EFFECTS OF FIBER CONTENT AND EXTRUSION PARAMETERS ON THE PROPERTIES OF FLAX FIBER – POLYETHYLENE COMPOSITES

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ABSTRACT

Extrusion compounding addresses such problems as the non-homogeneity of the mixture and separation of fiber from the polymer during rotational molding, which consequently affect the mechanical and physical properties of the resulting composites.

Using triethoxyvinylsilane as chemical pre-treatment on flax fibers and linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) as polymer matrices, this study focused on the effects of flax fiber content (0%, 12.5% or 25%) and extrusion parameters such as barrel zone temperatures (75-110-120-130-140°C or 75-120-130-140-150°C) and screw speed (110 or 150 rpm) on the extrudate and composite properties (extrudate color, extrudate density, extrudate melt flow index, extrudate morphology, composite color, composite density, composite morphology, composite tensile strength and composite water absorption).

A mixture of chemically pre-treated flax fibers and powdered polyethylene matrices underwent extrusion compounding using a twin-screw extruder. The extrudates were then pelletized, ground, rotationally molded and cut into test specimens (composites). The mechanical and physical properties of both the extrudates and the composites from different treatments were then measured and compared.

Using multiple linear regression, models were generated to show quantitatively the significant effects of the process variables on the response variables. Finally, using response surface methodology and superposition surface methodology on the preceding data, the following optimum values for fiber content and extrusion parameters were determined: for LLDPE composites, fiber content = 6.25%, temperatures = 75-117.3-127.3-137.3-147.3°C, screw speed = 117.5 rpm; for HDPE composites, fiber content = 5.02%, temperatures = 75-118.1-128.1-138.1-148.1°C, screw speed = 125.56 rpm.

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DEDICATION

This thesis is dedicated to my family: Daddy, Mommy, Kuyang Jojo, Ate Lynfel, Mikki, Kookie, Amber, Kuya Giovee, Manong Boyet, Ping, Nica, Giolo, Neneng, Bobeep, Anna, Steph, Michael, Liza, Michelle and Kirby.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. INTRODUCTION

Flax belongs to the genus *Linum*, one of the 10 genera in the family Linaceae. The genus contains more than 100 annual and perennial species. Cultivated flax belongs to the species, *L. usitatissimum*, and its varieties are of two types: one is grown for oil and the other for fiber. Presently in Canada, oilseed flax is one of the main commercially produced crops. There is also a growing trend to return to utilizing natural fibers for both industrial applications and textiles. This trend will only continue as pressures increase to produce materials that are recyclable or biodegradable. As a result, Western Canadian businesses are realizing the value of flax straw, and are developing technologies to handle and produce fiber from it for industrial purposes. The extraction and processing of fiber from existing flax straw residue and the dedicated planting of fiber flax will create new production and value-added processing opportunities for Western Canadian flax producers (Fridfinnson and Hale, 2002).

The major commercial users and buyers of prairie flax straw have been two flax straw processing companies based in Winkler, MB that extract flax fiber for use in the production of specialty papers. In recent years, a flax straw processing plant was also set up in Canora, SK. In addition to extracting flax fiber for use in specialty paper production, this plant produced fibers to replace the fiberglass presently used to make composites for use as automotive parts like dashboards and headliners. However, this plant ceased operation and has been bought by a business person in the region producing flax fibers for use in decks and fences, with all of its production going to the United States.

Despite the technology used in the aforementioned processing plants, the problems in quantity (variable fiber content of the straw) and quality (inconsistency of fibers extracted from flax straw) have not yet been addressed. This was also observed by Mercedes-Benz who, among other automotive companies, has studied many materials and was using animal hair and fibers from flax, sisal, coconut and cotton in upholstery, door panels and rear shelves of its cars. The company was looking to replace glass fiber with natural fiber alternatives, but has found it difficult. Not only are natural materials usually sensitive to temperature, but they also tend to absorb water and often exhibit extreme variation in quality (Murphy, 1998).

As well as temperature sensitivity, degradation by moisture and variation in quality, disadvantages of flax fibers include poor surface adhesion to hydrophobic polymers, susceptibility to fungal and insect attack (Murphy, 1998), and separation from the polymer during rotational molding and a resulting non-homogenous mixture, all of which contribute to the low performance of the composite. However, there are advantages to using flax fibers, including biodegradability, low density, low cost, better damage tolerance in composites and high specific strength and stiffness (Murphy, 1998) that cannot be ignored. Hence, a large number of researchers have investigated techniques to improve the performance of composites using flax fibers.

Numerous studies have dealt with the effect of retting, physical modifications and chemical pre-treatments on composite properties. Van de Weyenberg and co-workers (2003) found that during the consecutive decortication stages of flax fibers (retting, scutching and hackling), the fiber properties changed due to mechanical modifications. They concluded that the better the degree of retting of the fibers, the better the properties of the composite.

The high level of moisture adsorption by the fiber, its poor wettability, as well as the insufficient adhesion between untreated fibers and the polymer matrix led to debonding with age. In the study of vegetable fibers, Bledzki and co-workers (1996) reported that in order to build composites with high mechanical properties, surface modification of the fibers is necessary. George and co-workers (2001) agreed, stating that an important aspect with respect to optimal mechanical performance of natural-fiber-reinforced composites in general, and durability in particular, is the optimization of the interfacial bond between fiber and polymer matrix. This was reinforced by Ceres and Pott (2002) whose main focus in their study was on the hydrothermal treatment (physical modification) of green rippled flax straw, the Duralin™ process in particular. This process involved three steps: hydrothermolysis, drying and curing. The process was found to reduce moisture absorption and biological degradation. Duralin™ fibers had equal or higher tensile strength and higher flexural modulus than fibers extracted from dew-retted flax.

Sreekala and Thomas (2003) used various fiber surface modification methods, such as mercerization, latex coating, gamma irradiation, silane treatment, isocyanate treatment, acetylation and peroxide treatment, to reduce the hydrophilicity of oil palm fibers, thereby altering their sorption characteristics. In their study, Bledzki and co-workers (1996) employed chemical surface modification of vegetable fibers. With the use of a coupling agent, like silane or stearic acid, the Young's modulus and the tensile strength increased. Simultaneously, the moisture absorption of the composites decreased by about 60%. With other surface modifications of vegetable fibers, similar results were obtained. Panigrahi and co-workers (2003) also used silane, along with two other chemical treatments (benzoylation and peroxide treatment), for flax fiber and polyolefin-based (LLDPE, HDPE) composites. They concluded that the mechanical properties of the composites were modified by chemical modification of flax fiber, but recommended that further work be undertaken to quantify the effects of the pre-treatments. In their research, Cantero and co-workers (2003) compounded polypropylene-based composites with two kinds of flax fibers (natural flax and flax pulp). The treatments applied were maleic anhydride (MA), maleic anhydride – polypropylene copolymer (MAPP) and vinyltrimethoxysilane (VTMO). The three treatments reduced the polar component of the surface energy of the fiber. Composites containing MAPP-treated fibers had the highest mechanical properties, while composites with the MA and VTMO-treated fiber gave values similar to that of the untreated ones. Van de Weyenberg and co-workers (2003) also studied the influence of certain chemical treatments, performed on flax fibers, on composite properties. Treatments with alkali, dilute epoxy, acetone and silane were conducted. A treatment consisting of a combination of alkali and dilute epoxy gave the highest improvement of flexural properties.

Despite the numerous studies on retting, physical modification and chemical modification, there are only a limited number of investigations on extrusion of natural fiber and polymer matrix and the extrusion parameters involved. Extrusion compounding addresses composite rotational molding problems such as a non-homogeneous mixture and separation of fiber from polymer during the molding process. The goal of this study, therefore, was to focus on extrusion as a solution to these problems.

Extrusion compounding is a process of melting the polymer, thoroughly mixing the flax fibers with the molten plastic, and conveying the mixture through a die to produce extrudates. This process ensures that the flax fibers are uniformly dispersed within the melt, which results in extrudates and composites with better properties. However, there are certain extrusion parameters that must be considered to optimize the effect of extrusion on composite properties. These are screw speed and temperature (Hanawalt, 2002).

Screw speed must be maximized in order to minimize residence time and maximize throughput. However, when a product is heat sensitive (as flax fibers are), the extruder screw speed is limited by the maximum shear rate that the product can experience without degradation. Another reason for limiting screw speed is to avoid air entrapment and to prevent excessive melt temperatures. If the polymer is extruded at rates that are too high, air entrapment can occur, resulting in tiny bubbles in the extrudate.

Temperature limitations in extrusion result from either the inability to add enough heat to get a consistent melt or the inability to remove enough heat from a melt to prevent product degradation. Flax fibers are heat sensitive. If the barrel temperatures and/or the screw speed are high enough, it is possible to make a product consisting of plastic and degraded fiber.

This study further examined the effects of extrusion parameters (temperature and screw speed) and flax fiber content on the physical and mechanical properties of the composites. The composites were produced using rotational molding.

Rotational molding is a highly versatile manufacturing option that allows unlimited design possibilities with the added benefit of low production costs. It is utilized to produce hollow parts by placing a limited amount of the polymer in the mold and heating and rotating simultaneously so that the walls of the mold become coated with a thin layer of the polymer. After the entire polymer mass becomes fused into one continuous part, the mold is cooled and the product removed (Miller, 1996).

This study utilized the shuttle-type rotational molding machine at Quality Molded Products Inc, Saskatoon, SK, Canada.

The objectives (Chapter Two) follow the introduction. Chapter Three further delves into the literature available on flax fiber composites and the extrusion and rotational molding technologies. Chapter Four elaborates more on the materials and methods used to achieve the objectives of this study. The results are presented and discussed in Chapter Five, while summary and conclusions and recommendations are presented in Chapters Six and Seven, respectively.

2. OBJECTIVES

Extrusion compounding addresses problems such as non-homogeneous mixture and separation of fiber from polymer during rotational molding. It is, therefore, necessary to optimize the extrusion parameters to obtain the desired mechanical and physical properties of the polyethylene (LLDPE and HDPE) composites. To achieve this goal, the following objectives were set:

1) to compare the effects of fiber content and extrusion parameters on extrudate properties, namely color, density, melt flow index and morphology (dispersion and adhesion of fibers and porosity);
2) to compare the effects of fiber content and extrusion parameters on rotationally-molded composite properties such as color, density, morphology (dispersion and adhesion of fibers and porosity), tensile strength and water absorption;
3) to quantify through regression models the effects of fiber content, screw speed and temperatures on the aforementioned extrudate and composite properties; and
4) to determine the optimum values of fiber content and extrusion parameters (screw speed and barrel zone temperatures) in the production of rotationally-molded composites using linear low density polyethylene (LLDPE) and high density polyethylene (HDPE).

3. LITERATURE REVIEW

To achieve the preceding objectives, it was imperative to have a prior knowledge and understanding of the properties of rotationally-molded composites and their components (flax fiber and polymer) as well as the processing methods (extrusion and rotational molding) employed and their parameters.

3.1 Composites

Many everyday plastic products contain fiberglass to give strength, reduce volume and/or reduce cost. When plastic is combined with another material as reinforcement, the resultant product is called a plastic composite. Tractor fenders, car dashboards, decking and fencing materials, sewer pipes and septic tanks are but a few examples of products that are being made from plastic composites (Fridfinnson and Hale, 2002).

3.1.1 Reinforcing fibers

The reinforcement used with plastics is mainly fiber or filament, used singly or in mixtures. Fibrous materials act to reinforce a matrix material by transferring the stress under an applied load from the weaker resin to the much stronger fiber. Polymers provide valuable and versatile materials for use as matrices, but other materials, such as metals, ceramics and cements, are also used as matrices for fibrous reinforcement. Glass fiber is predominantly the most important and widely used fiber in reinforced plastics. Other fibers include natural (cotton, flax, sisal, jute and other cellulosics), synthetic (nylon, polyester, acetate and rayon), and organic and inorganic high performance fibers (aramid, boron and carbon/graphite) (Murphy, 1998).

3.1.2 Natural fibers

Natural fibers (usually derived from vegetable matter) are receiving increasing attention from where there is a strong urge to use materials that are friendlier to the environment. There is growing interest in the possible use of natural fibers in reinforced plastics, not only in the developing countries that produce them, but also in industrialized countries, where some believe they might help in solving waste disposal and recycling problems. However, based on present evidence, it appears that to match the performance and consistency offered by existing reinforcement materials (such as glass), natural fibers may well have to be treated with coatings, which might mitigate against easy recycling of the base fiber. Mercedes-Benz, among other automotive companies, has studied many materials and has used animal hair and fibers from flax, sisal, coconut and cotton in upholstery, door panels and rear shelves of its cars. The company is looking to replace glass fiber with natural fiber alternatives (Murphy, 1998).

3.1.2.1 Flax fibers

It has been found that in many plastic composite applications, flax fibers can be used in place of fiberglass. Flax fibers are generally cheaper, lighter in weight and impart more springiness than fiberglass. In addition, flax fibers take less energy to manufacture and are easier to decompose or burn than is fiberglass. The demand for flax fibers in plastic composites is growing by more than 50% annually in Europe and this trend has now started in North America. By far, the largest users are automotive parts manufacturers who are being pressured to make cheaper and lighter weight vehicles with lower fuel consumption and to use more environmentally friendly materials in their manufacture. Fiberglass comes in many grades and prices. At the present time, flax fiber is able to substitute only for lower grade, lower priced fiberglass. This is mainly because the flax straw that processors buy is quite inconsistent in quality. It will take time for processors and growers to learn the management techniques needed and to make the necessary capital investments to produce more consistent, higher-grade types of flax fiber. As quality improvements take place, an increase in demand, and a corresponding increase in the average price, of both the fiber and the straw can be expected (Fridfinnson and Hale, 2002).

3.1.2.2 Properties of flax fibers

The morphological structure of multicellular fibers makes them analogous to the modern reinforced rigid matrix composites. The properties of fibers are also determined by the physical, mechanical and chemical properties of their constituents and their interfaces. The polymeric constituents in flax fibers are cellulose (64.1%), hemicellullose (16.7%), lignin (2.0%) and pectin (1.8%). Other components are wax, water and water solubles. Lignin and pectin act mainly as bonding agents, whereas hemicellulose is known for its hydrophilicity. The flax fiber consists of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicellulose and lignin (Baley, 2002).

Following is a comparison of some physical and mechanical properties of flax, glass, hemp and other natural fibers (Table 3.1).

Table 3.1 Properties of glass and natural fibers (Brouwer, 2000).

Properties	Fiber							
	E-glass	Flax	Hemp	Jute	Ramie	Coir	Sisal	Cotton
Density, g/cm^3	2.55	1.4	1.48	1.46	1.5	1.25	1.33	1.51
Tensile strength, MPa	2400	800-1500	550-900	400-800	500	220	600-700	400
E-modulus, GPa	73	60-80	70	10-30	44	6	38	12
Elongation at failure, %	3	1.2-1.6	1.6	1.8	2	15-25	2-3	3-10
Moisture absorption, %	-	7	8	12	12-17	10	11	8-25

As shown in Table 3.1, some of the physical and mechanical properties of flax fibers are better than those of other natural fibers and are not far from those of glass fibers except for the tensile strength (which is almost half the value of that of the glass fibers) and the water absorption with the glass fibers having none at all compared with the flax fibers’ 7%. However, despite having good properties, flax fibers also have some defects. As a general rule in materials science, defects determine the mechanical properties of materials. It turns out to be equally true in the case of flax fibers. Flax fibers have cross-marks (deformed zones), presumably kink bands, called “nodes” or “dislocations”. During a tensile test, the break often occurs where the defect is situated. Defects in fibers are produced irreversibly either during plant growth or during the decortication process by which the fibers are isolated from the plant. As a result, defects can hardly be controlled and are one reason for the large spread (inconsistency) in the mechanical properties of fibers. Nodes, often in the form of an X, are easily observable in diascopic microscopy with polarized light (Baley, 2002).

3.1.3 Plastics

One of the major industries where flax fiber could be of major use is the composite industry, where flax fibers are mixed with plastics. Plastics are superior to many conventional materials, in both physical properties and in the variety of ways in which they can be processed. This fact became recognized particularly during the period of great economic growth after 1950, and has led, during the rapid development since then, to the present world production of over 100 million tonnes annually. Despite this large amount, sufficient quantities of raw materials are available to meet foreseeable future demand for plastics. The particularly useful chemical and physical properties of plastics make possible an extraordinarily large number and variety of applications. Molding during processing owes its simplicity to the basic characteristic of thermoplastic resins: they change reversibly from solid to the molten state within a relatively low temperature range, over which the plastic materials are highly viscous. This behavior pattern is related to their macromolecular structure. It is the reversibility of the change of state, in particular, that permits the molding operation to be shifted from the raw material producer to the processor (Hensen, 1997).

Thermoplastics offer a wide range of matrix materials for reinforcement by fibers, flakes, beads or particulate materials such as talc and mica. Their great advantage is that they are more easily molded in mass-production quantities (by injection molding) than are reinforced thermosets. One such kind of thermoplastic is polyethylene. Polyethylene (PE) comes in a range of densities, of which those relevant to reinforced plastics are low density (LDPE) and high density (HDPE). It is produced from ethylene, which is a direct product of naphtha (produced from cracking of crude oil). By far, the largest volumes of these materials go into film for packaging and many other applications. Polyethylene is rarely encountered as a matrix for reinforced plastics, although it forms a useful neutral carrier for specialty concentrates and master batches for pigments, conductive/antistatic compounds and other specialties. Recent work, however, has produced high performance PE fibers, which might have a useful role to play in the future, as reinforcing materials (Murphy, 1998).

3.1.4 Rotationally-molded plastics

Presently in Saskatoon, SK, one of the major products manufactured locally from plastics is the rotationally-molded agricultural water storage tank. Quality Molded Products, Inc. (Saskatoon, SK) is producing these tanks, as well as other hollow products for agricultural purposes, using polyethylene.

Rotational molding is used to manufacture hollow plastic articles. It has economical advantages over other more widespread processes, such as injection molding or blow molding, when products are large or the production runs are small. The majority of rotational molding products are made from polyethylene. It is quite different from other molding processes in that the heating and cooling rates are slower, and the shaping is done in the absence of pressure or shear (Oliveira and Cramez, 2001).

A number of researchers have studied rotational molding. Olinek and co-workers (2005) examined the nature of powder and its effect on the melt deposition of polymeric powder particles in rotationally molded parts. Experimental results confirmed that polymeric powders are cohesive enough to prevent size segregation when mixed at ambient temperature. Segregation was observed when smooth particle shapes, such as micropellets and olive stone, were used. During processing, the gradual heating of the polymer leads to the development of adhesive forces between the particles and the mold surface. These forces preferentially affect smaller particles and are the primary cause for the development of reverse segregation patterns. Under the conditions considered in their work, only a partial and gradual separation between different types of polymeric particles was obtained across the thickness of the rotomolded parts. It was shown that the degree of mixing and segregation, as well as the sharpness in the separation between different layers of materials are strongly affected by the heating rate and the rotation speed. The initial distribution of particles in the solid bed, which is primarily affected by the particle shape, size and density, also influences the final segregation patterns seen in the molded part, especially at higher rates. In their study on polyolefins, Oliveira and Cramez (2001) observed that, over a range of typical processing conditions, the morphology is affected by the processing temperature. Especially at the inner surface that is in contact with air, the sensitivity to temperature is higher, and the degradation is more likely to occur. In the case of polyethylene, the degradation is revealed in the morphology by the suppression of crystallization.

3.2 Flax Fiber Modification

Aside from biodegradability, the advantages of flax fibers include low density and cost, better damage tolerance in composites and high specific strength and stiffness (Murphy, 1998). Other advantages include renewability and utilization of otherwise waste materials. On the negative side, however, are degradation by moisture, poor surface adhesion to hydrophobic polymers, susceptibility to fungal and insect attack (Murphy, 1998), fiber quality inconsistency, sensitivity to temperature, separation from polymer during rotational molding and non-homogeneous mixture. All of these consequently contribute to the low performance of the composite. Various ways to improve performance have been studied. Numerous papers have dealt with the effect of retting, physical modifications and chemical pre-treatments on composite properties.

3.2.1 Retting

Van de Weyenberg and co-workers (2003) reported that during the consecutive decortication stages of flax fibers (retting, scutching and hackling), the fiber properties change tremendously due to mechanical modifications. It was concluded that the better the retting degree of the fibers, the better the properties of the composite.

3.2.2 Surface modification

The high level of moisture absorption by the fiber, its poor wettability, as well as the insufficient adhesion between untreated fibers and the polymer matrix, lead to debonding with age. To build composites with high mechanical properties, surface modification of the fibers is, therefore, necessary (Bledzki et al., 1996). Moreover, an important aspect with respect to optimal mechanical performance of fiber-reinforced composites in general, and durability in particular, is the optimization of the interfacial bond between fiber and polymer matrix. The quality of the fiber-matrix interface is significant for the application of natural fibers as reinforcement for plastics. Since the fibers and matrices are chemically different, strong adhesion at their interfaces is needed for an effective transfer of stress and bond distribution throughout an interface (George et al., 2001). The interface acts as a “binder” and transfers load between the matrix and the reinforcing fibers. Furthermore, because each fiber forms an individual interface with the matrix, the interfacial area is very large. The interface, therefore, plays a key role in controlling the mechanical properties of a composite (Jayaraman, 2003).

3.2.3 Physical modification

Ceres and Pott (2002) contended that when natural fibers are applied as reinforcement in polymer composites, moisture sensitivity, causing fiber swell and, ultimately, rotting through fungal attack, can be a very serious problem. A number of methods for dealing with this problem have been developed. These methods change the chemical and/or physical composition of the fiber, resulting in reduced moisture sensitivity. To this category belong acetylation and hydrothermal treatment. For acetylation, acetic anhydride reacts with reactive OH-groups of the lignocellulosic material, increasing hydrophobicity. In hydrothermal treatment, no chemicals are used, only water and energy.

Ceres and Pott (2002) focused on hydrothermal treatment, the Duralin^{TM} process in particular, which involves three steps: hydro-thermolysis, drying and curing. Bundles of flax straw are heated in water in a pressure vessel at a temperature of between 160-180°C for about 15 minutes (hydro-thermolysis). After drying, the flax straw is heated in air or dry steam for about 30 min at temperatures of up to 180°C (curing). The Duralin^{TM} process reduces moisture absorption and biological degradation. The fiber yield is higher than after dew-retting, and the shives can be used as a filler material in polymers or for making a water-proof particle board.

Duralin^{TM} fibers have equal or higher tensile strength and higher flexural modulus than fibers extracted from dew-retted flax. Compounds reinforced with these fibers have, apart from decreased moisture sensitivity, better mechanical performance. Both the amount and the release rate of decomposition products resulting from compounding with polypropylene are significantly lower for Duralin^{TM} fibers than for dew-retted or green fibers. Duralin^{TM} fibers are, on a weight basis, competitive with glass fibers.

3.2.4 Chemical modification

Chemical treatment of natural fiber reinforcements can enhance their adhesion to polymer matrices. This is due to alteration of the characteristics of the surface topography, the removal of non-crystalline constituents of the fibers such as hemicellulose (which is hydrophilic), lignin and pectin (Zafeiropoulos et al., 2002) and the removal of waxes and fatty acids present on the surfaces which can adversely affect interfacial bonding (Jayaraman, 2003).

Various fiber surface modifications, such as mercerization, latex coating, silane treatment, isocyanate treatment, acetylation and peroxide treatment, were investigated in the reduction of hydrophilicity and, thereby, altering the sorption characteristics (Sreekala and Thomas, 2003).

The use of coupling agents, such as silanes or stearic acid, increases the Young’s modulus and tensile strength. Simultaneously, the moisture absorption of the composites decreases by about 60%. With other surface modifications, similar results are obtained (Bledzki et al., 1996). Panigrahi and co-workers (2003) also used silane along with two other chemical treatments (benzoylation and peroxide treatment) for flax fiber and polyolefin-based (LLDPE, HDPE) composites. It was concluded that the mechanical properties of the composites were modified by chemical treatment of flax fiber, but recommended that further work is required to quantify the effects of the pretreatments.

Cantero and co-workers (2003) compounded polypropylene composites with two kinds of flax fibers (natural flax and flax pulp) (30%, w/w). The treatments applied were maleic anhydride (MA), maleic anhydride-polypropylene copolymer (MAPP) and vinyl trimethoxy silane (VTMO). The three treatments reduced the polar component of the surface energy of the fiber. Composites containing MAPP-treated fibers did have the best mechanical properties, whereas the MA and VTMO-treated fiber gave values similar to those of untreated ones.

Van de Weyenberg and co-workers (2003) also studied the influence of certain chemical treatments, performed on flax fibers, on composite (fiber volume fraction of 40%) properties. Treatments with alkali, dilute epoxy, acetone and silane were carried out. A treatment consisting of a combination of alkali and dilute epoxy gave the highest improvement in flexural properties.

In a study of the pre-treatment of flax fibers for use in rotationally-molded biocomposites using polyethylene as the matrix, Wang (2004) concluded that the use of a silane coupling agent resulted in composites with better mechanical and physical properties.

3.3 Extrusion Compounding

Despite the numerous studies on retting, physical modification and chemical modification, there are only a limited number of investigations on extrusion of natural fiber and polymer matrices and the extrusion parameters involved. Extrusion compounding addresses composite molding problems such as non-homogeneous mixture and separation of fiber from polymer during rotational molding, which consequently affect engineering properties.

3.3.1 Extrusion process

The main function of an extruder is to develop sufficient pressure in the material to force the material through the die. The pressure necessary for this depends on the geometry of the die, the flow properties of the material and the flow rate. Basically, an extruder is a machine capable of developing pressure. In other words, an extruder is a pump. A plastics extruder is a pump for plastic materials. Extruders are the most common machines in the plastics processing industry. Extruders are used not only in extrusion operations; most molding operations also use an extruder, injection molding and blow molding, for example. Essentially, every plastic part manufactured has gone though an extruder at one point or another; in many cases, more than once (Rauwendaal, 1998).

3.3.2 Extruders

In the plastics industry, there are three main extruder types: the screw extruder, which is the most common, the ram extruder, and the drum or disk extruder, which is the least common. In a screw extruder, a screw rotates in a cylinder; the rotation of the screw creates a pumping action.

A screw extruder can have one screw or more. An extruder with one screw is called a single screw extruder; it is the most common machine in the plastics processing industry. An extruder with more than one screw is called a multi-screw extruder, the most common of which is the twin-screw extruder (which has two screws). There are several types of twin-screw extruders. In most twin-screw extruders, the screws are located side by side. If both screws rotate in the same direction, the extruder is called a co-rotating twin-screw extruder. If the screws rotate in opposite directions, it is called a counter-rotating twin-screw extruder. Twin-screw extruders can run at high or low speed, depending on the application. High-speed extruders run at approximately 200-500 rpm or higher; they are primarily used in compounding. Low speed extruders run at approximately 10-40 rpm and are used mostly in profile extrusion applications. Most twin-screw extruders for profile extrusion are counter-rotating extruders. This is because counter-rotating extruders tend to have better conveying characteristics than co-rotating extruders. Most twin-screw extruders have parallel screws, but some extruders have conical screws where the screws are not parallel. Another distinguishing feature of twin extruders is the extent that the screws intermesh. The screws can be fully intermeshing, partially intermeshing or non-intermeshing. Most twin-screw extruders are intermeshing. The advantage of non-intermeshing extruders is that they can have a very long length without problems with respect to metal-to-metal contact between the screws. The length to diameter ratio (L/D) can be 100:1 or higher. The L/D of intermeshing twin-screw extruders is generally limited to values less than 50:1. A disadvantage of current non-intermeshing twin screws is that they have limited dispersive mixing capability. Mixing takes place both in the melting zone as well as in the melt conveying zone of the extruder. The solid plastic typically moves in plug flow, which means that there is no relative motion between the solid plastic particles. As a result, there is little or no mixing in the solids conveying zone. This means that complete mixing does not start until all the plastic has melted (Rauwendaal, 1998).

3.4 Extrusion Parameters

Extrusion engineers identify five factors that limit product throughput and quality: power/screw speed, temperature, feed, vacuum, and downstream processing (Hanawalt, 2002).

3.4.1 Screw speed

Screw speed must be maintained at a high rate in order to minimize residence time and maximize throughput. However, when a product is heat sensitive (as flax fibers are), extruder screw speed is limited by the maximum shear rate that the product can experience without degradation (Hanawalt, 2002). Another reason for limiting screw speed is to avoid air entrapment and to prevent excessive melt temperatures. If the polymer is extruded at rates that are too high, air entrapment can occur, resulting in tiny bubbles in the extrudate (Cisneros, 2002).

3.4.2 Temperature

Temperature limitations in extrusion result from either the inability to add enough heat to get a consistent melt (130.34°C for LLDPE with silane treated fibers and 133.38°C for HDPE with silane treated fibers) (Wang, 2004) or the inability to remove enough heat from a melt to prevent product degradation (200-220°C for flax fibers) (Composite Materials Group, 2001; Powell et al., 2002; Wielage, et al., 1999). Flax fibers are heat sensitive. If the barrel temperatures and/or the screw speed are very high, it is possible to make a product consisting of plastic and degraded fiber. This scenario results particularly when the melting point of a polymer is higher than the degradation temperature of the fiber. Thus, the melting point of the matrix should be lower than the degradation temperature of the fibers to prevent fiber degradation (Hanawalt, 2002).

3.4.3 Studies on extrusion parameters of food (and other fibers)

Studies on the extrusion of flax fibers are scarce. Despite the scarcity of literature on flax fiber extrusion, there are studies on the extrusion of food and other fibers that focus on the effect of extrusion parameters. For instance, the effect of extrusion process variables, such as the length to diameter ratio (L/D) of the extruder, feed ratio (ratio of the solids of fish and wheat flour), temperature and screw speed on the product texture of an extruded blend of partially-dried minced fish and wheat flour was studied by Bhattacharya and co-workers (1993). It was reported that among the process variables, an increase in L/D or feed ratio increased the texture parameters; the effects of temperature of extrusion and screw speed on the texture parameters were complex in nature. In another study, Gogoi and Yam (1994) investigated the relationships between residence time and process variables in a co-rotating, twin-screw extruder using yellow corn meal. The most significant process variables affecting mean residence time were screw speed followed by throughput. Moisture content had only a borderline effect, while die pressure and temperature had no significant effect.

Moreover, a number of studies discussed the effects of extrusion parameters. Chang and co-workers (1998) examined the effect of extrusion variables such as barrel temperature, feed rate, screw speed and slit die rheometer configuration on the rheological properties of yellow corn meal. Effects of processing variables, such as screw speed, feed moisture and barrel temperature at zone-six on system variables were discussed by Wang and co-workers (2001) on their study of twin-screw extrusion texturization of compound soybean proteins. Ha and Padua (2001) investigated the effect of three extrusion parameters (barrel temperature, screw speed and the amount of solvent added during extrusion) on the mechanical properties of zein-fatty acid sheets. Hull-less barley flours from CDC-Candle (waxy) and Phoenix (regular) were extrusion cooked under various combinations of temperature (90, 100, 120, 140 and 160°C), moisture content (20%, 25%, 30%, 35% and 40%) and screw speed (60, 80 and 100 rpm) by Faraj and co-workers (2004). The effect of processing on the formation of resistant starch (RS3) in extruded flour was determined. In the study of Guha and co-workers (1997), rice flour with 14% moisture content was extruded at different barrel temperatures (80-120°C) and screw speeds (200-400 rpm) through a twin-screw extruder without a die. Unmodified corn starch from dent corn was used in the study of Cunningham (1996) to determine the effect of twin-screw extrusion conditions on the intrinsic viscosity of this polysaccharide in water. Bhattacharya (1997) extruded a rice and green gram blend using a co-rotating twin-screw extruder with a barrel diameter of 31 mm. The effects of barrel temperature (100-175°C) and screw speed (100-400 rpm) on extrusion system parameters and extrudate characteristics were studied. In the paper of Guan and co-workers (2004), starch acetate was extruded with wood fiber, oat fiber and cellulose in a C. W. Brabender twin-screw laboratory extruder at 160°C barrel temperature and 225 rpm screw speed. Lue and co-workers (1994) established a statistical model for extrusion cooking of corn meal and sugar beet fiber mixtures in a twin-screw extruder. The operational variables included screw speed, addition level of sugar beet fiber and fiber particle size.

Based on the preceding studies, there are some differences between extrusion studies of food and that of composites. One obvious processing condition considered in food extrusion and not in the extrusion of composites is the moisture content. Food materials fed to an extruder always have moisture content. On the other hand, plastic and other composite materials fed into an extruder almost always have zero moisture content. Another difference is the aim of extrusion. One of the aims of extrusion for expanded food products is to ensure void fraction in the final product so as to obtain the desired product textural properties, while the aim of composite extrusion is to ensure that there is consistent melting of the matrix, the reinforcing fibers are uniformly dispersed within the melt and pore spaces are minimized in the final product, resulting in extrudates and composites with better properties. Despite these differences, both extrusion processes deal with temperature and screw speed as process variables. The succeeding sections describe the effects of these variables on the properties of extruded food products which can be of use to better understand the properties of extruded composites.

3.5 Effect of Extrusion Parameters on Extrudate Characteristics

The effect of extrusion parameters on extrudate characteristics have been studied by a number of researchers. The following are studies on the effect on polymer and extrudate properties, effect on density and effect on melt flow index.

3.5.1 Effect on polymer properties

In a study by Carneiro and co-workers (2000), the flow of polypropylene (PP) in a self-wiping, co-rotating, twin-screw extruder was characterized by measuring the pressure, temperature and residence time along the screw profile. The influence of operating conditions (feed rate, screw speed, barrel temperature) and screw profile were studied. Flow modeling was performed using the Ludovic© software (Ecole des Mines de Paris – CEMEF, Paris, France). Measured and calculated pressure, temperature, residence time and energy consumption were compared. It was observed that melt temperature increased with increasing rotation speed due to viscous dissipation, with a decreasing feed rate due to higher specific energy, and with an increasing barrel temperature due to more heat conduction. Results also showed that screw speed seemed to have a stronger influence on the process than did feed rate because the former only influences viscous dissipation, while the latter affects both viscous dissipation and heat transfer, which have conflicting effects.

Sombatsompop and Panapoy (2000) investigated the effect of screw speed on two-dimensional temperature profiles of flowing polypropylene melt in the barrel of a counter-rotating twin screw extruder using a designed experimental apparatus and a thermocouple temperature sensing device, the experimental apparatus being connected to a high speed data logger and a computer. The flow patterns of the polymer melt in the barrel of the extruder were also revealed. Changes in melt temperature profiles with extrusion time were discussed in terms of the flow patterns of the polymer melt during the flow, the increase in melt temperature being closely associated with total flow length of the melt and shear heating and heat conduction effects.

Steward and Bradley (1991) studied the extrusion characteristics of various screws used to process PP. The influence of various extrusion variables such as screw type, extruder diameter, length to diameter ratio, temperature profile and screw speed on the degradation of the material as seen through the melt flow rate (MFR) increase of PP was examined. It was shown that some of the findings will allow improved extrusion parameters to the producer desiring minimized property reductions of the PP being used. The performance trends measured from these two PP materials should be useful over a wider range of MFR levels.

3.5.2 Effect on extrudate properties

In the study of Guha and co-workers (1997) on the extrusion of rice flour at variable temperatures and screw speeds, the system parameters as well as the extrudate attributes were mainly dependent on temperature, whereas the screw speed imparted a lesser effect. Bhattacharya (1997) investigated the extrusion of rice and green gram blend using a co-rotating twin-screw extruder and studied the effects of barrel temperature and screw speed on extrusion system parameters and extrudate characteristics. Results showed that temperature and screw speed imparted curvilinear effects on extrusion and extrudate characteristics (torque, specific mechanical energy [SME], expansion ratio, density and maximum stress). It was concluded that high barrel temperature combined with a low screw speed was suitable for obtaining an expanded product. Lue co-workers (1994) established a statistical model for extrusion cooking of corn meal and sugar beet fiber mixtures in a twin-extruder. Specific mechanical energy (SME) input, product temperature (T), pressure before die (DP) and gelatinized starch content (GS) were measured and used to characterize the physical and chemical properties of extrudates. The results showed that predictor variables could explain 79-96% of the variations in product length, diameter, specific volume, breaking strength and water absorption index. Color attributes of the product also depended on fiber particle size.

3.5.3 Effect on density

In a study on the extrusion of rice flour by Guha and co-workers (1997) conducted at variable temperatures and screw speeds, optimum extrusion conditions for obtaining minimum torque, specific mechanical energy (SME) and bulk density were determined. A positive, linear ($r = 0.78$, $P<0.01$) relationship existed between SME and bulk density, indicating that a low density extrudate could be obtained with low SME. In the Bhattacharya (1997) study on the extrusion of a rice and green gram blend using a co-rotating twin-screw extruder, the response functions (torque, SME, expansion ratio, density and maximum stress) were related (r=0.870, P<0.01) to the process variables (screw speed and temperature) by second-order polynomials.

3.5.4 Effect on melt flow index

The melt flow index (MFI) or melt flow rate (MFR) test measures the rate of extrusion of a thermoplastic material through an orifice of specific length and diameter under prescribed conditions of temperature and load. This test is primarily used as a means of measuring the uniformity of the flow rate of the material. The reported melt flow index values help to distinguish between the different grades of a polymer or a composite (Shah, 1998).

Liang and co-workers (1999) studied the effect of pressure and temperature on the MFR of low-density polyethylene (LDPE) and a glass bead-filled LDPE composite (LDPE/GB) using a capillary plastometer. It was reported that the MFRs increased as an exponential function with temperature and increased as a quadratic function with pressure.

In the investigation of Sombatsompop and Panapoy (2000) on the effect of screw speed on two-dimensional temperature profiles of a flowing polypropylene melt, the flow patterns of the polymer melt in the barrel of the extruder were revealed. Changes in melt temperature profiles with extruding time were discussed in terms of flow patterns of the polymer melt during flow, the increase in melt temperature being closely associated with the total flow length of the melt, and with shear heating and heat conduction effects.

Unmodified cornstarch from dent corn was used in a study to determine the effect of twin-screw extrusion conditions on the intrinsic viscosity of this polysaccharide in water (Cunningham, 1996). The study focused on the intrinsic viscosity of cornstarch as a function of the key variables. Primary variables examined were temperature (75, 100 and 125°C), starch concentration or consistency (35, 50 and 65%), and screw speed (100, 200 and 300 rpm) during extrusion processing. The most favorable conditions examined were the extrusion of cornstarch at 35% consistency, a temperature of 100°C, and a screw speed of 200 rpm. Two-thirds of the original intrinsic viscosity of the unmodified starch was retained upon extrusion at 35% consistency at all temperatures and screw speeds of 200 and 300 rpm. Similar values were observed at 50% consistency for 75°C at 100 and 200 rpm and for 100°C at all three screw speeds.

Lo and co-workers (1998) studied the effect of operating conditions on melt rheological characteristics during twin-screw food extrusion. Data on operating variables (feed rate, feed moisture content, screw speed and temperature) and process variables (product/barrel/die temperatures, zones 4-5/die pressures and total power consumption) of a co-rotating, twin-screw food extruder and extrudate moisture content were collected. The steady-state data were analyzed and the mean residence time and average apparent viscosity of melted cornmeal were determined. The addition of two extra reverse paddles to the screw caused a decrease in the fluid consistency coefficient and an increase in the shear-thinning behavior of the melt.

To study the effects of processing conditions on the viscoelastic and mechanical properties of biodegradable composites, Ali and co-workers (2003) prepared several composites based on sisal fibers and biodegradable polymers. The effects of processing conditions such as screw speed, temperature and time of mixing were investigated. The mechanical and viscoelastic properties of these composites were affected by processing conditions. This was principally due to the modification of the initial aspect ratio of the natural fibers as a result of the shear stresses that developed in the mixer during compounding.

3.6 Effect of Extrusion Parameters on Composite Properties

There have been a few studies on the effects of temperature and screw speed on composite properties. In one study (Matuana and Li, 2004), a regression model was constructed to optimize the relationships among the void fraction of foamed HDPE/wood-flour composites, the processing conditions (extruder die temperature and screw speed) and the formulation compositions by applying a four-factor, central composite design (CCD) statistical approach. The analysis of variance (ANOVA) of the model showed that the void fraction of HDPE/wood-flour composites was a strong function of the extruder die temperature, screw speed, and the moisture content of the wood flour. The response surface optimization generated using the regression model suggested that HDPE/wood-flour composite foams with the highest void fraction could be achieved at the highest levels of extruder screw speed (120 rpm) and moisture content of wood flour (12%), together with the lowest levels of extruder die temperature (170°C) and no chemical foaming agent.

In another study, Matuana and Li (2001) performed a factorial design to determine the statistical effects of material composition and extrusion processing variables on the foamability of polypropylene/wood-flour composites. The experimental results indicated that the void fraction of extrusion-foamed composites is a strong function of the extruder die temperature. This can be explained by the cell growth mechanism that requires optimum viscoelastic properties of the matrix during foaming. Since the cell growth occurs due to the diffusion of gas from the polymer matrix, the stiffness and melt viscosity of the polymer has a strong influence on the rate of gas diffusion between cells. At an elevated temperature, the melt strength of the polymer and its extensional viscosity decreased significantly. When the melt viscosity was low, the diffusion of gas through the matrix was favored and the cells could grow more easily. Thus, the higher the temperature, the greater the void fraction.

3.6.1 Degree of degradation

Screw speed must be maintained at a high rate in order to minimize residence time and maximize throughput. However, when a product is heat sensitive (as flax fibers are), the extruder screw speed is limited by the maximum shear rate that the product can experience without degradation. Similarly, temperature limitations in extrusion result from either the inability to add enough heat to get a consistent melt or the inability to remove enough heat from a melt to prevent product degradation (Hanawalt, 2002).

Chang and co-workers (1998) studied the effect of extrusion variables on the rheological properties of yellow corn meal and discovered that the most important factor in starch degradation was the screw speed. Increasing the screw speed completely modified the organized structure of starch (crystalline region).

Fiber degradation has been investigated by a number of researchers. Jayaraman (2003) stated that the common methods for manufacturing fiber-reinforced thermoplastic composites, injection molding and extrusion, tended to degrade the fibers during processing, hence the development of a simple manufacturing technique for natural fiber-reinforced thermoplastic composites that minimizes fiber degradation. This was further confirmed by Fung and co-workers (2003) in an investigation on the processing of sisal fiber-reinforced polypropylene composites. It was found that an elevated injection molding temperature can cause severe thermal degradation of the reinforcing sisal fibers giving rise to the darkened color and odor emission of the molded sisal fiber-polypropylene composites. It was also pointed out that the stability of sisal fibers at a high melt processing temperature is of major concern because if serious degradation of the sisal fibers took place during the melt processing of the composites, the mechanical reinforcement effects of the sisal fibers would be lost.

Studies on flax fiber showed similar results. In an overview of several properties of biopolymers, Van de Velde and Kiekens (2002) reported that in the specific case of a flax-reinforced plastic, the application temperature of the product should remain relatively low because of the possible degradation of flax when exposed to elevated temperatures for a prolonged time. This led to the conclusion that polyglycolic acid (PGA) is not suited for use in combination with flax because the former would require process temperatures possibly higher than 250°C, which would lead to thermal degradation of the flax. In an overview of several properties of thermoplastic polymers, Van de Velde and Kiekens (2001) concluded that temperature-related properties seem to be the limiting criteria for the choice of a suitable polymer because of the heat sensitive nature of flax. In a study on flax-fiber-reinforced polypropylene in the melt mixing process, Jakobsson (2000) found that a mixing temperature of 195°C could optimize the strength of the compression molded composite and further explained that fiber degradation affected mechanical properties and was one of the functions of the processing variables.

In view of the gravity of the problem of fiber degradation, a number of researchers have tried to determine the degradation temperature of flax fibers. Van de Weyenberg (Composite Materials Group, 2001) conducted degradation tests on flax fibers and the respective composites. It was determined that the fiber starts to rapidly degrade at a temperature above 200°C. Wielage and co-workers (1999) studied the thermal stability of flax and hemp fibers using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

In that study, there was a slight decrease in the mass (onset of degradation or decomposition) of natural fibers between 200 and 220°C. Above the latter temperature, irreversible degradation was observed. In a study of the engineering properties of flax fibers, Powell and co-workers (2002) concluded that pure flax fiber generally followed a decomposition curve beginning at approximately 200-210°C and ending at 400°C.

3.6.2 Dispersion of fibers and porosity

Extrusion compounding is a process of melting a polymer, thoroughly mixing fibers (e.g. flax fibers) with the molten plastic, and conveying the mixture through a die to produce extrudates. This process ensures that the fibers are uniformly dispersed within the melt and that the porosity is minimized to achieve better properties in the extrudates and the composites.

Torres and Diaz (2004) described a methodology for applying conventional morphological characterization techniques to some of the manufacturing processes of natural-fiber-reinforced thermoplastics (NFRTP). The composites studied consisted of a matrix of polypropylene or polyethylene, and of discrete jute, sisal and other natural fibers as the reinforcement. Different microscopic techniques were used to characterize the processing stages and the structure-property relationships during the manufacture of NFRTPs using single screw extrusion, compression and rotational molding. Important issues in the processing of discrete fiber composites, such as fiber length distribution, fiber orientation and overall fiber dispersion in the matrix, were studied.

Transcrystallinity in the case of PP/sisal and PP/jute composites was reported. In all cases, the characterization procedures described were related to the manufacturing processes studied in each particular case (Torres and Diaz, 2004). In fact, a systematic approach to morphological characterization was presented in the study. It is believed that all or some of the procedures mentioned could be implemented as quality control techniques in manufacturing NFRTPs.

In the study by Mwaikambo and Ansell (2003), hemp fiber bundles were alkalized at concentrations between 0.8 and 8.0% NaOH and the change in surface morphology was elucidated using scanning electron microscopy. The treated fibers with the highest strength were used as reinforcement for a cashew nut shell liquid matrix. Non-woven fiber mats and unidirectional fiber composites were manufactured by hand lay-up compression molding. Tensile properties, porosity and fracture surface topography of the composites were analyzed. The unidirectional fiber composites exhibited the best mechanical properties and composites with the lowest porosity offered the highest mechanical properties.

In cable covering, void formation is due to the fact that since the outer part of the polymer solidifies first, it becomes impossible for the inner region to shrink freely upon its solidification. The adhesion of the plastic to the metal decreases, and macroscopic voids can form within the polymer, reducing the dielectric strength of the cable (Stevens and Covas, 1995).

3.6.3 Tensile strength and water absorption

In an investigation of the effect of three extrusion parameters (barrel temperature, screw speed and the amount of solvent added during extrusion) on mechanical properties of zein-fatty acid sheets, Ha and Padua (2001) observed that extrusion temperatures included in the experiment affected the mechanical properties and water resistance of zein sheets. Higher temperatures increased tensile strength but decreased elongation at break of the resulting sheets.

In the study by Pan and Sun (2003), the effects of moisture content (MC) and extrusion parameters on the tensile strength of starch and polylactic acid (PLA) blends were investigated. Temperatures at the first heating zone (T1) and the second-third heating zones (T2-T3), screw speed and MC injected into the first heating zone during extrusion were the variables. It was reported that MC and screw speed had a significant effect on the tensile strength of starch/PLA blends. Furthermore, it was reported that T1 was important in controlling the tensile strength of the blends. Lastly, it was found that blends with higher tensile strength had lower water absorption, less than 15% after a ten-day soaking test.

Huang and co-workers (1999) optimized processing conditions, ingredient ratio and moisture content for making soy protein/starch based plastics using a twin-screw extruder and an injection molding machine. Processing effects were investigated by measuring the tensile properties and water resistance of specimens. Results showed that the water absorption of the specimens was reduced by adding acid to adjust the pH to the isoelectric point of soy proteins (pH 4.5).

3.7 Summary

There are a number of works reported in literature on the different methods of enhancing the mechanical properties of flax fibers and flax-fiber-reinforced composites, including retting, physical modification and chemical modification but the need for extrusion and the study on the effects of its parameters cannot be ignored. Due to the dearth of work on the effect of extrusion parameters on flax-fiber-reinforced composites, it is hoped that results from studies on the effect of extrusion parameters (temperature, screw speed, feed rate) on the properties of extruded food products (tensile strength, water resistance, degradation, viscosity, dispersion and porosity) can be adapted to the study of the effects of extrusion processing conditions (temperature and screw speed) on the mechanical and physical properties (tensile strength, water absorption, melt flow index, degradation [color], dispersion, porosity and density) of flax fiber-reinforced polyethylene composites. In making these composites, the rotational molding process is used. Literature studies on the effect of temperature on the morphology and melt deposition of pure polyolefins would somehow aid in the understanding of the rotational molding of flax-fiber-reinforced polyethylene composites.

4. MATERIALS AND METHODS

A series of experiments were carried out to attain the objectives outlined in Chapter 2. These experiments included the chemical treatment of flax fibers to modify the surface, consequently making them more compatible with the matrix, extrusion compounding (using different parameters) to homogeneously disperse fibers in the polymer matrix, rotational molding to produce test specimens, and testing and characterization to compare the effects of fiber content and the different extrusion parameters on the engineering properties of the composite. This chapter outlines the materials, equipment and methods used in these experiments.

4.1 Materials

For use as a reinforcing material in the production of polyethylene composites, oilseed flax fibers (provided by Biolin Research, Saskatoon, SK, Canada) were subjected to mercerization using sodium hydroxide and fiber surface treatment with the use of vinyltrimethoxysilane (Sigma-Aldrich, Inc., St. Louis, MO, USA). Treated flax fibers were ground and mixed with powdered linear low-density polyethylene (LLDPE 8460.29) and high density polyethylene (HDPE 8760.29) (Exxon Mobil, Toronto, ON, Canada) as polymer matrices. Table 4.1 shows some properties of these polymer matrices. Table 3.1 shows some properties of the flax fiber compared with other fibers and glass.

Table 4.1 Properties of ExxonMobil LLDPE and HDPE Rotational Molding Resins (Matweb.com).

Property	LLDPE LL 8460.29	HDPE HD 8760.29
Density	0.938 g/cm^3	0.948g/cm^3
Melt Flow	3.3 g/10 min	5 g/10 min
Tensile Strength at Yield	17.8 MPa	23.4 MPa
Elongation at Yield	17.7%	15.3%
Flexural Modulus	0.772 GPa	1.06 GPa
Impact Test	258 J (at -40°C, 6.35 mm; ARM)	176 J (at -40°C, ¼” thickness, ARM)
Melting Point	127°C	131°C
Crystallization Temperature	112.7°C	115.3°C

4.2 Fiber Surface Treatment and Preparation

In the study of the pre-treatment of flax fibers for use in rotationally-molded biocomposites using polyethylene as matrix, Wang (2004) concluded that the use of silane coupling agent resulted to better mechanical and physical properties of the composites. Since this study involved using polyethylene as a matrix and the rotational molding process to produce composites, the chemical treatment used was silane. Following are the procedures for such treatment.

The flax fibers were washed with detergent and warm tap water, and then soaked in hot water (approximately 50°C) for 30 minutes. The fibers were then soaked in a 5% sodium hydroxide (NaOH) solution for 30 min to activate the hydroxyl groups so that they would effectively react with silane in the succeeding treatment. The fibers were then soaked for 30 min in a 60:40

ethanol/water mixture with vinyltrimethoxysilane. The pH of the solution was maintained acidic (pH 3-4) (Wang, 2004). Finally, the fibers were washed with deionized water and dried using a low-temperature-heat-pump dryer (University of Saskatchewan, Saskatoon, SK, Canada) for at least 24 h at 50°C (a low temperature was maintained to prevent fiber degradation with time). The dryer utilized was a partitioned cabinet with nine trays (for the materials being dried) on one side and a stack of two small household type dehumidifier on the other side (these units have condenser and evaporator coils, which provided the heating and cooling/dehumidification of air in the dryer). Air was re-circulated through the material from bottom to the top. The walls of the chamber were insulated with 51 mm thick fiberglass insulation. The doors of the cabinet were sealed to avoid air leaks using rubber strips (Adapa, 2001). Drying processes at the initial stage of this study were conducted at 104°C and 80°C for 24 h, as suggested by some researchers, but these resulted in the onset of fiber degradation as evidenced by browning of the fibers. Thus, the final temperature used later was 50°C. The dried fibers were then ground to pass a 1.59 mm screen using Retsch GmbH grinder (type SM1) (5657 Haan, West Germany).

While there are other standards for determining the particle size of powdered particles, the ground fibers and the polymers were subjected to particle size distribution according to ASAE S319.3 (ASAE, 1997) (calculation equations are included in this reference) using a Ro-Tap testing sieve shaker (Tyler Industrial Products, Mentor, Ohio). Sieve numbers and nominal openings (in parenthesis) used for the polymers were US sieve nos. 30 (0.595 mm), 40

(0.420 mm), 50 (0.297 mm), 70 (0.210 mm), 100 (0.149 mm) and 140 (0.105 mm), while those for the ground fibers were US sieve nos. 16 (1.190 mm), 20 (0.841 mm), 30 (0.595 mm), 40 (0.420 mm), 50 (0.297 mm) and 70 (0.210 mm). Table 4.2 summarizes the data analysis.

Table 4.2 Particle size distribution of ground flax fibers, LLDPE and HDPE.

Material	d_{gw}*	s_{gw}**
Ground Flax Fiber	0.46 mm	0.31 mm
LLDPE 8460.29	0.22 mm	0.09 mm
HDPE 8760.29	0.21 mm	0.09 mm

* 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

Due to the size difference (as well as the difference in density) between polymer and flax fibers, ordinary mixing resulted in non-homogeneous mixtures. Thus, extrusion was used to ensure a homogeneous mixture. Sufficient ground flax fiber was mixed with polymer at several fiber loadings by mass (0%, 12.5% and 25%) to generate a 6 kg sample for each extrusion treatment.

4.3 Experimental Process Variables

Most of the studies mentioned in the literature review focused on process variables such as temperature and screw speed. Therefore, the experimental process variables used in this study were extrusion parameters such as screw speed and barrel zone temperatures and fiber content. The response variables used are discussed in the materials testing and characterization section (section 4.7).

4.3.1 Fiber content

The presence of flax fiber would make the composite better in terms of mechanical properties, cost, renewability and biodegradability. Fiber loadings used were 0% (F1), 12.5% (F2) and 25% (F3) fiber content by mass in the composites.

4.3.2 Screw speed

Screw speed values used were 110 (S1) and 150 (S2) rpm.

4.3.3 Temperature

Temperatures for each of the five barrel zones (zones 1 to 5), which can be controlled and measured by the main control system, were set at 75-110-120-130-140°C (T1) or 75-120-130-140-150°C (T2). These temperatures where chosen with the melting points of the polymers and the degradation temperature of the flax fibers in mind. The melting points of LLDPE and HDPE with silane-treated fibers are at 130.34°C and 133.38°C, respectively (Wang, 2004), while degradation of flax fibers starts between 200 and 220°C (Composite Materials Group, 2001; Powell et al., 2002; Wielage, et al., 1999).

Higher temperatures (75-130-140-150-160°C) were used during the initial stage of experimentation, but such temperatures resulted in extrudates that did not have enough time to solidify when cooled and, therefore, were not used in later experiments.

Table 4.3 summarizes the experimental design based on the preceding process variables.

Table 4.3 Experimental design for extrusion and rotational molding trials.

Treatment*	Polymer Type	Fiber Content (%)	Temperature regime** (°C)	Screw Speed (rpm)
LF1T1S1***	LLDPE	0	75-110-120-130-140	110
LF1T1S2	LLDPE	0	75-110-120-130-140	150
LF1T2S1	LLDPE	0	75-120-130-140-150	110
LF1T2S2	LLDPE	0	75-120-130-140-150	150
LF2T1S1	LLDPE	12.5	75-110-120-130-140	110
LF2T1S2	LLDPE	12.5	75-110-120-130-140	150
LF2T2S1	LLDPE	12.5	75-120-130-140-150	110
LF2T2S2	LLDPE	12.5	75-120-130-140-150	150
LF3T1S1	LLDPE	25	75-110-120-130-140	110
LF3T1S2	LLDPE	25	75-110-120-130-140	150
LF3T2S1	LLDPE	25	75-120-130-140-150	110
LF3T2S2	LLDPE	25	75-120-130-140-150	150
HF1T1S1***	HDPE	0	75-110-120-130-140	110
HF1T1S2	HDPE	0	75-110-120-130-140	150
HF1T2S1	HDPE	0	75-120-130-140-150	110
HF1T2S2	HDPE	0	75-120-130-140-150	150
HF2T1S1	HDPE	12.5	75-110-120-130-140	110
HF2T1S2	HDPE	12.5	75-110-120-130-140	150
HF2T2S1	HDPE	12.5	75-120-130-140-150	110
HF2T2S2	HDPE	12.5	75-120-130-140-150	150
HF3T1S1	HDPE	25	75-110-120-130-140	110
HF3T1S2	HDPE	25	75-110-120-130-140	150
HF3T2S1	HDPE	25	75-120-130-140-150	110
HF3T2S2	HDPE	25	75-120-130-140-150	150

*does not correspond to order of processing
**zone1-zone2-zone3-zone4-zone5 temperatures
***L stands for LLDPE while H stands for HDPE

4.4 Extrusion Compounding

A major task of extrusion is polymer compounding, such as the melt blending of thermoplastics, and the incorporation of fibrous additives to modify engineering properties. Polymer compounding is performed in order to create a more uniform dispersion of the fiber within the matrix (Panigrahi et al., 2003). This is to address such composite problems (unfortunately not solved by retting, physical modification or chemical treatments) as non-homogeneous mixture and separation of fiber from polymer during rotational molding (Figure 4.1), which consequently affect engineering properties.

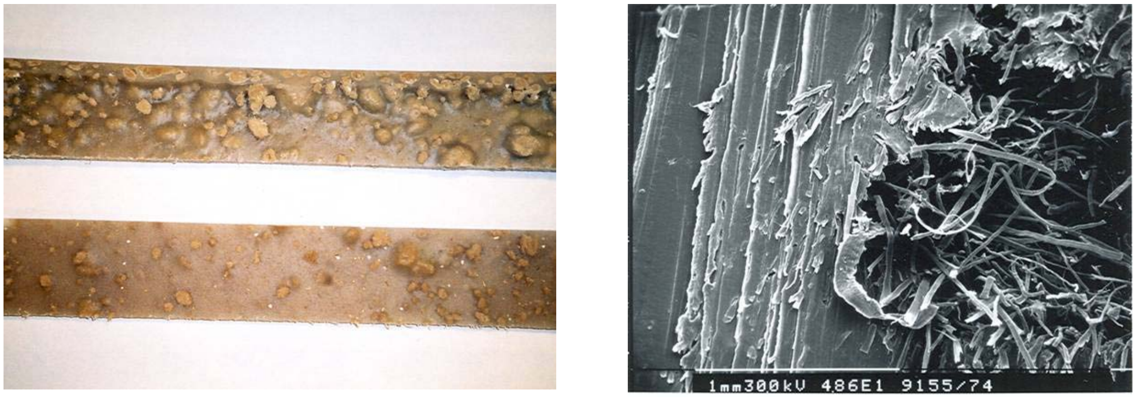


Figure 4.1 Actual appearance (left) and scanning electron microscope (SEM) micrograph (right) of the non-homogeneous mixture and the separation of fiber from polymer during rotational molding.

4.4.1 Extrusion equipment

In this study, the twin screw extruder was used because, compared to the single screw extruder, it had a shorter melting length, thus giving more time for the mixing of melted polymer and the dispersed flax fibers.

Extrusion was done with a co-rotating twin-screw extruder (Werner and Fleiderer, Stuttgart, Germany) at the Center for Agri-Industrial Technology (CAIT) in Edmonton, AB, Canada (Figure 4.2). The twin screw extruder was of type ZSK – 57 – M50/2. The length to diameter ratio (L/D) was 38:1. Screws were 38 mm in diameter and 1440 mm in length and were intermeshing. The extruder was electrically heated, water cooled and driven via variable speed drive 60 hp/24 kW (optimum power output of the shaft drive motor was 60 hp, and the same motor required 24 kW of energy). The screw speed was variable (36-350 rpm). The volumetric feeder system was gravity fed with the help of an auger type system to move and meter the material. It oscillated front to back. The augering or metering system was a screw style shaft with a larger outer coil moving at the same speed to help break up the material for consistent metering. The material was then conveyed to a belt conveyor to the extruder opening.

Figure 4.2 Twin-screw extruder at CAIT, Edmonton, Alberta, Canada.

The extruder was equipped with a temperature controller and had a digital display of temperature during extrusion. Of the three zones (solid conveying zone; melting, pumping and mixing zone; and pumping and mixing zone) (Figure 4.3), two zones (melting, pumping and mixing zone and pumping and mixing zone), where the barrel surface was heated, along with the die, were collectively subdivided into five separate heating zones (Figure 4.4). The die was a six-hole die with a diameter of 3 mm for each hole (Figure 4.5).

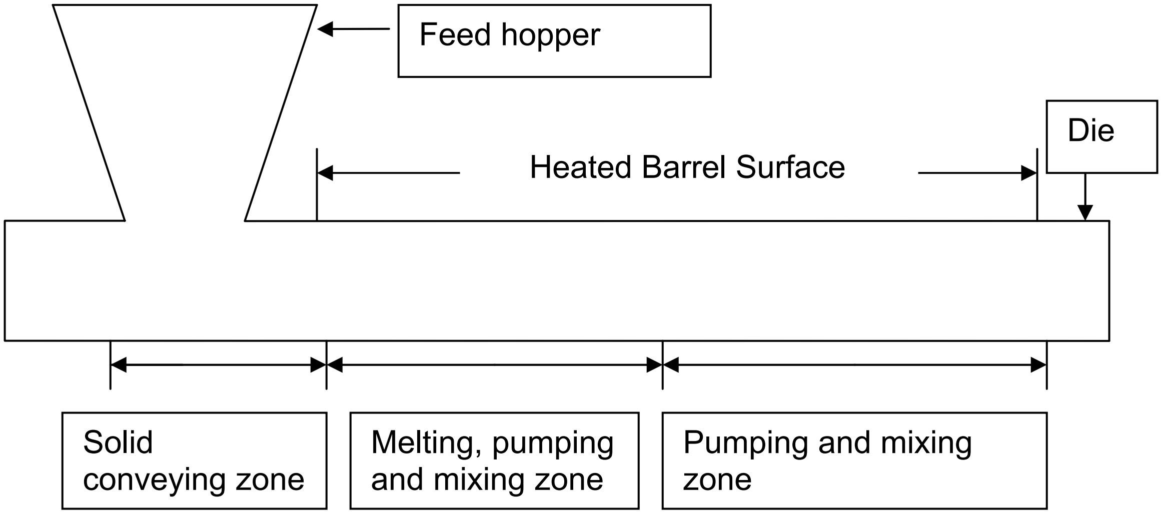


Figure 4.3 Schematic diagram of the extruder with the three zones.

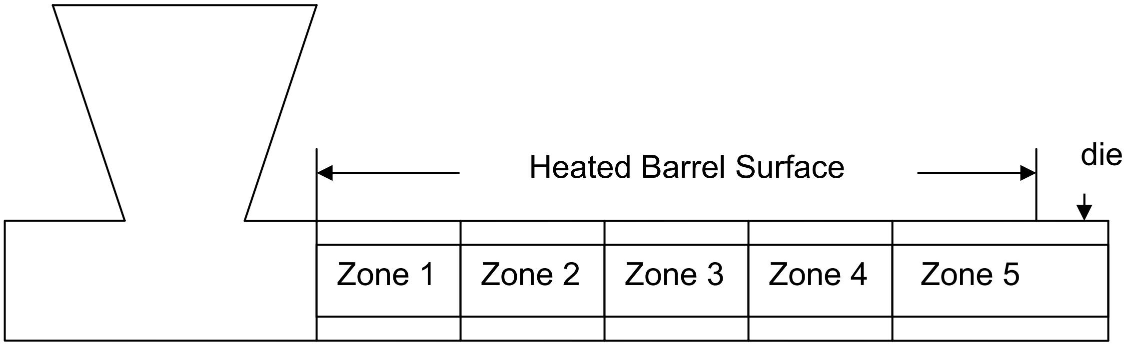


Figure 4.4 Schematic diagram of the extruder with the five separate heating zones.

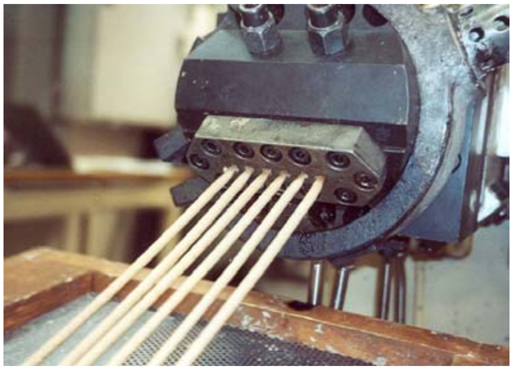


Figure 4.5 Six-hole die with extrudates coming out.

4.4.2 Extrusion methodology

Extrusion was done in such a way that there was time for purging materials that were being extruded. Thus, samples with fiber in them were alternately fed between samples that were pure plastic. This also helped in identifying which sample was exiting the die. Also, extrusion started with low temperatures first before proceeding to high temperatures. Barrel zone temperatures and pressures were logged for the duration of the extrusion.

Extrusion began with material feeding. Materials/samples were fed into the feeder to ensure that agglomeration did not occur. If agglomeration and bridging occurred, a rubber mallet was used to pound on the walls of the feeder to disintegrate agglomerates. Materials were then conveyed from the feeder to the feed hopper at a rate of 22 kg/h and then to the solid conveying zone. By the action of the screws, the materials were then conveyed to the melting, pumping and mixing zone where the plastic was melted and fibers were mixed, and the mixture was conveyed to the pumping and mixing zone where mixing and conveying continued until the materials were extruded from the six-hole die as extruded strands.

Once the extruded strands exited the die, they were cooled using air blown from a fan through a duct then through a perforated metal sheet on a platform (Figure 4.6).

Figure 4.6 Perforated metal sheet on a platform with extruded strands being air-cooled.

4.5 Pelletizing and Powdering

The extrudates were pelletized using an AEC Nelmor granulator model G1215P1 (Nelmor Co, Inc., Uxbridge, MA, USA) (Figure 4.7). The LLDPE pellets were then powdered using a Wedco size reduction system model SE12TC (Thermofine Mills, Wedco, Inc., Grand Junction, TN, USA) (Figure 4.7) equipped with a 1-mm screen.

Due to the non-availability of the latter equipment for the succeeding powdering, the HDPE pellets were powdered in three stages using different pieces of equipment. The first stage was done using a Retsch GmbH knife mill (5657 Haan, West Germany) equipped with a 3.37-mm screen. The next two stages were done using a Thomas Scientific^{TM} laboratory mill (Thomas Scientific, Swedesboro, NJ, USA) equipped with 2-mm and 1-mm screens, respectively. It was foreseen that no significant differences would occur due to the use of different equipment.

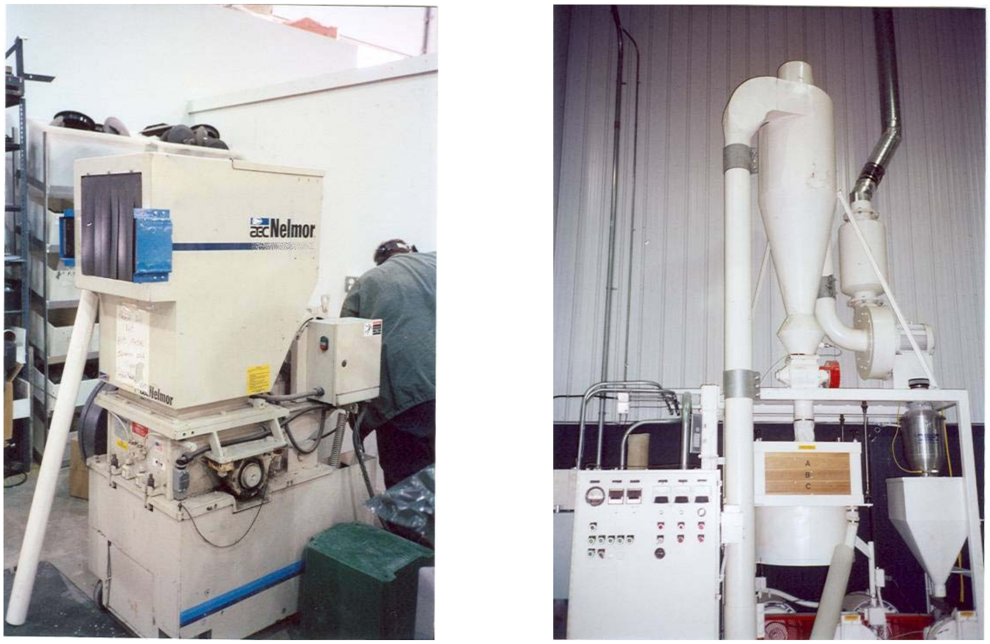


Figure 4.7 AEC Nelmor granulator (left) and Wedco size reduction system (right).

4.6 Rotational Molding

Rotational molding is a highly versatile manufacturing option that allows unlimited design possibilities with the added benefit of low production costs. This study utilized the shuttle-type rotational molding machine at Quality Molded Products Inc, Saskatoon, SK, Canada.

The molding process utilized an oven where the mold was heated at a pre-determined and pre-set temperature, a cooling chamber where the mold was cooled, a control system that set the heating temperature and the heating time and a shuttle where the mold was attached. The mold's shape was box-like. The material used was powdered extrudates and the amount of charge per run was 2 kg.

Preliminary results of this study showed that rotational molding temperature had a major effect on the degradation of flax fiber. One major problem was the inadvertent use of high rotational molding temperatures (275°C and 285°C) which caused fiber degradation (as evidenced by darkening of the product and odor emission) and air bubble formation which produced porous composites and weakened the final product. It was recommended to conduct a further study on the determination of the optimum values of temperature and heating/residence time in rotational molding to prevent the degradation of the flax fiber. It was later found out that the optimum temperature for rotational molding was at 180°C and the optimum heating time was at 20 min (refer to appendix A)

Rotational molding involved a three-step process. The first step was to load a mold cavity with a plastic material (ground pelletized extrudates). Next, the mold was moved, or indexed, to the heating chamber with a temperature between 180 and 200°C (refer to appendix A) where it was heated while on constant biaxial rotation.

The mold was attached to a secondary axis which rotated around the major axis (Figure 4.8). The major axis, on the other hand rotated horizontally. The ratio of rotation of the major axis to the rotation of the secondary axis was 5:1.

While on constant biaxial rotation, the mold was heated for 20 minutes (refer to appendix A). In this step, the melting extrudates began sticking to the hot mold, coating every surface evenly. Finally, the mold was indexed to the cooling chamber where it again was rotated biaxially so that the parts retained an even wall thickness. Once the parts were cooled, they were released from the mold. The rotational speed and heating and cooling times were all controlled throughout the process.

Figure 4.8 Mold mounted on the secondary axis rotating around the major axis.

4.7 Materials Testing and Characterization

The effects of the different variables were analyzed in terms of the color (degree of degradation), density, melt flow index and morphology (dispersion and adhesion of fibers and porosity) of extrudates, and the color (degree of degradation), density, morphology (dispersion and adhesion of fibers and porosity), tensile strength and water absorption of composites. For this, color analysis, a density test, a melt flow index test, scanning electron microscope image analysis, a tensile test and a water absorption test were used.

4.7.1 Color analysis

Color, as an indicator of the degree of degradation brought about by the extrusion parameters (temperature and screw speed), was measured (and compared) using the HunterLab Color Analyzer – LabScan System (Hunter Associates Laboratory, Inc., Reston, Virginia, USA) (Figure 4.9). Values of L (0=black to 100=white), a (-a=green to +a=red) and b (-b=blue to +b=yellow) were measured.

Figure 4.9 HunterLab Color Analyzer.

For this study, powdered extrudates and 25.4 mm by 76.2 mm (1” x 3”) specimens cut from rotationally-molded composites were exposed to the reflectance port. The port size used was 25.4 mm (1 in.) while the viewing area used was 12.77 mm (0.50 in.). To examine the degree of degradation of the extrudates and the composites, the index ΔE, as given by equation 4.1 (Patil et al., 1997), was calculated by taking the color of the first treatment for LLPDE extrudates (LF1T1S1), HDPE extrudates (HF1T1S1) and HDPE composites (HF1T1S1) as base values.

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (4.1)$$

where:

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

L, a, b = color coordinates of the samples

L_{base}, a_{base}, b_{base} = color coordinates of the first treatment for LLDPE extrudates (LF1T1S1), HDPE extrudates (HF1T1S1) and HDPE composites (HF1T1S1)

4.7.2 Density test

The density of plastic materials is defined as the mass per unit volume and is expressed in grams per cubic centimeter. Portions of the extruded strands of each of the 24 treatments were cut into fifteen rod-like pieces (five pieces per replication with three replications) at a length of approximately 30 mm to serve as samples for the extrudate density test, while 25.4 mm by 76.2 mm specimens (with three replications for each treatment) served as samples for the composite density test. The volume of the samples was measured using a gas-operated pycnometer (Quantachrome Corporation, Boynton Beach, FL, USA) (Fig. 4.10) and the mass of the samples was measured using a Galaxy 160D weighing scale (OHAUS Scale Corporation, Florham Park, NJ, USA). Measurements were conducted at a temperature of ca. 23°C and a pressure of 101.3 kPa. Density was calculated by dividing the mass by the volume. Three trials per treatment were conducted. The average of the three was calculated as actual density. Deviations (%) in the actual densities of the treatments from ideal densities (0% fiber content, 12.5% fiber content and 25% fiber content) were computed (equation 4.2) and compared. Ideal densities (equation 4.3) were calculated using the densities of the ground flax fibers, LLDPE and HDPE. The densities of the ground flax fibers, LLDPE and HDPE were calculated using their respective masses and volumes measured in the same way as the samples were measured. Table 4.4 shows the ideal densities of the extrudates.

Figure 4.10 Gas-operated pycnometer used to measure volume.

Density deviation was computed using the following equation:

$$\rho_{\text{deviation}} = \frac{\rho_{\text{actual}} - \rho_{\text{ideal}}}{\rho_{\text{ideal}}} \text{x}100 \tag{4.2}$$

where:

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

ρ_{actual} = actual density (g/cm^3)

ρ_{ideal} = ideal density (g/cm^3)

Ideal density was computed using the following equation (Stroshine, 2000):

$$\rho_{\text{ideal}} = \frac{1}{\frac{m_{\text{plastic}}}{\rho_{\text{plastic}}} + \frac{m_{\text{fiber}}}{\rho_{\text{fiber}}}} \tag{4.3}$$

where:

ρ_{ideal} = ideal density (g/cm^3)

m_{plastic} = mass fraction of plastic

m_{fiber} = mass fraction of fiber

ρ_{plastic} = density of plastic (g/cm^3)

ρ_{fiber} = density of fiber (g/cm^3)

Table 4.4 Ideal densities of the three types of extrudates based on fiber content.

Ground Flax Fiber Density	LLDPE/HDPE Density	Extrudate Type	Ideal Density (g/cm^3)
1.618 g/cm^{3*} (0.085)**	LLDPE = 0.969 g/cm^{3*} (0.007)**	0% fiber content	0.969 g/ cm^3
		12.5% fiber content	1.020 g/ cm^3
		25% fiber content	1.077 g/cm^3
	HDPE = 0.977 g/cm^{3*} (0.002)**	0% fiber content	0.977 g/cm^3
		12.5% fiber content	1.028 g/cm^3
		25% fiber content	1.084 g/cm^3

*average of 3 values
**standard deviation

It must be noted that the computed densities for LLDPE and HDPE were slightly higher than those presented in Table 4.1. This may be attributed to the use of the pycnometer during the volume measurement.

4.7.3 Melt flow index test

The melt flow index test, more appropriately known as the melt flow rate (MFR) test (ASTM D1238 – standard test method for melt flow rates of thermoplastics by extrusion plastometer) (ASTM, 2003a), measures the rate of extrusion of a thermoplastic material through an orifice of specific length and diameter under prescribed conditions of temperature and load (Shah, 1998). The test specimen was in the form of powder. Since the polymer used in this study was polyethylene, the condition used was 190/2.16 which means that the temperature was 190°C and the total load including the piston was 2.16 kg. Procedure A (manual operation) was used. The equipment used was the Thermodyne shell development design of the Tinius Olsen Testing Machine Company (Hallikainen Instruments, Richmond, CA, USA) (Figure 4.11). The measured value was expressed in g/10 min.

Figure 4.11 Melt indexer used for melt flow index test.

4.7.4 Scanning electron microscope image analysis

The mechanical properties of reinforced thermoplastics depend on such characteristics of the filler as granulometry, orientation and dispersion. In their study, Averous and co-workers (1998) determined these parameters by using image analysis coupled with optical and electron microscopy. In this study, the homogeneity of the mixture or uniform dispersion of flax fibers in the thermoplastic matrix and porosity were examined using a scanning electron microscope (SEM 505, Philips, Holland) (Figure 4.12). Samples were prepared by slicing a thin cross-section (approximately 1 mm) from each of the treatments. These samples were then coated with gold to provide the necessary conductive surface for the electron microscope, since the sample was a biological material and, therefore, not a conductor. The coated samples were then stuck to a stud with double-sided tape and then analyzed using the SEM.

Figure 4.12 Scanning electron microscope.

4.7.5 Tensile test

The tensile test was conducted using an Instron reversible load cell (5 kN) (Instron, Canton, MA, USA) (Figure 4.13) in accordance with ASTM D638-02a (standard test method for tensile properties of plastics) (ASTM, 2003b). Since the material was isotropic, only five specimens for each treatment were made. The test specimens, being part of a reinforced composite, conformed to the dimensions of a Type I specimen (Figure 4.14). These were conditioned at 24°C and 50% relative humidity for 72 h. Tests were conducted under the same conditions. The speed of testing used was 5 mm/min. Only the specimens that broke in the center were considered. The specimens that broke on the grips were discarded. Tensile strength at yield (σ_{ty}) was calculated using the following equation:

$$\sigma_{ty} = \frac{F_{max}}{A} \qquad (4.4)$$

where:

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

A = original cross-sectional area (m^2).

Figure 4.13 Instron reversible load cell (5 kN) (Instron, Canton, MA, USA) used to perform the tensile strength test.

Figure 4.14 Tensile test specimen

4.7.6 Water absorption test

The water absorption test was carried out following ASTM D570-98 (standard test method for water absorption of plastics) (ASTM, 2003c). The test specimens were cut in the form of bars 76.2 mm (3 in.) long by 25.4 mm (1 in.) wide (Figure 4.15). Cut specimens were dried in an air oven for 24 h at 50°C, cooled in a desiccator, and immediately weighed to the nearest 0.001 g (conditioned mass). Conditioned specimens were then subjected to the 24-h immersion procedure as specified in the standard. After the 24 h immersion, the samples were again weighed to the nearest 0.001 g (wet mass). Water absorption was measured as the increase in mass using the following equation:

$$\%mass.increase = \frac{m_{wet} - m_{conditioned}}{m_{conditioned}} x100 \qquad (4.5)$$

where:

m_{wet} = wet mass (g)

$m_{conditioned}$ = conditioned mass (g)

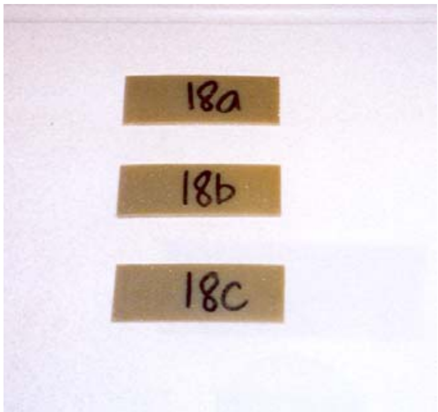


Figure 4.15 Water absorption test specimens.

4.8 Statistical Analyses, Modeling and Optimization

The experiment was a 3 x 2 x 2 factorial design with fiber content having three levels, barrel zone temperature having 2 levels and screw speed having 2 levels, resulting to 12 treatments each for LLDPE and HDPE composites. The effects of the three process variables on the color, density, melt index, and morphology (dispersion and adhesion of fibers and porosity) of extrudates, and the color, density, morphology (dispersion and adhesion of fibers and porosity), tensile strength, and water absorption of composites, were studied.

Treatment means were analyzed using analysis of variance (Factorial ANOVA) and compared using Duncan's multiple range test (DMRT). Response surface plots (3D graphs) were generated using Tecplot 9.2 (Tecplot, 2001) to visually show the effects of the three process variables on the response variables.

The effects of the three process variables on each of the response variables were modeled and the equations determined using multiple linear regression and the stepwise method of the SAS software (SAS, 2003).

The graphical method was applied as an optimization technique (Carrillo et al., 2002). Generated using Tecplot 9.2 (Tecplot, 2001), contour plots of the response variables were utilized by applying superposition surface methodology to obtain three contour plots (for each of LLDPE and HDPE composites) for observation and selection of the best (optimum) combination of fiber content (FC), temperature (T) and screw speed (SS) for the production of flax-fiber-reinforced polyethylene composites.

5. RESULTS AND DISCUSSIONS

The extrusion trials yielded six kilograms of extrudate for each of the 24 treatments. The extrudate for each of the 24 treatments was subjected to four material testing and characterization techniques, namely color analysis, a density test, a melt flow index test and SEM image analysis.

The rotational molding trials produced 24 box-shaped composites from which test specimens were made for five material testing and characterization techniques, namely color analysis, a density test, SEM image analysis, a tensile test and a water absorption test.

5.1 Extrusion Barrel Zone Temperatures and Pressures

The temperature log revealed that the extruder temperature control accurately set the actual barrel zone temperatures. The plots of actual temperatures followed the three settings: the 1st setting at 0 s (75-110-120-130-140°C); the 2nd setting after 4900 s (75-120-130-140-150°C); and the 3rd setting after 9000 s (75-130-140-150-160°C), with minimal deviations between actual temperatures and set temperatures (except for zone 4 where some thermocouple-related and cooling zone-related problems were experienced) (refer to appendix B for the graphs).

Figure 5.1 shows a typical graph of actual barrel zone temperatures which were set at 75-110-120-130-140°C.

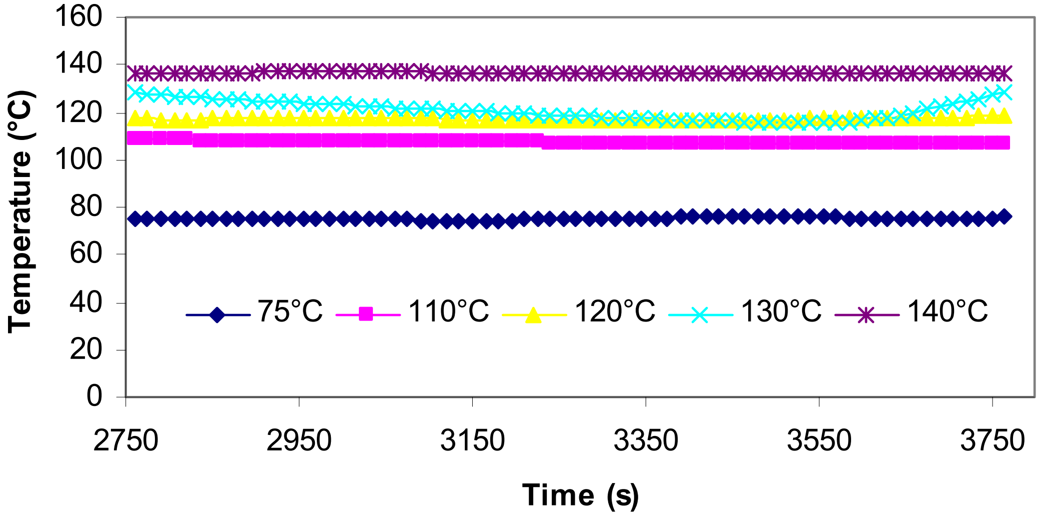


Figure 5.1 Actual barrel zone temperatures during extrusion of HF1T1S2 (HDPE, 0% fiber content, 75-110-120-130-140°C temperatures, 150 rpm screw speed).

The pressures fluctuated between 1.3 MPa and 2.8 MPa, without any particular pattern (Figure 5.2) (refer to appendix C for pressure readings for each treatment). It was observed, though, that fluctuations were more evident during the extrusion of flax fiber and plastic mixtures than during the extrusion of the pure plastic. If there was uniform mixing of fiber and PE, we would have seen less variation in pressure readings, however, that was not the case. The fibers tended to form agglomerates which caused the fluctuations in the pressure readings.

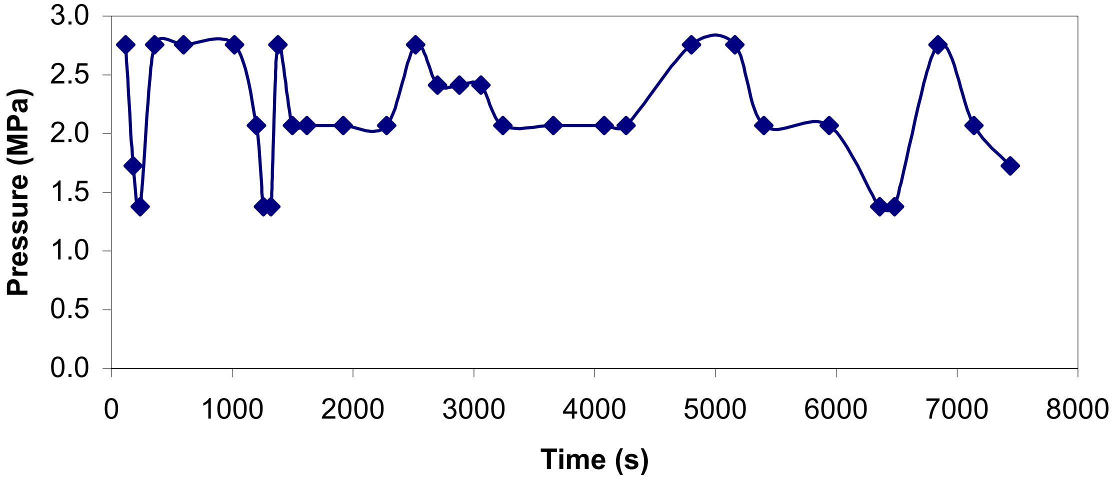


Figure 5.2 Pressure readings during extrusion of HDPE composites.

5.2 Extrudate Color

Experimental results for the response variable ΔE (color index) at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.1 for LLDPE extrudates and in Table 5.2 for HDPE extrudates. HunterLab values L, a, and b are averages of nine values (three replications with three readings for each replication). The five barrel zone temperatures from here on will be represented in the tables by the temperature at zone 5 (preferred by some researchers).

Table 5.1 L, a, b color coordinates and color index (ΔE) of LLDPE extrudates.

Process Variables			Response Variable							DMRT
FC*	T*	SS*	L**		a**		b**		ΔE	Grouping
(%)	(°C)	(rpm)	Mean	SD	Mean	SD	Mean	SD		
0	140	110	74.04	1.33	0.57	0.08	6.57	0.32	0.00	J
0	140	150	73.26	0.51	1.46	0.03	8.40	0.16	2.18	I
0	150	110	71.31	0.19	1.14	0.02	8.10	0.40	3.18	H
0	150	150	68.09	0.55	1.27	0.01	8.99	0.07	6.46	G
12.5	140	110	47.75	1.09	1.90	0.13	8.43	0.37	26.39	D
12.5	140	150	52.19	1.12	1.71	0.17	8.56	0.69	21.97	F
12.5	150	110	48.95	0.77	2.65	0.15	9.72	0.09	25.37	E
12.5	150	150	44.61	0.89	2.27	0.10	9.05	0.44	29.58	B
25	140	110	45.20	1.54	3.24	0.21	10.91	0.60	29.29	B
25	140	150	45.43	1.34	3.27	0.22	11.34	0.67	29.13	B
25	150	110	46.34	0.40	2.89	0.12	10.88	0.36	28.13	C
25	150	150	43.89	1.29	3.43	0.22	11.16	0.49	30.63	A

*FC=fiber content, T= temperatures, SS=screw speed
**Average of 9 values

For LLDPE extrudates, ΔE varied from 0 to 30.63. The analysis of variance (ANOVA) (refer to Appendix D.1) showed that ΔE was significantly dependent on fiber content (FC) ($P < 0.05$), temperature ($P < 0.05$), and screw speed ($P < 0.05$). The higher the fiber content, the higher the ΔE. This can be explained by the fact that flax fibers have a brown color. Thus, the more fibers there are in the extrudate, the browner the extrudate would be. The higher temperatures (T2 = 75-120-130-140-150°C) resulted in higher ΔEs because high product temperatures result in darkening. The higher screw speed resulted in higher ΔEs because of higher shear rate, which would result in a higher product temperature (Carneiro et al., 2000), consequently resulting in darkening. It must be noted that the measured temperature represented the temperature at the jacket rather than the actual temperature of the product, which is more complicated to determine.

Sombatsompop and Panapoy (2000) investigated the effect of screw speed on two-dimensional temperature profiles of flowing polypropylene melt in the barrel of a counter-rotating, twin-screw extruder and concluded that the increase in melt temperature was closely associated with the total flow length of the melt, shear heating and heat conduction effects.

The response surface plot (Figure 5.3) for the effect of screw speed and temperature on ΔE shows the same result for the latter variables (refer to appendix E for other response surface plots).

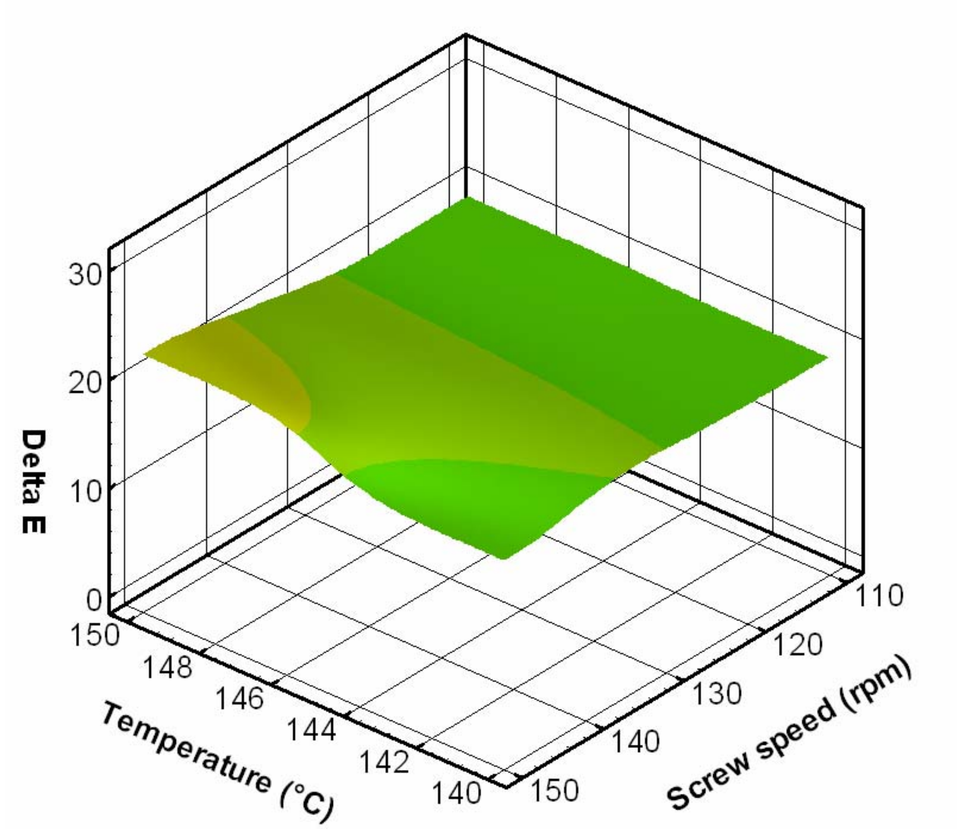


Figure 5.3 Response surface plot for the effects of temperature and screw speed on the color index (ΔE) of LLDPE extrudates.

Table 5.2 L, a, b color coordinates and color index (ΔE) of HDPE extrudates.

Process Variables			Response Variable							DMRT
FC* (%)	T* (°C)	SS* (rpm)	L** Mean	L** SD	a** Mean	a** SD	b** Mean	b** SD	ΔE	Grouping
0	140	110	75.92	0.98	1.06	0.11	5.03	0.15	0.00	H
0	140	150	72.62	0.50	1.20	0.05	8.15	0.08	4.55	G
0	150	110	73.52	0.43	1.31	0.12	9.05	0.20	4.69	G
0	150	150	70.40	0.71	1.58	0.03	10.07	0.26	7.50	F
12.5	140	110	50.91	0.53	1.67	0.22	8.05	0.58	25.20	E
12.5	140	150	48.83	0.54	2.24	0.22	9.16	0.30	27.44	D
12.5	150	110	47.57	0.57	1.78	0.12	8.38	0.28	28.56	C
12.5	150	150	50.86	0.69	1.67	0.06	7.81	0.23	25.23	E
25	140	110	44.98	0.66	3.43	0.21	11.31	0.23	31.66	A
25	140	150	46.11	0.33	2.56	0.08	10.29	0.20	30.31	B
25	150	110	47.93	1.66	1.96	0.13	8.96	0.27	28.28	C
25	150	150	47.86	1.31	1.86	0.15	9.12	0.31	28.37	C

*FC=fiber content, T= temperatures, SS=screw speed
**Average of 9 values

For HDPE extrudates, ΔE varied from 0 to 31.66. The ANOVA (refer to Appendix D.2) showed that ΔE was significantly dependent on fiber content (FC) ($P < 0.05$) only. Thus, the two temperature regimes and the two screw speeds used in this experiment did not have any measurable effect on this quality parameter. This is probably due to the fact that HDPE had a higher ability to absorb heat from the fibers than LLDPE. The melting point of HDPE with silane-treated fibers is 133.38°C while that of LLDPE with silane-treated fibers is 130.34°C (Wang, 2004). The response surface plot (Figure 5.4) for the effect of fiber content and screw speed also shows that only the fiber content has an effect on ΔE (the higher the fiber content, the higher the ΔE).

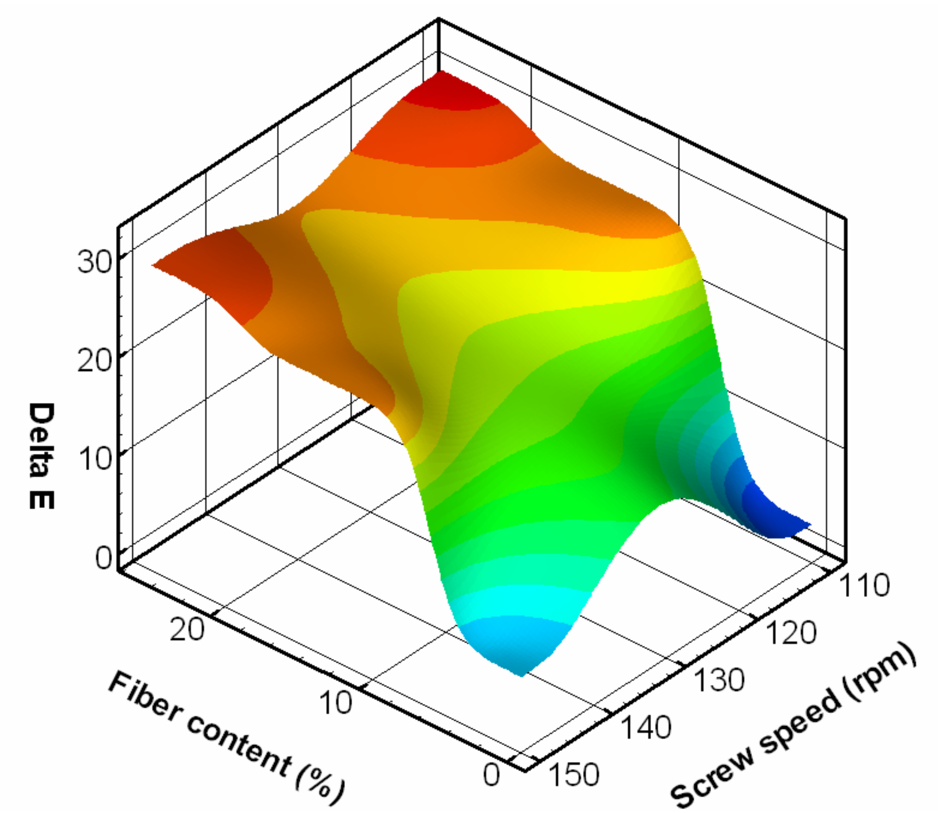


Figure 5.4 Response surface plot for the effects of fiber content and screw speed on the color index (ΔE) of HDPE extrudates.

5.3 Extrudate Density

Experimental results for the density deviation at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.3 for LLDPE extrudates and in Table 5.4 for HDPE extrudates.

For LLDPE extrudates, the density deviation varied from -16.99% (at 25% fiber content) to 30.18% (at 12.5% fiber content).

Table 5.3 Density and density deviation (%) of LLDPE extrudates.

Process Variables			Response Variable				DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Actual Density (g/cm^3) Mean**	SD	Ideal Density (g/cm^3)	Density Deviation (%)	
0	140	110	0.92	0.18	0.97	-5.53	B C
0	140	150	0.96	0.08	0.97	-0.71	B C
0	150	110	0.88	0.15	0.97	-9.15	C
0	150	150	0.99	0.01	0.97	2.64	A B C
12.5	140	110	0.94	0.03	1.02	-8.16	C
12.5	140	150	0.87	0.21	1.02	-14.46	C
12.5	150	110	1.33	0.31	1.02	30.18	A
12.5	150	150	1.25	0.14	1.02	22.81	A B
25	140	110	0.95	0.19	1.08	-12.19	C
25	140	150	1.12	0.20	1.08	4.12	A B C
25	150	110	1.06	0.12	1.08	-1.57	B C
25	150	150	0.89	0.04	1.08	-16.99	C

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

The response surface plots (Figure 5.5) show that a 12.5% fiber content, higher temperatures (T2 = 75-120-130-140-150°C) and lower screw speed (110 rpm) resulted in the highest density deviation, whereas the 25% fiber content resulted in the lowest density deviation.

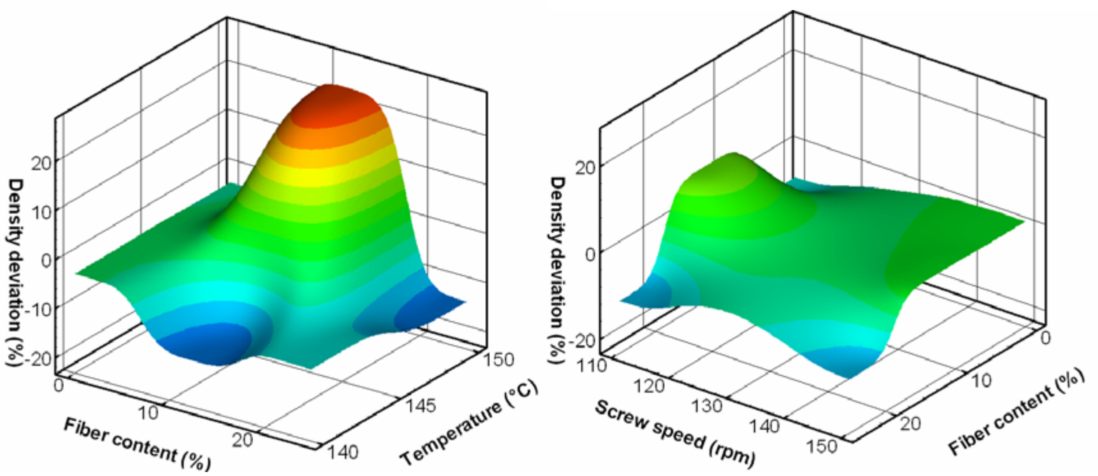


Figure 5.5 Response surface plots for the effects of fiber content, temperature, and screw speed on the density deviation (%) LLDPE extrudates.

The addition of 12.5% fibers made the materials denser because flax fibers are denser than pure plastics. The addition of 25% fiber, however, made the extrudates very porous, which means that air was incorporated into the extrudates. Air density is low, thus bringing down the actual density from the ideal. The higher barrel zone temperatures (T2 = 75-120-130-140-150°C) resulted in more dense materials, because it enabled the plastic to melt more consistently, thus thoroughly mixing with the fiber without introducing much air. The lower screw speed (110 rpm) resulted in more dense materials because it allowed the materials more residence time, and thus more time for effective melting and mixing with fibers, again introducing less air. The ANOVA (refer to Appendix D.3), however, revealed that the effects of the three variables, namely fiber content, temperature and screw speed, were not significant in any of the LLDPE treatments.

Table 5.4 Density and density deviation (%) of HDPE extrudates.

Process Variables			Response Variable				DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Actual Density (g/cm^3) Mean**	SD	Ideal Density (g/cm^3)	Density Deviation (%)	
0	140	110	0.93	0.00	0.98	-4.59	C
0	140	150	1.05	0.03	0.98	7.81	A B C
0	150	110	1.30	0.16	0.98	33.47	A
0	150	150	1.22	0.10	0.98	25.01	A
12.5	140	110	1.30	0.06	1.03	26.81	A
12.5	140	150	1.20	0.12	1.03	16.79	A B C
12.5	150	110	1.33	0.08	1.03	29.34	A
12.5	150	150	1.27	0.24	1.03	23.08	A B
25	140	110	1.06	0.06	1.08	-2.39	B C
25	140	150	1.30	0.21	1.08	19.60	A B C
25	150	110	1.39	0.19	1.08	27.83	A
25	150	150	1.37	0.25	1.08	26.57	A

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For HDPE extrudates, the density deviation varied from -4.59% to 33.47%. The analysis of variance showed that the density deviation was significantly dependent on temperature (T) ($P < 0.05$) only. The response surface plot (Figure 5.6) for the effect of temperature and screw speed agreed with the results of the ANOVA (refer to Appendix D.4). The higher temperatures (T2 = 75-120-130-140-150°C) resulted in the highest density deviation. The lower screw speed (110 rpm) also resulted in the highest density deviation.

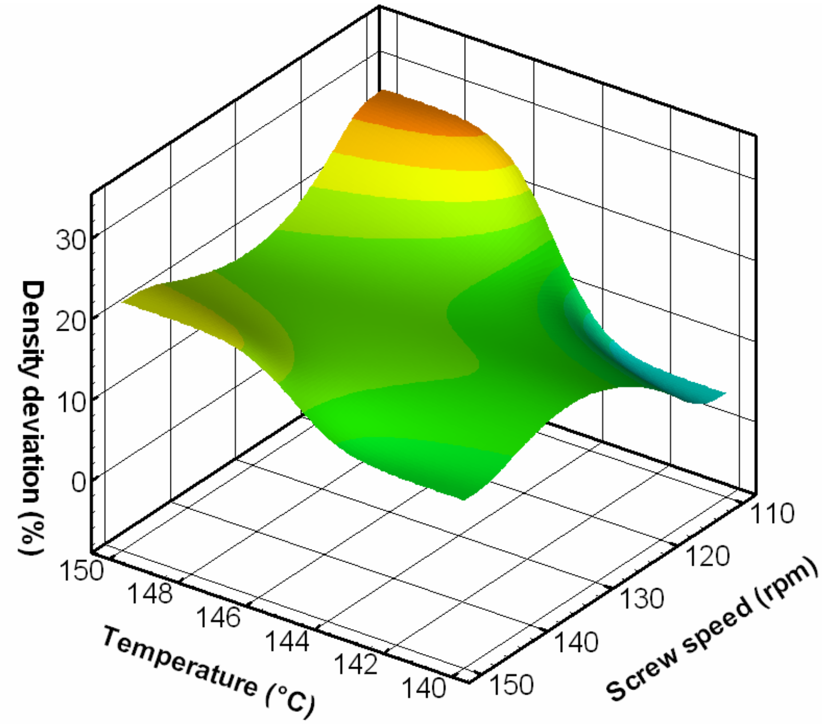


Figure 5.6 Response surface plot for the effects of temperature and screw speed on the density deviation (%) HDPE extrudates.

In the study by Bhattacharya (1997) on the extrusion of rice and green gram blend using a co-rotating, twin-screw extruder, the response functions (torque, specific mechanical energy, expansion ratio, density and maximum stress) were related (r=0.870, P≤0.01) to the process variables (screw speed and temperature) by second-order polynomials.

5.4 Extrudate Melt Flow Index

Experimental results for the melt flow index (MFI) at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.5 for LLDPE extrudates and in Table 5.6 for HDPE extrudates.

Table 5.5 Melt flow index (g/10 min) of LLDPE extrudates.

Process Variables			Response Variable		DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Melt Flow Index (g/10 min) Mean**	SD	
0	140	110	2.96	0.14	A B
0	140	150	3.10	0.06	A
0	150	110	2.94	0.17	B
0	150	150	3.04	0.11	A B
12.5	140	110	1.89	0.06	C
12.5	140	150	1.57	0.07	D
12.5	150	110	1.74	0.07	C
12.5	150	150	1.86	0.02	C
25	140	110	0.66	0.02	F
25	140	150	0.54	0.01	F
25	150	110	1.34	0.11	E
25	150	150	0.61	0.04	F

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For LLDPE extrudates, the MFI varied from 0.54 g/10 min (at 25% fiber content) to 3.10 g/10 min (at 0% fiber content). Values of pure plastic extrudate (0% fiber content) were slightly lower than the actual MFI of pure LLDPE powder (3.3 g/10 min – from Table 4.1) because the pure plastic extrudate has gone through extrusion, which altered some of its characteristics and probably introduced some foreign materials.

The response surface plot (Figure 5.7) shows that the extrudates with 0% fiber content had the highest melt index while the extrudates with 25% fiber content had the lowest melt index.

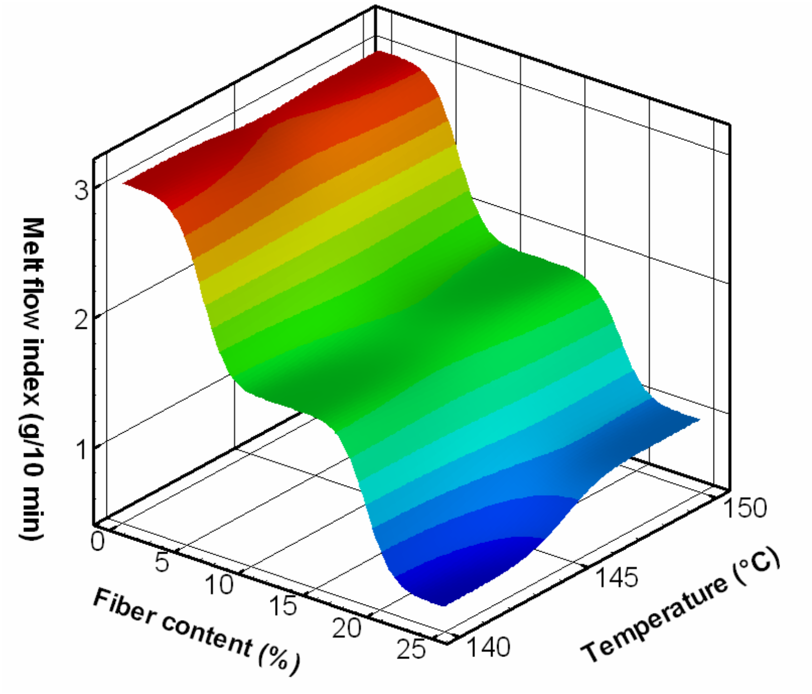


Figure 5.7 Response surface plot for the effects of temperature and fiber content on the melt index of LLDPE extrudates.

The ANOVA (refer to Appendix D.5) revealed that only the fiber content had a significant effect on the MFI ($P < 0.05$).

For HDPE extrudates, the MFI varied from 0.56 g/10 min (at 25% fiber content) to 5.02 g/10 min (at 0% fiber content). The MFI of pure HDPE powder was approximately 5 g/10 min.

Table 5.6 Melt flow index (g/10 min) of HDPE extrudates.

Process Variables			Response Variable		DMRT
FC* (%)	T* (°C)	SS* (rpm)	Melt Flow Index (g/10 min) Mean**	SD	Grouping
0	140	110	5.02	0.02	A
0	140	150	4.96	0.06	A
0	150	110	4.97	0.03	A
0	150	150	5.05	0.12	A
12.5	140	110	2.96	0.01	C D
12.5	140	150	2.93	0.08	D
12.5	150	110	3.13	0.03	B
12.5	150	150	3.04	0.09	B C
25	140	110	0.88	0.04	E
25	140	150	0.65	0.05	F
25	150	110	0.97	0.04	E
25	150	150	0.56	0.03	F

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

The response surface plot (Figure 5.8) reveals that the 0% fiber content and the lower screw speed (110 rpm) resulted in higher values of melt index.

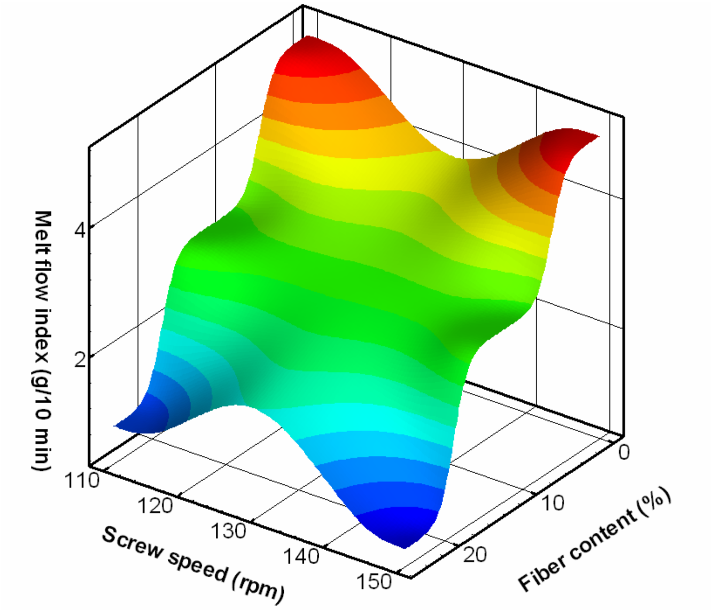


Figure 5.8 Response surface plot for the effects of screw speed and fiber content on the melt index of HDPE extrudates.

The ANOVA (refer to Appendix D.6) also showed that fiber content (FC) and screw speed (SS) had significant effects on the melt index of HDPE extrudates ($P < 0.05$).

For both LLDPE and HDPE extrudates, the melt flow indices decreased as fiber content increased. This has a substantial effect on molding operations such as rotational molding, since the latter process requires greater flowability to evenly apply heat to the materials. With lower flowability (as in the case of the extrudates with 12.5% and 25% fiber content), heat is applied unevenly, thus melting is inconsistent which results in high porosity and, consequently, low composite properties (Mwaikambo and Ansell, 2003).

To study the effects of processing conditions on the viscoelastic and mechanical properties of biodegradable composites, Ali and co-workers (2003) prepared several composites based on sisal fibers and biodegradable polymers. The effects of processing conditions such as screw speed, temperature and time of mixing were investigated. The mechanical and viscoelastic properties of these composites were affected by the processing conditions. Both the tensile strength and melt flow index depended strongly on the nature of the polymeric matrix and on the processing conditions, such as the temperature, screw speed and time of mixing.

5.5 Extrudate Morphology

Comparing the results of the density test and SEM analysis proved that there is a relationship between the density deviation and the porosity of the material. LF2T1S1 and LF2T1S2 (using T1 = 75-110-120-130-140°C), which had negative deviations from the ideal densities, contained a large number of pores as viewed from the SEM micrographs (Figure 5.9).

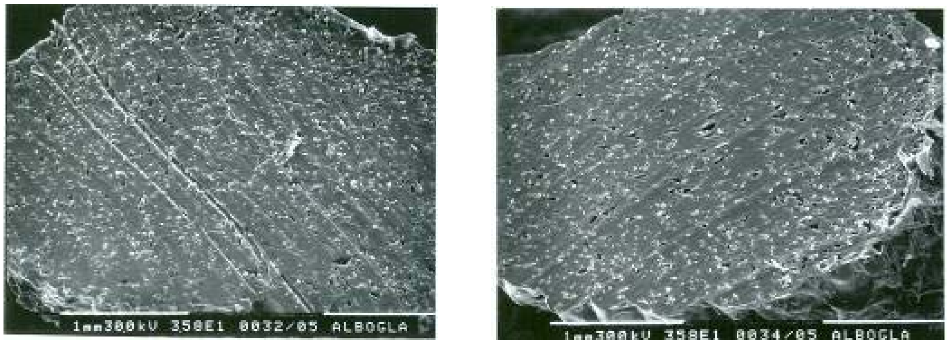


Figure 5.9 SEM micrographs of LF2T1S1 (LLDPE, 12.5% fiber content, 75-110-120-130-140°C, and 110 rpm) (left) and LF2T1S2 (LLDPE, 12.5% fiber content, 75-110-120-130-140°C, and 150 rpm) (right).

The treatments LF2T2S1 and LF2T2S2 (using T2 = 75-120-130-140-150°C), on the other hand, had positive deviations from the ideal densities. Based on the SEM micrographs (Figure 5.10), the two treatments contained only very few pores compared with the previous two treatments.

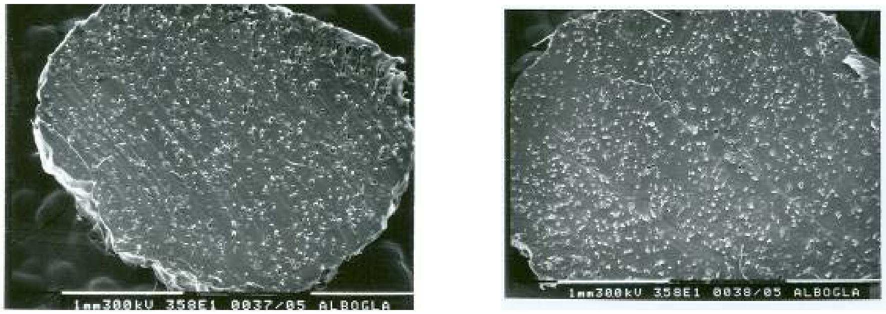


Figure 5.10 SEM micrographs of LF2T2S1 (LLDPE, 12.5% fiber content, 75-120-130-140-150°C, and 110 rpm) (left) and LF2T2S2 (LLDPE, 12.5% fiber content, 75-120-130-140-150°C, and 150 rpm) (right).

It can be observed from the four micrographs that the flax fibers were uniformly dispersed (with slight variations) within the polymer matrix. This proves that extrusion compounding was indeed effective in addressing the problem of a non-homogeneous mixture. Moreover, extrusion enhanced adhesion between the fibers and the matrix.

In the study by Averous and co-workers (1998), it was concluded that dispersion was correlated with microstructural parameters and that variations in the average fiber length caused variations in the dispersion. In this study, since the flax fibers had slight variations in length (mean of 0.46 mm, with a standard deviation of 0.31 mm), slight variations in the dispersion of fibers were also observed.

5.6 Composite Color

Experimental results for the response variable ΔE (color index) at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.7 for LLDPE composites and in Table 5.8 for HDPE composites.

For LLDPE composites, ΔE varied from 11.30 to 35.81. The ANOVA (refer to Appendix D.7) showed that ΔE was significantly dependent on fiber content (FC) ($P < 0.05$) and screw speed ($P < 0.05$). The higher the fiber content, the higher the ΔE. This can be explained by the fact that flax fibers have a brown color. Thus, the more fibers in the composite, the browner the composite would be. The lower the screw speed, the longer the residence time, thus the longer the exposure to heat, which results to darkening.

Table 5.7 Color index (ΔE) of LLDPE composites.

Process Variables			Response Variable		DMRT
FC*	T*	SS*	ΔE		Grouping
(%)	(°C)	(rpm)	Mean**	SD	
0	140	110	15.84	1.10	H
0	140	150	15.24	1.17	H
0	150	110	20.12	0.30	G
0	150	150	11.30	0.46	I
12.5	140	110	30.20	0.19	C
12.5	140	150	31.64	0.59	B C
12.5	150	110	30.22	0.39	C
12.5	150	150	31.88	0.29	B
25	140	110	27.62	0.63	D
25	140	150	23.61	1.15	F
25	150	110	35.81	0.73	A
25	150	150	25.74	2.07	E

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

The response surface plot (Figure 5.11) for the effect of fiber content and screw speed on ΔE shows the same result for the latter variables.

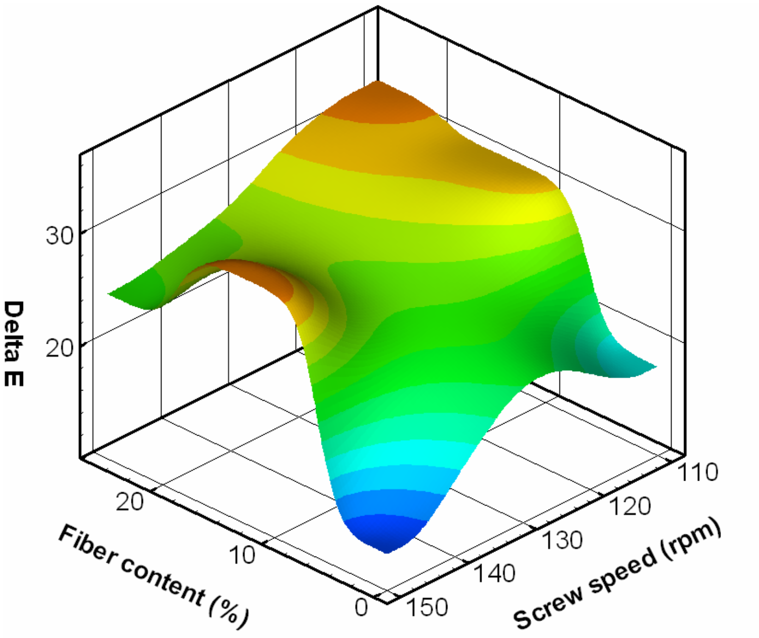


Figure 5.11 Response surface plot for the effects of fiber content and screw speed on the color index of LLDPE composites.

Table 5.8 Color index (ΔE) of HDPE composites.

Process Variables			Response Variable		DMRT
FC*	T*	SS*	ΔE		Grouping
(%)	(°C)	(rpm)	Mean**	SD	
0	140	110	0.76	0.58	H
0	140	150	2.27	0.09	G
0	150	110	3.76	0.23	F
0	150	150	2.94	0.23	F G
12.5	140	110	26.16	0.47	C
12.5	140	150	27.22	0.47	B
12.5	150	110	27.52	0.68	B
12.5	150	150	27.57	0.21	B
25	140	110	29.70	0.73	A
25	140	150	26.28	0.54	C
25	150	110	23.07	0.66	D
25	150	150	19.72	0.53	E

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For HDPE composites, ΔE varied from 0 to 31.66. The ANOVA (refer to Appendix D.8) showed that ΔE was significantly dependent on fiber content (FC) ($P < 0.05$) only. Thus, the two temperature regimes and the two screw speeds used in this experiment did not have any measurable effect on ΔE. As in the case of the extrudate color, this is probably due to the fact that HDPE had a higher ability to absorb heat from the fibers than LLDPE.

The response surface plot (Figure 5.12) for the effect of fiber content and temperature shows that only the fiber content had an effect on ΔE (the higher the fiber content, the higher the ΔE).

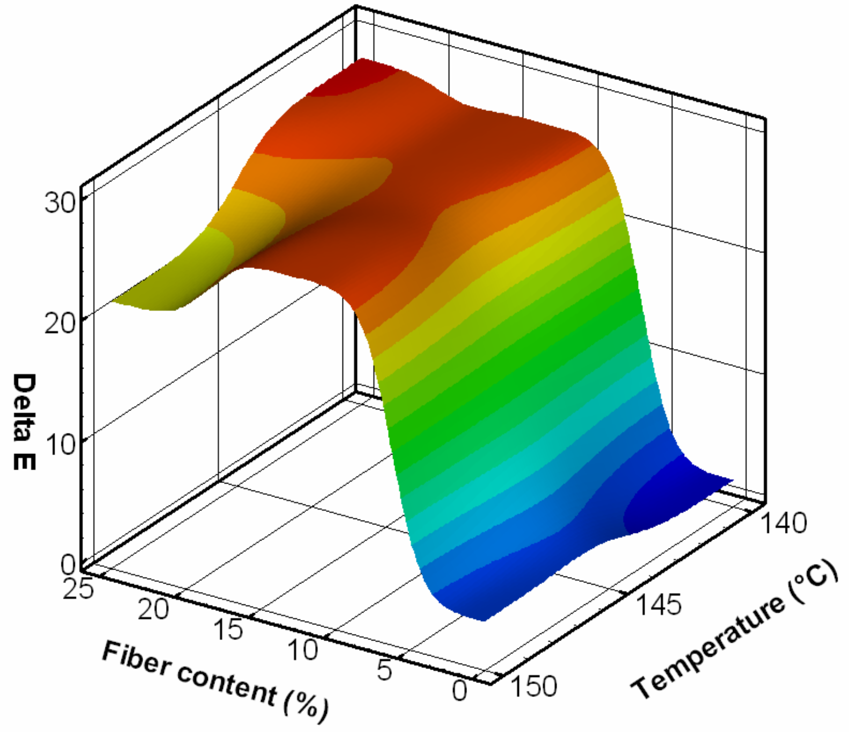


Figure 5.12 Response surface plot for the effects of fiber content and temperature on the color index of HDPE composites.

5.7 Composite Density

Experimental results for the density deviation at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.9 for LLDPE composites and in Table 5.10 for HDPE composites.

For LLDPE composites, the density deviation varied from -9.63% (at 25% fiber content) to 7.67% (at 12.5% fiber content).

The response surface plot (Figure 5.13) shows that the 12.5% fiber content and the lower screw speed (110 rpm) resulted in the highest density deviation, while the 25% fiber content resulted in the lowest density deviation.

Table 5.9 Density and density deviation (%) of LLDPE composites.

Process Variables			Response Variable				DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Actual Density (g/cm^3) Mean**	SD	Ideal Density (g/cm^3)	Density Deviation (%)	
0	140	110	0.93	0.01	0.97	-4.19	A B
0	140	150	0.93	0.00	0.97	-3.60	A B
0	150	110	0.98	0.04	0.97	0.72	A B
0	150	150	0.93	0.00	0.97	-3.72	A B
12.5	140	110	1.10	0.15	1.02	7.67	A
12.5	140	150	1.05	0.11	1.02	2.62	A B
12.5	150	110	1.02	0.08	1.02	-0.32	A B
12.5	150	150	1.04	0.12	1.02	1.72	A B
25	140	110	1.03	0.04	1.08	-4.45	A B
25	140	150	1.01	0.02	1.08	-6.67	B
25	150	110	0.97	0.00	1.08	-9.63	B
25	150	150	1.01	0.00	1.08	-6.63	B

*FC=fiber content, T=temperatures, SS=screw speed

**Average of 3 values

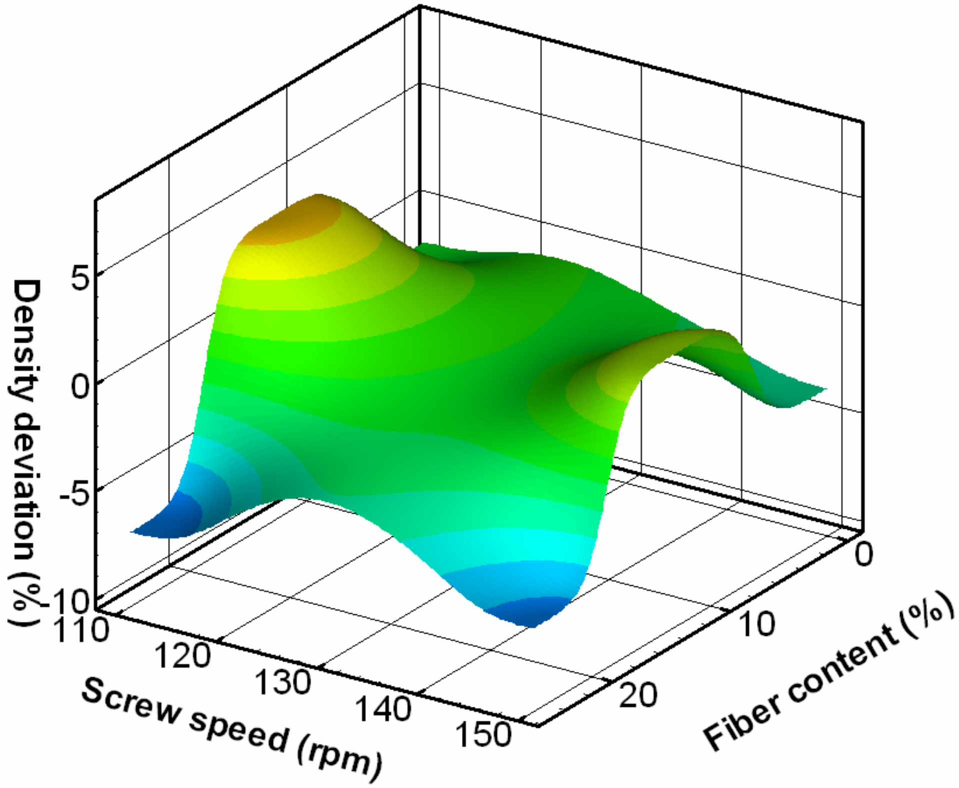


Figure 5.13 Response surface plot for the effects of fiber content and screw speed on the density deviation of LLDPE composites.

As in the case of the extrudates, the addition of 12.5% fibers made the composites denser because flax fibers are denser than pure plastic. The addition of 25% fiber, however, made the composites very porous, which means that air was incorporated during molding. The density of air is low, thus bringing down the actual density from the ideal. The lower screw speed (110 rpm) resulted in more dense materials because it allowed the materials more residence time, thus more time for effective melting and mixing with fibers, again introducing less air. The ANOVA (refer to Appendix D.9), however, revealed that only the fiber content had a significant effect on the density deviation ($P < 0.05$).

Table 5.10 Density and density deviation (%) of HDPE composites.

Process Variables			Response Variable				DMRT
FC* (%)	T* (°C)	SS* (rpm)	Actual Density (g/cm^3) Mean**	SD	Ideal Density (g/cm^3)	Density Deviation (%)	Grouping
0	140	110	0.94	0.00	0.98	-3.55	A
0	140	150	0.96	0.04	0.98	-1.33	A
0	150	110	1.04	0.15	0.98	6.39	A
0	150	150	0.94	0.00	0.98	-4.00	A
12.5	140	110	1.09	0.10	1.03	6.27	A
12.5	140	150	0.97	0.01	1.03	-5.63	A
12.5	150	110	0.97	0.00	1.03	-6.11	A
12.5	150	150	1.10	0.16	1.03	7.33	A
25	140	110	1.03	0.01	1.08	-4.99	A
25	140	150	1.03	0.02	1.08	-4.73	A
25	150	110	1.07	0.06	1.08	-1.71	A
25	150	150	1.02	0.05	1.08	-6.33	A

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For HDPE composites, the density deviation varied from -6.33% (at 25% fiber content) to 7.33% (at 12.5% fiber content).

The response surface plot (Figure 5.14) for the effect of temperature and screw speed reveals that the higher temperatures (T2 = 75-120-130-140-150°C) and the lower screw speed (110 rpm) resulted in higher density deviations.

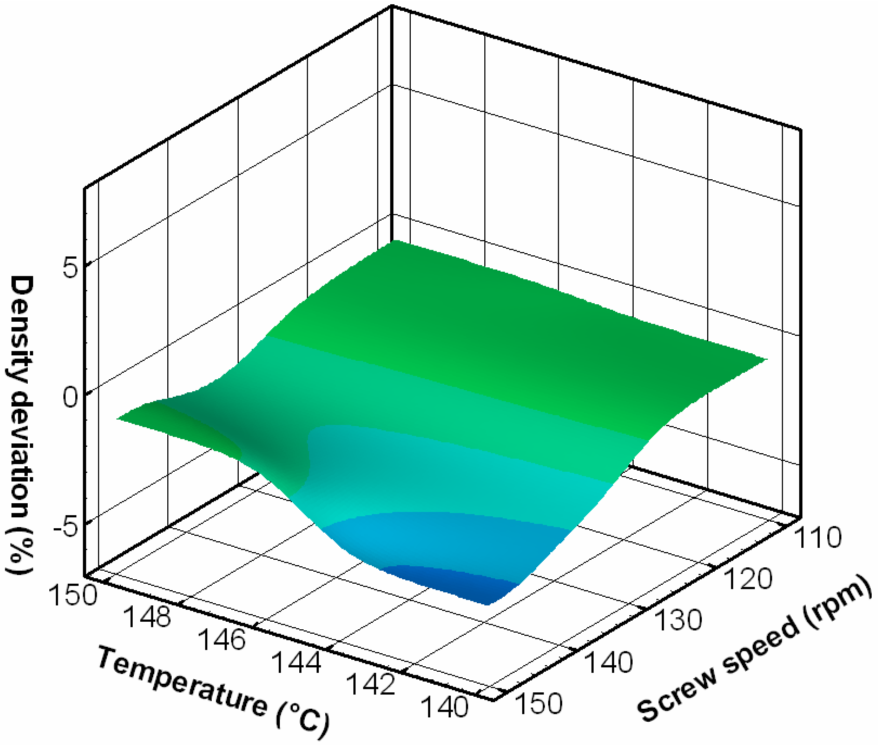
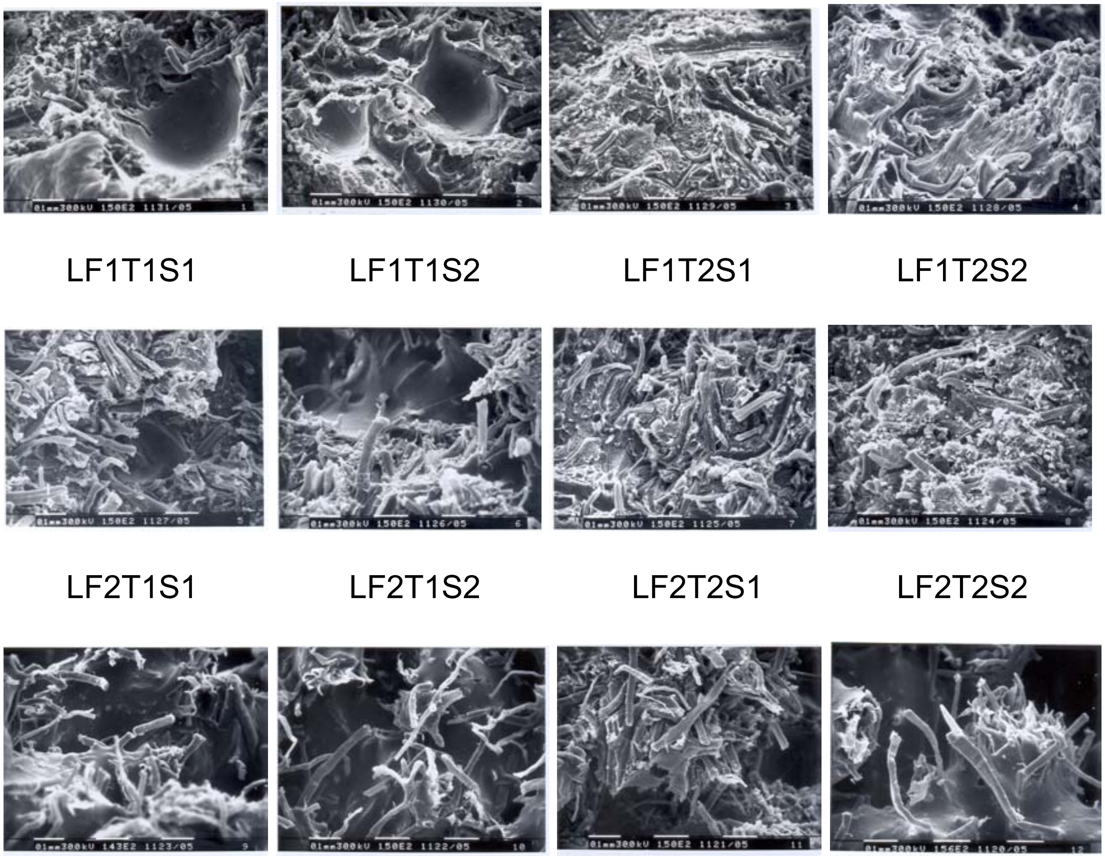


Figure 5.14 Response surface plot for the effects of temperature and screw speed on the density deviation of HDPE composites.

It is expected that a higher density will result in better mechanical properties, such as tensile strength, because of lower porosity (Mwaikambo and Ansell, 2003).

5.8 Composite Morphology



LF1T1S1 LF1T1S2 LF1T2S1 LF1T2S2

LF2T1S1 LF2T1S2 LF2T2S1 LF2T2S2

LF3T1S1 LF3T1S2 LF3T2S1 LF2T2S2

Figure 5.15 SEM micrographs of LLDPE composites.

The preceding photographs (Figure 5.15) are scanning electron microscope (SEM) micrographs of LLDPE composites. L stands for LLDPE, F stands for fiber content, T stands for temperature and S stands for screw speed. The numbers stand for the different levels.

It can be observed from the micrographs that for F1 (0% fiber content) and F2 (12.5% fiber content), composites subjected to the lower extrusion temperatures (T1 = 75-110-120-130-140°C) were more porous than those subjected to the higher extrusion temperatures (T2 = 75-120-130-140-150°C). This means that the lower extrusion temperature regime did not generate enough heat to consistently melt the plastic, thus resulting in higher porosity. The higher temperature regime, however, generated enough heat energy to melt the plastic, thus resulting in greater bonding between fibers and matrix. Likewise, the lower speed resulted in lower porosity.

For 25% fiber content, all treatments were porous because there was too much fiber, which served as insulation, thus preventing consistent melting and thorough mixing of the fibers within the matrix, resulting in high porosity.

Temperature and screw speed effects on porosity were also studied by Matuana and Li (2004), and it was observed that the response surface optimization generated using the regression model suggested that HDPE/wood-flour composite foams with the highest void fraction could be achieved at the highest levels of extruder screw speed and moisture content of wood flour, together with the lowest levels of extruder die temperature. Thus, lower porosity can be achieved by the opposite, i.e. lower levels of screw speed and higher levels of temperature.

5.9 Composite Tensile Strength

Experimental results for the tensile strength at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.11 for LLDPE composites and in Table 5.12 for HDPE composites.

Table 5.11 Tensile strength (MPa) of LLDPE composites.

Process Variables			Response Variable Tensile Strength (MPa)		DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Mean**	SD	
0	140	110	16.53	0.25	B
0	140	150	16.92	0.15	A B
0	150	110	16.55	0.21	B
0	150	150	17.09	0.29	A
12.5	140	110	14.11	0.30	C
12.5	140	150	10.80	0.38	E
12.5	150	110	12.06	0.22	D
12.5	150	150	14.23	0.64	C
25	140	110	2.71	0.12	F
25	140	150	1.78	0.16	G
25	150	110	12.25	0.35	D
25	150	150	1.76	0.46	G

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 5 values

For LLDPE composites, tensile strength varied from 1.76 MPa to 16.92 MPa. The ANOVA (refer to Appendix D.11) showed that the tensile strength was significantly dependent on fiber content (FC) ($P < 0.05$), temperature ($P < 0.05$) and screw speed ($P < 0.05$).

The response surface plots (Figure 5.16) for the effect of fiber content, temperature and screw speed reveal that the 0% fiber content, the higher temperatures (T2 = 75-120-130-140-150°C) and the lower screw speed (110 rpm) resulted in higher tensile strengths.

The effect of temperature on tensile strength was also studied by Ha and Padua (2001). In their investigation of the effect of three extrusion parameters (barrel temperature, screw speed and amount of solvent added during extrusion) on the mechanical properties of zein-fatty acid sheets, it was observed that high temperatures increased tensile strength.

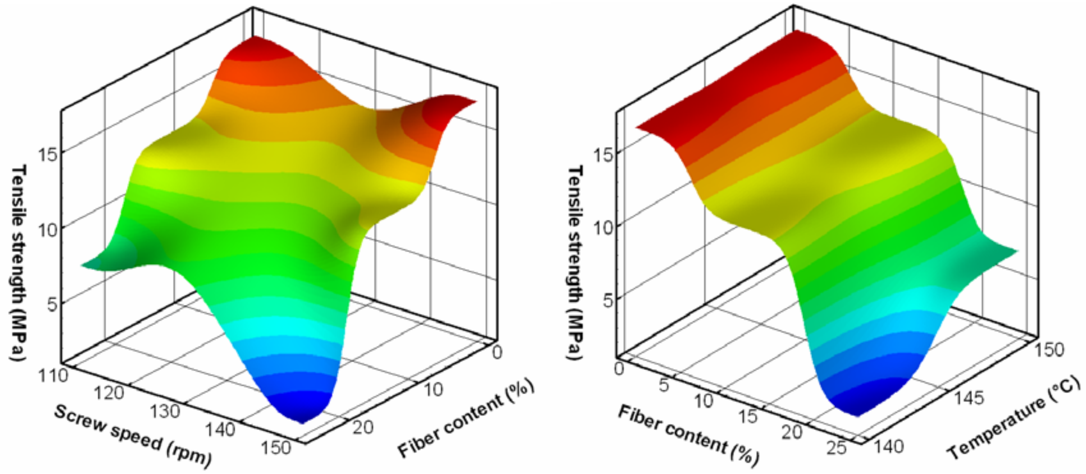


Figure 5.16 Response surface plots for the effects of fiber content, screw speed and temperature on the tensile strength LLDPE composites.

In the study by Mwaikambo and Ansell (2003), hemp fiber bundles were alkalized at concentrations between 0.8 and 8.0% NaOH and the change in surface morphology was elucidated using SEM. The treated fibers with the highest strength were used as reinforcement for cashew nut shell liquid matrix. Non-woven fiber mats and unidirectional fiber composites were manufactured by hand lay-up compression molding. Tensile properties, porosity and fracture surface topography of the composites were analyzed. The unidirectional fiber composites exhibited the best mechanical properties and composites with the lowest porosity (which was achieved in the current study by the use of higher temperatures) offered the best mechanical properties.

Table 5.12 Tensile strength (MPa) of HDPE composites.

Process Variables			Response Variable		DMRT
FC* (%)	T* (°C)	SS* (rpm)	Tensile Strength (MPa) Mean**	SD	Grouping
0	140	110	21.70	0.32	A
0	140	150	20.97	0.93	A
0	150	110	21.70	0.11	A
0	150	150	21.37	0.51	A
12.5	140	110	13.81	0.87	C
12.5	140	150	12.05	1.05	D
12.5	150	110	13.92	1.00	C
12.5	150	150	15.15	0.89	B
25	140	110	3.11	0.52	E
25	140	150	2.05	0.30	F G
25	150	110	2.72	0.39	E F
25	150	150	1.39	0.18	G

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 5 values

For HDPE composites, tensile strength varied from 1.39 MPa to 21.70 MPa. The ANOVA (refer to Appendix D.12) showed it significantly dependent on fiber content (FC) ($P < 0.05$) and screw speed ($P < 0.05$) only.

The response surface plot (Figure 5.17) for the effects of fiber content and screw speed reveals that the 0% fiber content and the lower screw speed (110 rpm) resulted in higher tensile strengths.

Tensile strengths at 25% fiber content, however, were found to be low because the latter had a very high porosity, which led to weaker mechanical properties (Mwaikambo and Ansell, 2003).

5.10 Composite Water Absorption

Experimental results for the water absorption (% mass increase) at different fiber contents (FC), temperatures (T) and screw speeds (SS) are presented in Table 5.13 for LLDPE composites and in Table 5.14 for HDPE composites.

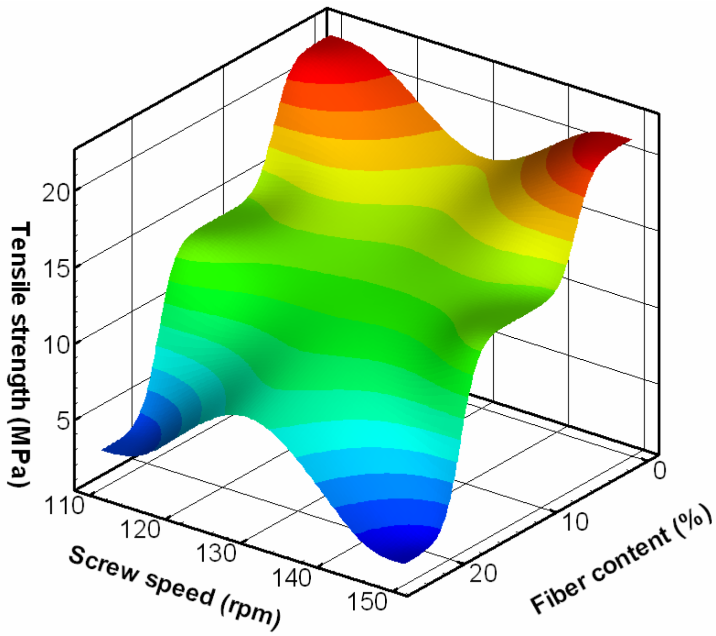


Figure 5.17 Response surface plot for the effects of fiber content and screw speed on the tensile strength HDPE composites.

Table 5.13 Mass increase (%) of LLDPE composites.

Process Variables			Response Variable Mass Increase (%)		DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Mean**	SD	
0	140	110	0.03	0.02	C
0	140	150	0.02	0.01	C
0	150	110	0.01	0.01	C
0	150	150	0.00	0.01	C
12.5	140	110	0.28	0.05	C
12.5	140	150	1.66	0.14	C
12.5	150	110	0.49	0.20	C
12.5	150	150	0.16	0.02	C
25	140	110	6.14	1.68	B
25	140	150	9.32	5.22	A
25	150	110	1.09	0.09	C
25	150	150	9.97	2.11	A

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For LLDPE composites, the mass increase varied from 0% to 9.97%. The ANOVA (refer to Appendix D.13) showed that the mass increase was significantly dependent on fiber content (FC) ($P < 0.05$) and screw speed ($P < 0.05$).

It can be observed from the table that the treatment means for the 0% fiber content were not significantly different from the treatment means for the 12.5% fiber content. This signifies that the chemical treatment was effective in decreasing the water absorption capacity of the flax fibers. The reason for the high mass increase of the treatments with 25% fiber content was not the water absorption capacity of the fibers present but, instead, the porosity of the composites.

The response surface plots (Figure 5.18) for the effects of fiber content, temperature and screw speed reveal that 0% and 12.5% fiber content, higher temperatures (T2 = 75-120-130-140-150°C) and lower screw speed (110 rpm) resulted in lower mass increases.

It must be noted that these parameters also resulted in lower porosity, thus the lower the porosity, the lower the mass increase (water absorption).

It was also observed that the higher the water absorption, the lower the tensile strength (found with treatments with 25% fiber content). This agrees with the study by Pan and Sun (2003) where the effects of moisture content (MC) and extrusion parameters on water absorption and tensile strength of starch and polylactic acid (PLA) blends were investigated. It was determined that blends with higher tensile strength had lower water absorption, less than 15% after a 10-day soaking test.

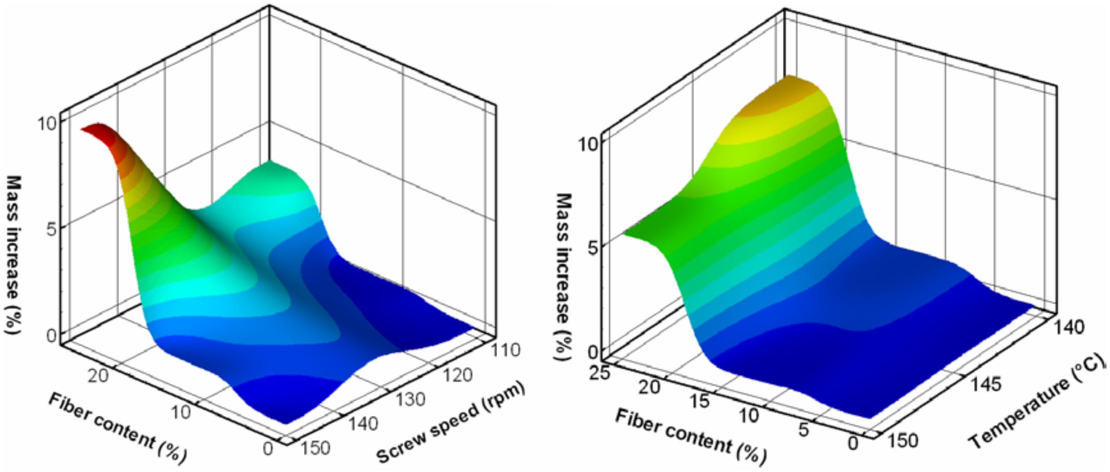


Figure 5.18 Response surface plots for the effects of fiber content, temperature and screw speed on the water absorption (%mass increase) LLDPE composites.

Table 5.14 Mass increase (%) of HDPE composites.

Process Variables			Response Variable		DMRT Grouping
FC* (%)	T* (°C)	SS* (rpm)	Mass Increase (%) Mean**	SD	
0	140	110	0.00	0.00	B
0	140	150	0.00	0.00	B
0	150	110	0.01	0.01	B
0	150	150	0.01	0.01	B
12.5	140	110	0.43	0.05	B
12.5	140	150	0.46	0.06	B
12.5	150	110	0.19	0.01	B
12.5	150	150	0.17	0.02	B
25	140	110	5.95	4.44	A
25	140	150	1.37	0.27	B
25	150	110	1.31	0.24	B
25	150	150	1.73	0.11	B

*FC=fiber content, T=temperatures, SS=screw speed
**Average of 3 values

For HDPE composites, the mass increase varied from 0% (0% fiber content) to 5.95% (25% fiber content). The ANOVA (refer to Appendix D.14) showed that the mass increase was significantly dependent on fiber content (FC) ($P < 0.05$) only.

The response surface plot (Figure 5.19) for the effects of fiber content and temperature reveals that the 0% and 12.5% fiber content and the higher temperatures (T2 = 75-120-130-140-150°C) resulted in lower mass increases.

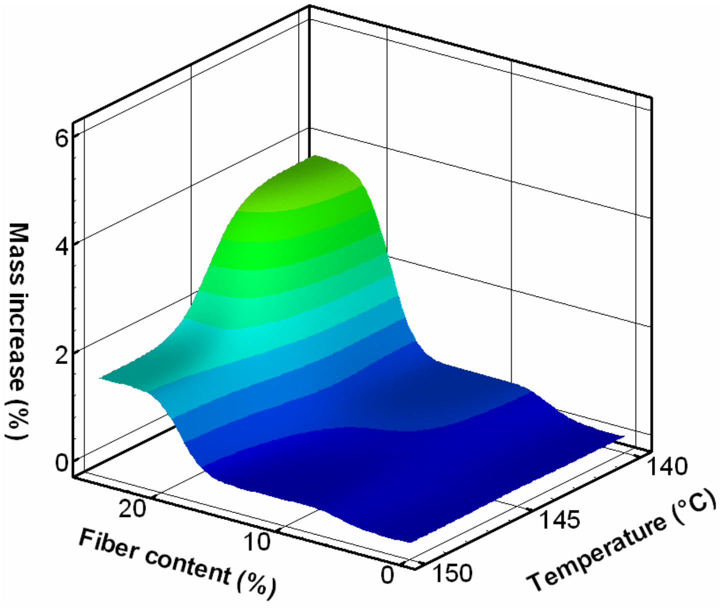


Figure 5.19 Response surface plots for the effects of fiber content, temperature and screw speed on the water absorption (%mass increase) HDPE composites.

5.11 Modeling

The effects of the three process variables (fiber content, temperature and screw speed) on each of the response variables (extrudate color, extrudate density, extrudate melt flow index, composite color, composite density, composite tensile strength and composite water absorption) were modeled and the equations determined using multiple linear regression and the stepwise method of the SAS software (SAS, 2003).

The limitation of this modeling, however, was that it only generated equations of the first order since there were only two levels (or factors) used in two process variables – temperature and screw speed (Cochran and Cox, 1957).

Following are the models generated:

a) Extrudate color (LLDPE):

Model: $\Delta E = 1.04(FC) + 6.44$

$R^2 = 0.82$

Fiber content (FC) $P < 0.05$

b) Extrudate color (HDPE):

Model: $\Delta E = 1.01(FC) + 7.61$

$R^2 = 0.81$

Fiber content (FC) $P < 0.05$

c) Extrudate density (LLDPE):

No variable met the 0.05 significance level for entry into the model.

d) Extrudate density (HDPE):

The R^2 value was too low (0.26) for the model to be reported.

e) Extrudate melt index (LLDPE):

Model: $MI = 2.96 - 0.09(FC)$

$R^2 = 0.94$

Fiber content (FC) $P < 0.05$

f) Extrudate melt index (HDPE):

Model: $MI = 5.45 - 0.17(FC) - 0.01(SS)$

$R^2 = 0.99$

Fiber content (FC) $P < 0.05$

Screw speed (SS) $P < 0.05$

g) Composite color (LLDPE):

The R^2 value was too low (0.47) for the model to be reported.

h) Composite color (HDPE):

Model: $\Delta E = 0.89(FC) + 6.95$

$R^2 = 0.64$

Fiber content (FC) $P < 0.05$

i) Composite density (LLDPE and HDPE):

No variable met the 0.05 significance level for entry into the model.

k) Composite tensile strength (LLDPE):

Model: $TS = 23.78 – 0.49(FC) – 0.05(SS)$

$R^2 = 0.78$

Fiber content (FC) $P < 0.05$

Screw speed (SS) $P < 0.05$

l) Composite tensile strength (HDPE):

Model: $TS = 22.05115 – 0.76(FC)$

$R^2 = 0.97$

Fiber content (FC) $P < 0.05$

m) Composite water absorption (LLDPE):

The R^2 value was too low (0.56) for the model to be reported.

n) Composite water absorption (HDPE):

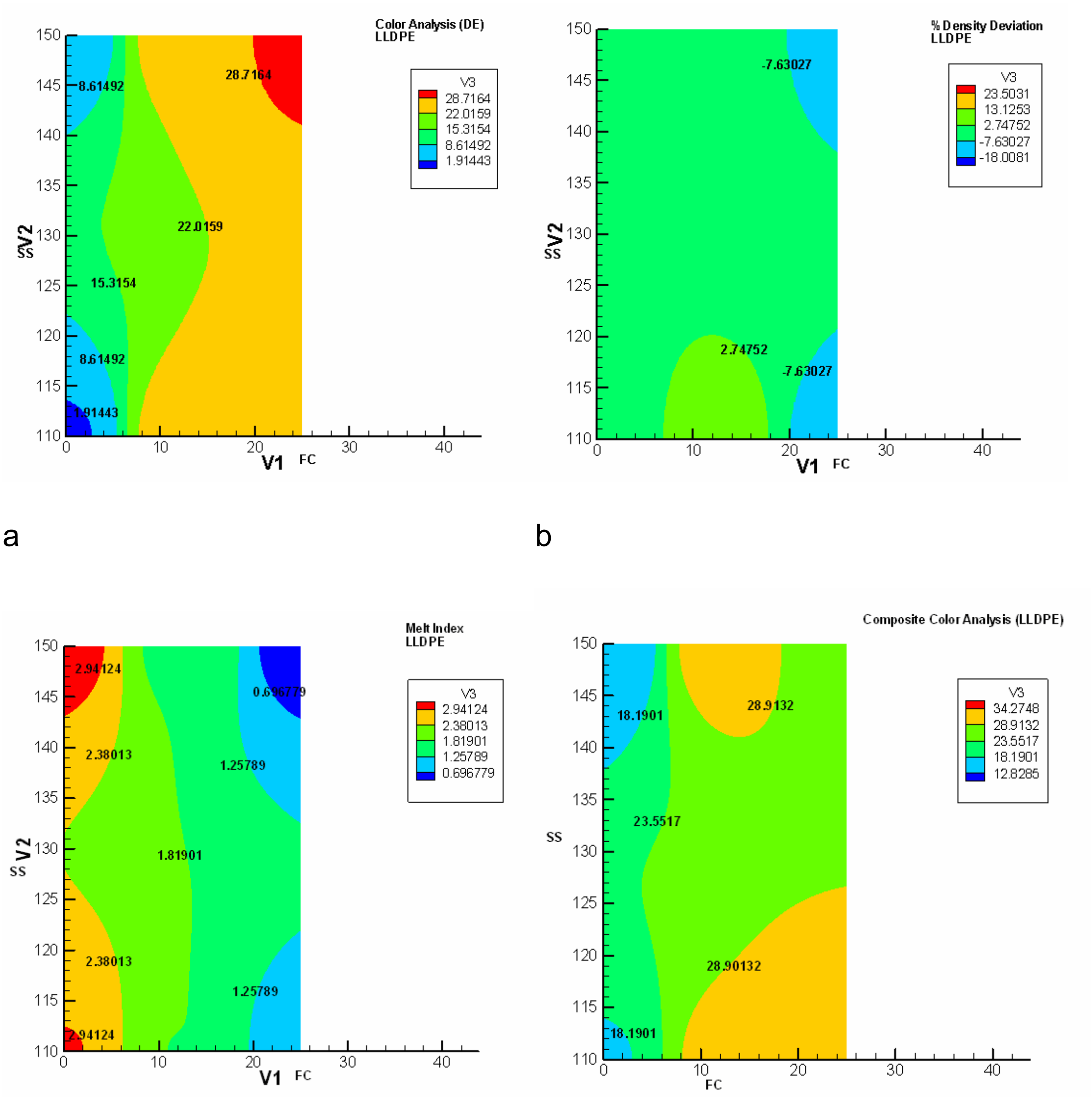
The R^2 value was too low (0.30) for the model to be reported.

5.12 Optimization

The graphical method was applied as an optimization technique (Carrillo et al., 2002). For LLDPE and HDPE composites, contour plots of the response variables (refer to appendix G) were utilized by applying superposition surface methodology to obtain three contour plots for observation and selection of the best (optimum) combination of fiber content (FC), temperature (T) and screw speed (SS) for the production of flax-fiber-reinforced polyethylene composites.

Contour plots were generated using Tecplot 9.2. The plots of LLDPE were separated from the plots of HDPE. LLDPE plots were again subdivided into three groups according to the two process variables involved: FC-SS (fiber content – screw speed) plots (1), FC-T (fiber content – temperature) plots (2) and T-SS (Temperature – Screw speed) plots (3). The same was done for the HDPE plots. Superposition of the plots within a group was carried out to determine the best combination of process variables (FC-SS, FC-T, and T-SS). Since there were two values for each variable, the two values were averaged to obtain the optimum value for each of the variables FC, T, and SS. This was done both for the LLDPE and HDPE treatments.

A sample computation follows. The following are LLDPE plots grouped according to the two variables [fiber content (FC) and screw speed (SS)] involved.

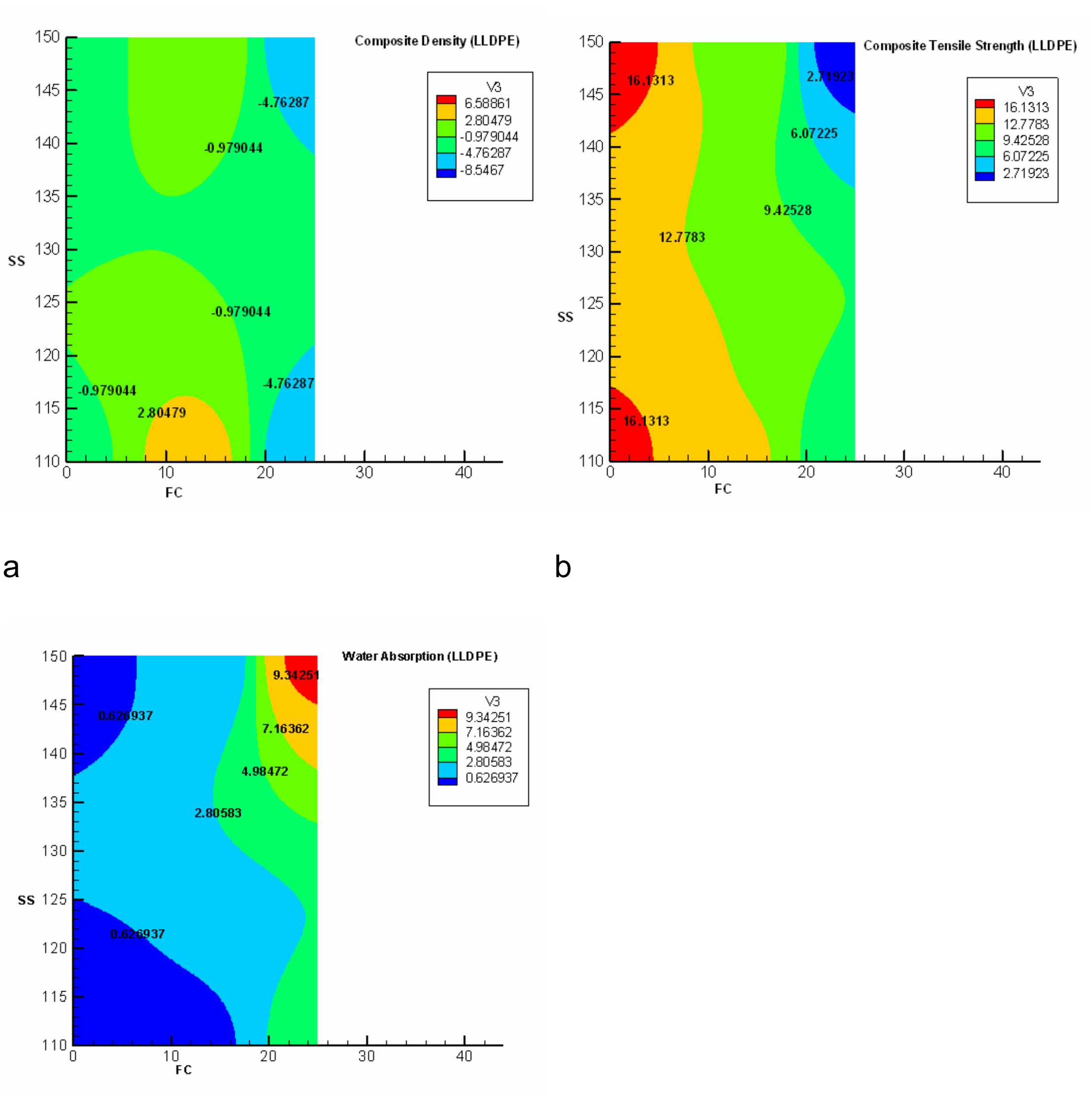

a

b

c

d

Figure 5.20 Contour plots (LLDPE) for the effects of fiber content (FC) and screw speed (SS) on the different response variables (extrudate color, extrudate density, extrudate melt flow index, and composite color).



a

b

c

Figure 5.21 Contour plots (LLDPE) for the effects of fiber content (FC) and screw speed (SS) on the different response variables (composite density, composite tensile strength, and composite water absorption).

Since the superposition could not be shown here, the contour plots were analyzed one by one.

The first plot (Figure 5.20a) shows the effect of fiber content (FC) and screw speed (SS) on extrudate color. The desired value would be the lowest value since it signifies proximity to the pure plastic color. The lowest value can be found on the FC level of 0% and the SS level of 110 rpm.

The second plot (Figure 5.20b) shows the effect of FC and SS on extrudate density. The desired value would be the highest value (most dense). The highest value lies on the FC level of 12.5% and the SS level of 110 rpm.

The third plot (Figure 5.20c) shows the effect of FC and SS on melt flow index. The desired value would be the highest value since this signifies the greatest flowability. The highest value lies on the FC level of 0% and the SS levels of 110 rpm and 150 rpm.

The fourth plot (Figure 5.20d) shows the effect of FC and SS on composite color. The desired value is the lowest value which can be found on the FC level of 0% and the SS levels of 110 rpm and 150 rpm.

The fifth plot (Figure 5.21a) shows the effect of FC and SS on composite density. The desired value (highest value) lies on the FC level of 12.5% and the SS level of 110 rpm.

The sixth plot (Figure 5.21b) shows the effect of FC and SS on composite tensile strength. The desired value is the highest value which lies on the FC level of 0% and SS levels of 110 rpm and 150 rpm.

The seventh plot (Figure 5.21c) shows the effect of FC and SS on the composite water absorption. The desired value would be the lowest value (least absorbent) and this can be found on the FC levels of 0% and 12.5% and the SS levels of 110 rpm and 150 rpm.

Table 5.15 summarizes these results.

Table 5.15 Optimum levels of fiber content (FC) and screw speed (SS) for the different response variables.

Response Variable	Levels with desired values	
	Fiber content (%)	Screw speed (rpm)
Extrudate color	0%	110 rpm
Extrudate density	12.5%	110 rpm
Extrudate melt index	0%	110 rpm and 150 rpm
Composite color	0%	110 rpm and 150 rpm
Composite density	12.5%	110 rpm
Composite tensile strength	0%	110 rpm and 150 rpm
Composite water absorption	0% and 12.5%	110 rpm and 150 rpm

To obtain the optimum levels for fiber content (FC) and screw speed (SS), the values were averaged:

$$FC = \frac{0\%(5) + 12.5\%(3)}{8} = 4.69\%$$

$$SS = \frac{110(7) + 150(4)}{11} = 124.55 \text{ rpm}$$

The preceding values were the optimum levels derived from the subgroup LLDPE FC-SS contour plots. The same procedure was done for the subgroup LLDPE FC-T plots and the LLDPE T-SS plots, generating two values each for FC, T and SS variables. The two values were averaged to finally arrive at the optimum values of FC, T and SS for LLDPE. The same procedure was applied to the HDPE contour plots.

Table 5.16 presents the computed optimum values for both LLDPE and HDPE.

Table 5.16 Optimum values of process variables fiber content (FC), temperature (T), and screw speed (SS) for LLDPE and HDPE composites based on extrudate color, extrudate density, extrudate melt flow index, composite color, composite density, composite tensile strength and composite water absorption.

Process Variable	Optimum Values	
	LLDPE	HDPE
Fiber content (FC)	4.69%	3.96%
Temperatures (T)	146.7°C or 75-116.7-126.7-136.7-146.7°C	147.7°C or 75-117.7-127.7-137.7-147.7°C
Screw speed (SS)	120.13 rpm	125 rpm

The preceding table presents the optimum values of the three process variables FC, T and SS based on the seven response variables, including extrudate color and composite color.

The purpose of including the response variables extrudate color and composite color was to measure the degree of degradation of the flax fibers. However, it was observed that the fibers never underwent degradation during the whole process since process temperatures used for both extrusion and rotational molding did not go beyond the degradation temperature of flax fibers (213.9°C – refer to appendix A). Hence, we can exclude the two response variables in the optimization process.

Table 5.17 presents the optimum values of the three process variables FC, T and SS based on the remaining five response variables: extrudate density, extrudate melt flow index, composite density, composite tensile strength and composite water absorption.

Table 5.17 Optimum values of process variables fiber content (FC), temperature (T), and screw speed (SS) for LLDPE and HDPE composites based on extrudate density, extrudate melt flow index, composite density, composite tensile strength and composite water absorption.

Process Variable	Optimum Values	
	LLDPE	HDPE
Fiber content (FC)	6.25%	5.02%
Temperatures (T)	147.3°C or 75-117.3-127.3-137.3-147.3°C	148.1°C or 75-118.1-128.1-138.1-148.1°C
Screw speed (SS)	117.5 rpm	125.56 rpm

6. SUMMARY AND CONCLUSIONS

Flax fibers have the ability to reinforce plastics due to their low cost, high specific strength and biodegradability, but their use has been limited by temperature sensitivity, degradation by moisture, variation in quality, poor surface adhesion to hydrophobic polymers and separation from polymer during rotational molding and non-homogenous mixture. All of these disadvantages contribute to the poor performance of the composite. Numerous researches have dealt with the effect of retting, physical modifications and chemical pre-treatments on composite properties to address the first four disadvantages, but a very few have dealt with the process of extrusion compounding which addresses the last two disadvantages.

The goal of this study, therefore, was to focus on extrusion compounding and its parameters (barrel zone temperature and screw speed) as a solution to these problems and to ensure that the flax fibers were uniformly dispersed within the melt, thus yielding extrudates and composites with better properties.

The objectives of this study were: (1) to compare the effects of fiber content and extrusion parameters on extrudate properties, namely color, density, melt flow index and morphology (dispersion and adhesion of fibers and porosity); (2) to compare the effects of fiber content and extrusion parameters on rotationally-molded composite properties such as color, density, morphology (dispersion and adhesion of fibers and porosity), tensile strength and water absorption; (3) to quantify, through regression models, the effects of fiber content, screw speed and temperature on the aforementioned extrudate and composite properties; and, (4) to determine the optimum values for fiber content and extrusion parameters (screw speed and barrel zone temperatures) in the production of rotationally-molded composites using linear low density polyethylene (LLDPE) and high density polyethylene (HDPE).

To address objectives 1 and 2, nine tests were conducted, namely extrudate color analysis, an extrudate density test, an extrudate melt flow index test, extrudate scanning electron microscope (SEM) image analysis, composite color analysis, a composite density test, composite scanning electron microscope (SEM) image analysis, a composite tensile test and a composite water absorption test. Results showed that the lowest level of fiber content (0%), the higher level of temperatures (T2 = 75-120-130-140-150°C) and the lower level of screw speed (110 rpm) resulted in better properties.

To address objective 3, multiple linear regression models were generated to quantitatively show the significant effects of the process variables on the response variables.

To address objective 4, superposition surface methodology was utilized to come up with the optimum values. The optimum level of temperature for HDPE was higher than that of LLDPE because HDPE composites have a higher melting point (130.34°C for LLDPE with silane treated fibers and 133.38°C for HDPE with silane treated fibers) (Wang, 2004).

The optimum values for temperatures (T) were closer to the higher levels (T2 = 75-120-130-140-150°C) because the lower temperatures resulted in inconsistent and uneven melting, leading to higher porosity, lower density, higher water absorption, non-uniform dispersion of the fibers and, eventually, poorer mechanical properties.

The optimum values for screw speed (SS) were closer to the lower level (110 rpm) because the higher screw speed led to shorter residence time, uneven melting, non-uniform dispersion of fibers, higher porosity, lower density, higher water absorption and, consequently, poorer mechanical properties.

What was unexpected, though, was the very low optimum level of the fiber content. The flax fibers should have improved the mechanical properties of the composites, yet the results for tensile strength negated this. The higher fiber content resulted in a slower melt flow, especially in the rotational molding process, uneven melting, non-uniform dispersion of fibers, higher porosity, lower density, higher water absorption and, hence, poorer mechanical properties.

7. RECOMMENDATIONS

Extrusion compounding is a process that solves the problems of non-homogeneous mixture and separation of dry-blended flax fibers from the polymer matrix during rotational molding. Until now, there has never been a study that determined the optimum values for extrusion parameters such as temperature and screw speed in producing flax-fiber-reinforced LLDPE and HDPE composites. Temperature limitations include inconsistent melting (and, thus, non-uniform dispersion of fibers) in the low range and fiber degradation in the high range. Screw speed limitations, on the other hand, include longer residence time and low throughput in the low range and fiber degradation through shear and air entrapment in the high range. Using superposition surface methodology over five response variables (extrudate density, extrudate melt flow index, composite density, composite tensile strength, and composite water absorption), this study has identified optimum values for extrusion parameters to be used for LLDPE composites (temperature = 75-117.3-127.3-137.3-147.3°C and screw speed = 117.5 rpm) and HDPE composites (temperature = 75-118.1-128.1-138.1-148.1°C and screw speed = 125.56 rpm). It is recommended that the optimum values obtained in these experiments for temperature (T) and screw speed (SS) be used for future extrusion compounding experiments.

Along with the values for extrusion parameters, this study has also determined optimum values for fiber content. However, the optimum values were too low (fiber content = 6.25% for LLDPE composites and 5.02% for HDPE composites) to be recommended for use. This could be attributed to rotational molding. During the rotational molding trials, the parameters used (temperature of 180-200°C and time of 20 minutes) were already the maximum threshold values, in that the fibers would have degraded beyond 200°C and it would have been less economical for the plant to use more than 20 minutes of processing time (average time of processing in the plastics plant). Yet, these maximum threshold values were not enough to ensure a consistent melt, which resulted in high porosity, especially for treatments with 25% fiber content. Further study, therefore, is recommended, with a focus on rotational molding parameters (heating temperature, heating time and ratio of biaxial rotation) and the inclusion of additives such as flow enhancers and heat stabilizers. Flow enhancers would, hopefully, increase melt flow, thus preventing porosity and ensuring uniform dispersion of fibers for effective use of the flax fibers as reinforcement and not just as fillers. The heat stabilizer would, hopefully, enable working at higher temperatures to ensure consistent melting and minimizing porosity without degrading the flax fibers.

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APPENDICES

APPENDIX A

Optimum processing conditions for rotational molding in making flax fiber-reinforced polyethylene composites

ABSTRACT

Rotational molding processing conditions are important considerations in the making of flax-fiber-reinforced polyethylene composites. Low temperatures and short heating times result in inconsistent melt of the polymer matrix while high temperatures and longer times result in flax fiber degradation. An optimal mix of temperature and heating time is thus required. In this study it was found that the optimum processing conditions are a temperature of 180°C and a heating time of 20 minutes.

Keywords. Rotational molding temperature, heating time, degradation, flax fiber

INTRODUCTION

Applications of flax fiber-reinforced thermoplastic composites are becoming popular, yet problems of low performance are still being encountered. To address this problem, various ways to improve the performance have been studied. These include retting, physical modification, chemical pre-treatment and extrusion compounding.

In their study on the extrusion compounding of flax-fiber-reinforced thermoplastic composites, the researcher and co-workers (Siaotong et al., 2004) concluded that the extrusion process had a positive effect on the composite, i.e. uniform dispersion of flax fibers in the thermoplastic matrix.

One major problem of the aforementioned study, however, was the inadvertent use of relatively high rotational molding temperatures (275°C and 285°C) and heating times (15 and 30 min) which caused fiber degradation (as evidenced by darkening of the product and odor emission), and air bubble formation consequently producing porous composites, thereby weakening the final product. A further study on the determination of the optimum values for temperature and heating time in rotational molding was recommended to prevent degradation of the flax fiber.

Fiber degradation has been investigated by a number of researchers. In a study on the manufacturing of sisal-polypropylene composites, Jayaraman (2003) noted that the common methods of manufacturing fiber-reinforced thermoplastic composites, namely injection molding and extrusion, tended to degrade the fibers during processing. This was further confirmed by Fung and co-workers (2003) in an investigation on the processing of sisal-fiber-reinforced polypropylene composites. It was found that an elevated injection molding temperature can cause severe thermal degradation of the reinforcing sisal fibers, giving rise to darkening of color and odor emission of the molded sisal fiber-polypropylene composites. Thermal gravimetric analysis (TGA) was employed to study the high temperature decomposition characteristics of the sisal fiber. It was further pointed out that the stability of sisal fibers under high melt processing temperature was of major concern because if serious degradation of the sisal fibers took place during the melt processing of the composites, the mechanical reinforcement effects of the sisal fibers would be lost.

Studies on flax fiber also showed similar results. In an overview of several properties of thermoplastic polymers, Van de Velde and Kiekens (2001) concluded that temperature-related properties seemed to be the limiting criteria for the choice of a suitable polymer because of the heat sensitivity of flax. In fact, in another overview of several properties of biopolymers, Van de Velde and Kiekens (2002) reported that in the specific case of a flax-reinforced plastic, the application temperature of the product should remain relatively low because of the possible degradation of flax when exposed to elevated temperatures for prolonged period of time. This led to the conclusion that polyglycolic acid (PGA) was not suited for use in combination with flax because the former would require a process temperature of 250°C or higher, which would lead to thermal degradation of the flax. In a study on the melt mixing process for flax-fiber-reinforced polypropylene, Jakobsson (2000) reported that fiber degradation affected the mechanical properties of the composites and was one of the functions of the process variables.

In view of the gravity of the problem of fiber degradation, a number of researchers tried to determine the degradation temperature of flax fibers. Van de Weyenberg (Composite Materials Group, 2001) conducted degradation tests on flax fibers and the respective composites. It was found that the fiber started to rapidly degrade at temperatures above 200°C. Wielage and co-researchers (1999) studied the thermal stability of flax and hemp fibers using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In that study, there was a slight decrease of the mass of natural fibers between 200 and 220°C. Above 220°C, irreversible degradation was observed. Finally, in the study of the engineering properties of flax fibers, Powell and co-workers (2002) concluded that pure flax fiber generally followed a decomposition curve beginning at approximately 200-210°C and ending at 400°C.

It was, therefore, the aim of this work to determine the optimum (to prevent fiber degradation) processing conditions (temperature and heating time) for flax-fiber-reinforced polyethylene composites during rotational molding. To do so, composites were prepared by chemically treating the fibers, extruding the flax fiber and polymer mixture, and rotationally molding the ground extrudates at different processing conditions.

MATERIALS AND METHODS

Materials

For use as a reinforcing material in the production of polyethylene composites, oilseed flax fibers (procured from by Biolin Research, Saskatoon, SK, Canada) were subjected to fiber surface treatment with the use of triethoxyvinylsilane, ground and mixed with powdered linear low-density polyethylene (LLDPE 8460.29) (Exxon Mobil, Toronto, ON, Canada) as polymer matrix.

Fiber surface treatment and preparation

The flax fibers were washed with warm water then soaked in hot water (approximately 50°C), after which, the fibers were dried and then soaked in 5% sodium hydroxide (NaOH) solution for 30 min to activate the hydroxyl groups. After 24 hours of oven-drying at 80ºC, the fibers were soaked for 30 minutes in a 60:40 ethanol/water mixture with triethoxyvinylsilane. Finally, the fibers were washed with deionized water and oven-dried for 24 hours at 80ºC (a low temperature was maintained to prevent fiber degradation over time). Oven-dried fibers were ground using Retsch GmbH grinder (type SM1) (5657 Haan, West Germany) equipped with a 4-mm screen. The preceding procedures were based on the methodology reported by Wang and co-workers (2003).

Experimental variables and constants

The experimental variables were rotational molding processing conditions: temperature and residence time. The constants were fiber content and extrusion temperatures.

Rotational molding temperature. Temperature limitations in rotational molding result from either the inability to add enough heat to get a consistent melt in the polyethylene or the inability to remove enough heat from a melt to prevent flax fiber degradation. Temperatures used were 160, 180, 200, and 240°C.

Rotational molding heating time. Heating time in rotational molding is important in that it has to be increased to properly melt the polyethylene at a given temperature, but it has to be maintained at a level where it will not degrade the fiber and it will not be costly to the rotational molding company. Heating times used were 18, 20, 25, and 30 min.

Fiber content. Fiber loading used was 12.5% w/w.

Extrusion temperature. Temperatures for each of the five barrel zones were 75,130,140,150, and 160ºC, respectively.

Extrusion compounding

Extrusion was done with a co-rotating, twin-screw (ZSK type) extruder (Werner and Pfleiderer, Stuttgart, Germany) at the Center for Agri-Industrial Technology (CAIT) in Edmonton, AB, Canada. The extruder barrel had both heating and cooling capability. Heating was done with electrical band heaters located along the length of the extruder. Most extruders have three to eight temperature zones. Each zone has its own heating and cooling capability and at least one temperature sensor to measure the zone temperature (Rauwendaal, 1998). The extruder used in this study had five temperature zones (Fig. 1), each of which had a heater, the temperature of which could be controlled. Barrel temperatures (of the five zones) used were 75-130-140-150-160ºC. The screw speed used was 110 rpm.

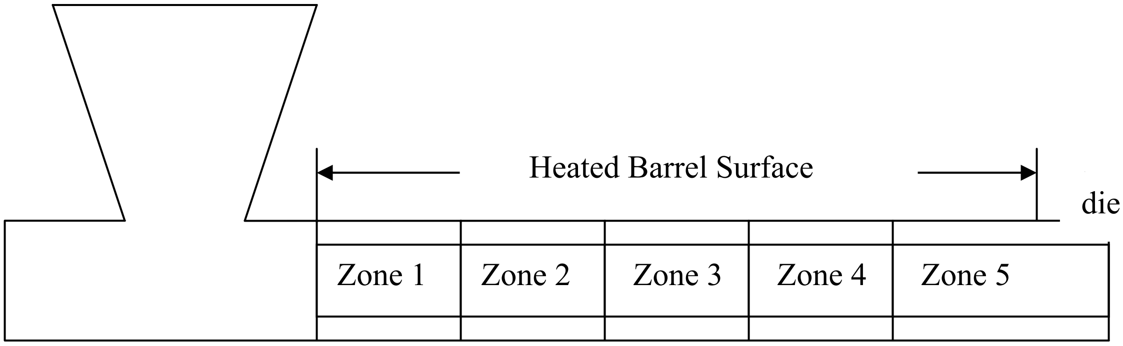

Figure 1. Schematic diagram of the extruder with the five separate heating. zones

Rotational molding

This study utilized the carousel rotational molding machine at Norwesco Canada Ltd., Saskatoon, SK, Canada. To make composites, pre-measured ground extrudates were first loaded into a mold. The mold was then moved into the oven at set temperatures (160, 180, 200, and 240°C) where it was slowly rotated on both the vertical and the horizontal axes with a rotation ratio of 5:1.

The molding process is described as follows. The melting extrudate sticks to the hot mold and coats every surface evenly. The mold continues to rotate during the cooling cycle so the parts retain an even wall thickness. Once the parts are cooled, they are released from the mold. The rotational speed, heating and cooling times were all controlled throughout the process. For this study, heating times used were 18, 20, 25, and 30 min, while the cooling time used was 16 min.

Materials characterization

The effects of the rotational molding variables were analyzed in terms of the degree of degradation (as indicated by color changes). For this, the HunterLab Color Analyzer was used. The differential scanning calorimeter was also used to determine the degradation temperature of the chemically treated flax fiber as a basis for the choice of the optimum temperature in rotational molding, along with values obtained from literature.

Color measurement. The color, as an indicator of the degree of degradation, was measured (and compared) using the HunterLab Color Analyzer–LabScan System (Hunter Associates Laboratory, Inc., Reston, Virginia, USA). The system generates values of L (0=black to 100=white), a (-a=green to +a=red) and b (-b=blue to +b=yellow).

For this study, three sides of the rotationally molded composites (boxes) were exposed to the reflectance port. Since the degree of degradation, which is evidenced by darkening, was the factor under consideration, only the L values (black to white) were used and averaged.

Differential scanning calorimetry. The differential scanning calorimetry experiment in this paper was performed using a temperature modulated DSC in conventional mode, a refrigerated cooling system (TA Instruments, New Castle, DE, USA), and a nitrogen gas DSC cell purge. The DSC 2910 system (TA Instruments, New Castle, DE, USA) was calibrated for enthalpy and temperature readings using a standard of high purity elemental indium. The samples were ground and immediately weighed into aluminium hermetic pans and then sealed. The sample weight was 7.3 mg. An empty crimped pan was used as a reference sample. The DSC system was operated in a dynamic mode with a heating scheme of 10ºC to 250ºC at a heating rate of 10ºC/min. A chart of heat flow versus temperature was produced.

RESULTS AND DISCUSSIONS

The choice of optimum values for temperature and heating time would be dependent on a number of factors, namely the degradation temperature of the flax fiber, the consistency of melt of the polyethylene, rotational molding cost efficiency, and the degree of degradation (as evidenced by a darkening in color and the emission of odors) of rotationally-molded products.

Degradation temperature of the flax fiber

Based on the literature, flax fibers begin to degrade between 200 and 220°C (Composite Materials Group, 2001; Wielage et al. 1999; Powell et al. 2002). For this study, it was found that chemically treated fibers began to degrade at 213.9°C (Fig. 2). This degradation temperature, along with the temperatures mentioned in literature, will be one of the bases for choosing the optimum rotational molding temperature.

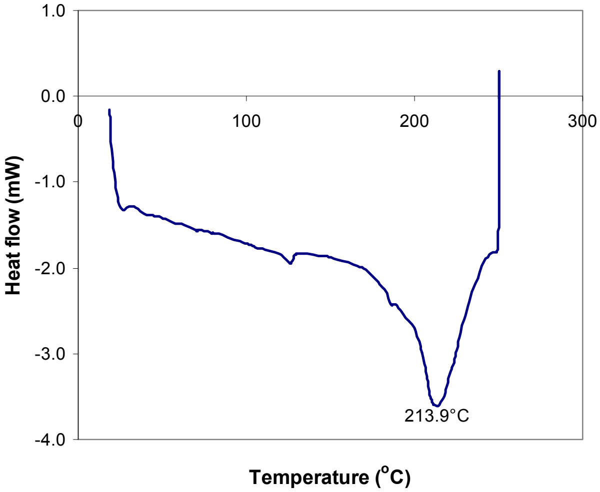

Figure 2. DSC analysis of the treated flax fiber. The value shown (213.9°C) is the onset of degradation.

Consistent melt of the polyethylene

Results showed that a temperature of 160°C and a heating time of 18 min did not result in a consistent melt of the polyethylene. However, with a temperature starting at 180°C and a heating time starting at 20 min, a consistent melt was attained. This is confirmed by the study of Liang and co-workers (1999) who were investigating the effects of pressure and temperature on melt density and the melt flow rate of LDPE and glass bead-filled LDPE composites. In their study, it was discovered that the melt flow rate (MFR) increased exponentially with temperature. Moreover, in the study on the effect of extrusion parameters on melt flow and the mechanical properties of high density polyethylene, Mokhtar and co-researchers (2003) concluded that at a given pressure and die length, the flow increases with temperature.

Rotational molding cost efficiency

Heating times used were 18, 20, 25, and 30 min. The use of 18 min as the heating time did not really result in a consistent melt for polyethylene, especially at lower temperatures. The heating times of 20, 25 and 30 min were enough to get a consistent melt. However, most of the products that the rotational molding company produces use a maximum of 20 minutes as heating time; therefore, it will be uneconomical to use 25 and 30 minutes as a heating time. Since 18 min did not produce a consistent melt, 20 minutes is being recommended at this.

Degree of degradation

Figure 3 shows a graph of the relationship between rotational molding temperature and degree of degradation based on the L-value of HunterLab color analysis. As expected, there is a decreasing trend in the Hunter Lab L-values (100 for white and 0 for black) which means that as the temperature rises, the fibers start to degrade as evidenced by the darkening color of the composites. Analysis of variance and linear regression proves that the temperature had a significant effect on the Hunter L-values with a probability of less than 0.01 and an R-square value of 0.96. Duncan's Multiple Range Test of Means reveals that all the means are significantly different from one another.

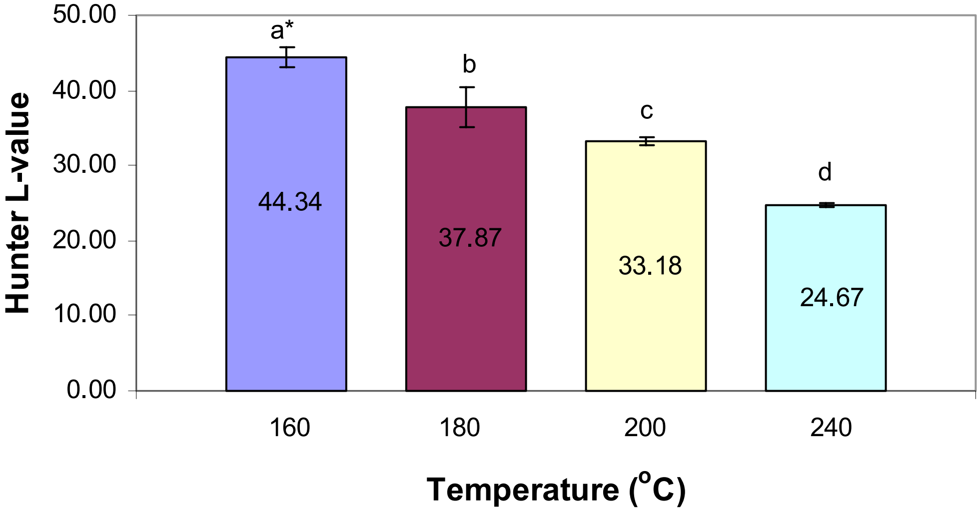

Figure 3. Hunter L-values of rotationally molded composites as affected by temperature. *Means with different letters are significantly different.

The value for 160°C is ideal but, unfortunately, it cannot be used since it did not yield a consistent melt in the polyethylene. The 180, 200, and 240°C treatments all yielded a consistent melt. However, the last two temperatures resulted in very low L-values and caused odor emissions in the final product. Hence, the use of 180°C as a heating temperature during rotational molding is recommended.

CONCLUSION

A temperature of 180°C was found to be the optimum value for rotational molding because: (1) it is less than the degradation temperature of the chemically-treated flax fibers (213.9°C); (2) it produces a consistent melt in the polyethylene; and (3) the color was not as dark as those with 200°C and 240°C.

The heating time of 20 minutes was found to be the optimum time for use in rotational molding because: (1) it yields a consistent melt in the polyethylene; and (2) it is more economical to use since most of the products molded at the rotational molding plant are molded at 17-20 minutes.

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APPENDIX B

Extruder Barrel Zones Temperature Log

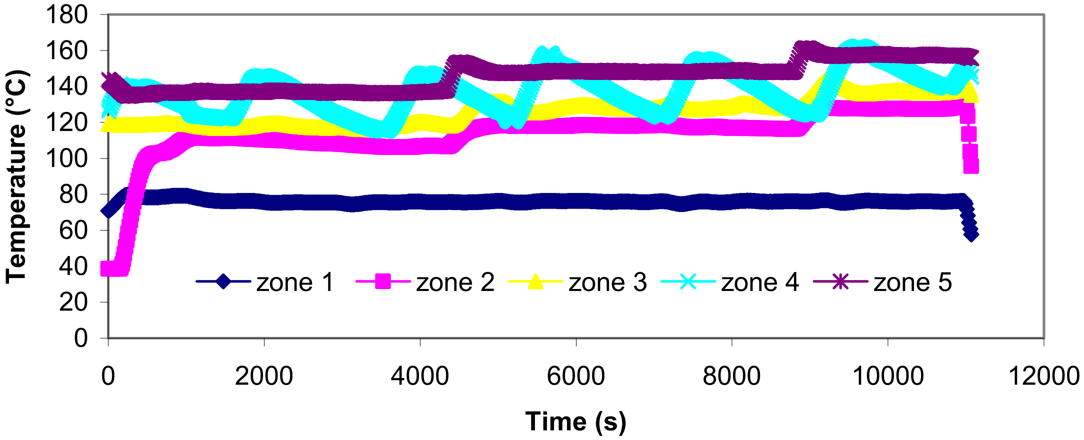


Figure B.1 Actual barrel zone temperatures set at the following settings: 1st setting at 0 s (75, 110, 120, 130, 140°C); 2nd setting after 4900 s (75, 120, 130, 140, 150°C) and 3rd setting after 9000 s (75, 130, 140, 150, 160°C).

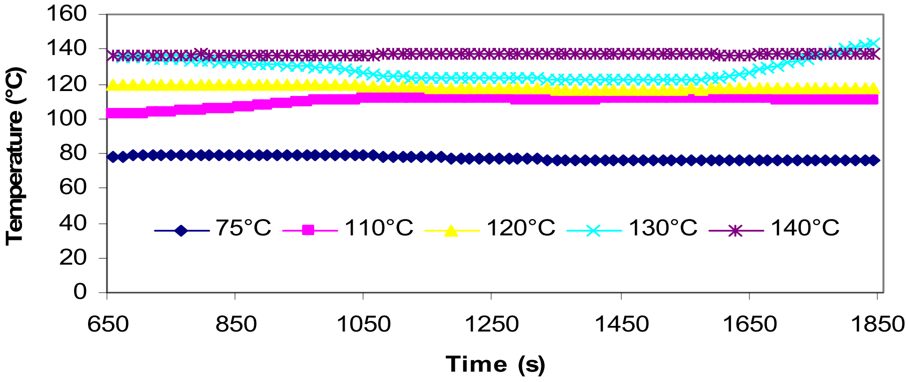


Figure B.2 Actual barrel zone temperatures during extrusion of HF1T1S1 (HDPE, 0% fiber content, 75°C, 110°C, 120°C, 130°C and 140°C temperatures, 110 rpm screw speed).

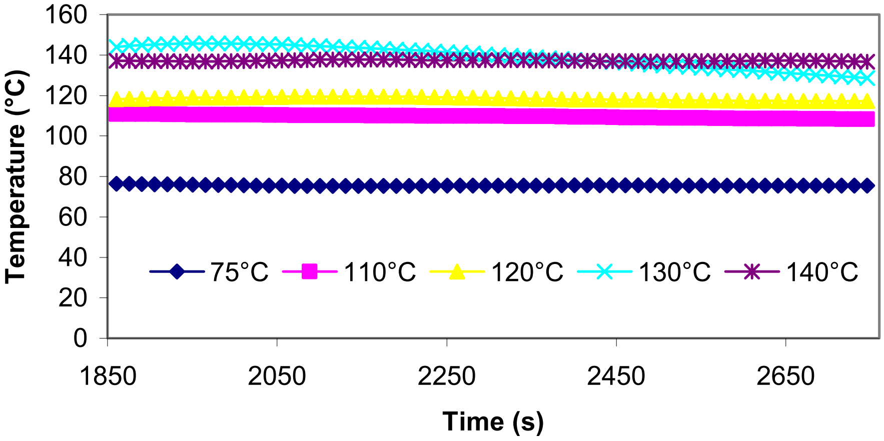


Figure B.3 Actual barrel zone temperatures during extrusion of HF2T1S1 (HDPE, 12.5% fiber content, 75°C, 110°C, 120°C, 130°C and 140°C temperatures, 110 rpm screw speed).

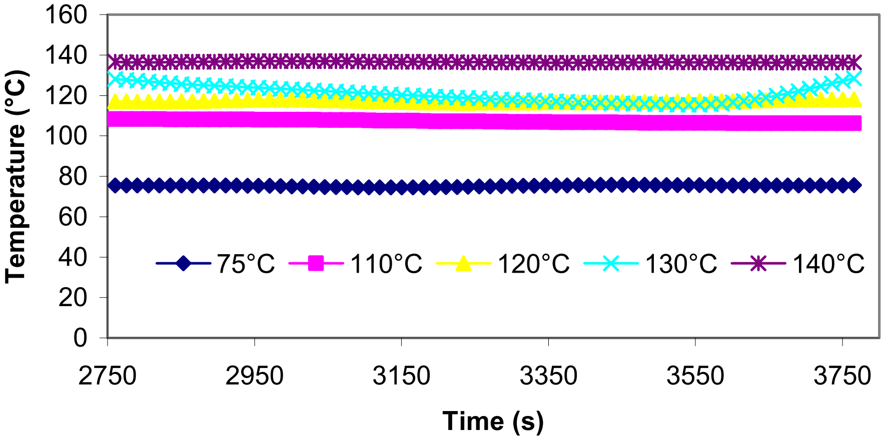


Figure B.4 Actual barrel zone temperatures during extrusion of HF1T1S2 (HDPE, 0% fiber content, 75°C, 110°C, 120°C, 130°C and 140°C temperatures, 150 rpm screw speed).

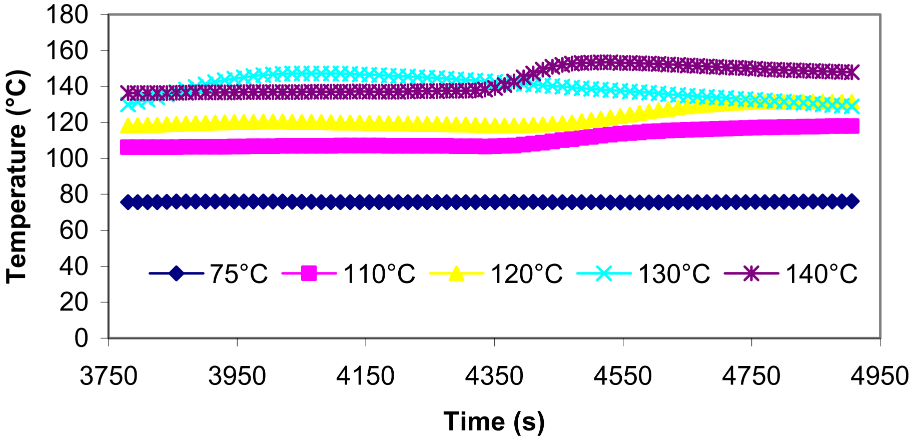


Figure B.5 Actual barrel zone temperatures during extrusion of HF2T1S2 (HDPE, 12.5% fiber content, 75°C, 110°C, 120°C, 130°C and 140°C temperatures, 150 rpm screw speed).

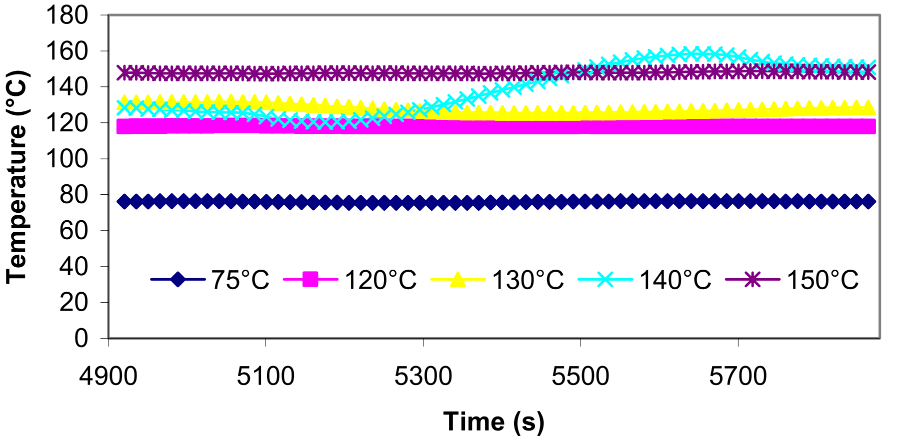


Figure B.6 Actual barrel zone temperatures during extrusion of HF1T2S1 (HDPE, 0% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 110 rpm screw speed).

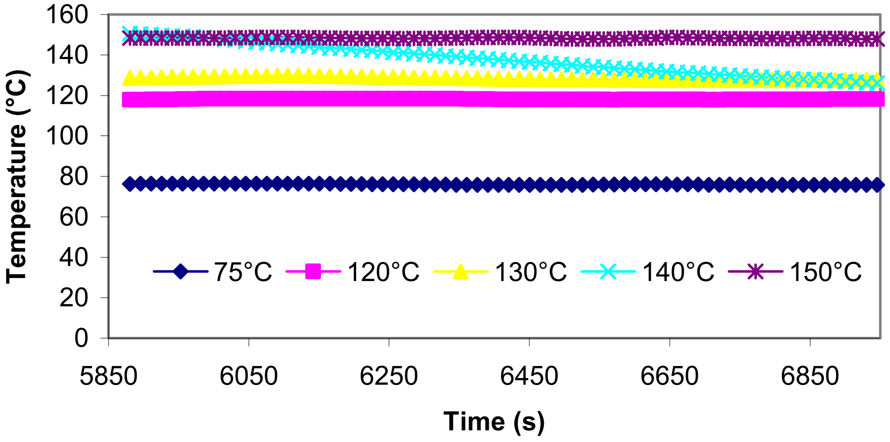


Figure B.7 Actual barrel zone temperatures during extrusion of HF2T2S1 (HDPE, 12.5% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 110 rpm screw speed).

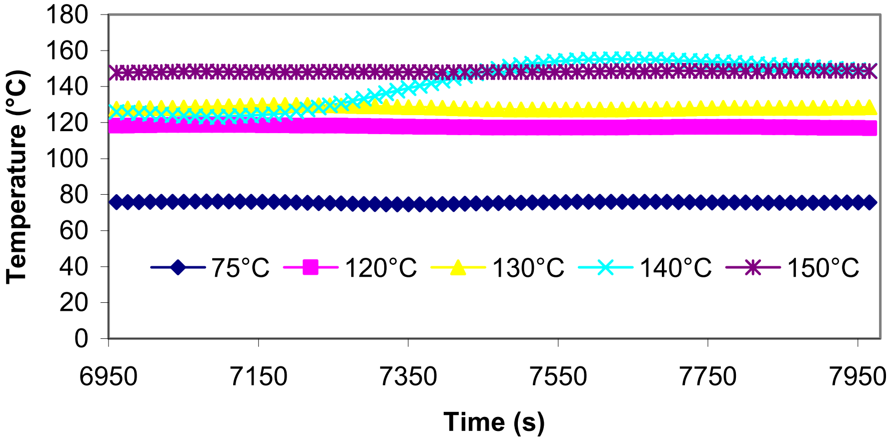


Figure B.8 Actual barrel zone temperatures during extrusion of HF1T2S2 (HDPE, 0% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 150 rpm screw speed).

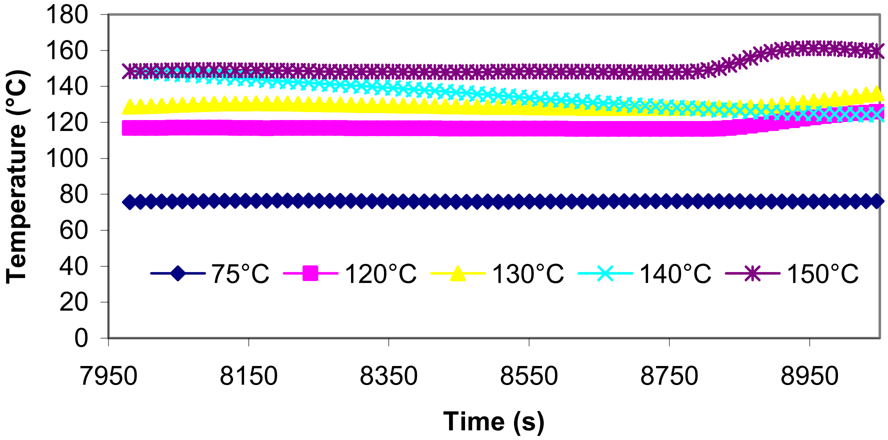


Figure B.9 Actual barrel zone temperatures during extrusion of HF2T2S2 (HDPE, 12.5% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 150 rpm screw speed).

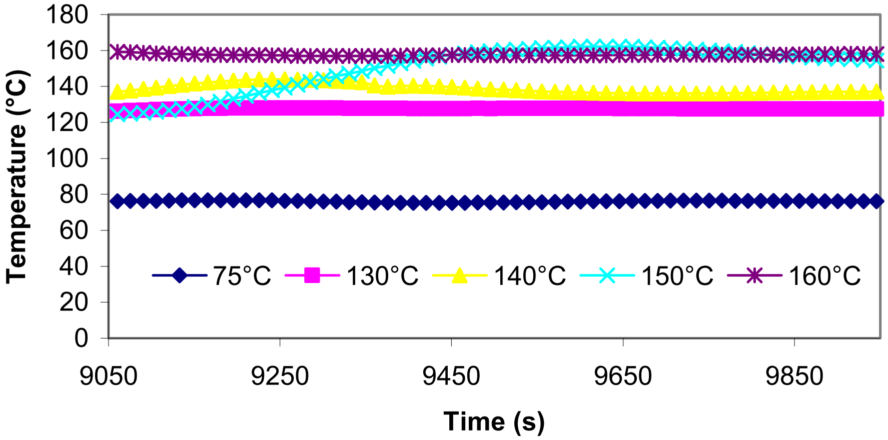


Figure B.10 Actual barrel zone temperatures during extrusion of HF1T3S1 (HDPE, 0% fiber content, 75°C, 130°C, 140°C, 150°C, and 160°C temperatures, 110 rpm screw speed).

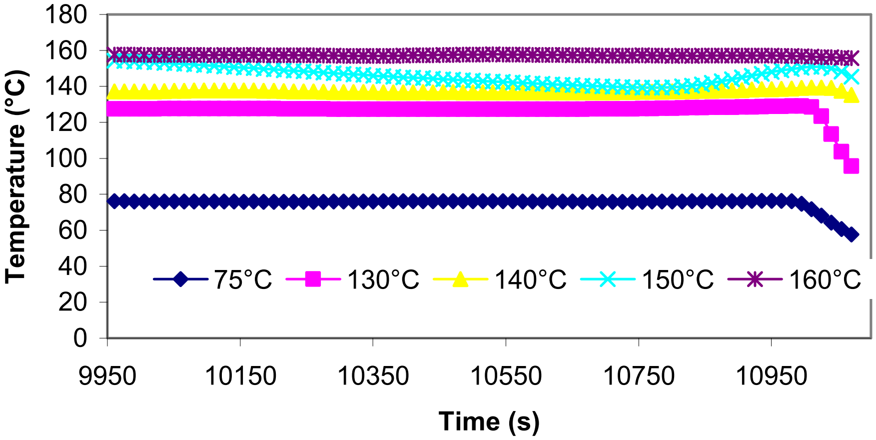


Figure B.11 Actual barrel zone temperatures during extrusion of HF1T3S2 (HDPE, 0% fiber content, 75°C, 130°C, 140°C, 150°C, and 160°C temperatures, 150 rpm screw speed).

APPENDIX C

Extruder Pressure Log

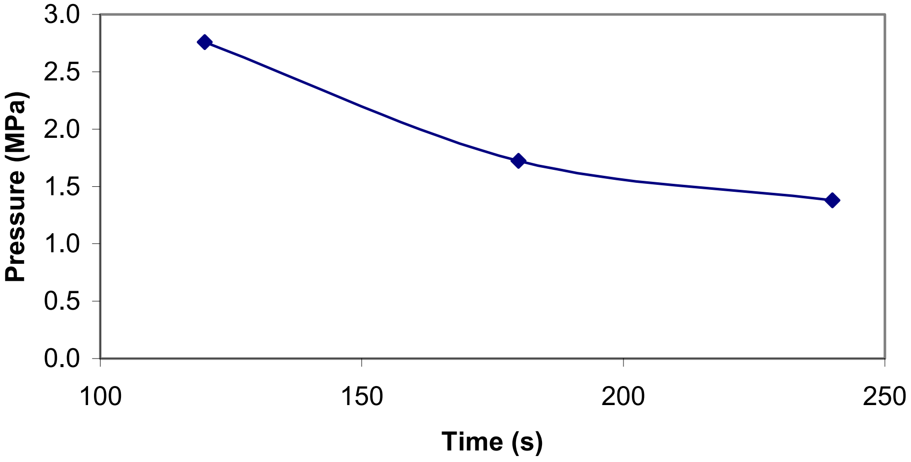


Figure C.1 Pressure readings during extrusion of HF1T1S1 (HDPE, 0% fiber content, 75°C, 110°C, 120°C, 130°C, and 140°C temperatures, 110 rpm screw speed).

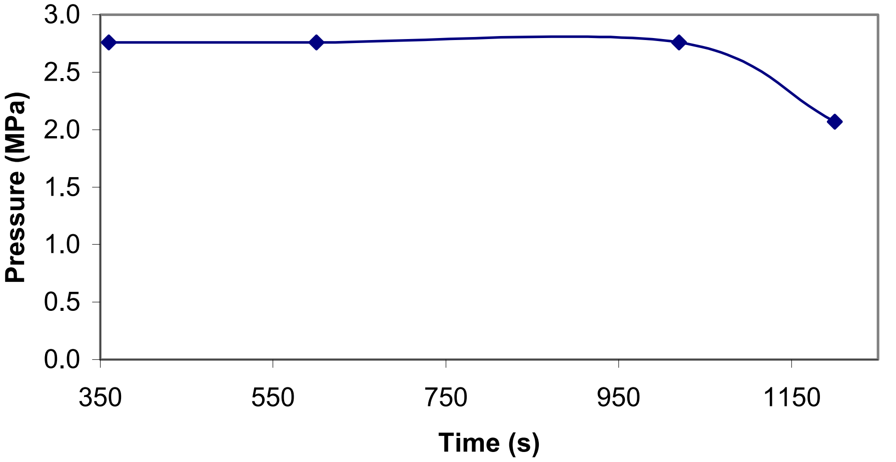


Figure C.2 Pressure readings during extrusion of HF2T1S1 (HDPE, 12.5% fiber content, 75°C, 110°C, 120°C, 130°C, and 140°C temperatures, 110 rpm screw speed).

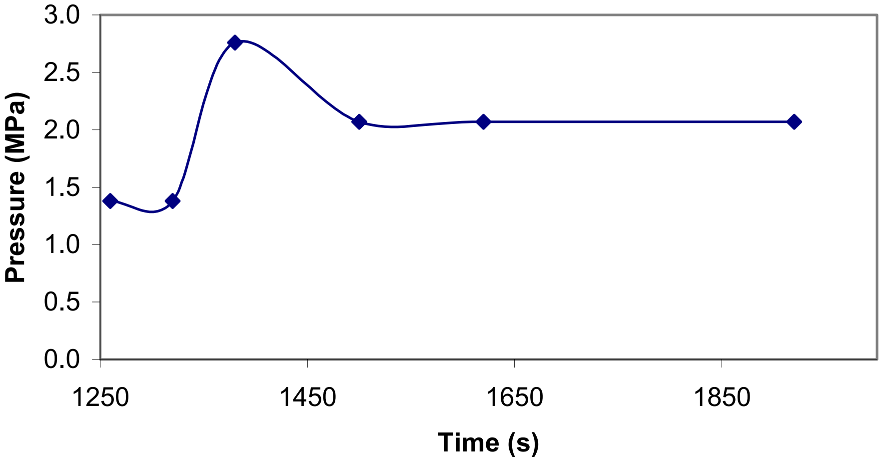


Figure C.3 Pressure readings during extrusion of HF1T1S2 (HDPE, 0% fiber content, 75°C, 110°C, 120°C, 130°C, and 140°C temperatures, 150 rpm screw speed).

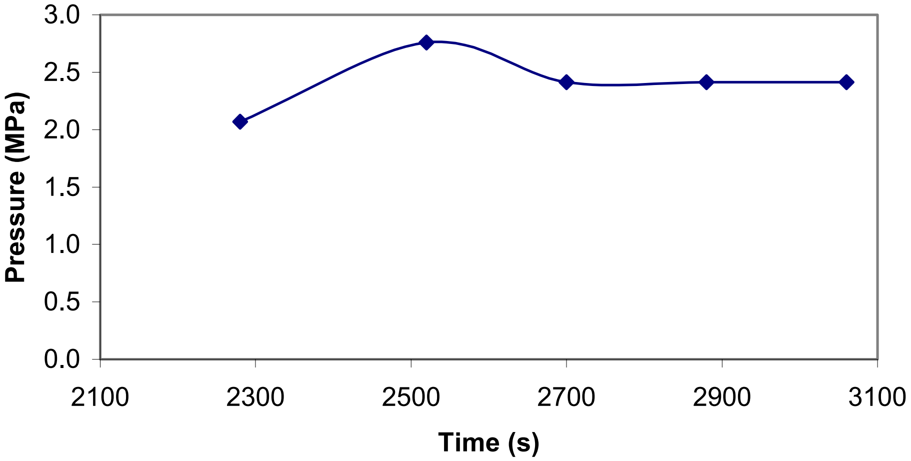


Figure C.4 Pressure readings during extrusion of HF2T1S2 (HDPE, 12.5% fiber content, 75°C, 110°C, 120°C, 130°C, and 140°C temperatures, 150 rpm screw speed).

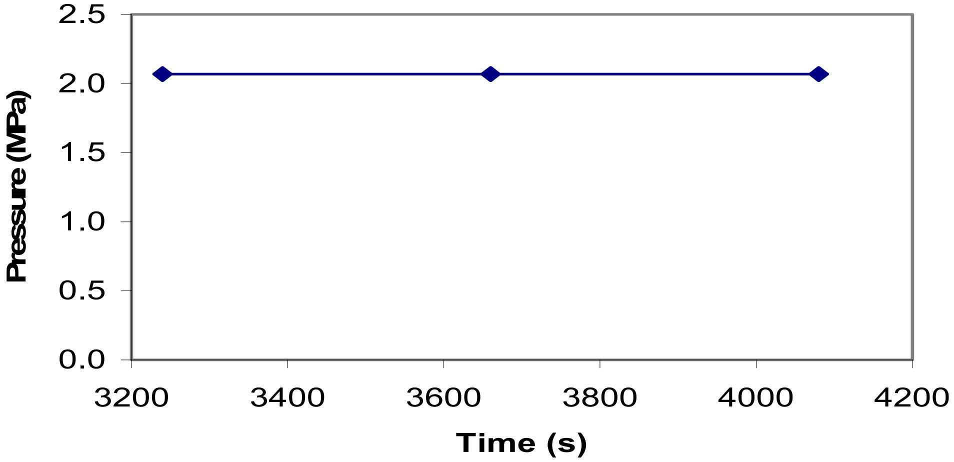


Figure C.5 Pressure readings during extrusion of HF1T2S1 (HDPE, 0% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 110 rpm screw speed).

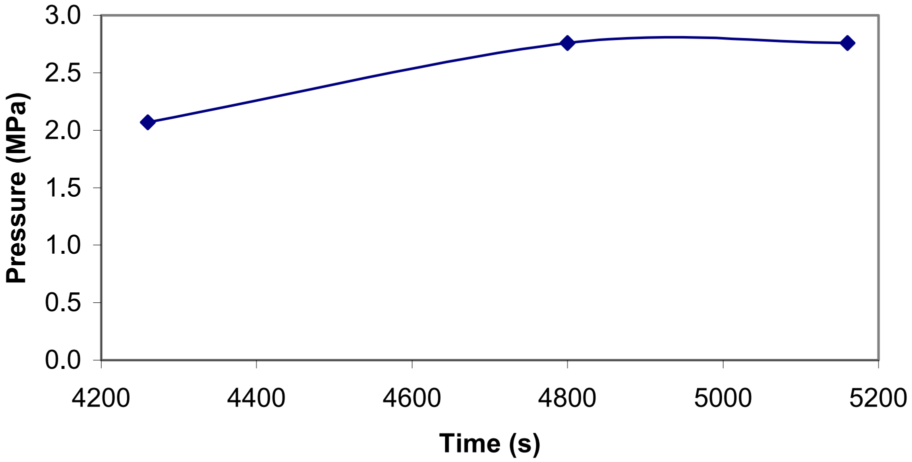


Figure C.6 Pressure readings during extrusion of HF2T2S1 (HDPE, 12.5% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 110 rpm screw speed).

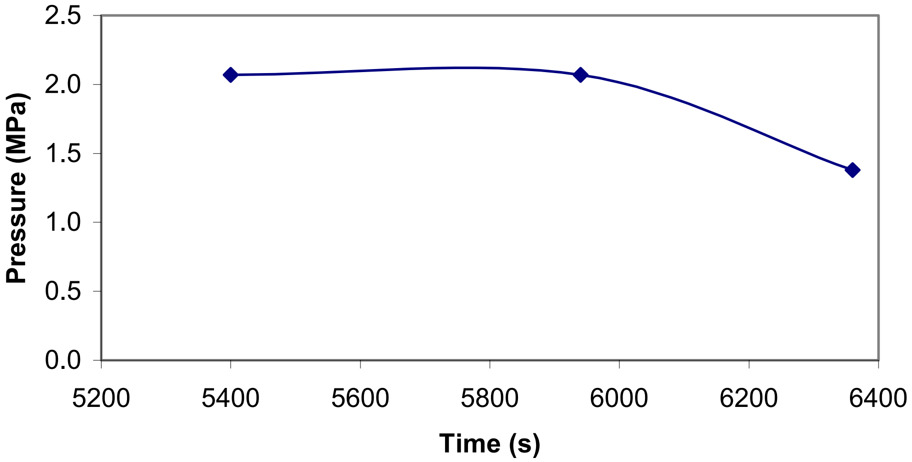


Figure C.7 Pressure readings during extrusion of HF1T2S2 (HDPE, 0% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 150 rpm screw speed).

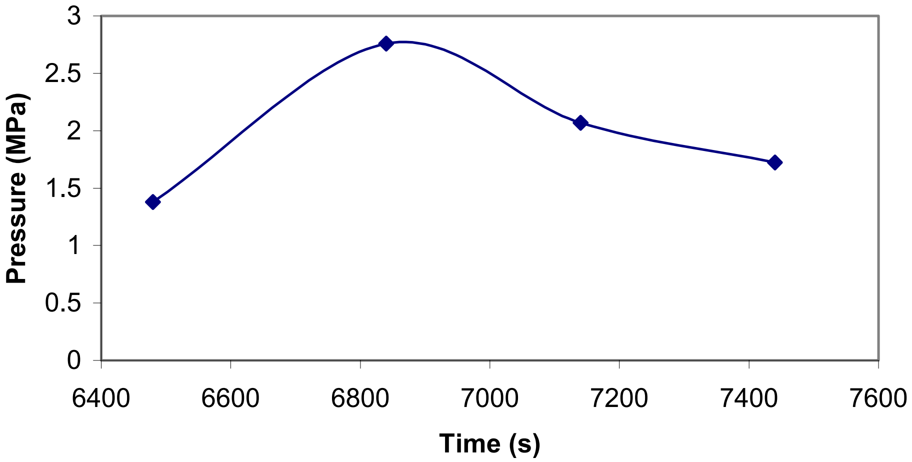


Figure C.8 Pressure readings during extrusion of HF2T2S2 (HDPE, 12.5% fiber content, 75°C, 120°C, 130°C, 140°C, and 150°C temperatures, 150 rpm screw speed).

APPENDIX D

Analyses of Variance (ANOVA)

Table D.1 Analysis of variance of color index for LLDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	14568.16	3642.04	1057.20	< 0.0001
Error	103	354.83	3.44		
Total	107	14923.00			
Fiber content	2	14405.18	7202.59	2090.75	< 0.0001
Temperature	1	131.14	131.14	38.07	< 0.0001
Screw speed	1	31.84	31.84	9.24	0.0030

Table D.2 Analysis of variance of color index for HDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	13688.81	3422.20	913.57	< 0.0001
Error	103	385.83	3.75		
Total	107	14074.64			
Fiber content	2	13670.89	6835.44	1824.75	< 0.0001
Temperature	1	5.42	5.42	1.45	< 0.0001
Screw speed	1	12.51	12.51	3.34	0.0030

Table D.3 Analysis of variance of density deviation for LLDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	2380.37	595.10	1.76	0.1612
Error	31	10453.35	337.20		
Total	35	12833.72			
Fiber content	2	1325.56	662.78	1.97	0.1572
Temperature	1	1051.18	1051.18	3.12	0.0873
Screw speed	1	3.63	3.63	0.01	0.9180

Table D.4 Analysis of variance of density deviation for HDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	3050.43	762.61	3.43	0.0196
Error	31	6887.68	222.18		
Total	35	9938.11			
Fiber content	2	468.03	234.02	1.05	0.3610
Temperature	1	2564.77	2564.77	11.54	0.0019
Screw speed	1	17.63	17.63	0.08	0.7800

Table D.5 Analysis of variance of melt index for LLDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	30.06	7.52	174.01	< 0.0001
Error	31	1.34	0.04		
Total	35	31.40			
Fiber content	2	29.74	14.87	344.25	< 0.0001
Temperature	1	0.16	0.16	3.64	0.0659
Screw speed	1	0.17	0.17	3.91	0.0569

Table D.6 Analysis of variance of melt index for HDPE extrudates.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	107.94	26.98	2442.23	< 0.0001
Error	31	0.34	0.01		
Total	35	108.28			
Fiber content	2	107.77	53.87	4877.08	< 0.0001
Temperature	1	0.02	0.02	2.18	0.1503
Screw speed	1	0.14	0.14	12.59	0.0013

Table D.7 Analysis of variance of color index for LLDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	1740.88	435.22	50.56	< 0.0001
Error	31	266.85	8.61		
Total	35	2007.73			
Fiber content	2	1607.13	803.56	93.35	< 0.0001
Temperature	1	29.68	29.68	3.45	0.0728
Screw speed	1	104.07	104.07	12.09	0.0015

Table D.8 Analysis of variance of color index for HDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	4463.67	1115.92	206.60	< 0.0001
Error	31	167.44	5.40		
Total	35	4631.11			
Fiber content	2	4442.19	2221.10	411.21	< 0.0001
Temperature	1	15.26	15.26	2.83	0.1028
Screw speed	1	6.22	6.22	1.15	0.2916

Table D.9 Analysis of variance of density deviation for LLDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	607.01	151.75	3.63	0.0155
Error	31	1297.46	41.85		
Total	35	1904.47			
Fiber content	2	576.40	288.20	6.89	0.0034
Temperature	1	21.39	21.39	0.51	0.4800
Screw speed	1	9.22	9.22	0.22	0.6421

Table D.10 Analysis of variance of density deviation for HDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	212.23	53.06	0.81	0.5284
Error	31	2030.75	65.51		
Total	35	2242.98			
Fiber content	2	159.21	79.60	1.22	0.3104
Temperature	1	22.78	22.78	0.35	0.5596
Screw speed	1	30.24	30.24	0.46	0.5019

Table D.11 Analysis of variance of tensile strength for LLDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	1642.16	410.54	68.26	< 0.0001
Error	55	330.77	6.01		
Total	59	1972.93			
Fiber content	2	1534.47	767.23	127.57	< 0.0001
Temperature	1	51.18	51.18	8.51	0.0051
Screw speed	1	56.52	56.52	9.40	0.0034

Table D.12 Analysis of variance of tensile strength for HDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	3708.53	927.13	1078.84	< 0.0001
Error	55	47.27	0.86		
Total	59	3755.79			
Fiber content	2	3699.19	1849.60	2152.24	< 0.0001
Temperature	1	2.72	2.72	3.17	0.0806
Screw speed	1	6.61	6.61	7.69	0.0076

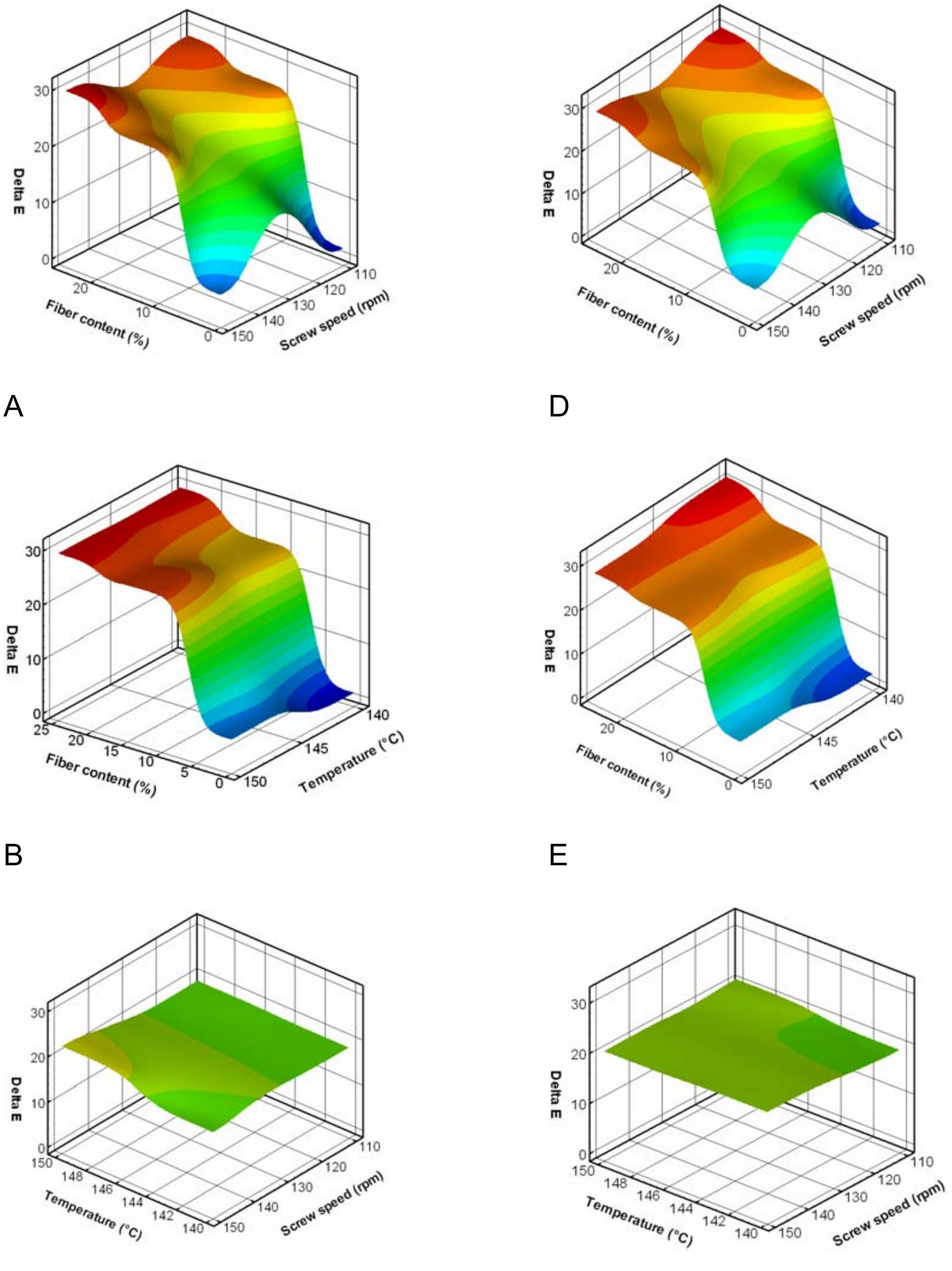
Table D.13 Analysis of variance of water absorption for LLDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	370.86	92.72	16.88	< 0.0001
Error	31	170.29	5.49		
Total	35	541.15			
Fiber content	2	319.67	159.84	29.10	< 0.0001
Temperature	1	8.25	8.25	1.50	0.2297
Screw speed	1	42.94	42.94	7.82	0.0088

Table D.14 Analysis of variance of water absorption for HDPE composites.

Source	DF	Sum of Squares	Mean Square	F value	Pr > F
Model	4	57.98	14.49	5.96	0.0011
Error	31	75.44	2.43		
Total	35	133.41			
Fiber content	2	47.92	23.96	9.85	0.0005
Temperature	1	5.75	5.75	2.36	0.1344
Screw speed	1	4.31	4.31	1.77	0.1931

APPENDIX E - Response Surface Plots



A

D

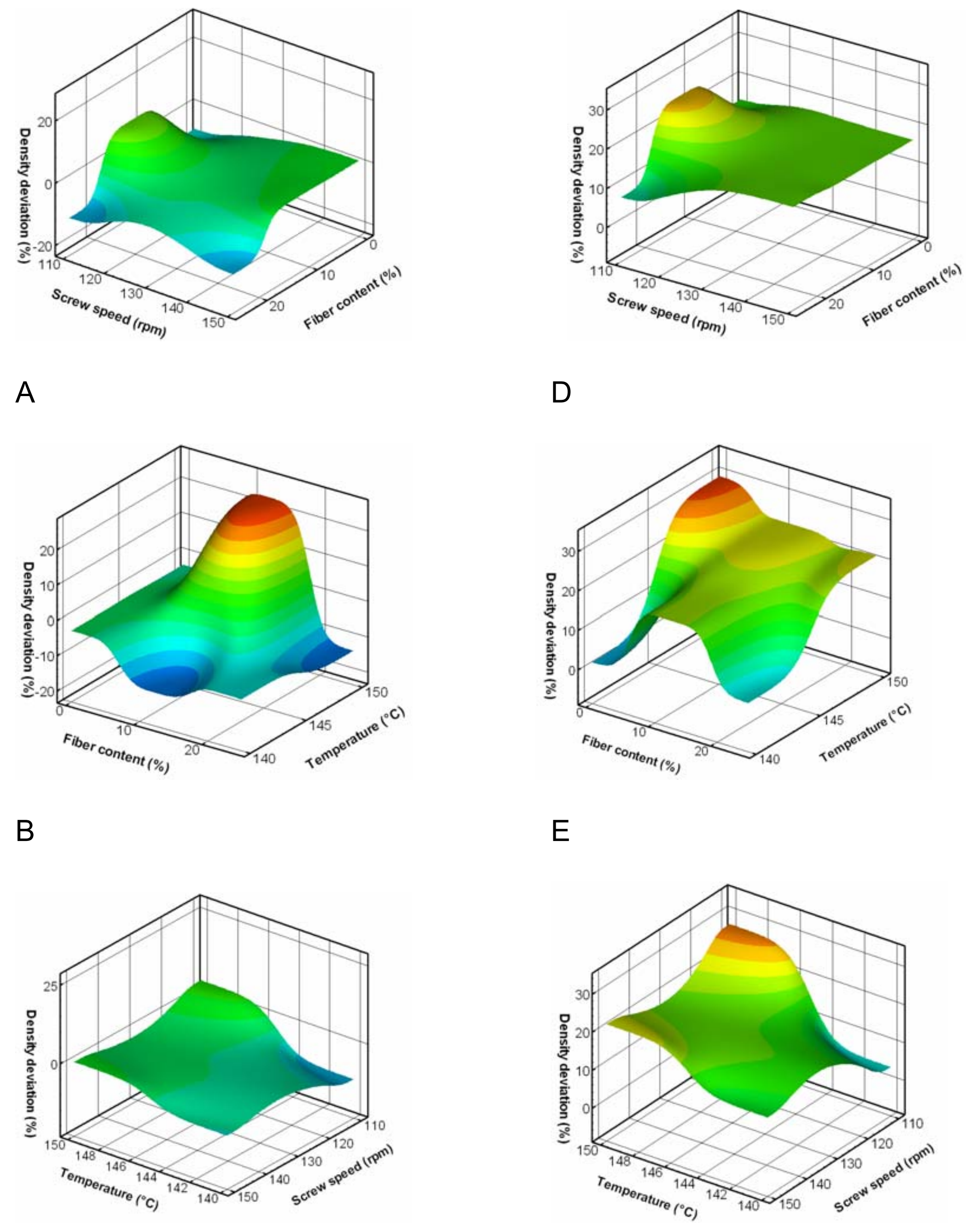
B

E

C

F

Figure E.1 Response surface plots for effects of fiber content, temperature, and screw speed on color index (ΔE) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) extrudates.



A

D

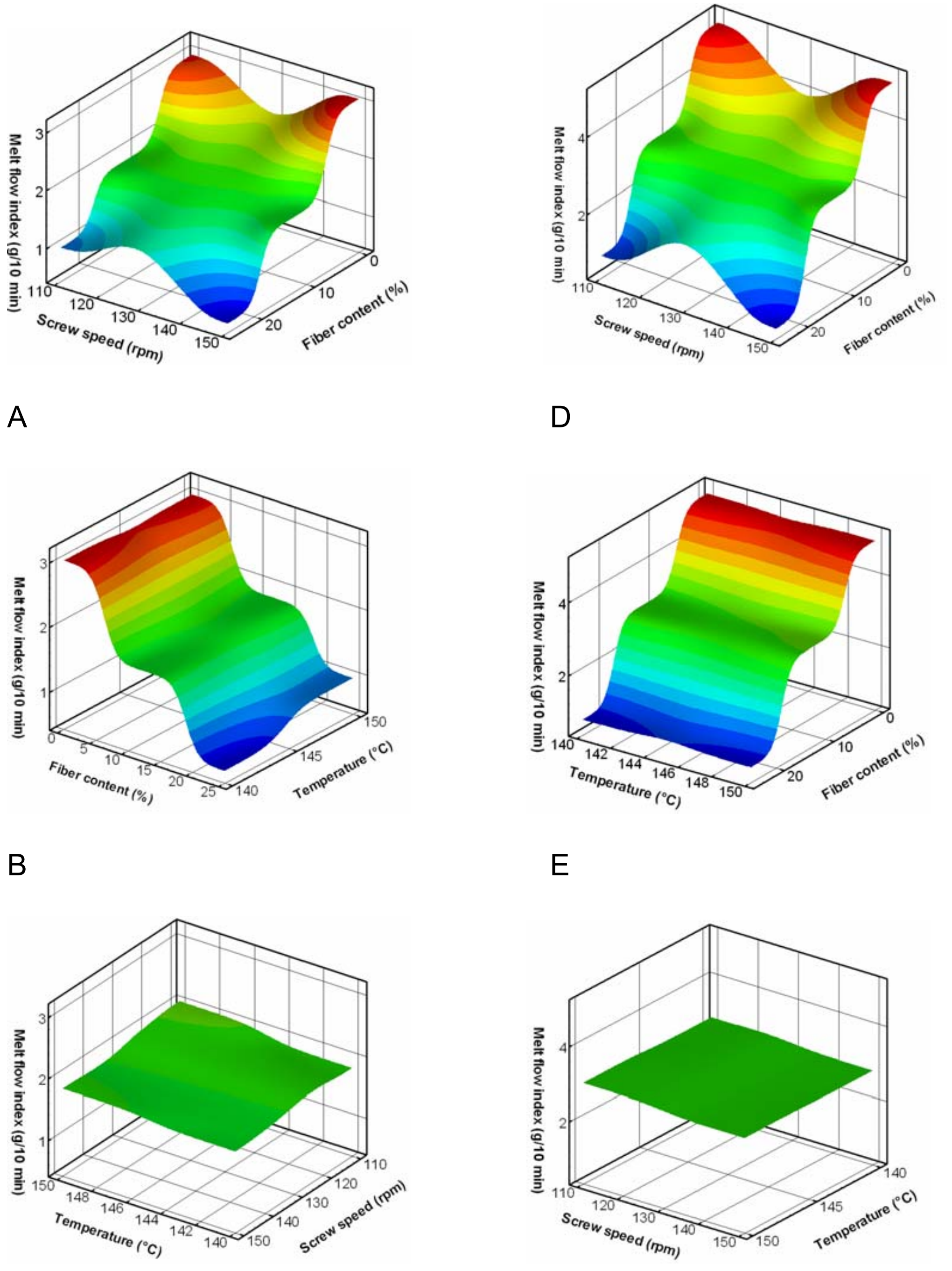
B

E

C

F

Figure E.2 Response surface plots for effects of fiber content, temperature, and screw speed on density deviation (%) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) extrudates.

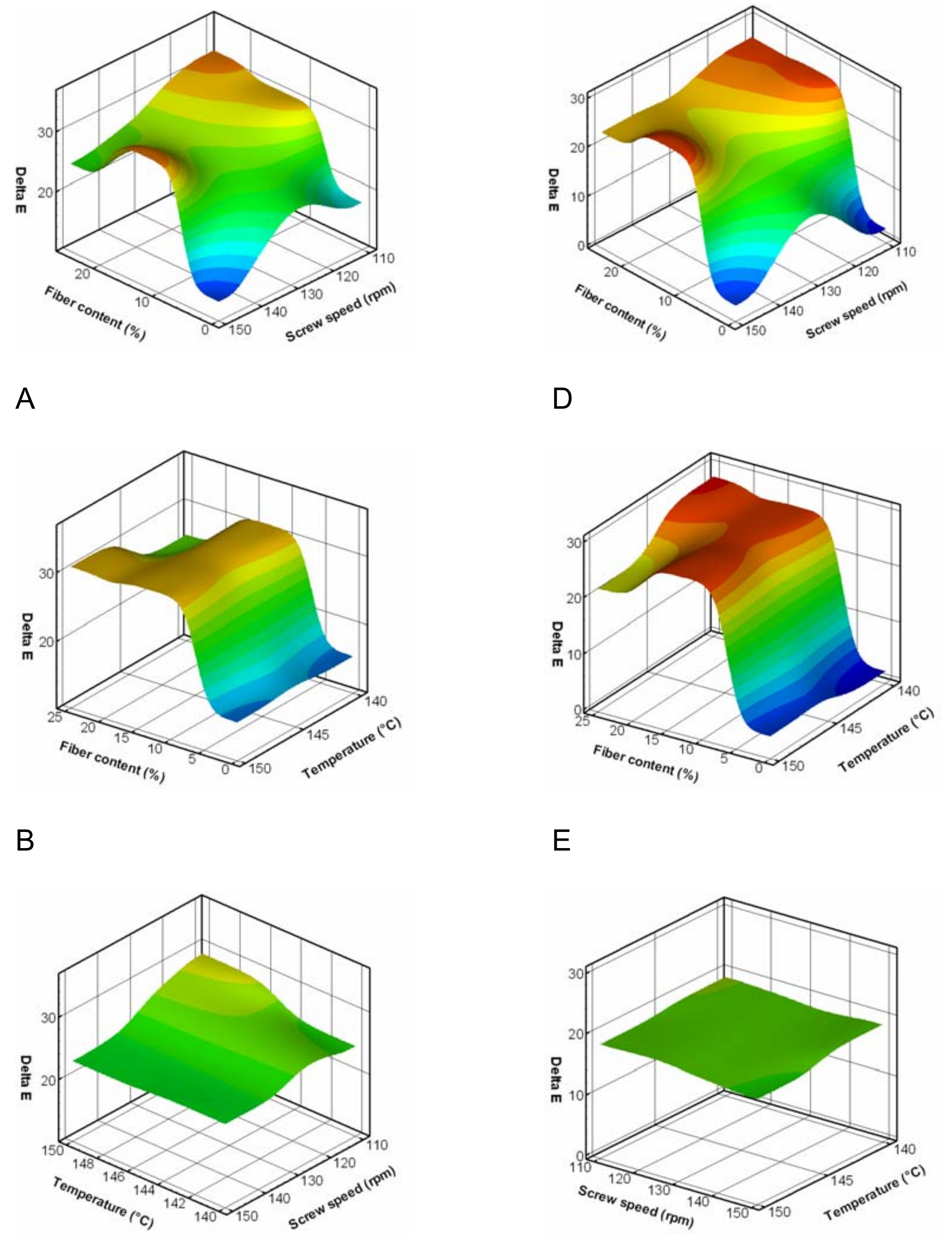


A D

B E

C F

Figure E.3 Response surface plots for effects of fiber content, temperature, and screw speed on melt index (g/10 min) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) extrudates.



A

D

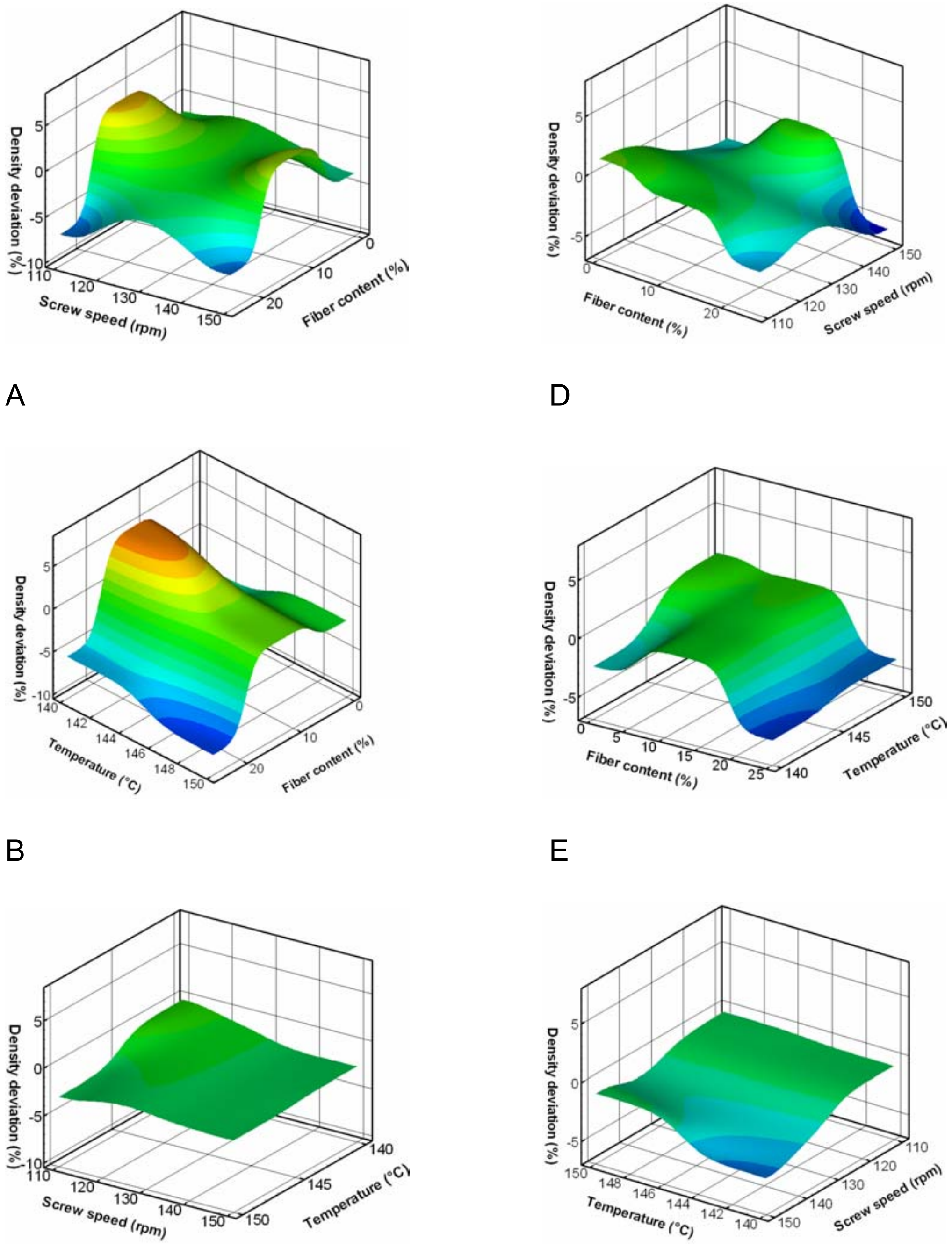
B

E

C

F

Figure E.4 Response surface plots for effects of fiber content, temperature, and screw speed on color index (ΔE) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) composites.



A

D

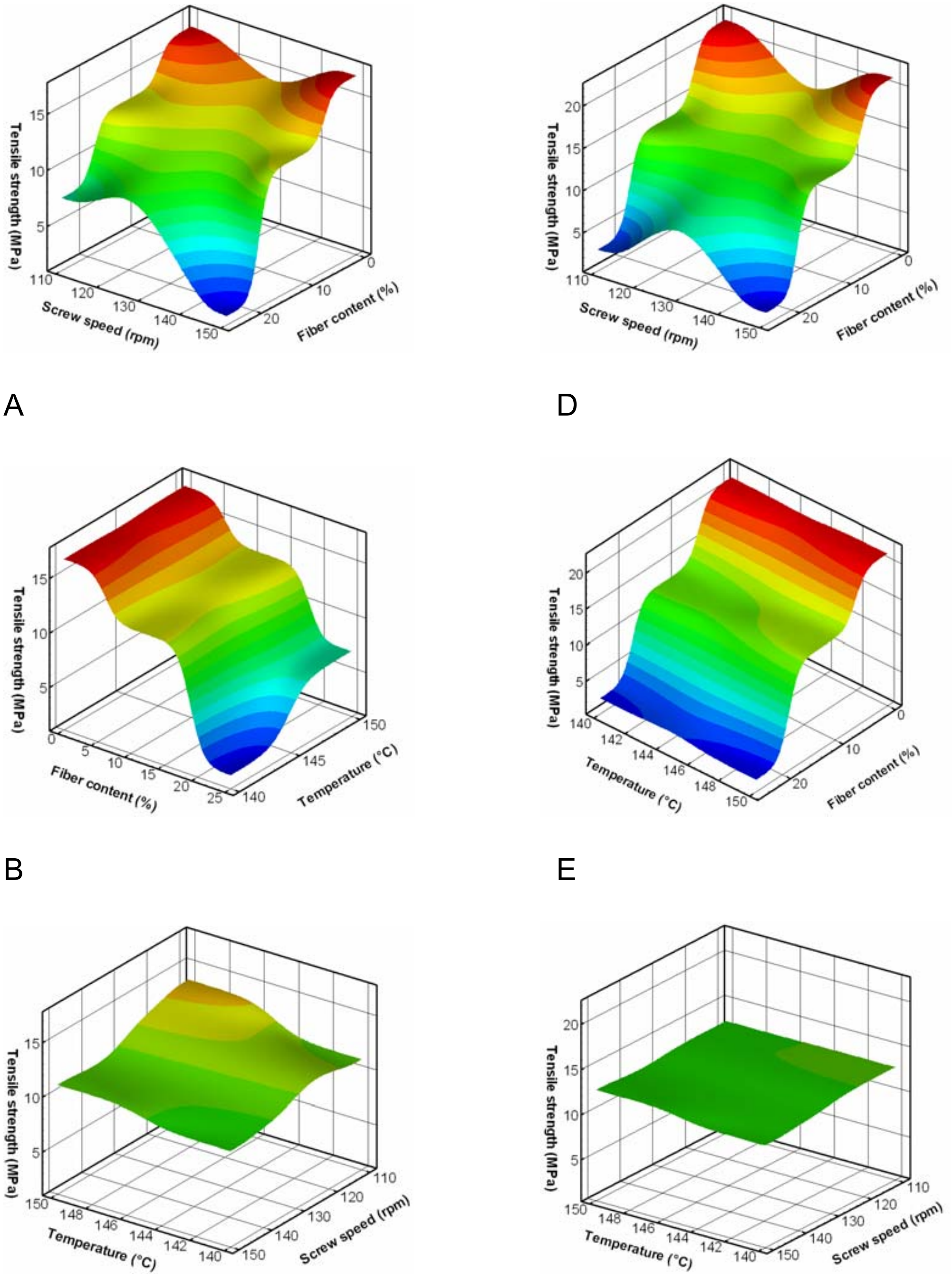
B

E

C

F

Figure E.5 Response surface plots for effects of fiber content, temperature, and screw speed on density deviation (%) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) composites.



A

D

B

E

C

F

Figure E.6 Response surface plots for effects of fiber content, temperature, and screw speed on tensile strength (MPa) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) composites.

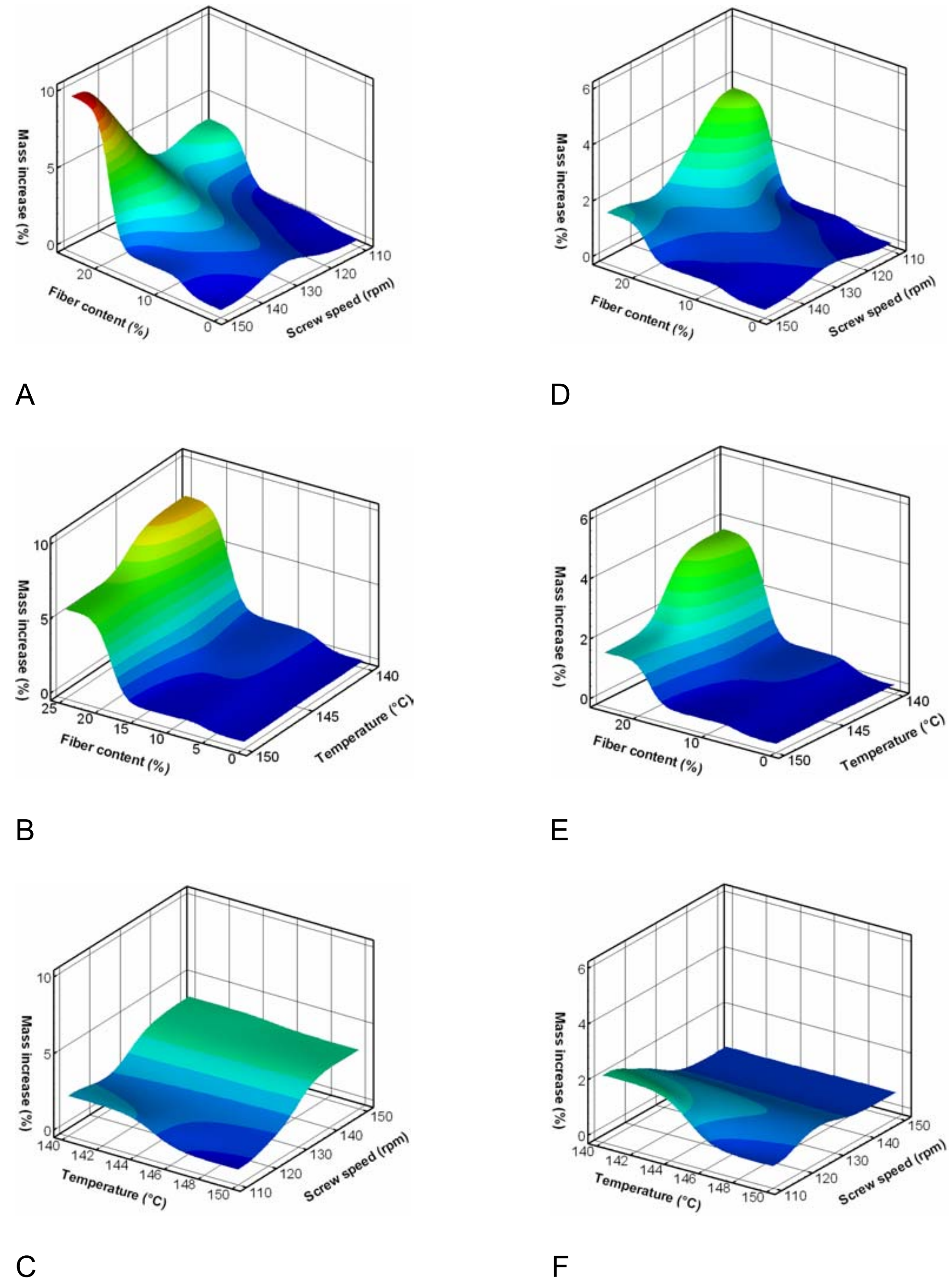


Figure E.7 Response surface plots for effects of fiber content, temperature, and screw speed on water absorption (%) of flax fiber-reinforced LLDPE (A, B, and C) and HDPE (D, E, and F) composites.

APPENDIX F

Multiple Linear Regression Analyses

Table F.1 Regression analysis of color index for LLDPE extrudates.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	6.44	1791.00	70.10	<0.0001
Fiber	1.04	12215.00	478.09	< 0.0001
Error		25.55		
R - square	0.82			

Table F.2 Regression analysis of color index for HDPE extrudates.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	7.61	2503.02	101.76	< 0.0001
Fiber	1.01	11467.00	466.17	< 0.0001
Error		24.60		
R - square	0.81			

Table F.3 Regression analysis of density deviation for LLDPE extrudates.

no variable met the 0.05 significance level for entry into the model

Table F.4 Regression analysis of density deviation for HDPE extrudates.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	-225.67	2177.32	10.04	0.0032
Temperature	1.67	2564.77	11.83	0.0016
Error		216.86		
R - square	0.26			

Table F.5 Regression analysis of melt index for LLDPE extrudates.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	2.96	126.48	2387.36	< 0.0001
Fiber	-0.09	29.60	558.74	< 0.0001
Error		0.05		
R - square	0.94			

Table F.6 Regression analysis of melt index for HDPE extrudates.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	5.45	23.87	1543.73	< 0.0001
Fiber	-0.17	107.63	6961.58	< 0.0001
Screw speed	-0.01	0.14	8.99	0.0051
Error		0.02		
R - square	0.99			

Table F.7 Regression analysis of color index for LLDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	18.65	5007.75	160.71	< 0.0001
Fiber	0.50	948.28	30.43	< 0.0001
Error		31.16		
R - square	0.47			

Table F.8 Regression analysis of color index for HDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	6.95	696.03	14.27	0.0006
Fiber	0.89	2972.38	60.93	< 0.0001
Error		48.79		
R - square	0.64			

Table F.9 Regression analysis of density deviation for LLDPE composites.

no variable met the 0.05 significance level for entry into the model

Table F.10 Regression analysis of density deviation for HDPE composites.

no variable met the 0.05 significance level for entry into the model

Table F.11 Regression analysis of tensile strength for LLDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	23.78	758.30	98.05	< 0.0001
Fiber	-0.49	1475.57	190.79	< 0.0001
Screw speed	-0.05	56.52	7.31	0.0090
Error		7.73		
R - square	0.78			

Table F.12 Regression analysis of tensile strength for HDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	22.05	11670.00	6608.38	< 0.0001
Fiber	-0.76	3653.37	2068.78	< 0.0001
Error		1.77		
R - square	0.97			

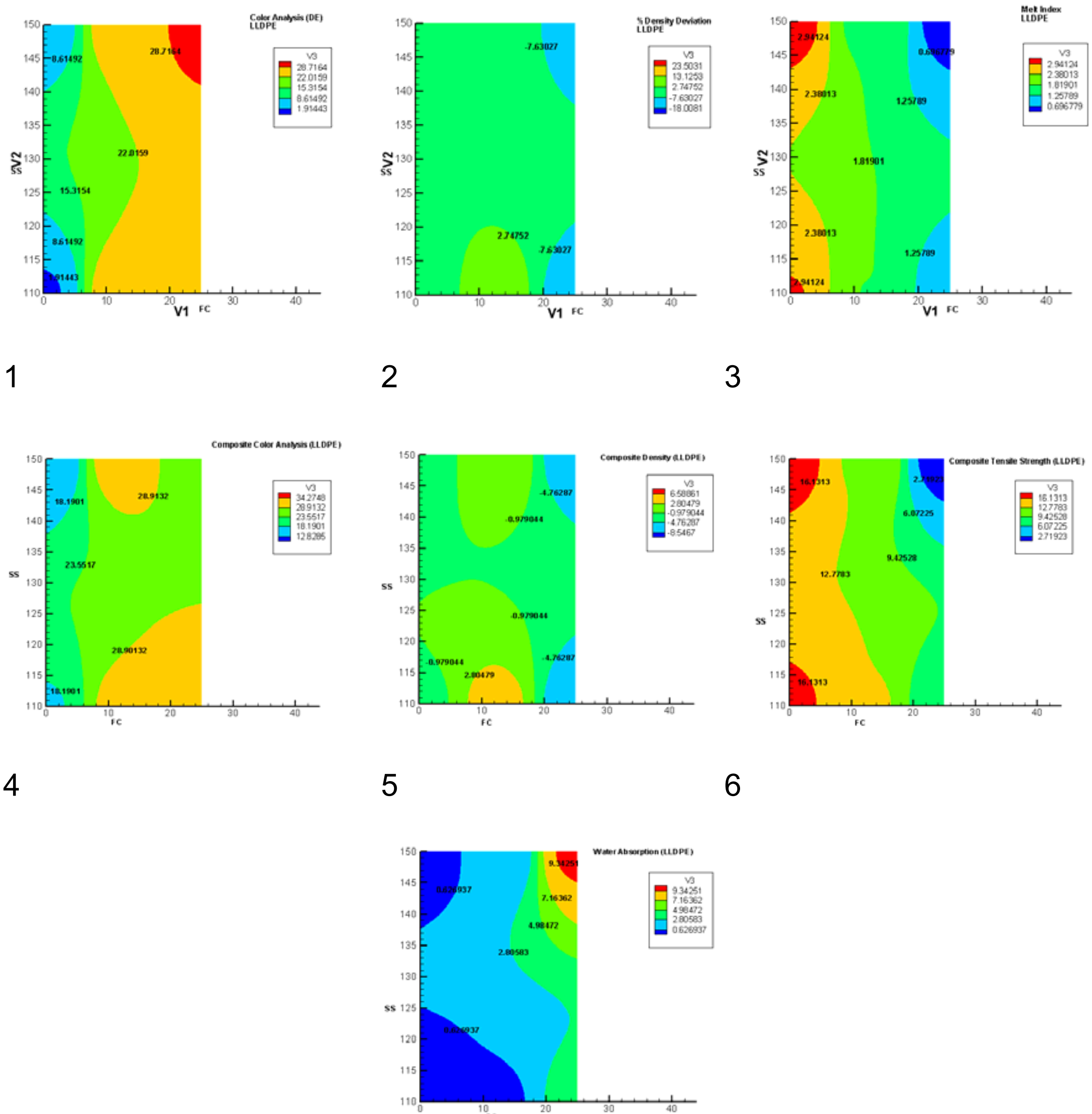
Table F.13 Regression analysis of water absorption for LLDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	-7.98	51.17	7.16	0.0115
Fiber	0.26	262.39	36.72	< 0.0001
Screw speed	0.05	42.94	6.01	0.0197
Error		7.15		
R - square	0.56			

Table F.14 Regression analysis of water absorption for HDPE composites.

Variable	Parameter Estimate	Sum of Squares	F value	Pr > F
Intercept	-0.32	1.52	0.55	0.4619
Fiber	0.10	40.16	14.64	0.0005
Error		2.74		
R - square	0.30			

APPENDIX G - Superposition Surface Methodology Contour Plots

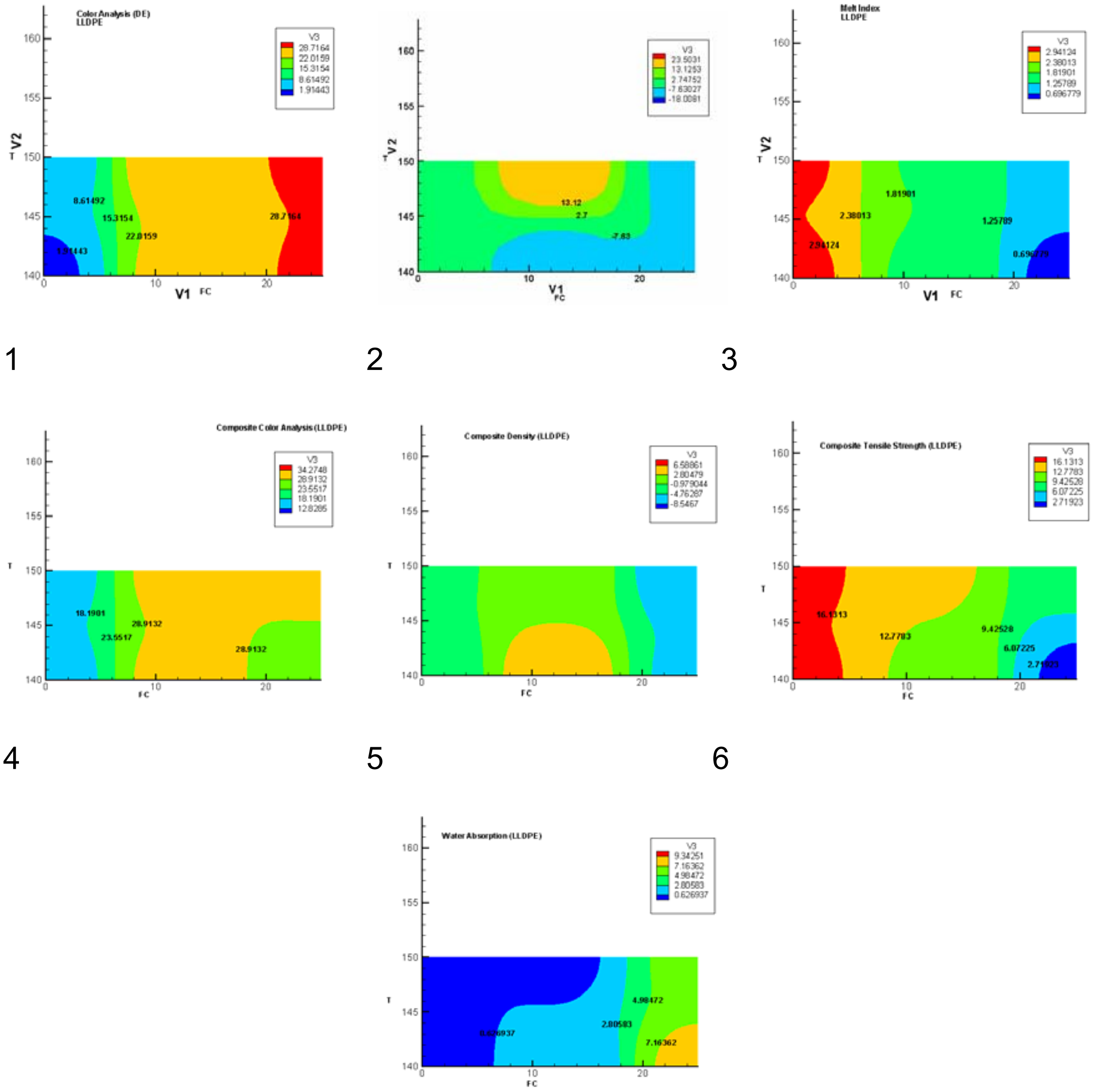


1 2 3

4 5 6

7

Figure G.1 Contour plots for effects of fiber content and screw speed on the different properties [extrudate color (1), extrudate density (2), melt index (3), composite color (4), composite density (5), tensile strength (6), and water absorption (7)] of flax fiber-reinforced LLDPE composites.

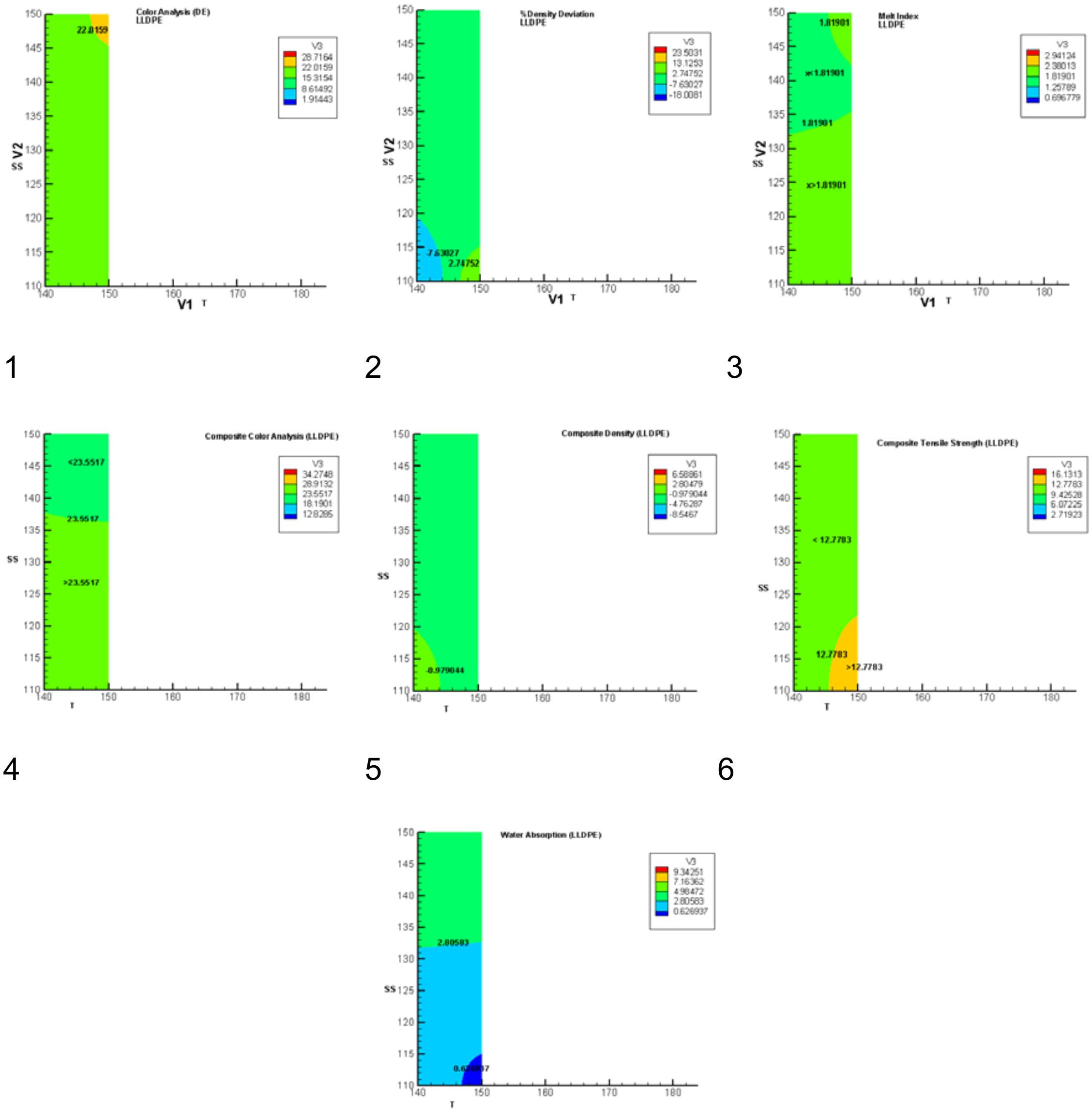


1 2 3

4 5 6

7

Figure G.2 Contour plots for effects of fiber content and temperature on the different properties [extrudate color (1), extrudate density (2), extudate melt index (3), composite color (4), composite density (5), composite tensile strength (6), and composite water absorption (7)] of flax fiber-reinforced LLDPE composites.

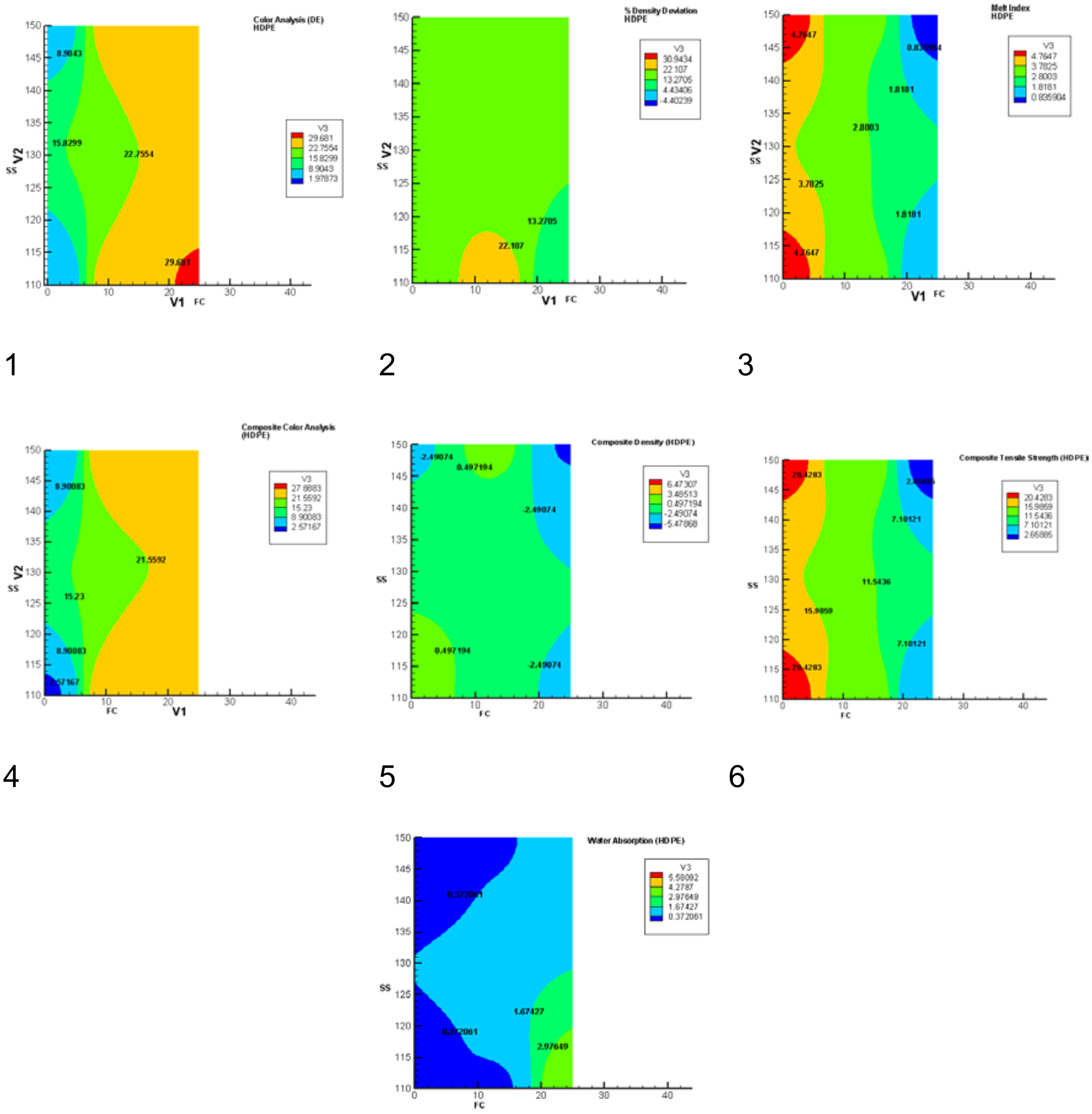


1 2 3

4 5 6

7

Figure G.3 Contour plots for effects of temperature and screw speed on the different properties [extrudate color (1), extrudate density (2), extudate melt index (3), composite color (4), composite density (5), composite tensile strength (6), and composite water absorption (7)] of flax fiber-reinforced LLDPE composites.

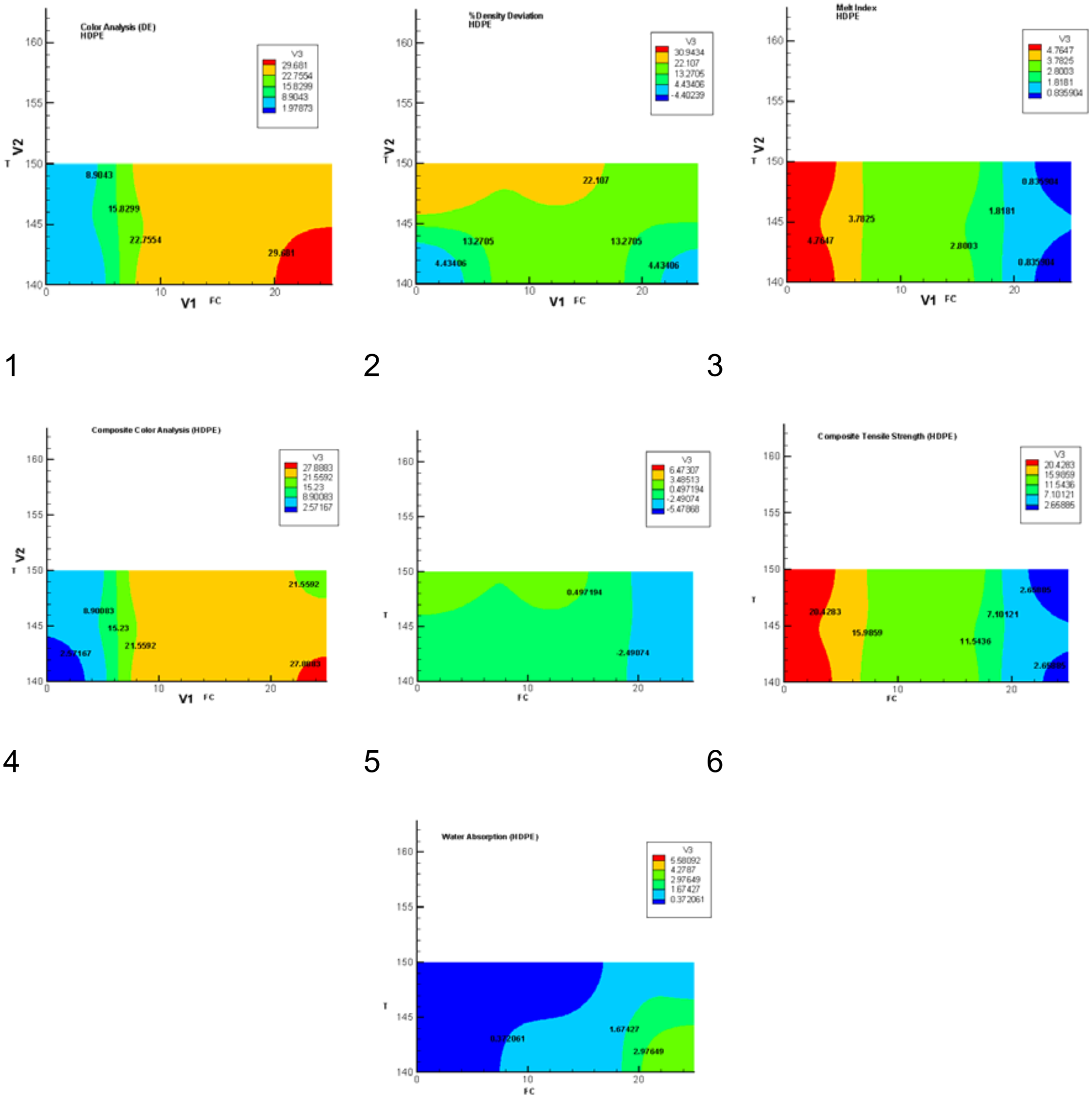


1 2 3

4 5 6

7

Figure G.4 Contour plots for effects of fiber content and screw speed on the different properties [extrudate color (1), extrudate density (2), extudate melt index (3), composite color (4), composite density (5), composite tensile strength (6), and composite water absorption (7)] of flax fiber-reinforced HDPE composites.

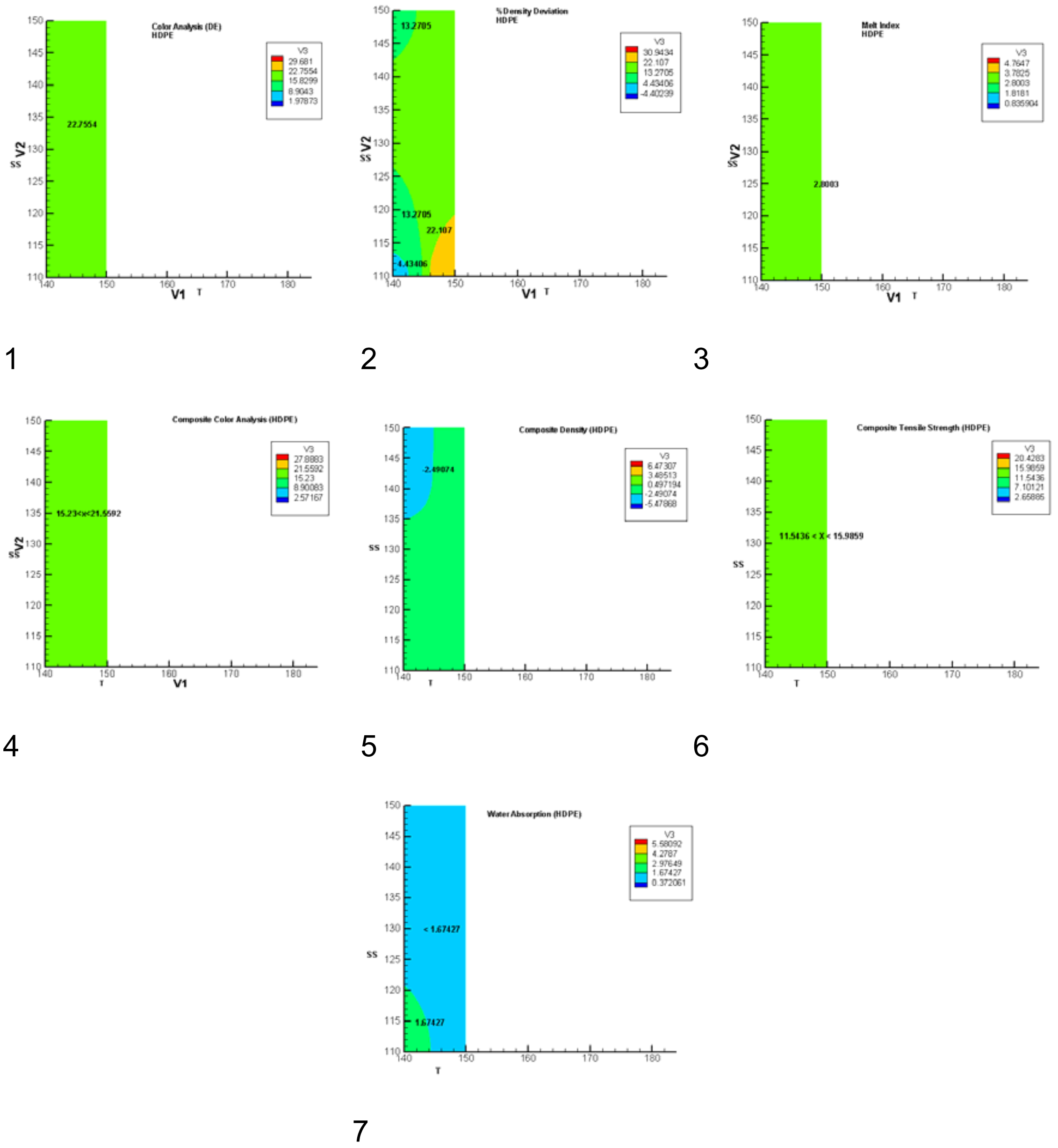


1 2 3

4 5 6

7

Figure G.5 Contour plots for effects of fiber content and temperature on the different properties [extrudate color (1), extrudate density (2), extudate melt index (3), composite color (4), composite density (5), composite tensile strength (6), and composite water absorption (7)] of flax fiber-reinforced HDPE composites.



1

2

3

4

5

6

7

Figure G.6 Contour plots for effects of temperature and screw speed on the different properties [extrudate color (1), extrudate density (2), extudate melt index (3), composite color (4), composite density (5), composite tensile strength (6), and composite water absorption (7)] of flax fiber-reinforced HDPE composites.