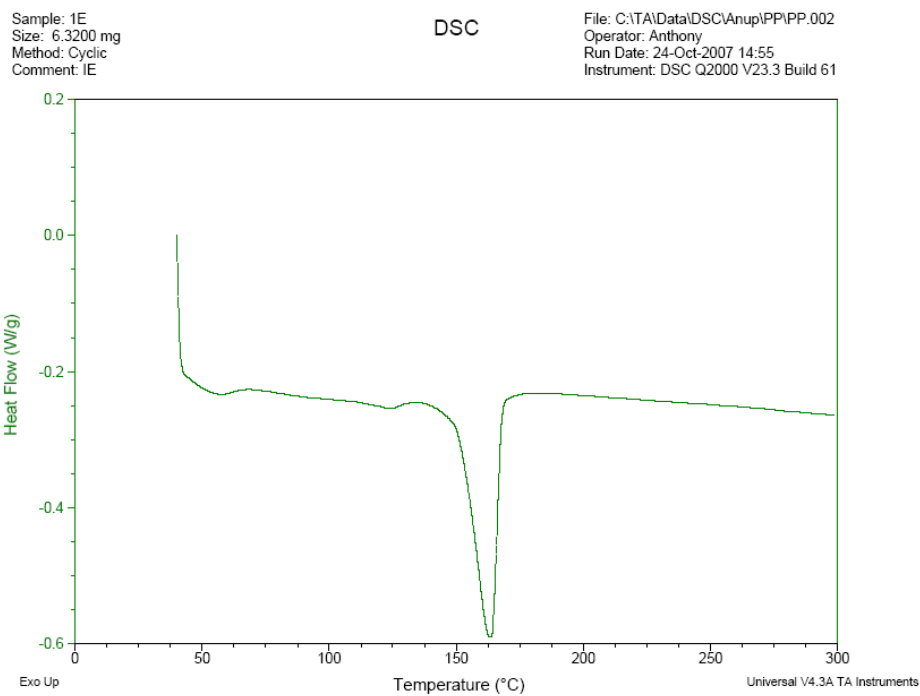


Figure B.13 DSC thermogram of PP with 20% untreated flax fiber.

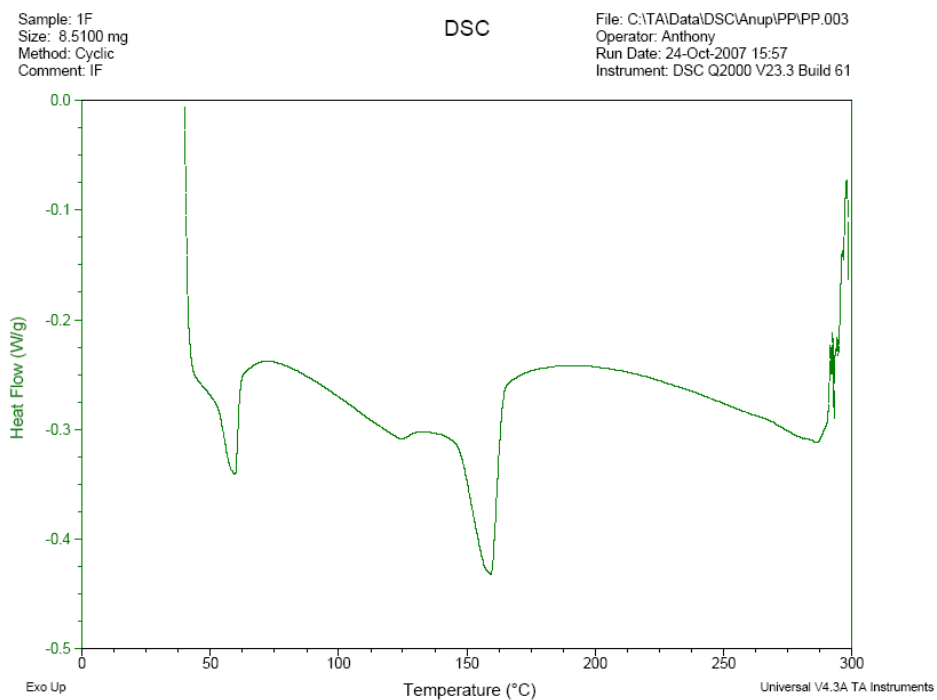


Figure B.14 DSC thermogram of PP with 30% untreated flax fiber.

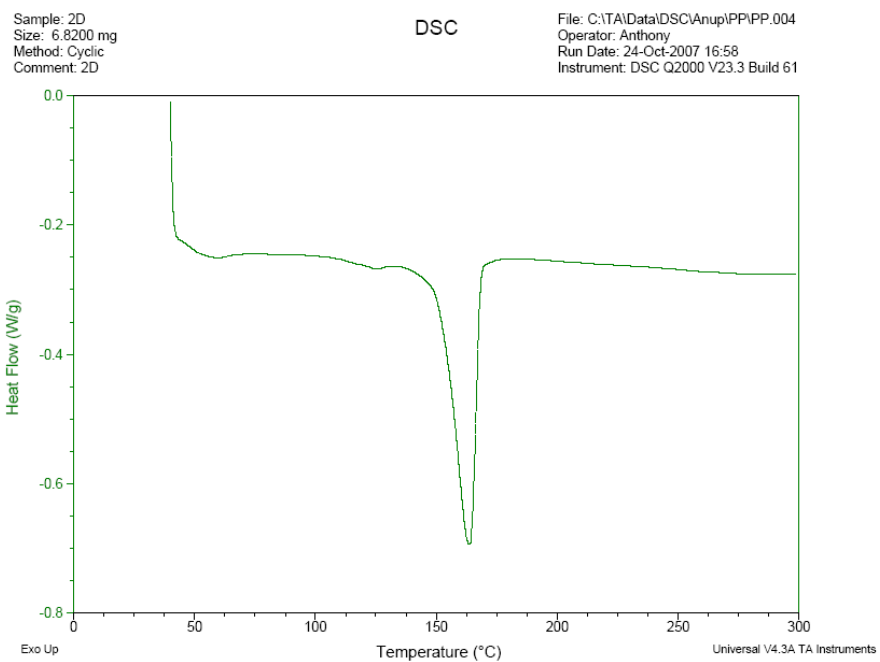


Figure B.15 DSC thermogram of PP with 10% alkaline treated flax fiber.

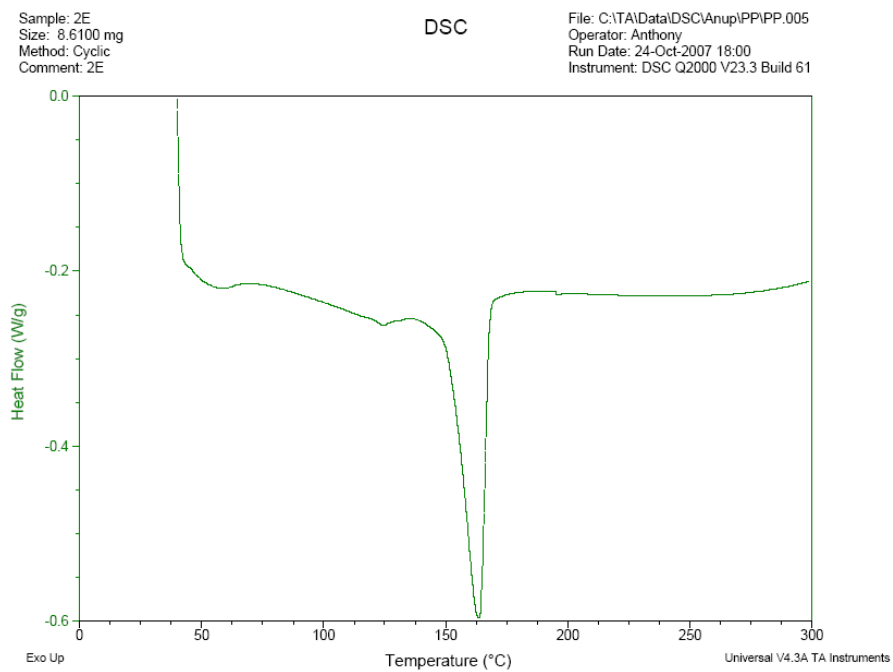


Figure B.16 DSC thermogram of PP with 20% alkaline treated flax fiber.

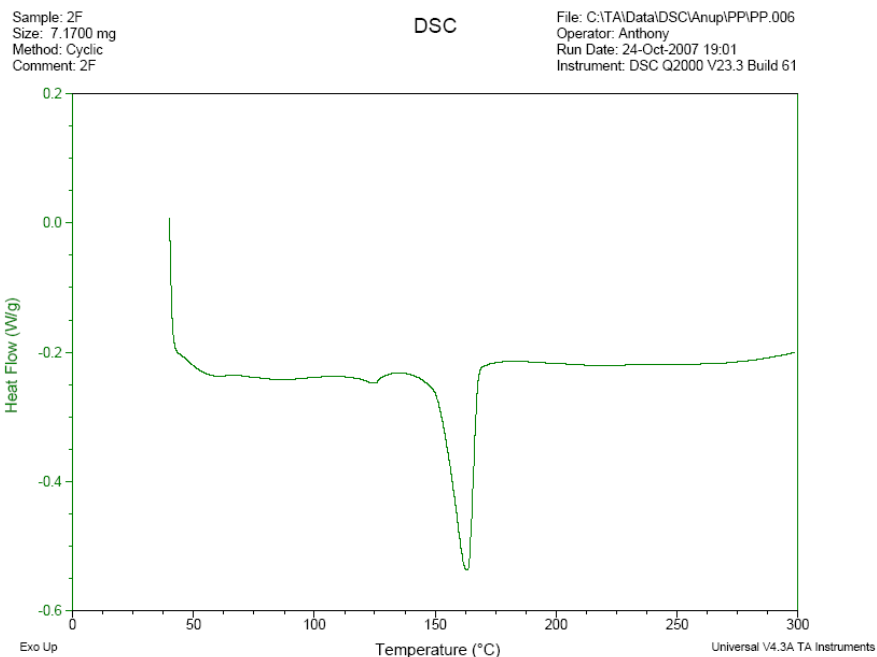


Figure B.17 DSC thermogram of PP with 30% alkaline treated flax fiber.

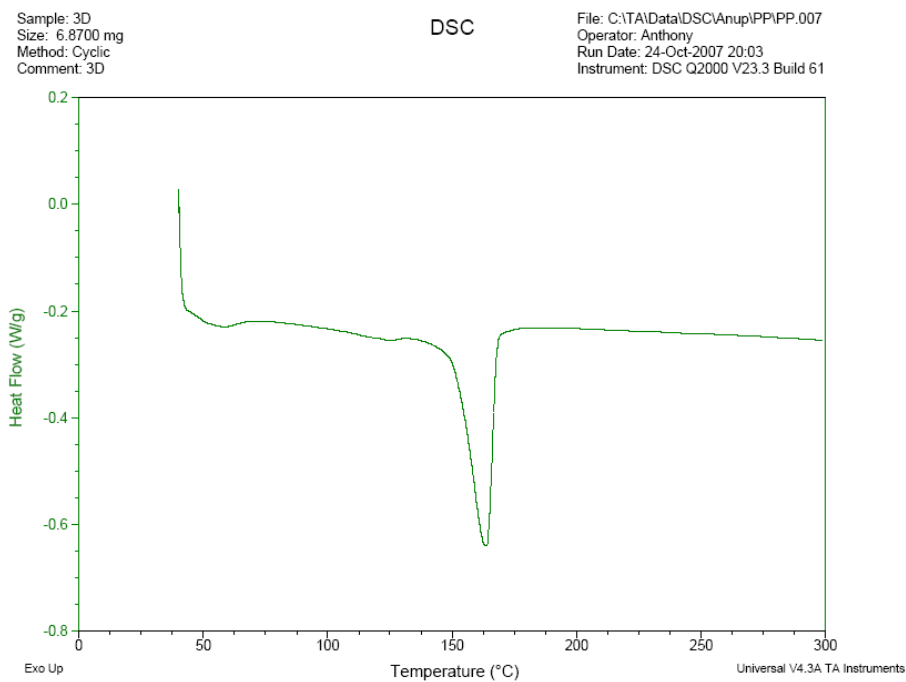


Figure B.18 DSC thermogram of PP with 10% silane treated flax fiber.

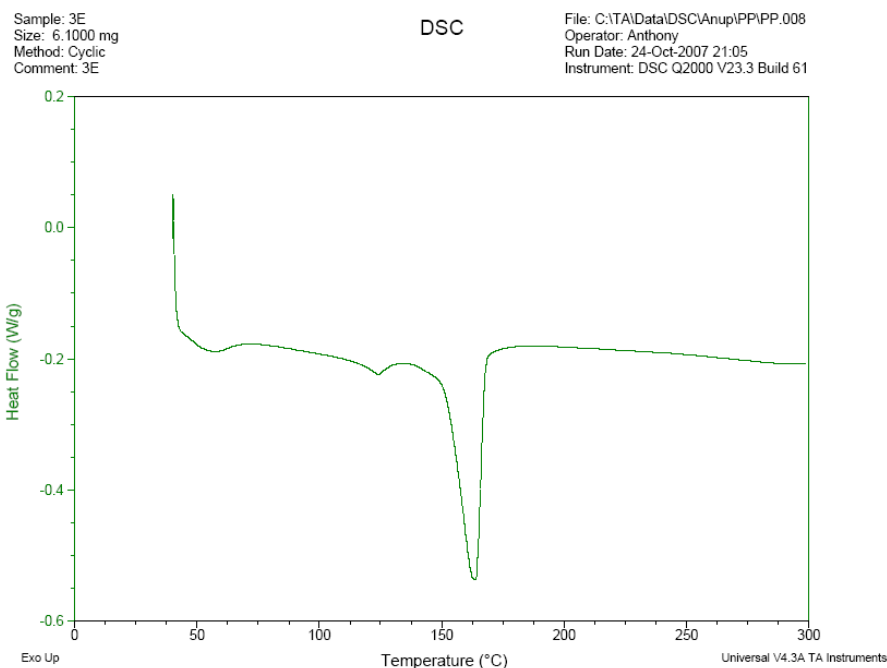


Figure B.19 DSC thermogram of PP with 20% silane treated flax fiber.

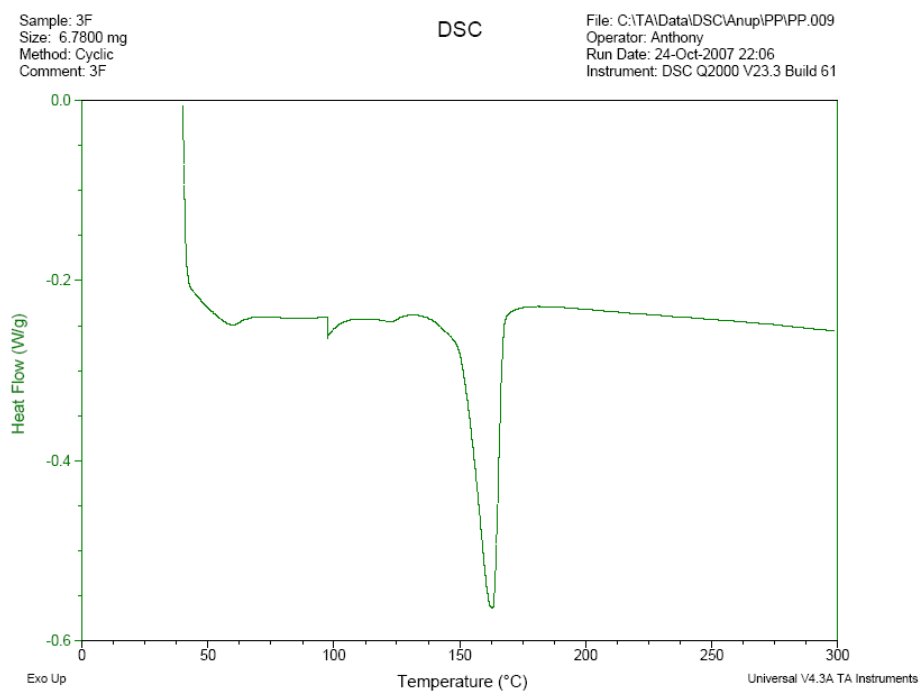


Figure B.20 DSC thermogram of PP with 30% silane treated flax fiber.

APPENDIX C

Surface Response Plots of HDPE AND PP Biocomposites

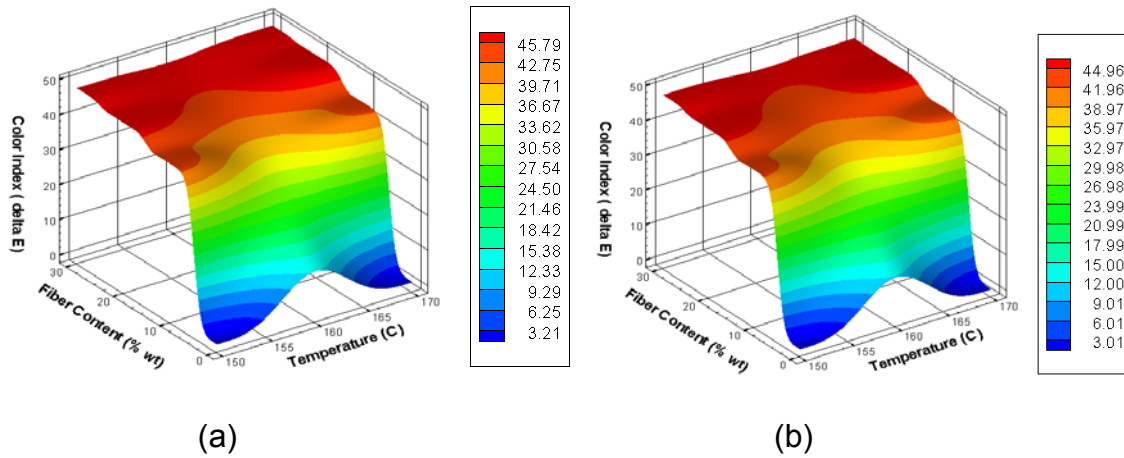


Figure C.1 Response surface plots for the effect of fiber content and temperature on color index of HDPE biocomposites at a) high pressure b) low pressure.

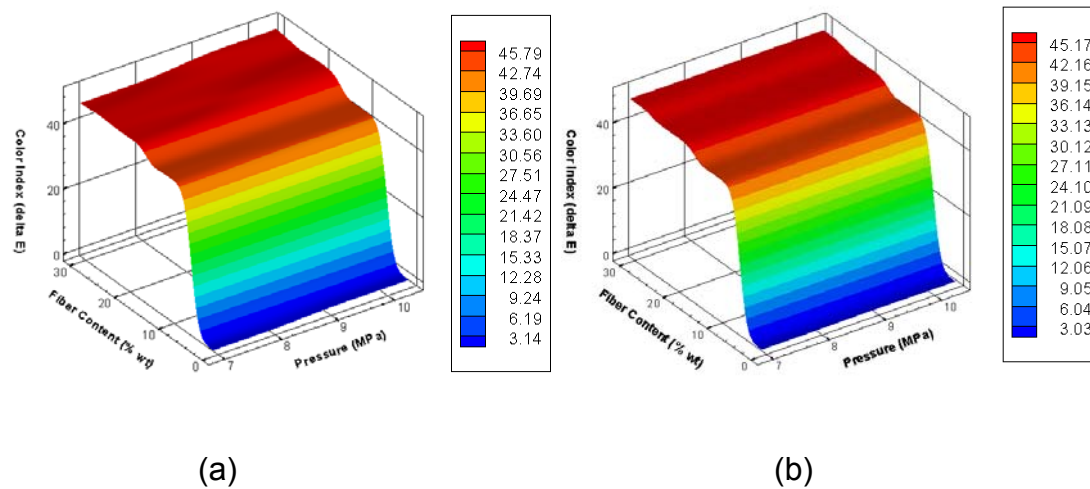


Figure C.2 Response surface plots for the effect of fiber content and pressure on color index of HDPE biocomposites at a) high temperature b) low temperature.

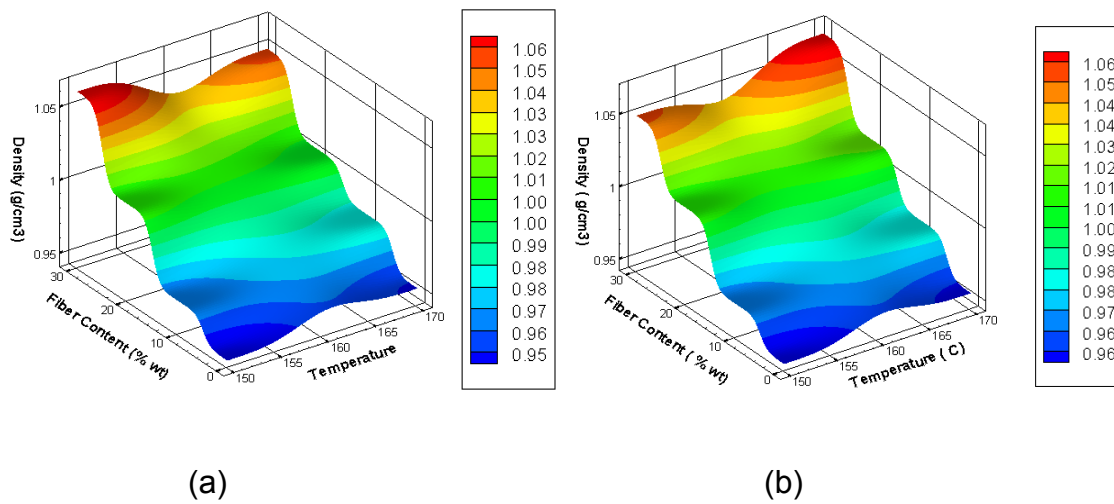


Figure C.3 Response surface plots for the effect of fiber content and temperature on HDPE biocomposites density at a) high pressure b) low pressure.

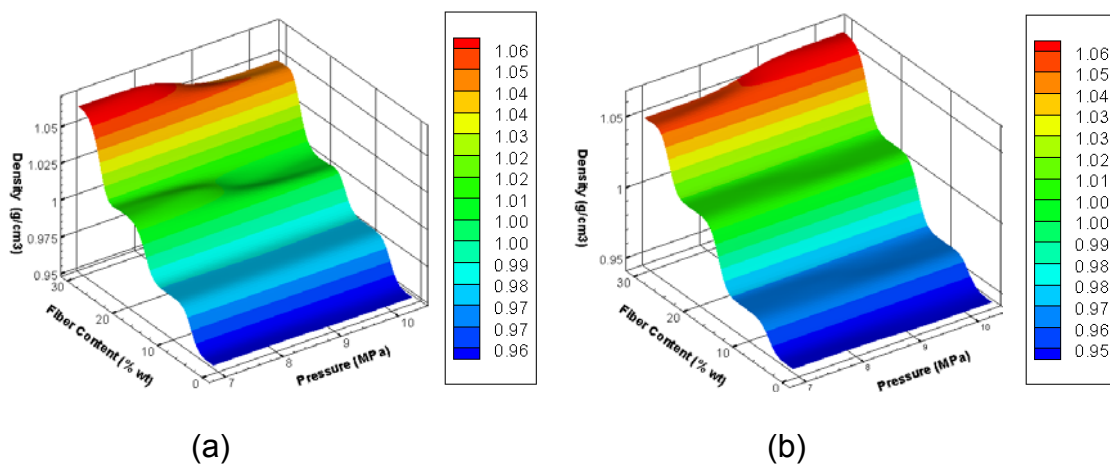


Figure C.4 Response surface plots for the effect of fiber content and pressure on HDPE biocomposites density at a) high temperature b) low temperature.

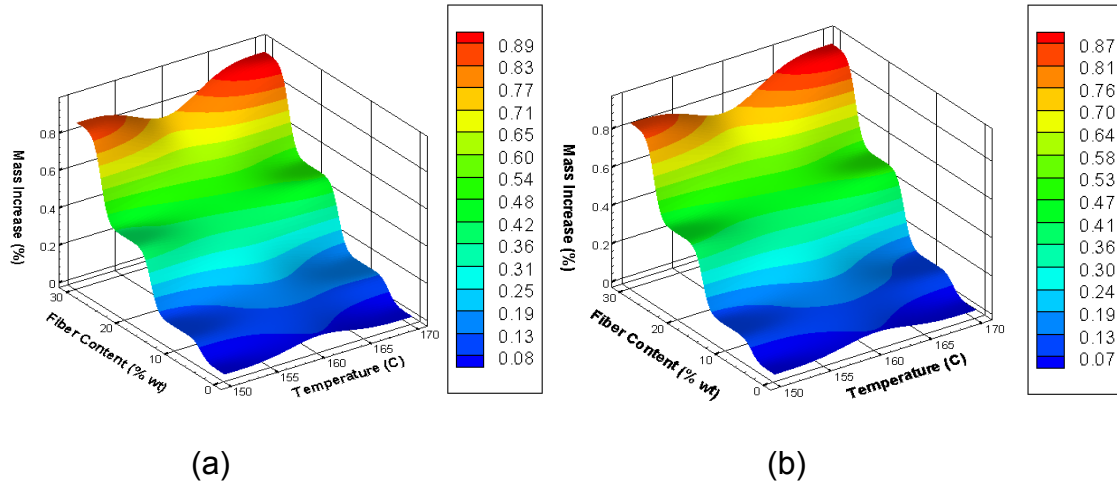


Figure C.5 Response surface plots for the effect of fiber content and temperature on water absorption characteristics of HDPE biocomposites at a) high pressure b) low pressure.

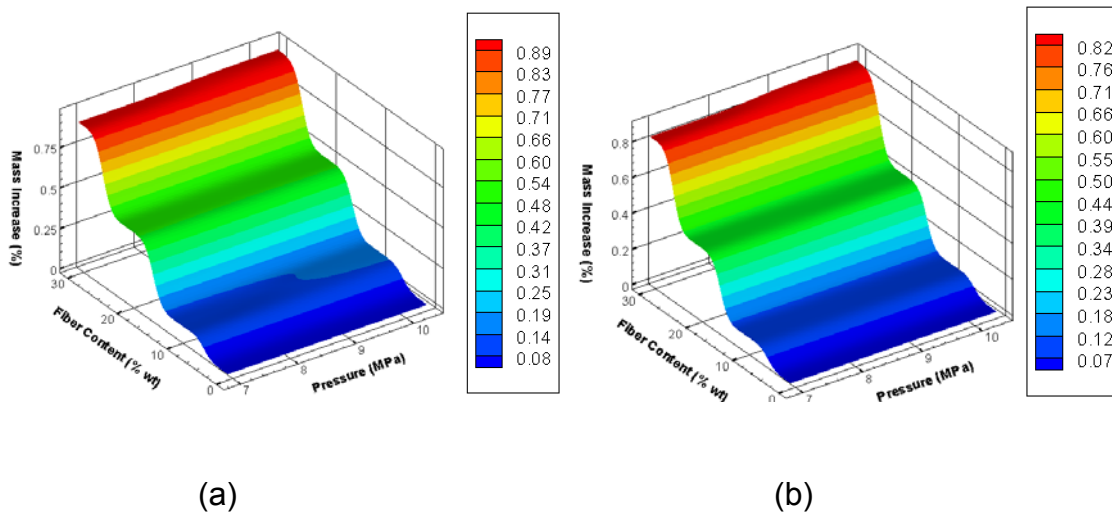
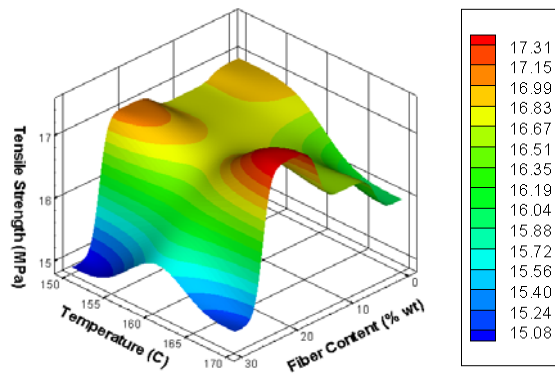
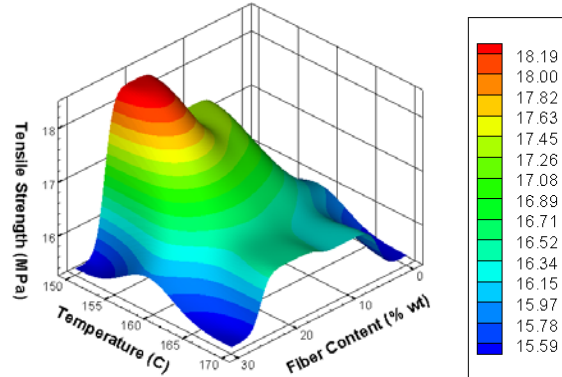


Figure C.6 Response surface plots for the effect of fiber content and pressure on water absorption characteristics of HDPE biocomposites at a) high temperature b) low temperature.

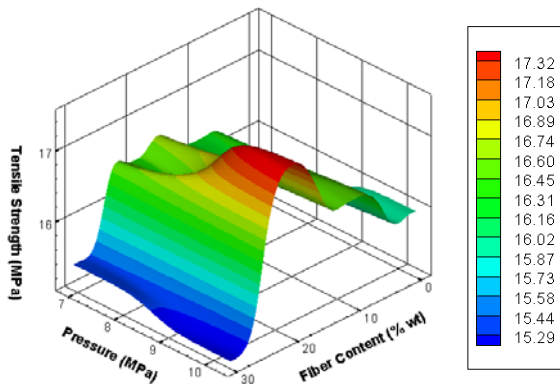


(a)

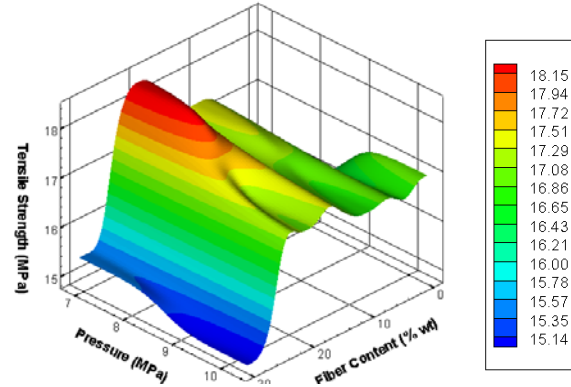


(b)

Figure C.7 Response surface plots for the effect of fiber content and temperature on tensile strength of HDPE biocomposites at a) high pressure b) low pressure.



(a)



(b)

Figure C.8 Response surface plots for the effect of fiber content and pressure on tensile strength of HDPE biocomposites at a) high temperature b) low temperature.

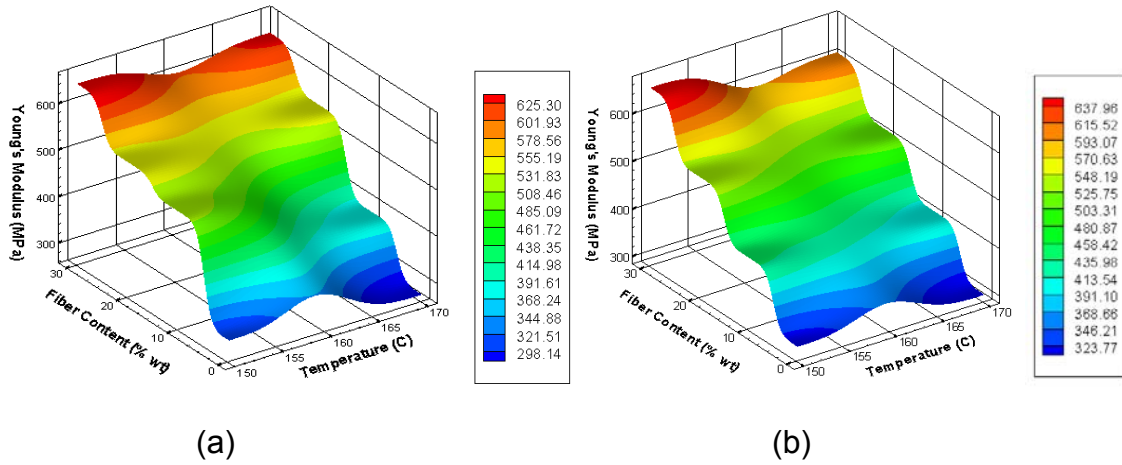


Figure C.9 Response surface plots for the effect of fiber content and temperature on young's modulus of HDPE biocomposites at a) high pressure b) low pressure.

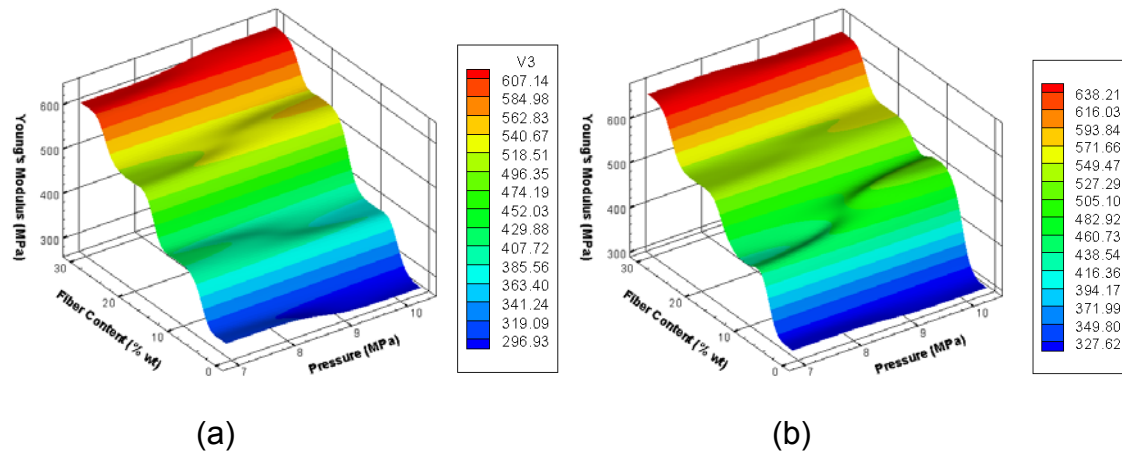


Figure C.10 Response surface plots for the effect of fiber content and pressure on young's modulus of HDPE biocomposites at a) high temperature b) low temperature.

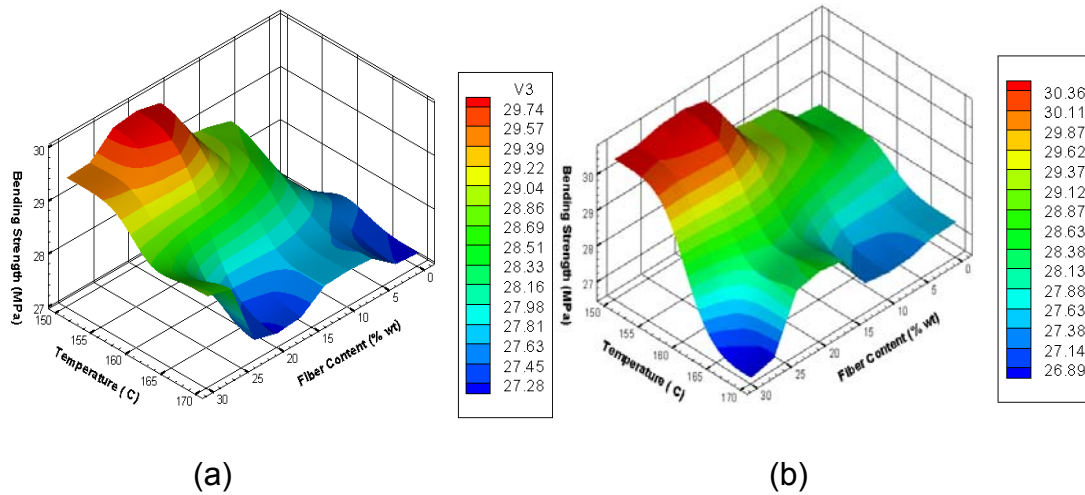


Figure C.11 Response surface plots for the effect of fiber content and temperature on bending strength of HDPE biocomposites at a) high pressure b) low pressure.

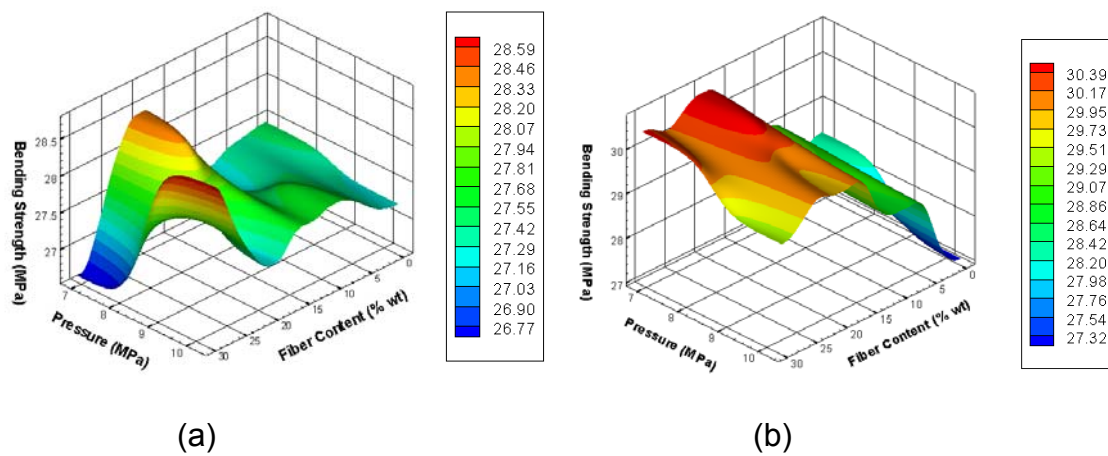


Figure C.12 Response surface plots for the effect of fiber content and pressure on bending strength of HDPE biocomposites at a) high temperature b) low temperature.

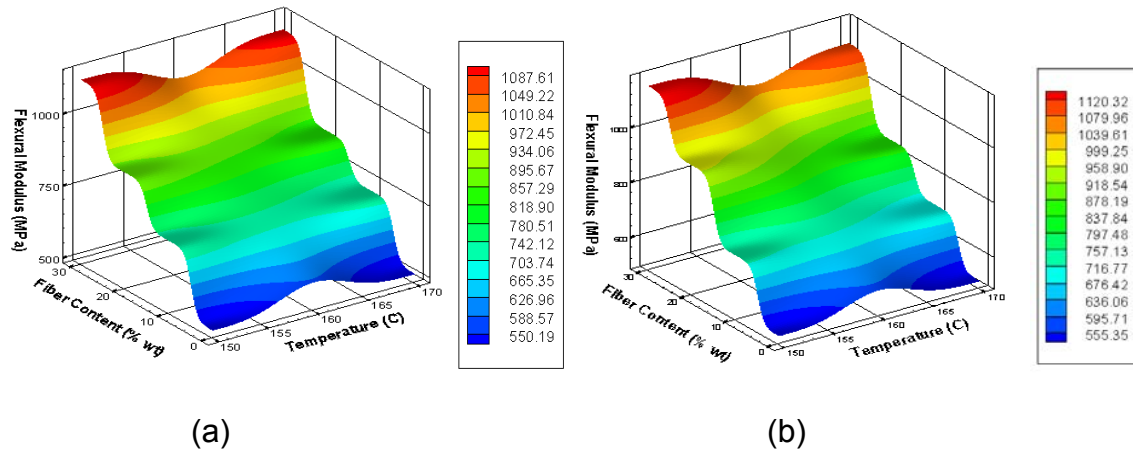


Figure C.13 Response surface plots for the effect of fiber content and temperature on flexural modulus of HDPE biocomposites at a) high pressure b) low pressure.

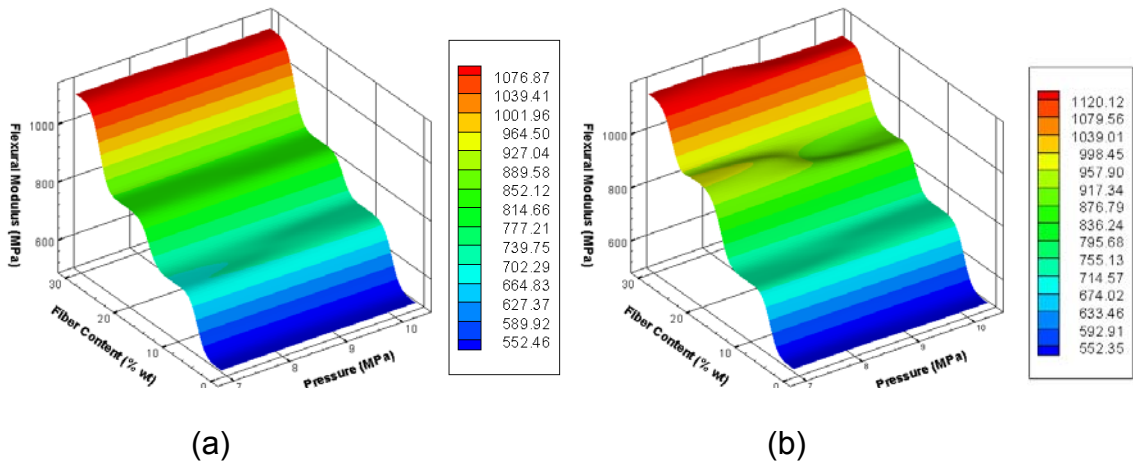
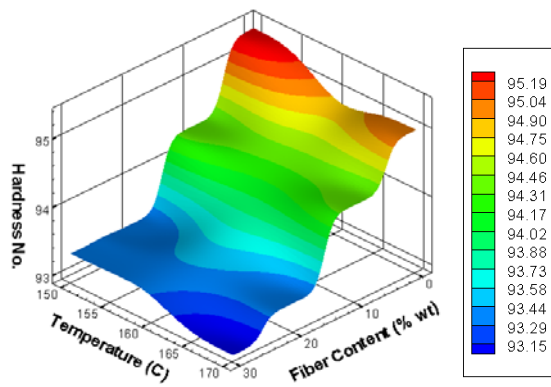
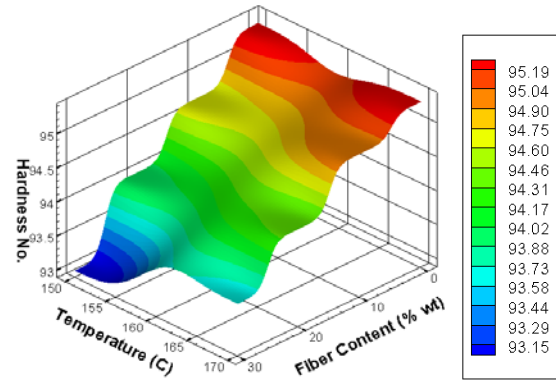


Figure C.14 Response surface plots for the effect of fiber content and pressure on flexural modulus of HDPE biocomposites at a) high temperature b) low temperature.

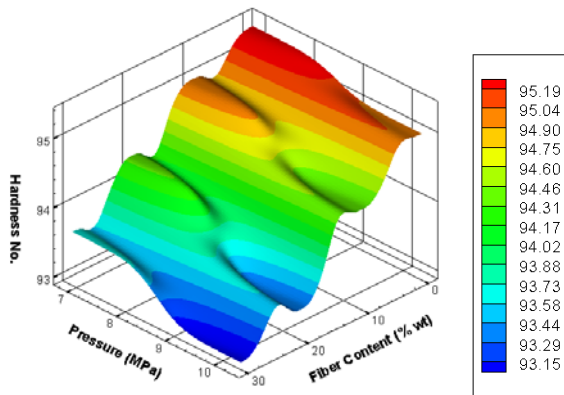


(a)

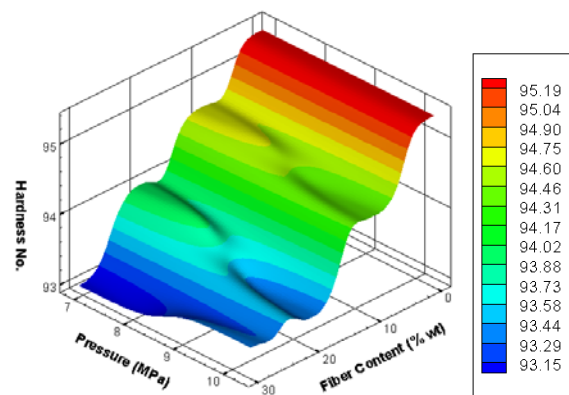


(b)

Figure C.15 Response surface plots for the effect of fiber content and temperature on hardness of HDPE biocomposites at a) high pressure b) low pressure.



(a)



(b)

Figure C.16 Response surface plots for the effect of fiber content and pressure on hardness of HDPE biocomposites at a) high temperature b) low temperature.

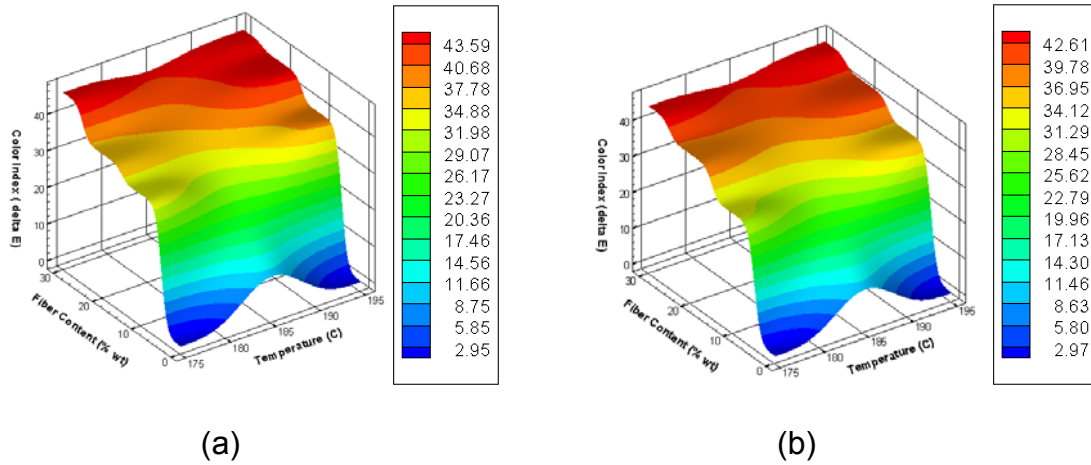


Figure C.17 Response surface plots for the effect of fiber content and temperature on color index of PP biocomposites at a) high pressure b) low pressure.

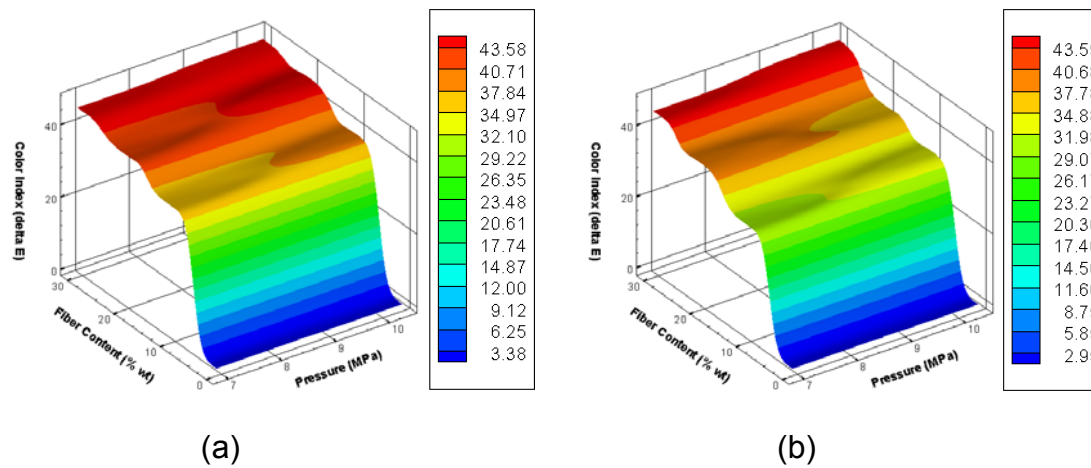
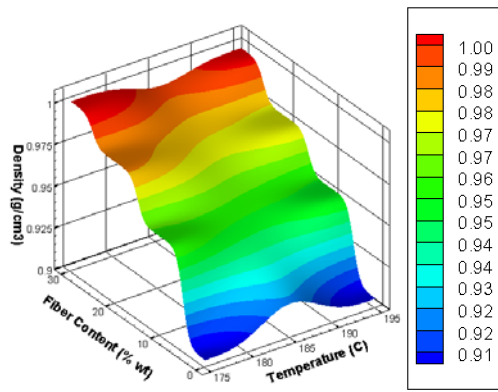
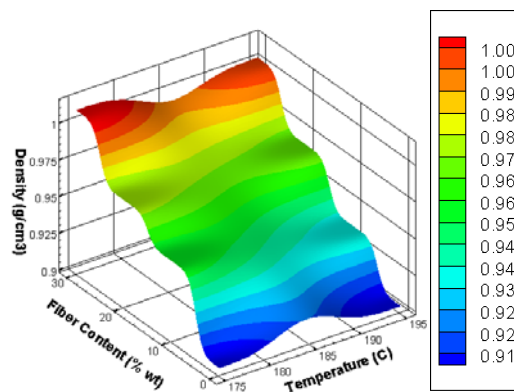


Figure C.18 Response surface plots for the effect of fiber content and pressure on color index of PP biocomposites at a) high temperature b) low temperature.

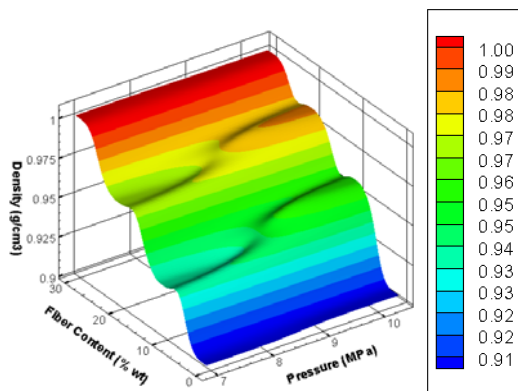


(a)

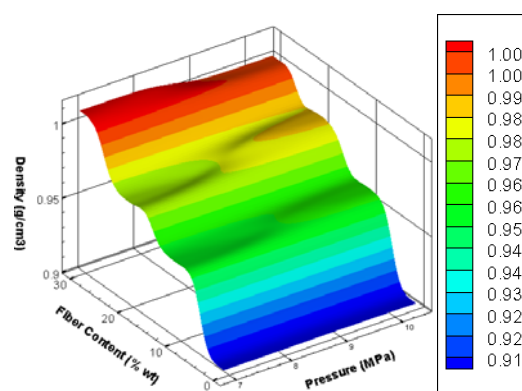


(b)

Figure C.19 Response surface plots for the effect of fiber content and temperature on PP biocomposites density at a) high pressure b) low pressure.



a)



(b)

Figure C.20 Response surface plots for the effect of fiber content and pressure on PP biocomposites density at a) high temperature b) low temperature.

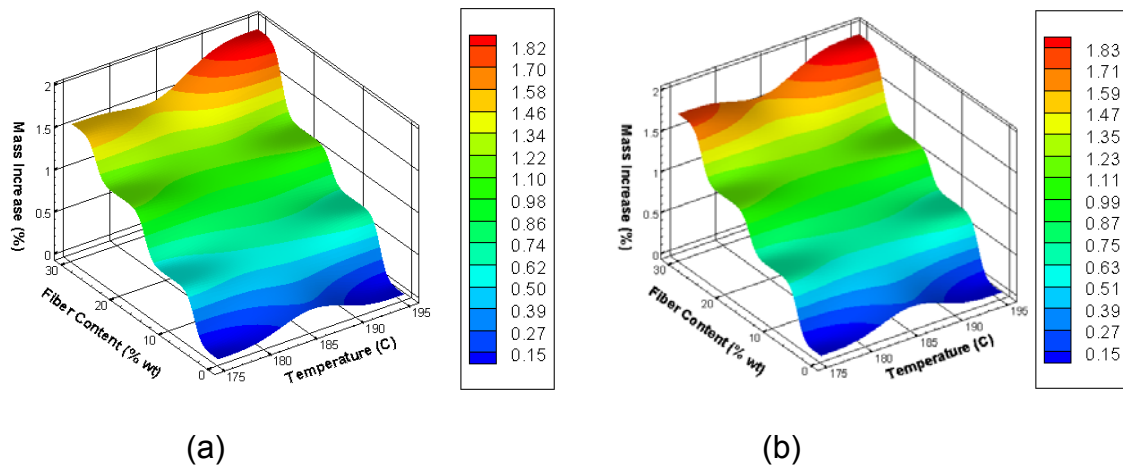


Figure C.21 Response surface plots for the effect of fiber content and temperature on water absorption characteristics of PP biocomposites at a) high pressure b) low pressure.

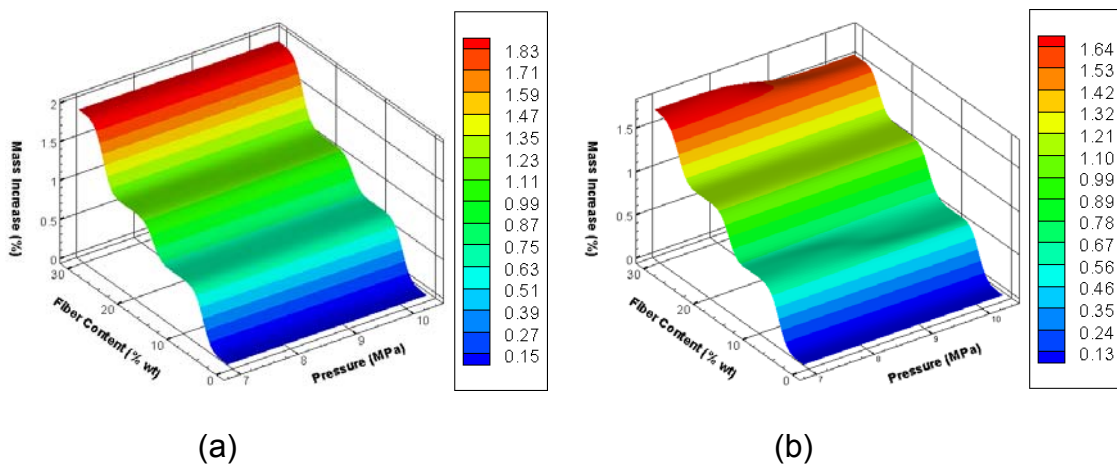
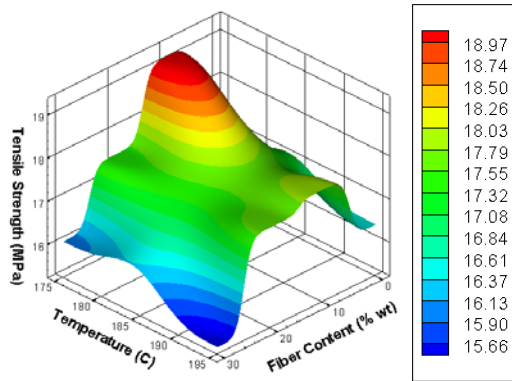
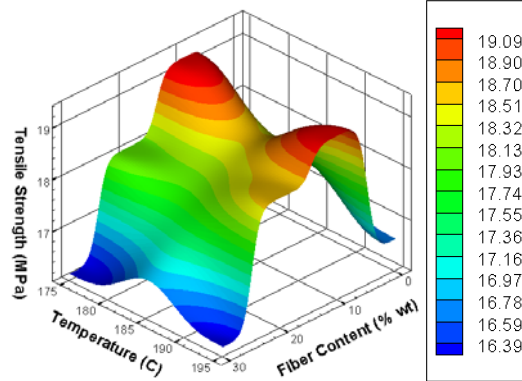


Figure C.22 Response surface plots for the effect of fiber content and pressure on water absorption characteristics of PP biocomposites at a) high temperature b) low temperature.

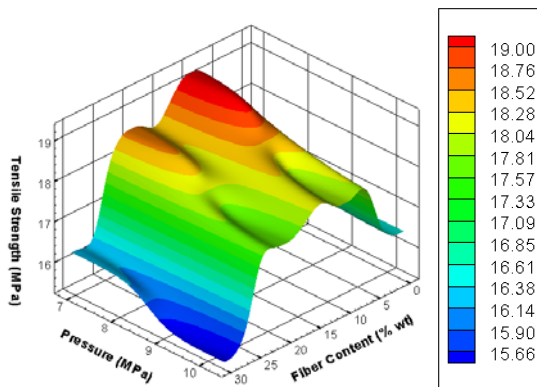


(a)

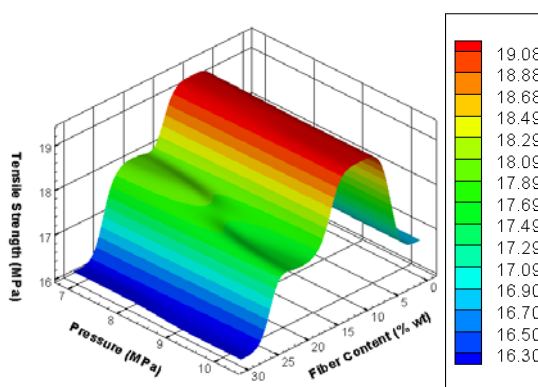


(b)

Figure C.23 Response surface plots for the effect of fiber content and temperature on tensile strength of PP biocomposites at a) high pressure b) low pressure.



(a)



(b)

Figure C.24 Response surface plots for the effect of fiber content and pressure on tensile strength of PP biocomposites at a) high temperature b) low temperature.

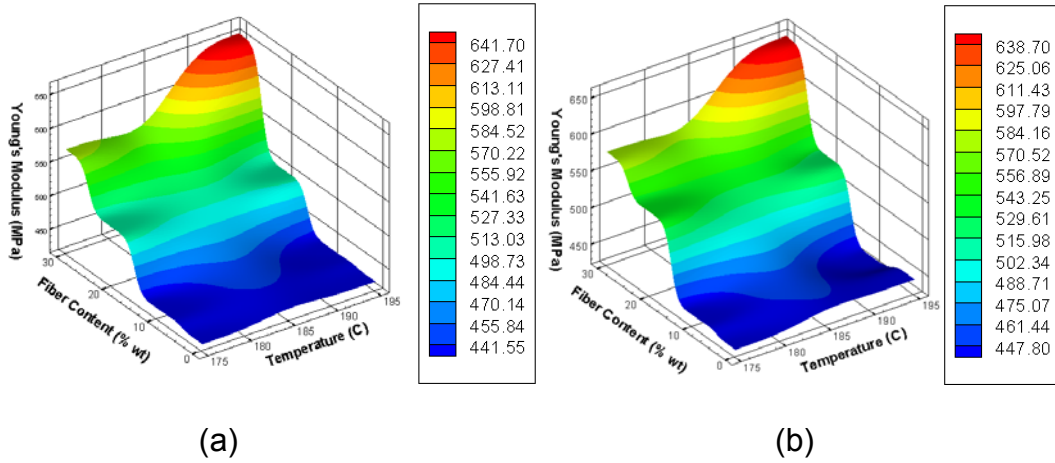


Figure C.25 Response surface plots for the effect of fiber content and temperature on Young's modulus of PP biocomposites at a) high pressure b) low pressure.

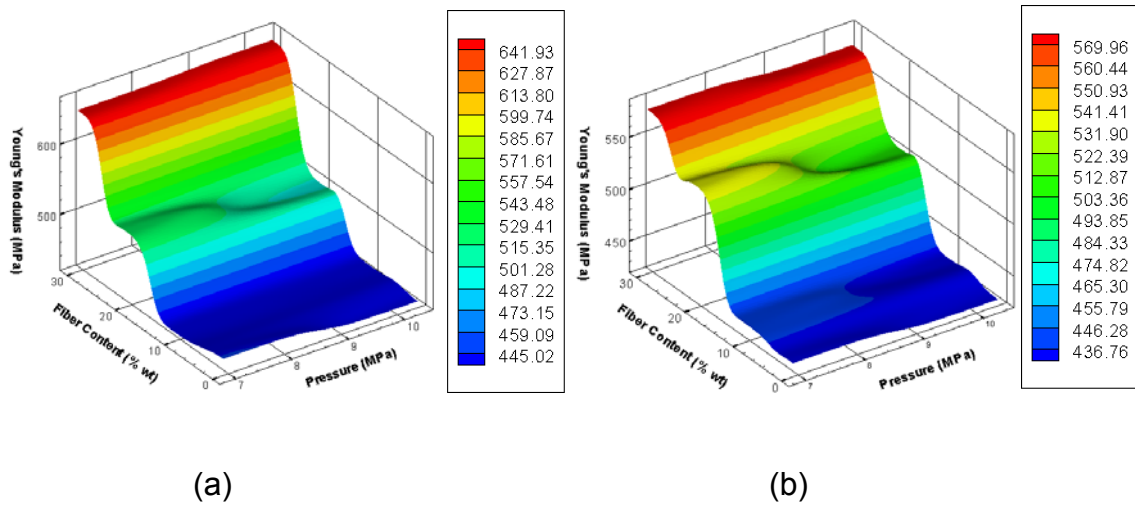
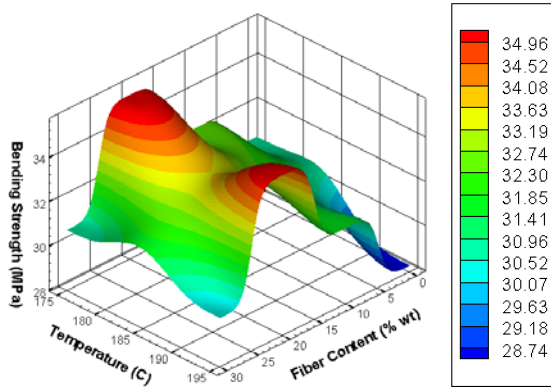
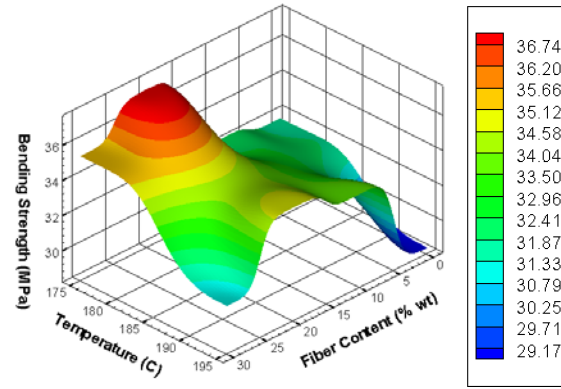


Figure C.26 Response surface plots for the effect of fiber content and pressure on Young's modulus of PP biocomposites at a) high temperature b) low temperature.

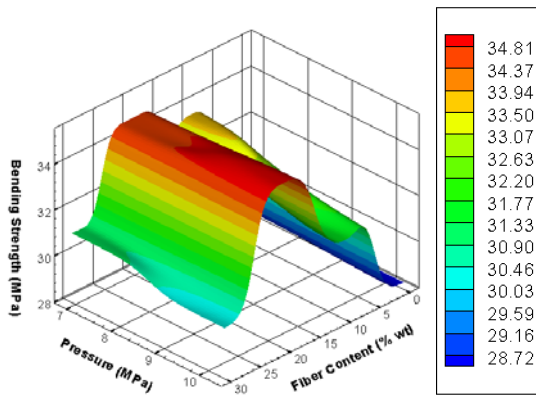


(a)

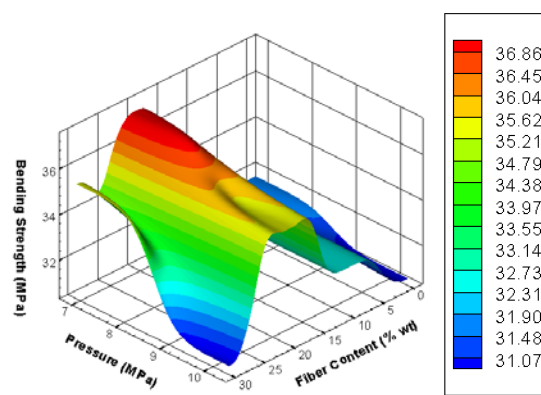


(b)

Figure C.27 Response surface plots for the effect of fiber content and temperature on bending strength of PP biocomposites at a) high pressure b) low pressure.



(a)



(b)

Figure C.28 Response surface plots for the effect of fiber content and pressure on bending strength of PP biocomposites at a) high temperature b) low temperature.

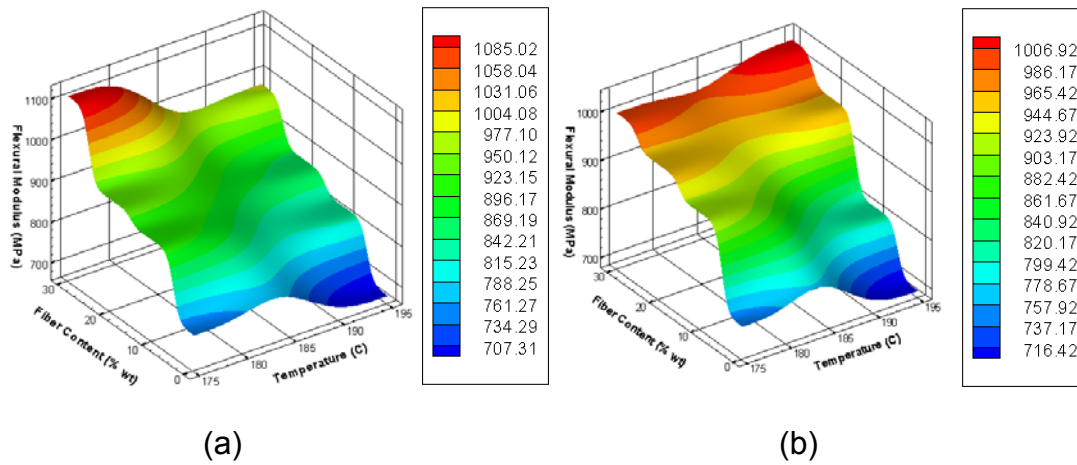


Figure C.29 Response surface plots for the effect of fiber content and temperature on flexural modulus of PP biocomposites at a) high pressure b) low pressure.

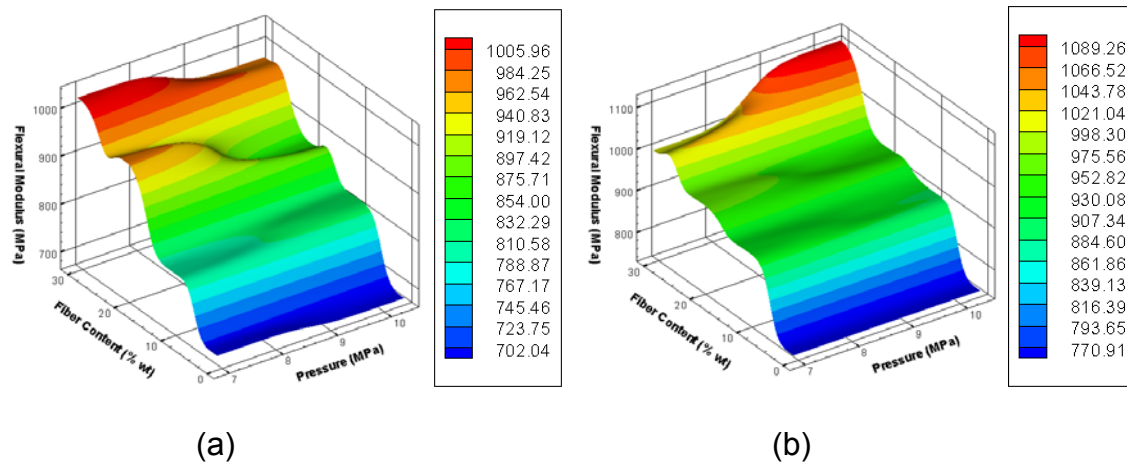


Figure C.30 Response surface plots for the effect of fiber content and pressure on flexural modulus of PP biocomposites at a) high temperature b) low temperature.

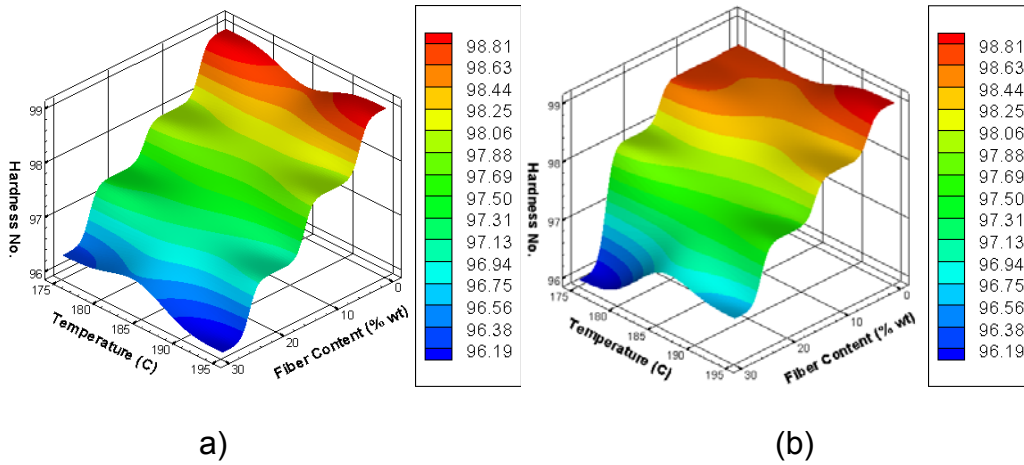


Figure C.31 Response surface plots for the effect of fiber content and temperature on hardness of PP biocomposites at a) high pressure b) low pressure.

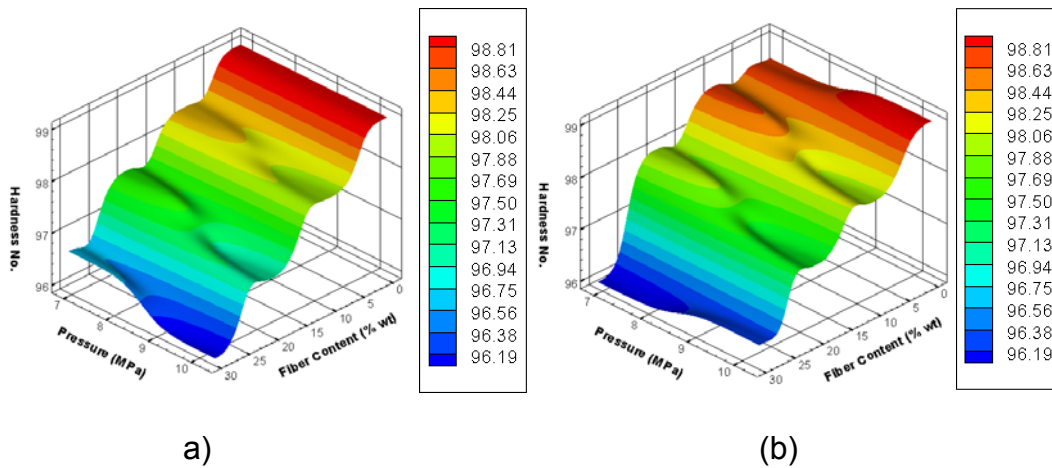


Figure C.32 Response surface plots for the effect of fiber content and pressure on hardness of PP biocomposites at a) high temperature b) low temperature.

APPENDIX D

Contour Plots for Superposition Surface Methodology

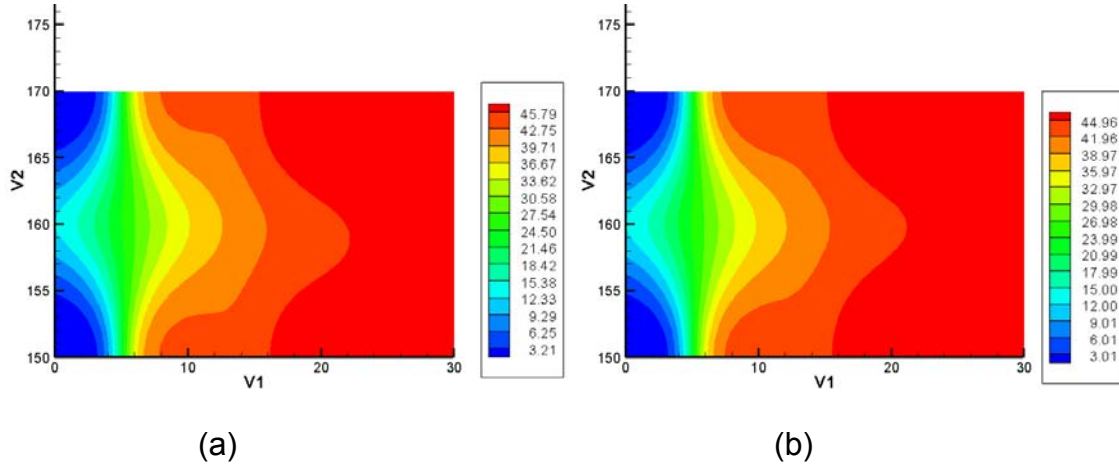


Figure D.1 Contour plots for the effect of fiber content (V1) and temperature (V2) on color index of HDPE biocomposites at a) high pressure b) low pressure.

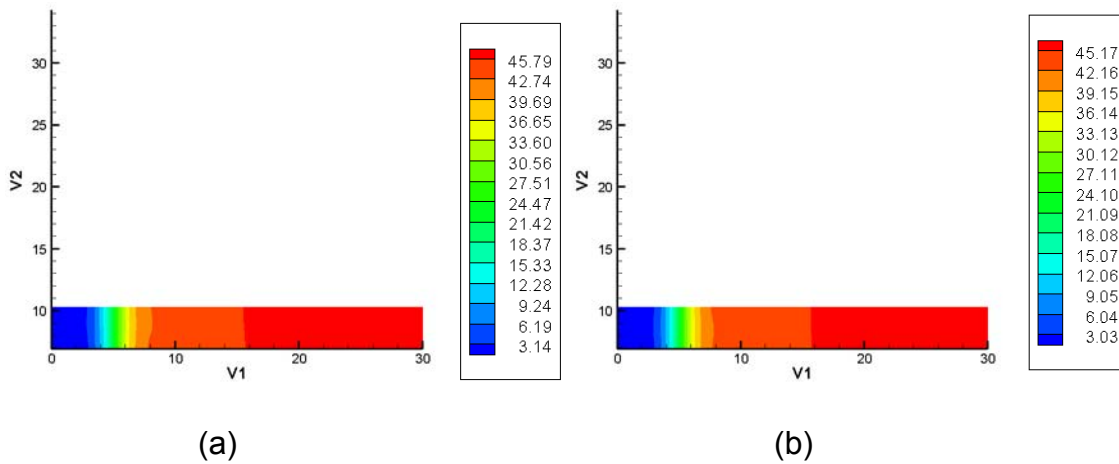


Figure D.2 Contour plots for the effect of fiber content (V1) and pressure (V2) on color index of HDPE biocomposites at a) high temperature b) low temperature.

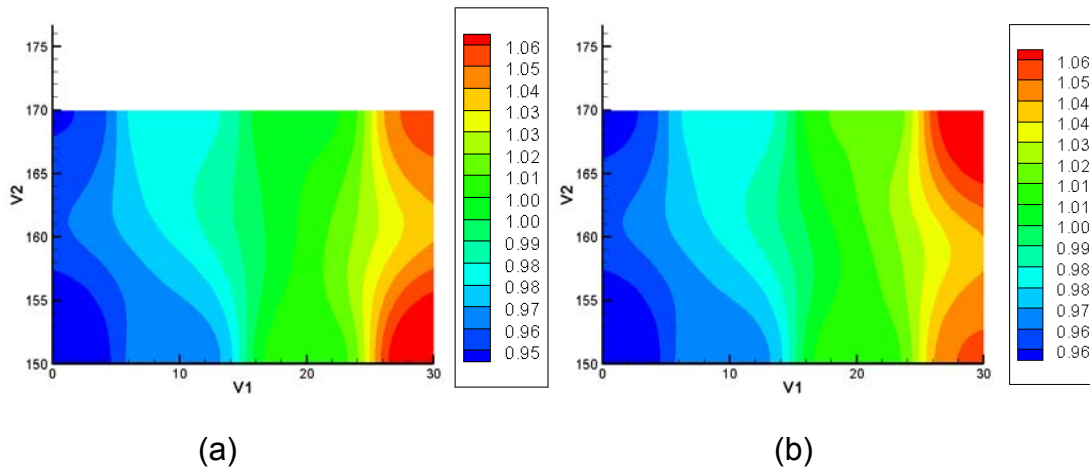


Figure D.3 Contour plots for the effect of fiber content (V1) and temperature (V2) on HDPE biocomposites density at a) high pressure b) low pressure.

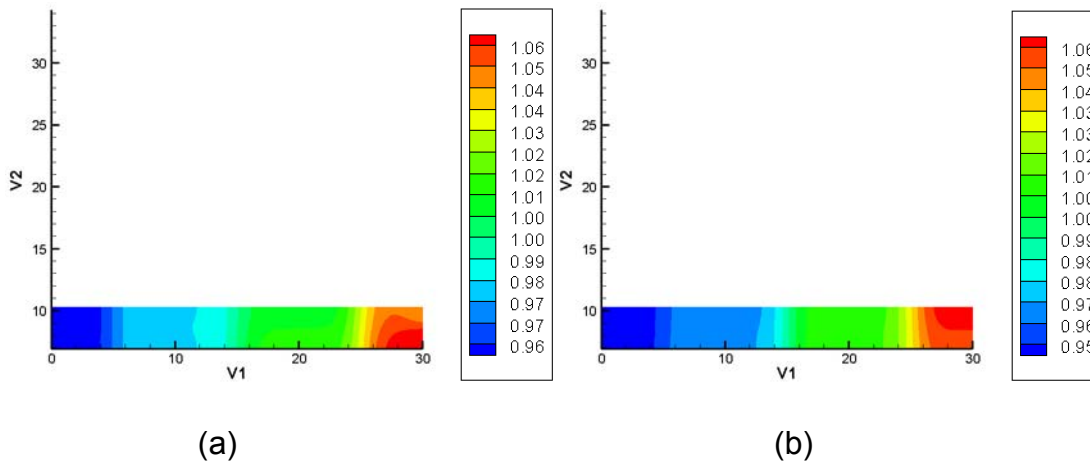


Figure D.4 Contour plots for the effect of fiber content (V1) and pressure (V2) on HDPE biocomposites density at a) high temperature b) low temperature.

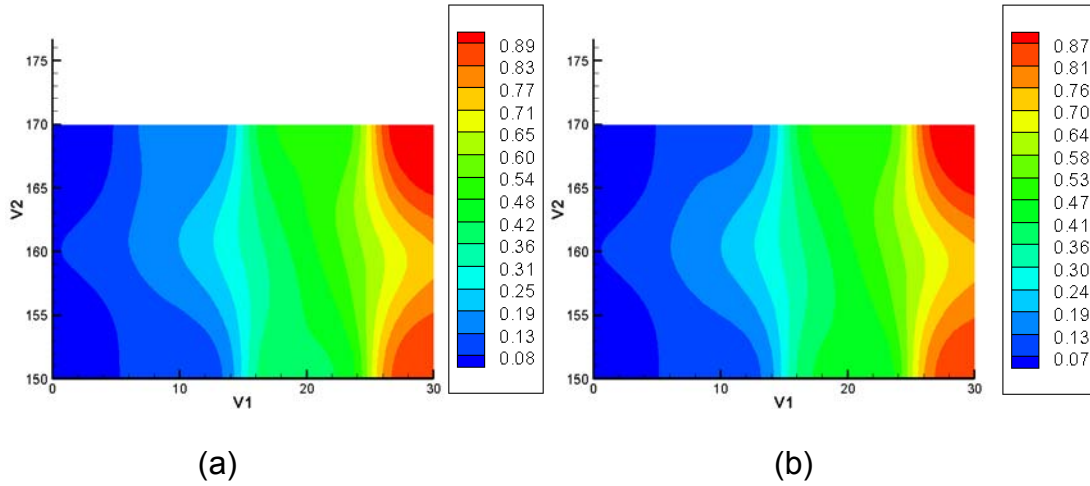


Figure D.5 Contour plots for the effect of fiber content (V1) and temperature (V2) on water absorption characteristics of HDPE biocomposites at a) high pressure b) low pressure.

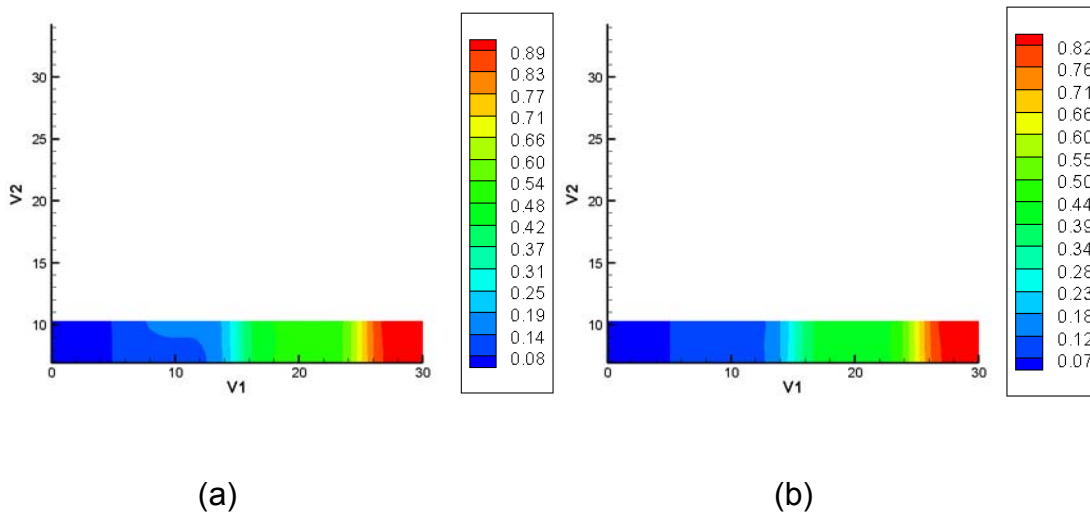


Figure D.6 Contour plots for the effect of fiber content (V1) and pressure (V2) on water absorption characteristics of HDPE biocomposites at a) high temperature b) low temperature.

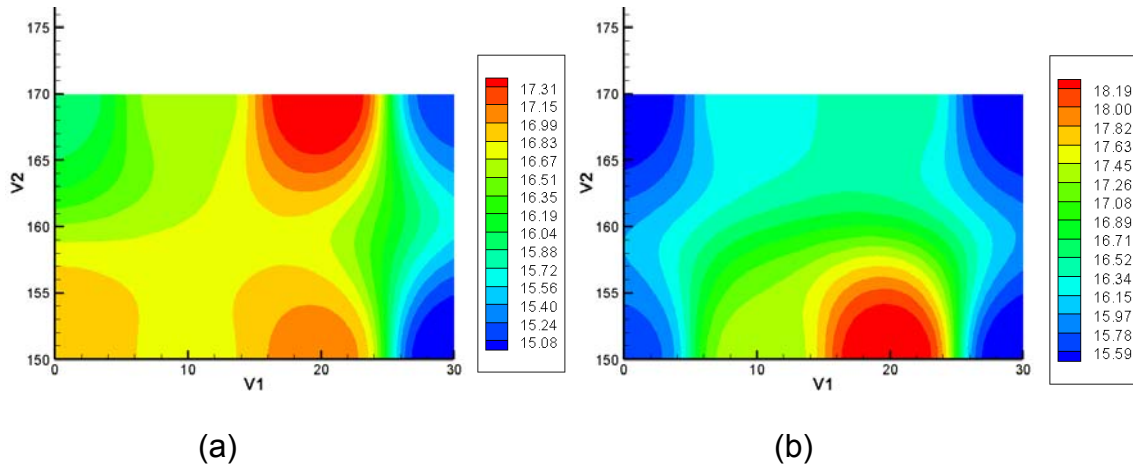


Figure D.7 Contour plots for the effect of fiber content (V1) and temperature (V2) on tensile strength of HDPE biocomposites at a) high pressure b) low pressure.

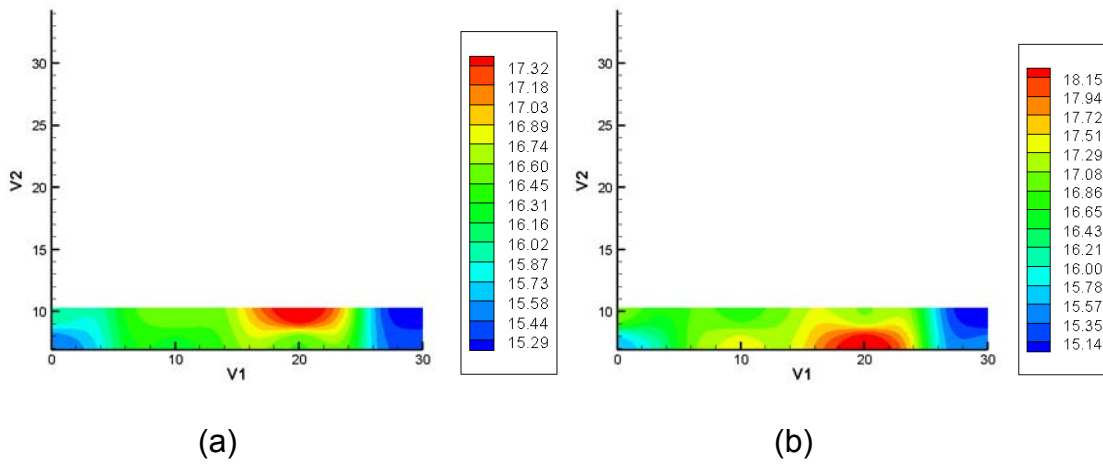


Figure D.8 Contour plots for the effect of fiber content (V1) and pressure (V2) on tensile strength of HDPE biocomposites at a) high temperature b) low temperature.

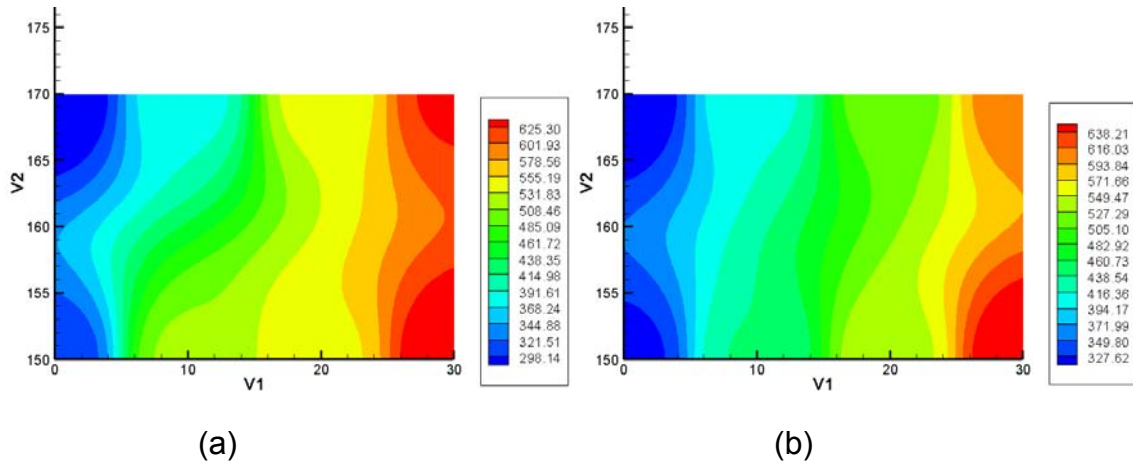


Figure D.9 Contour plots for the effect of fiber content (V1) and temperature (V2) on Young's modulus of HDPE biocomposites at a) high pressure b) low pressure.

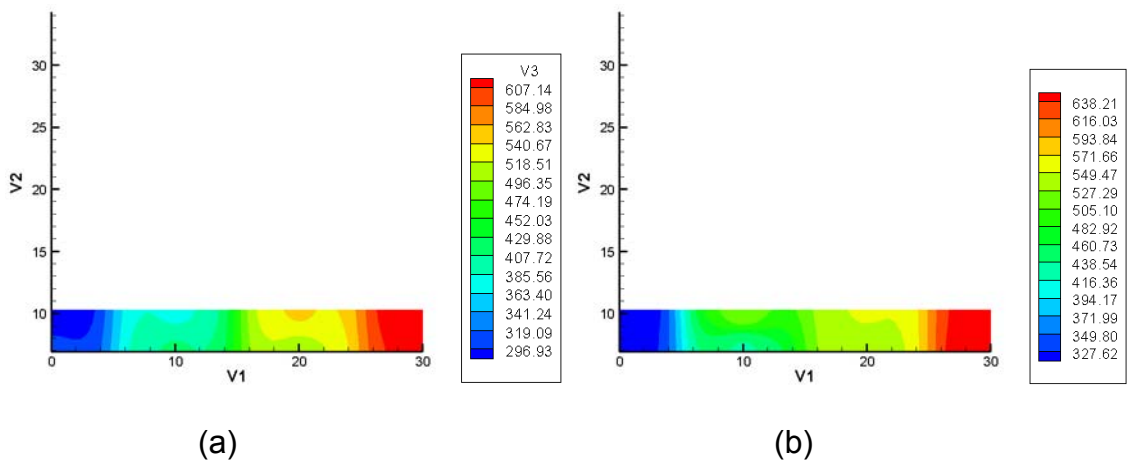


Figure D.10 Contour plots for the effect of fiber content (V1) and pressure (V2) on Young's modulus of HDPE biocomposites at a) high temperature b) low temperature.

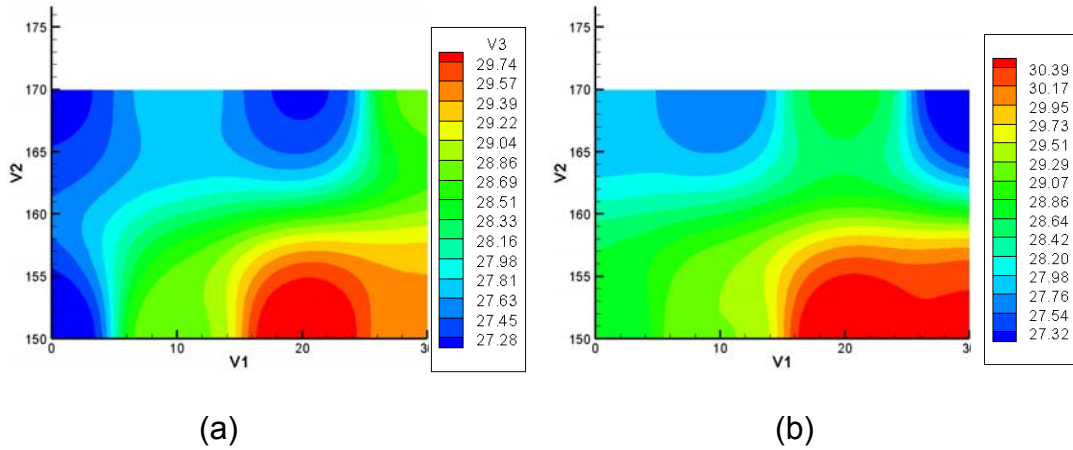


Figure D.11 Contour plots for the effect of fiber content (V1) and temperature (V2) on bending strength of HDPE biocomposites at a) high pressure b) low pressure.

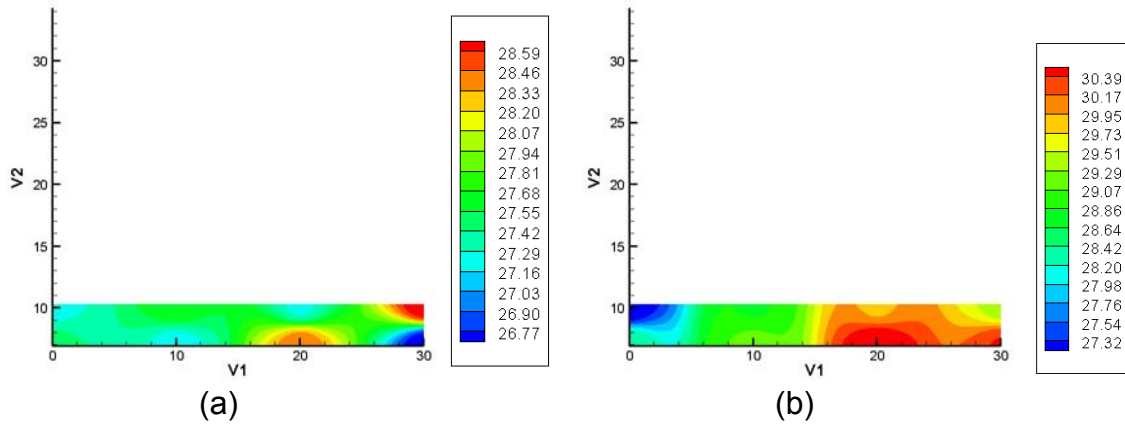


Figure D.12 Contour plots for the effect of fiber content (V1) and pressure (V2) on bending strength of HDPE biocomposites at a) high temperature b) low temperature.

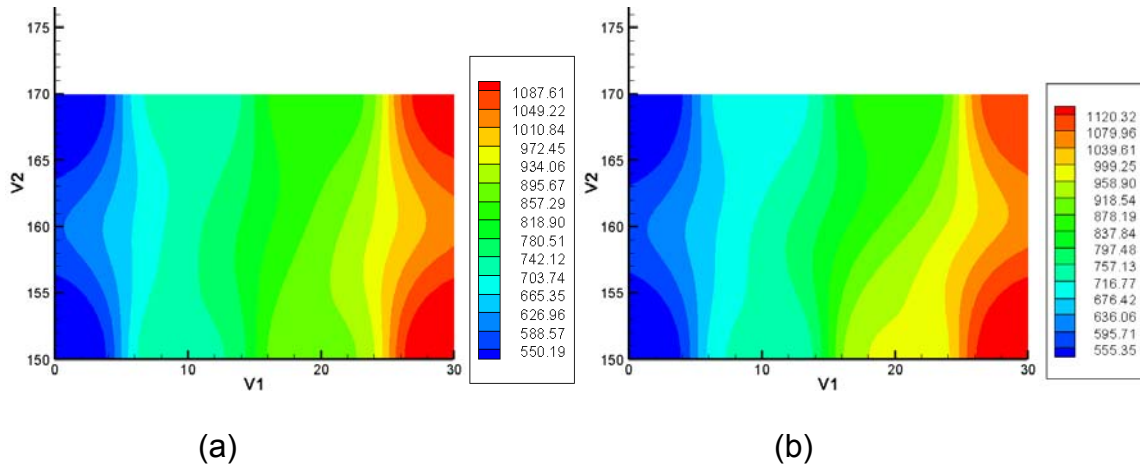


Figure D.13 Contour plots for the effect of fiber content (V1) and temperature (V2) on flexural modulus of HDPE biocomposites at a) high pressure b) low pressure.

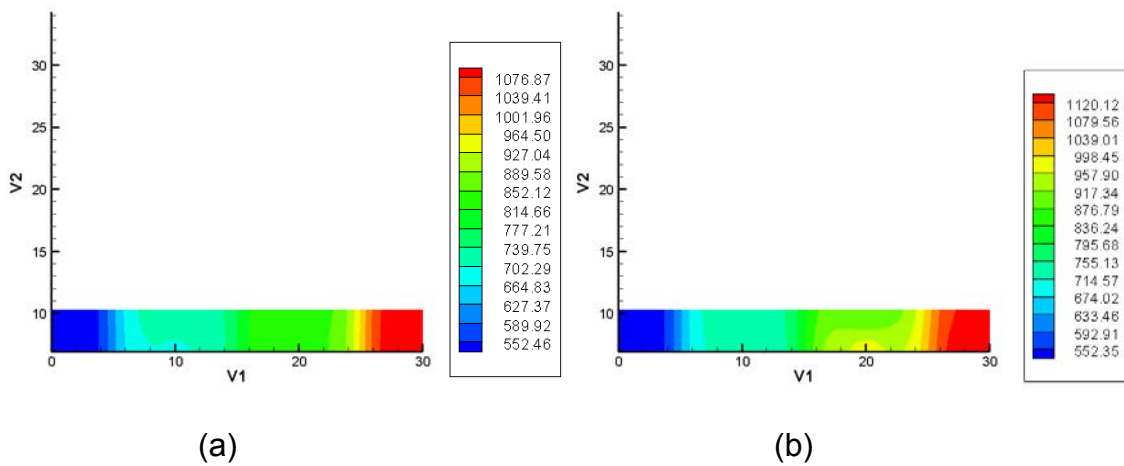


Figure D.14 Contour plots for the effect of fiber content (V1) and pressure (V2) on flexural modulus of HDPE biocomposites at a) high temperature b) low temperature.

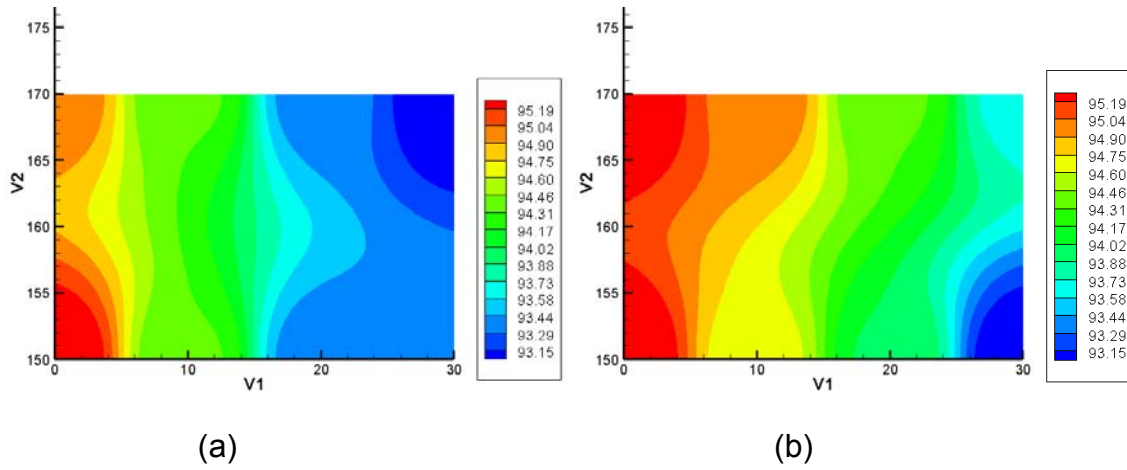


Figure D.15 Contour plots for the effect of fiber content (V1) and temperature (V2) on hardness of HDPE biocomposites at a) high pressure b) low pressure.

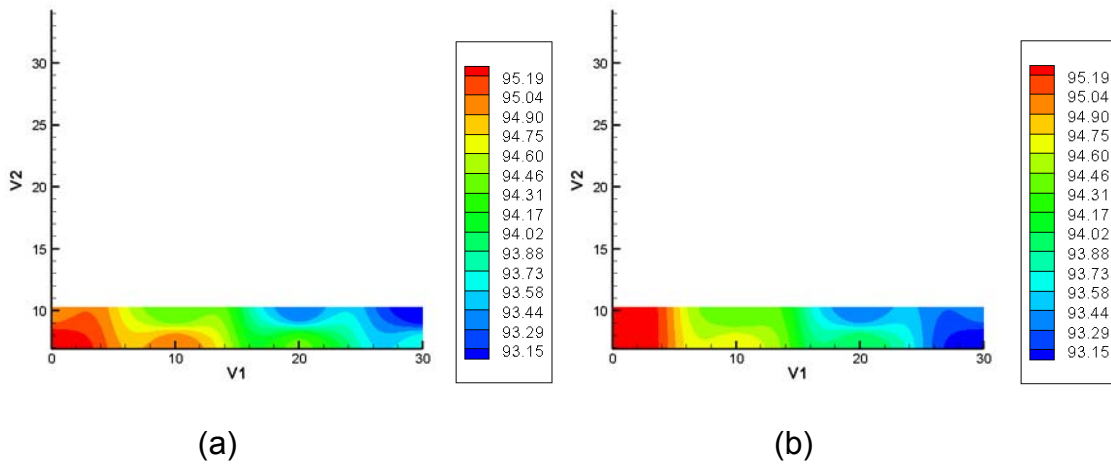


Figure D.16 Contour plots for the effect of fiber content (V1) and pressure (V2) on hardness of HDPE biocomposites at a) high temperature b) low temperature.

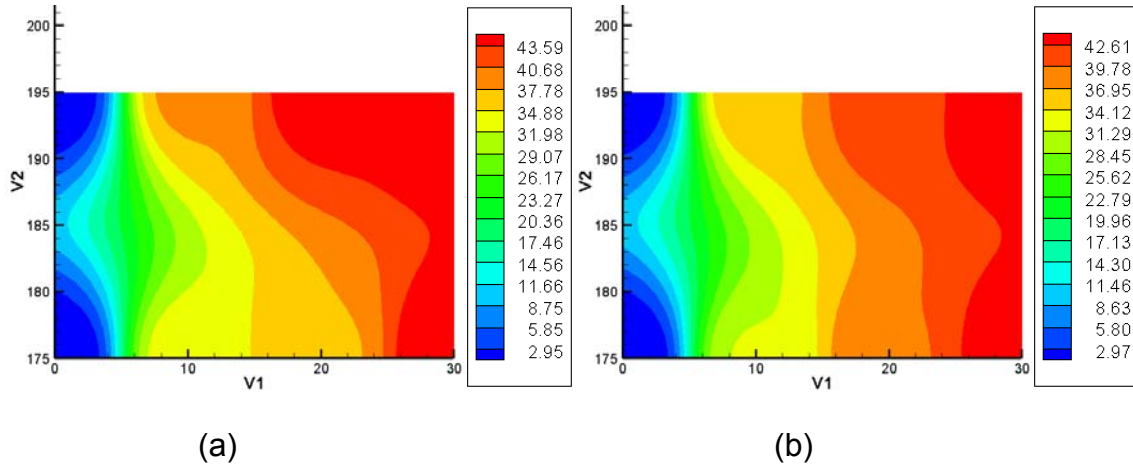


Figure D.17 Contour plots for the effect of fiber content (V1) and temperature (V2) on color index of PP biocomposites at a) high pressure b) low pressure.

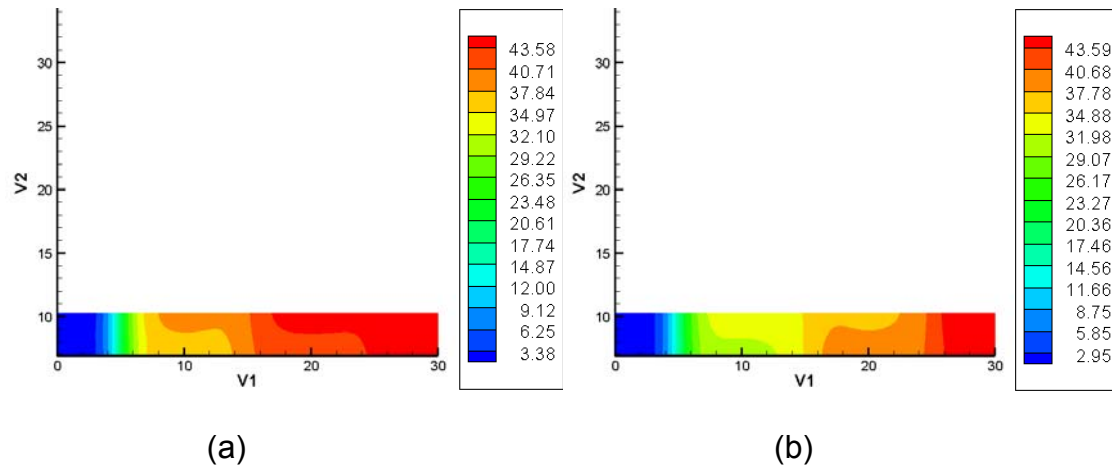


Figure D.18 Contour plots for the effect of fiber content (V1) and pressure (V2) on color index of PP biocomposites at a) high temperature b) low temperature.

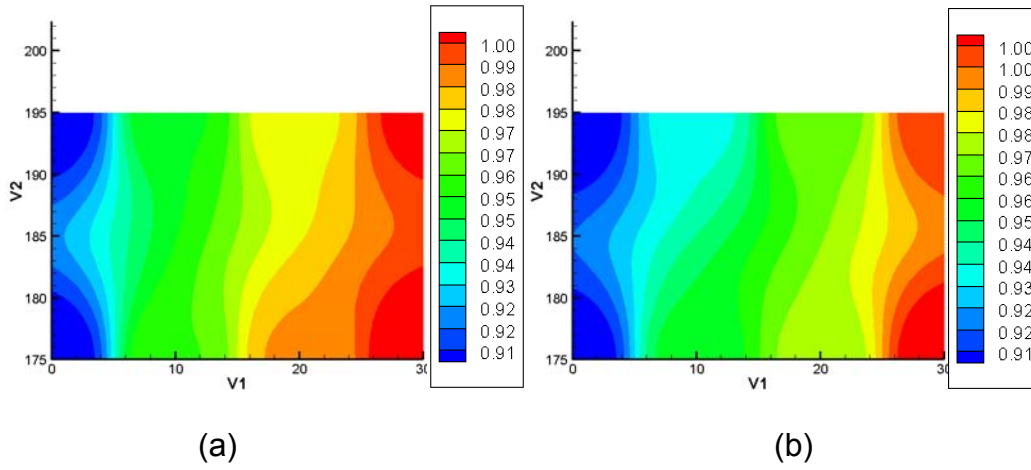


Figure D.19 Contour plots for the effect of fiber content (V1) and temperature (V2) on PP biocomposites density at a) high pressure b) low pressure.

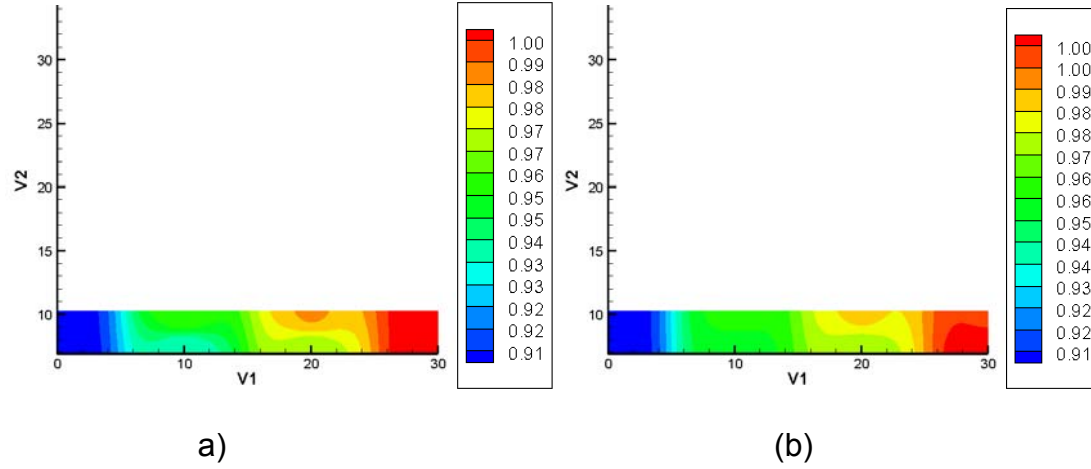


Figure D.20 Contour plots for the effect of fiber content (V1) and pressure (V2) on PP biocomposites density at a) high temperature b) low temperature.

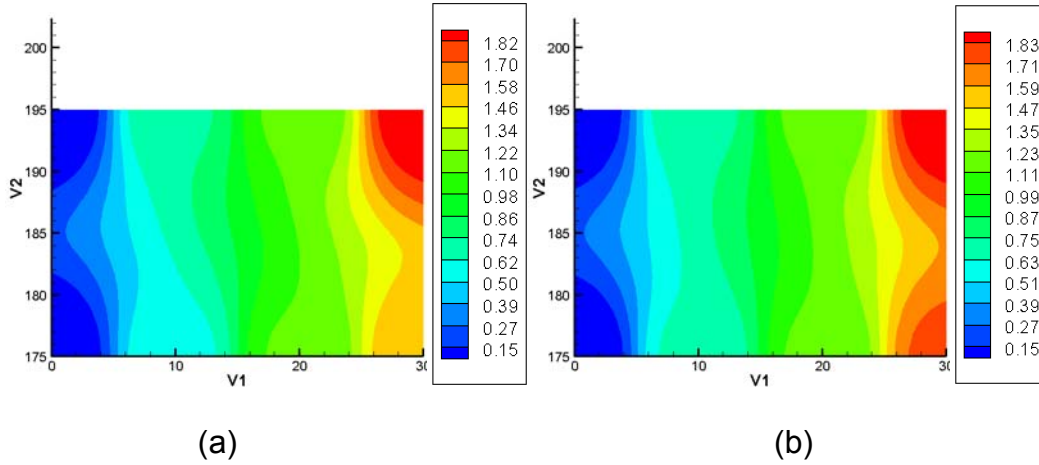


Figure D.21 Contour plots for the effect of fiber content (V1) and temperature (V2) on water absorption characteristics of PP biocomposites at a) high pressure b) low pressure.

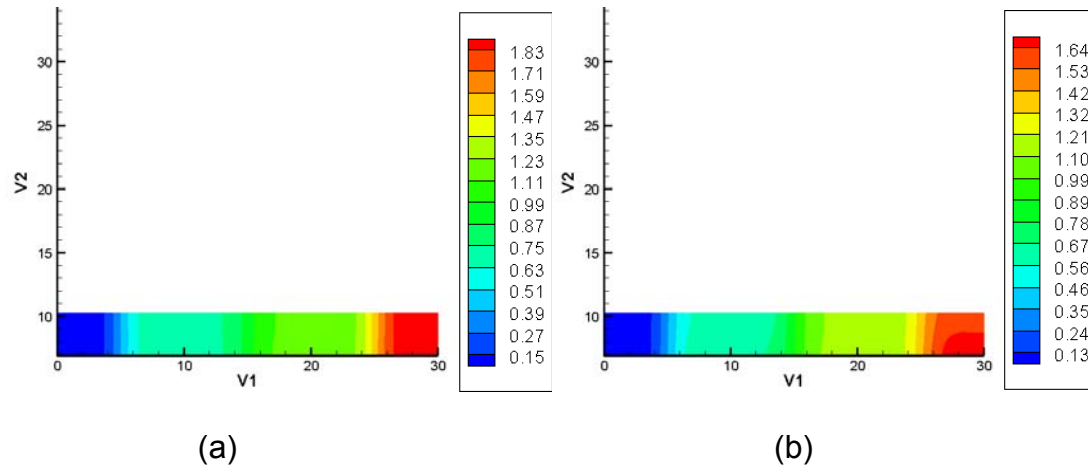


Figure D.22 Contour plots for the effect of fiber content (V1) and pressure (V2) on water absorption characteristics of PP biocomposites at a) high temperature b) low temperature.

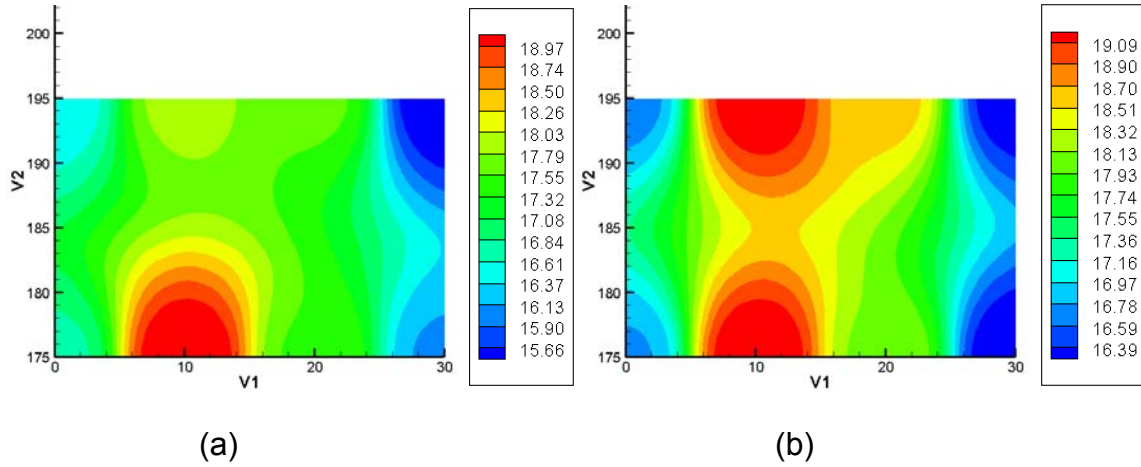


Figure D.23 Contour plots for the effect of fiber content (V1) and temperature (V2) on tensile strength of PP biocomposites at a) high pressure b) low pressure.

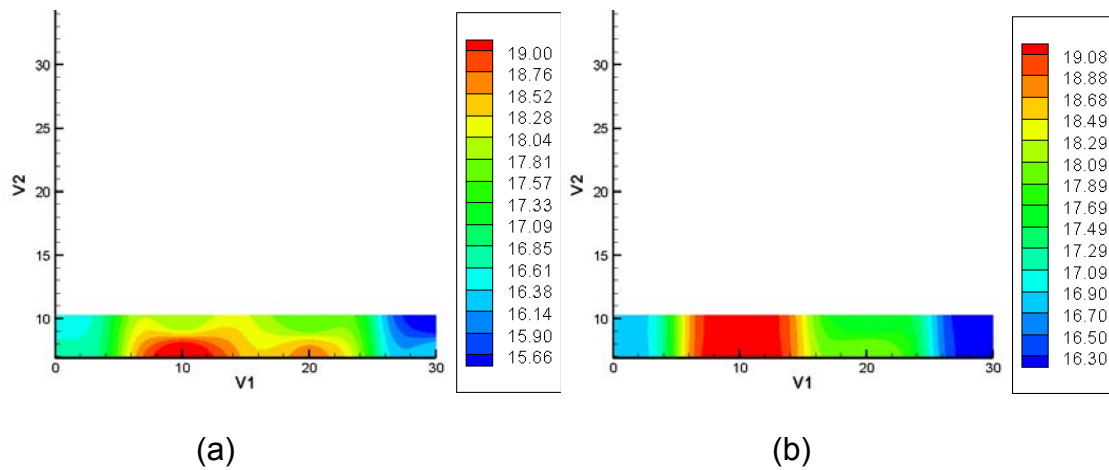


Figure D.24 Contour plots for the effect of fiber content (V1) and pressure (V2) on tensile strength of PP biocomposites at a) high temperature b) low temperature.

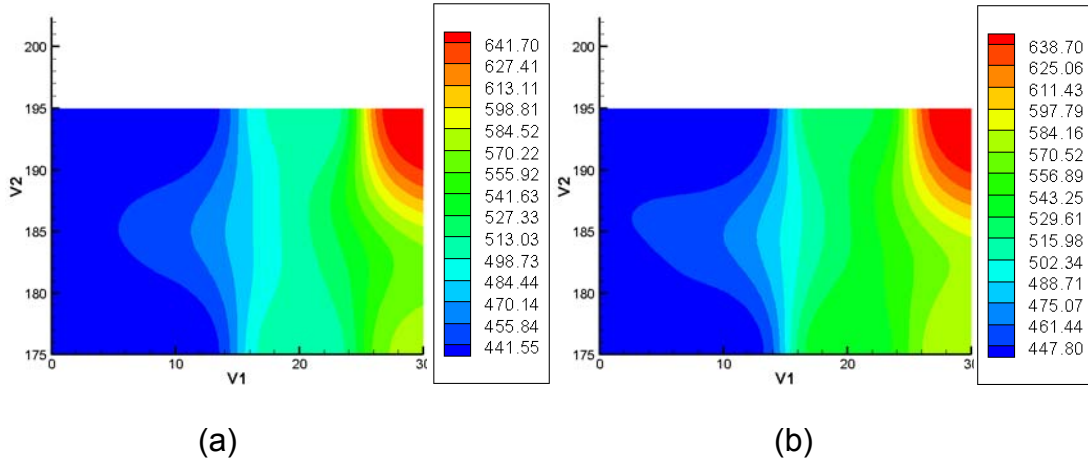


Figure D.25 Contour plots for the effect of fiber content (V1) and temperature (V2) on Young's modulus of PP biocomposites at a) high pressure b) low pressure.

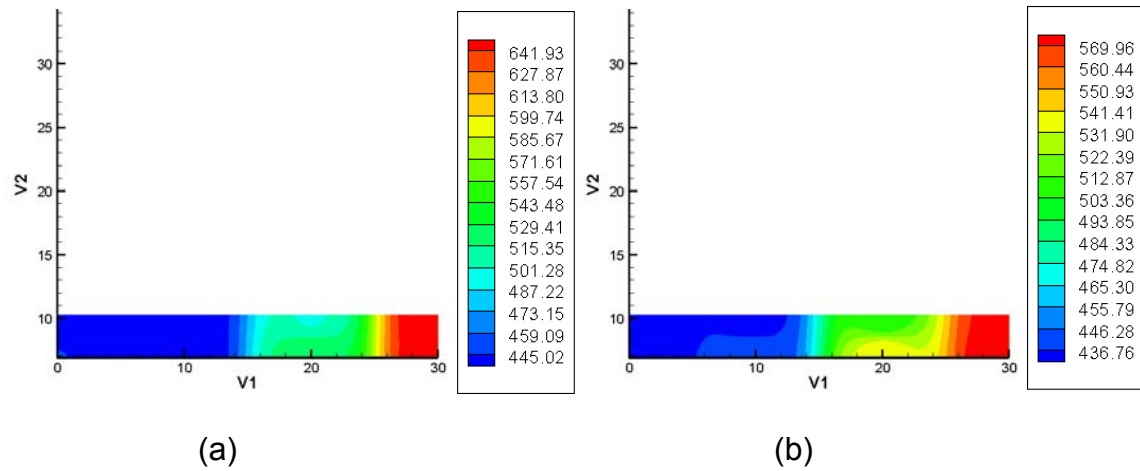


Figure D.26 Contour plots for the effect of fiber content (V1) and pressure (V2) on Young's modulus of PP biocomposites at a) high temperature b) low temperature.

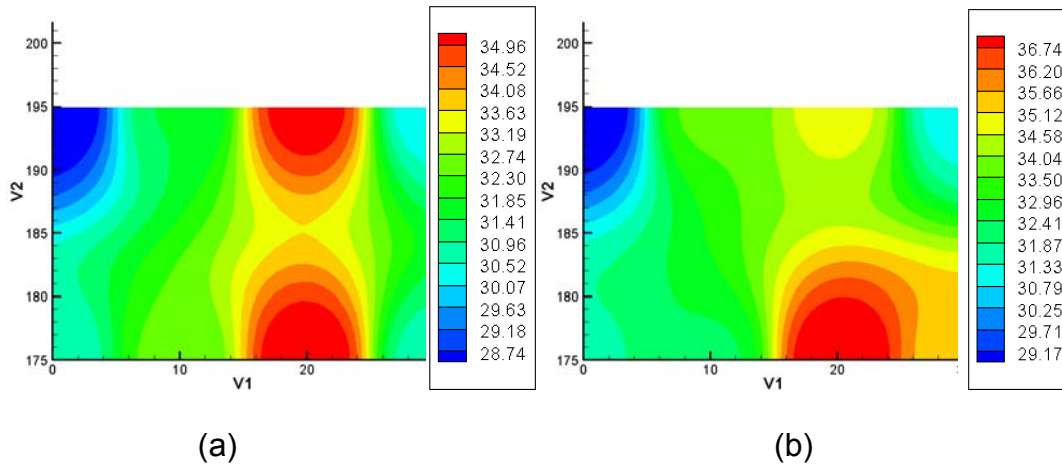


Figure D.27 Contour plots for the effect of fiber content (V1) and temperature (V2) on bending strength of PP biocomposites at a) high pressure b) low pressure.

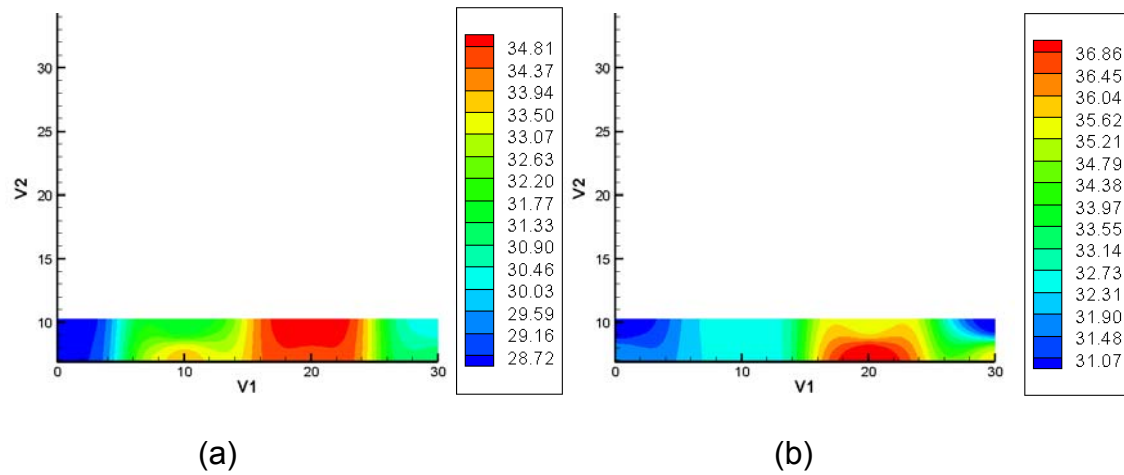


Figure D.28 Contour plots for the effect of fiber content (V1) and pressure (V2) on bending strength of PP biocomposites at a) high temperature b) low temperature.

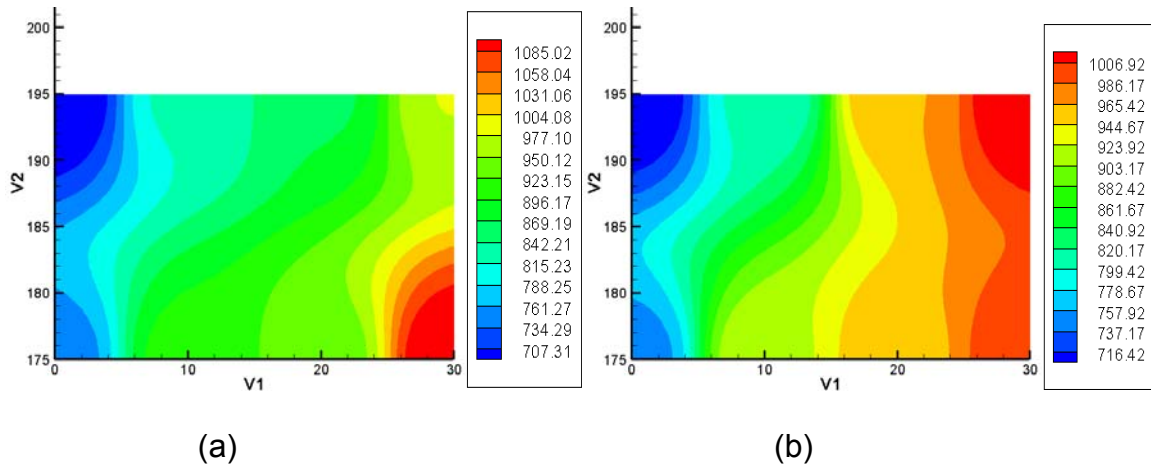


Figure D.29 Contour plots for the effect of fiber content (V1) and temperature (V2) on flexural modulus of PP biocomposites at a) high pressure b) low pressure.

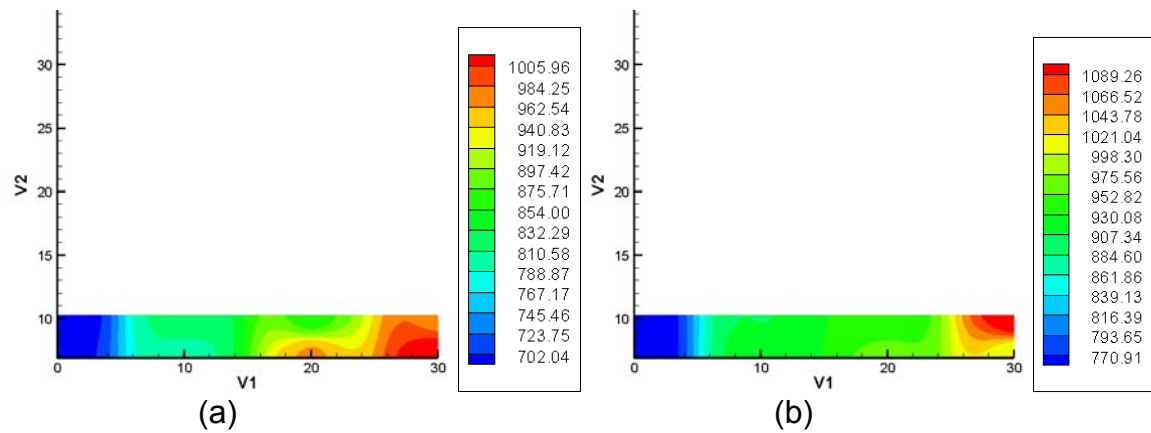


Figure D.30 Contour plots for the effect of fiber content (V1) and pressure (V2) on flexural modulus of PP biocomposites at a) high temperature b) low temperature.

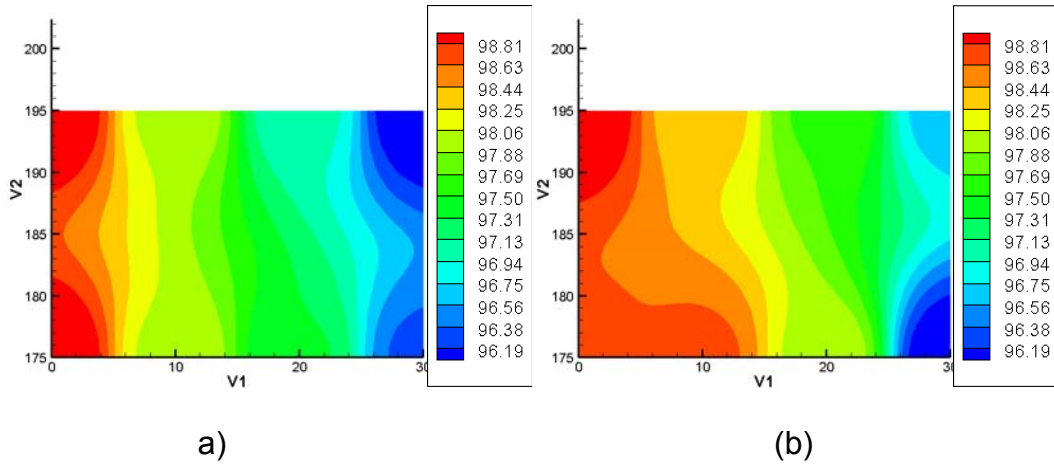


Figure D.31 Contour plots for the effect of fiber content (V1) and temperature (V2) on hardness of PP biocomposites at a) high pressure b) low pressure.

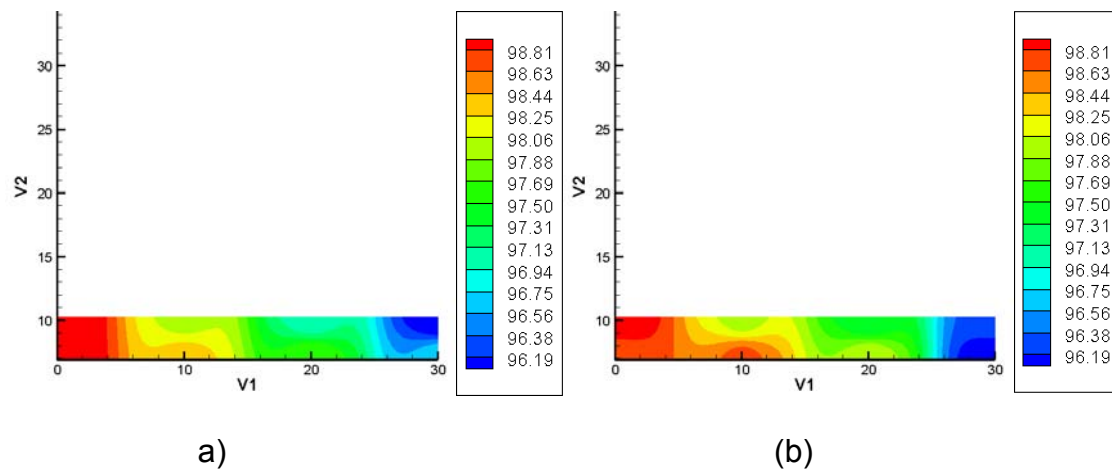


Figure D.32 Contour plots for the effect of fiber content (V1) and pressure (V2) on hardness of PP biocomposites at a) high temperature b) low temperature.

APPENDIX E

Swelling Data of HDPE and PP biocomposites

Table E.1 Swelling data of HDPE-based biocomposites.

Processing condition	Sample	Thickness (mm)			Width (mm)		
		Before water absorption test	After water absorption test	Swelling (%)	Before water absorption test	After water absorption test	Swelling (%)
C-I	HDPE	3.260	3.260	0.00%	24.080	24.080	0.00%
C-II	HDPE	3.950	3.950	0.00%	23.770	23.770	0.00%
C-III	HDPE	2.780	2.780	0.00%	24.150	24.150	0.00%
C-IV	HDPE	3.610	3.610	0.00%	23.820	23.820	0.00%
C-I	1a	3.180	3.210	0.94%	24.150	24.210	1.89%
C-II	1a	3.140	3.150	0.32%	24.130	24.150	0.64%
C-III	1a	1.940	1.950	0.52%	23.960	23.970	0.52%
C-IV	1a	2.210	2.230	0.90%	24.130	24.130	0.00%
C-I	1b	3.060	3.080	0.65%	24.160	24.170	0.33%
C-II	1b	3.160	3.190	0.95%	23.940	23.990	1.58%
C-III	1b	2.320	2.350	1.29%	23.960	23.970	0.43%
C-IV	1b	2.800	2.850	1.79%	24.160	24.200	1.43%
C-I	1c	3.120	3.150	0.96%	24.180	24.220	1.28%
C-II	1c	2.960	3.040	2.70%	23.500	23.530	1.01%
C-III	1c	3.350	3.420	2.09%	24.060	24.140	2.39%
C-IV	1c	2.650	2.690	1.51%	23.580	23.580	0.00%
C-I	2a	2.690	2.690	0.00%	24.120	24.150	1.12%
C-II	2a	2.710	2.720	0.37%	23.900	23.900	0.00%
C-III	2a	1.910	1.920	0.52%	24.010	24.030	1.05%
C-IV	2a	2.650	2.660	0.38%	23.980	23.980	0.00%
C-I	2b	3.380	3.390	0.30%	24.080	24.100	0.59%
C-II	2b	2.990	3.010	0.67%	24.150	24.150	0.00%
C-III	2b	2.910	2.940	1.03%	24.090	24.100	0.34%
C-IV	2b	3.080	3.090	0.32%	24.010	24.020	0.32%
C-I	2c	3.090	3.130	1.29%	24.060	24.070	0.32%
C-II	2c	2.700	2.730	1.11%	23.940	23.945	0.19%
C-III	2c	2.990	3.020	1.00%	23.950	23.960	0.33%
C-IV	2c	3.220	3.240	0.62%	23.830	23.850	0.62%
C-I	3a	2.840	2.843	0.11%	23.580	23.584	0.14%
C-II	3a	3.280	3.283	0.09%	23.850	23.853	0.09%
C-III	3a	2.530	2.540	0.40%	23.690	23.694	0.16%
C-IV	3a	2.050	2.054	0.20%	24.110	24.114	0.20%
C-I	3b	3.040	3.050	0.33%	24.090	24.100	0.33%
C-II	3b	2.760	2.770	0.36%	23.900	23.904	0.14%
C-III	3b	3.070	3.083	0.42%	23.980	23.984	0.13%
C-IV	3b	2.520	2.531	0.44%	24.040	24.044	0.16%
C-I	3c	3.310	3.330	0.60%	24.020	24.030	0.30%
C-II	3c	3.320	3.344	0.72%	23.310	23.323	0.39%
C-III	3c	3.060	3.084	0.78%	24.100	24.110	0.33%
C-IV	3c	2.970	2.992	0.74%	24.080	24.090	0.34%

Table E.2 Swelling data of PP-based biocomposites.

Processing condition	Sample	Thickness (mm)			Width (mm)		
		Before water absorption test	After water absorption test	Swelling (%)	Before water absorption test	After water absorption test	Swelling (%)
C-I	PP	3.280	3.280	0.00%	24.120	24.120	0.00%
C-II	PP	3.390	3.390	0.00%	24.150	24.150	0.00%
C-III	PP	3.210	3.210	0.00%	23.500	23.500	0.00%
C-IV	PP	3.450	3.620	0.00%	24.150	24.150	0.00%
C-I	1d	3.220	3.230	0.98%	24.010	24.020	0.99%
C-II	1d	3.240	3.246	0.62%	24.140	24.147	0.74%
C-III	1d	2.940	2.948	0.79%	24.050	24.054	0.42%
C-IV	1d	3.210	3.216	0.60%	23.950	23.956	0.56%
C-I	1e	3.280	3.297	1.65%	23.980	23.987	0.73%
C-II	1e	3.010	3.023	1.35%	24.030	24.042	1.24%
C-III	1e	3.210	3.230	1.99%	24.080	24.091	1.14%
C-IV	1e	3.340	3.357	1.69%	24.140	24.152	1.21%
C-I	1f	3.260	3.298	3.76%	24.070	24.082	1.16%
C-II	1f	3.460	3.494	3.40%	24.030	24.044	1.41%
C-III	1f	3.150	3.189	3.95%	23.940	23.956	1.59%
C-IV	1f	3.220	3.259	3.94%	24.070	24.081	1.14%
C-I	2d	3.120	3.128	0.84%	24.140	24.146	0.62%
C-II	2d	2.940	2.949	0.87%	24.160	24.169	0.89%
C-III	2d	2.980	2.988	0.82%	24.210	24.216	0.65%
C-IV	2d	3.170	3.179	0.88%	24.140	24.147	0.68%
C-I	2e	3.160	3.172	1.24%	24.060	24.067	0.74%
C-II	2e	3.290	3.304	1.38%	24.180	24.187	0.65%
C-III	2e	3.240	3.251	1.12%	24.060	24.067	0.72%
C-IV	2e	3.130	3.141	1.13%	24.080	24.087	0.74%
C-I	2f	3.250	3.271	2.13%	24.140	24.148	0.84%
C-II	2f	3.120	3.142	2.22%	24.130	24.136	0.56%
C-III	2f	3.350	3.372	2.18%	24.090	24.100	0.96%
C-IV	2f	2.940	2.962	2.16%	24.050	24.059	0.92%
C-I	3d	3.160	3.165	0.51%	24.080	24.081	0.14%
C-II	3d	2.950	2.955	0.49%	24.150	24.152	0.16%
C-III	3d	2.860	2.865	0.50%	24.140	24.142	0.20%
C-IV	3d	3.180	3.184	0.40%	23.940	23.943	0.30%
C-I	3e	3.250	3.260	1.04%	23.960	23.964	0.42%
C-II	3e	3.210	3.221	1.13%	24.210	24.213	0.25%
C-III	3e	3.170	3.182	1.21%	24.020	24.023	0.32%
C-IV	3e	3.280	3.292	1.24%	24.050	24.054	0.36%
C-I	3f	3.360	3.377	1.66%	24.180	24.185	0.45%
C-II	3f	3.200	3.214	1.42%	23.910	23.915	0.52%
C-III	3f	3.150	3.167	1.66%	24.020	24.025	0.45%
C-IV	3f	3.120	3.137	1.71%	24.110	24.114	0.39%