Product Design of Wheat Straw Polypropylene Composite

by

Rois Fatoni

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Doctor of Philosophy

in

Chemical Engineering

Waterloo, Ontario, Canada, 2012

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Rois Fatoni

Abstract

The use of wheat straw and other agricultural by-product fibers in polymer composite materials offers many economical and environmental benefits. Wheat straw has been recently commercialized as new filler for polypropylene thermoplastic composites in automotive applications. However, to expand its application in the automotive industry and other sectors where highly-engineered materials are needed, a systematic database and reliable composite property models are needed. For this purpose, this research was systematically conducted.

A *product design* approach is used in studying wheat straw polypropylene (WS-PP) composite. A set of thermoplastic composite specifications relevant to several automotive parts was used as a basis for the customer needs which give the direction to the entire product design of thermoplastic composites based on polypropylene and straw. Straw fibers were produced by grinding and sieving (without any other treatment). These fibers were used in the formulation of polypropylene thermoplastic composites to understand the variable that can contribute to minimize production cost, maximize product performance and maximize wheat straw utilization (fraction of renewable material).

The variation in chemical composition due to plant variety (parts of the plant, location of harvesting and seasonality), the bonding incompatibility between hydrophobic polypropylene matrix and hydrophilic straw fiber, along with the heterogeneity of fiber size and shape, has made wheat straw polypropylene composite a complex system. This complexity causes the mechanistic approach of composite modeling in the well-established composite theory difficult to be applied, since modeling the contribution of natural fibers to the performance of thermoplastic composites is not as straightforward like in the case of homogenous glass fiber (with same shape, diameter and narrow length distribution). Alternatively, a statistical approach of modeling by using designed experiments was used in this research.

The Mixture and Process-Mixture Experimental Design methodologies were applied to develop response surface models that can be used to correlate input properties and formulation of these thermoplastic composites to the final properties of the product. The models obtained can then be inverted to predict the required properties and formulations using fiber (straw), matrix (polypropylene), and additives (coupling agent) as the main components for a specified product

performance. The prediction includes the fiber grading (size and aspect ratio) and classification in order to maximize fiber utilization for different needs of composite products.

The experiments were designed based on the analysis of the existing data provided by previous research works of wheat straw polypropylene composite system in our laboratory and by experimental data generated during this research. The focus of the analysis was the determination of the factor(s), i.e., the independent variables of the experiments and their acceptable levels. The response variables being measured were chosen based on the required specifications of targeted products.

A constrained three-component mixture design of experiment was conducted to develop models for flexural properties of WS-PP composite. The three independent mixture variables in this experiment were the weight proportions of: straw (as fiber), polypropylene (as matrix), and maleic anhydride polypropylene (as coupling agent). Statistical analysis results showed that the obtained models have met standard requirements of response surface models with good predictive capability. One of the important finding of this study was the formulation for optimum coupling agent proportion which gives the best flexural properties of composite.

The effect of straw fiber size on composite properties was investigated by using fiber length and aspect ratio as parameters to describe fiber size, instead of the size of sieves used in fiber preparation. Two-stage separation method was applied in the straw fiber preparation process. In this method, width-based separation was followed by length-based separation to obtain fiber fractions with distinct fiber length and aspect ratio. Samples of thermoplastic composites for measurement of physical properties were produced from each fiber factions at two different levels of fiber loading. The samples were compounded by twin-screw extrusion and specimens were prepared by injection molding. The fibers were then extracted from the samples after injection molding (using solvent) and their sizes were measured to investigate the fiber size reduction during the compounding and molding process. A comprehensive analysis was then performed to study the responses of stiffness, impact resistance and specific properties of these composites by including initial fiber sizes, fiber chemical compositions (measured as cellulose, hemi-cellulose and lignin), fiber size reduction during compounding/molding process, and fiber loading as factors. One of the important contributions of this study is fiber grading in terms of their sizes and their respective contributions to the final composite product properties.

Based on the previous results, a mixture design of experiment was performed on wheat straw – polypropylene / impact copolymer polypropylene (WS-PP/ICP) composite system. The objective of the experiment was to obtain response surface models that can be used to estimate some important properties required by a set of automotive product specifications. The optimum formulation of coupling agent obtained in the previous study was used to determine the fixed recipe of coupling agent; simplifying the composite system into a three-component mixture, i.e. straw (as fiber) and polypropylene (homopolymer and impact copolymer (polypropylene blend as matrix). Simulation of the models shows the superiority of using a blend of polypropylenes to balance the stiffness and impact strength of the composites and being able to reach three targeted product specifications. A case study was also performed to demonstrate that the models can be used to find optimum formulations to minimize material cost while meeting specifications of all targeted products.

Finally, a framework for wheat straw polypropylene product design and development is presented in this thesis. The framework can be used for designing polypropylene-straw thermoplastic composites with various combinations of fiber - polymer matrix - additive systems with different product attributes and specifications suitable for several applications in the automotive industry.

Acknowledgements

First and foremost, all praise due to Allah The Lord of the universe. He who taught human being anything new and unknown before.

I would like to express my gratitude to my supervisors, Professor Ali Elkamel and Professor Leonardo Simon, for their supports and encouragement to me during my study in University of Waterloo. Professor Elkamel has introduced me to product design field while Professor Simon has involved me in his project on wheat straw polypropylene composite. It was such a joy and an honor to me to work and study with them. I was so fortunate to have them as supervisors and to learn a lot from them during my studies.

I would also like to thanks to Pouyan, Ravindra, Diogenes, Barbara, Andrew, Arif, Arathi, Kate, Kyu-Min, Manuel, and Charles in Professor Simon's research group, and Hui, Mohammed, Mujib, and other colleagues in Professor Elkamel's research group for their valuable helps and fruitful discussions.

I want to thank to the committee members: Professor David Potter (McMaster University), Professor Fatma Gzara, Professor Joao Soares, and Professor Boxin Zhao for their valuable comments and suggestions on my thesis.

I also want to thank to Directorate General of Higher Education, The Ministry of Education Republic of Indonesia for the scholarships for my studies. Supports from Muhammadiyah University of Surakarta, my home institution, are also highly appreciated.

The last but not the least, I would like to thank to my wife Ovie for her support, patience, and encouragement during my studies and our amazing four-year life in Waterloo.

Dedication

I dedicated this PhD thesis to:

- Suparmi Mustajab and Abdul Hamid, my mom and dad;
- Alpri Hayatus Shofia, my wife;
- Hannah, Yahya, Fiya and Mutia, my children;
- All my teachers and gurus.

Table of Contents

Lists of Figures

Lists of Tables

1 Introduction

1.1 Background and Motivation

During the last decade, there has been a tremendous growth of natural-plant-fiber polymer composite applications in automotive industries. Compared to the glass fiber and mineral filler, natural plant fibers are more attractive because of the economical and environmental benefits they offer. Plant fibers have better specific properties, i.e. the ratio of mechanical properties per mass, which makes them good candidates for lighter materials. They are annually renewable and recyclable which make them environmentally friendly. Those benefits, in addition to government regulations and initiatives in some countries, have become the main reasons for car manufacturers and suppliers for investigating and using natural plant fibers such as kenaf, hemp, flax, jute, and sisal as fillers in thermoplastic and thermoset composites. These composite materials have been used for automotive parts such as door panels, seat backs, headliners, packages, trays, dashboard, and other interior parts.

The automotive industry is not the only sector that has experienced an increase in natural fiber utilization. The use of natural fibers as filler and reinforcement materials in the industrial, building, and commercial market sectors has increased by 13% from 1996 to 2006 with an annual use of approximately 275 million kilograms (Suddell & Evans, 2005).

Despite that growth, however, there are some questions concerning the environmental impact of production processes of such natural fibers. The use of chemical fertilizer, lands, and water in growing the plants; the chemicals, electricity, and water as utilities in fiber extraction processes; and the waste produced in such processes, have been suspected to cause a similar or even greater environmental impact than the impact produced by the utilization of mineral fibers and fillers.

Fibers from agricultural by-products or waste, such as wheat straw, soy stalk and rice husk, have received considerable attention due to their nature as a by-product of food. The production and utilization of fibers produced using by-product feedstock are not associated with any cultivation-related environmental issues because the plant of origin was meant for food. Furthermore, the use of the agricultural fibers would result in a negative CO_2 emission

since in most cases the by-product fibers were merely burnt or decomposing in the field, thus releasing a significant amount of CO_2.

The insertion of wheat straw fiber in thermoplastic polymers for application in automotive parts has become real today, thanks to many researchers who contributed to a better understanding of fiber-matrix reinforcement mechanisms leading to the better, and easier product manufacturing of the composite. Ford Motors Company, for instance, announced on November 2009 the use of wheat straw polypropylene composite material for the quarter trim bin in the Ford Flex vehicle model 2010. This new technology was a result of the intense collaboration between Ford Motors, the University of Waterloo and other partners of the supply chain like A. Schulman (USA) and Omtec Inc. (Canada). Figure 1-1 shows the schematic representation of the utilization of the wheat straw in such application. This success was one of high impact contribution from part of the research presented in this thesis.

Figure 1-1 The Use of Wheat Straw Bio-Filled Polypropylene on 2010 Ford Flex (Ford Motor Company, 2009)

There are many car parts whose specifications are similar to the specifications of the quarter trim bin part so that there is a wide range of opportunities available for expansion of the use of wheat straw polypropylene composite. To this point, we arrive at the typical product design challenge: how to create a new product which meets (or even exceeds) the specified

needs? How can we accelerate the expansion of utilization of wheat straw and other agricultural by-product fibers in automotive and other industries?

1.2 Research Objectives

Based on the above discussions, there are three main objectives of this research:

1. To develop a methodology that can be used to effectively design the wheat straw polypropylene composite product in order to bring the product to market cheaper and faster.
2. To obtain additional data regarding the attributes of wheat straw for developing grades for products (fiber grading).
3. To develop an effective general framework for designing natural plant fiber plastic composite products.

1.3 Research Approach

Product design approach and strategy has been implemented to achieve the research objectives. In product design, a research effort is viewed as a whole, carried out by integrating research with market needs and manufacturing process. The choice of materials and methods used, as well as variables and responses being investigated in the research were directed by specified consumer needs and were subjected to constraints during manufacturing processes.

A set of thermoplastic composite specifications in automotive applications was used as a basis for the customer needs, thus giving the direction to the research of product design of wheat straw polypropylene composite. Ground wheat straw fibers, without any costly fiber pre-treatment such as fibrillation process or chemical treatment, were used as reinforcing dispersed phase in thermoplastic composites in order to minimize material costs.

Mixture and Process-Mixture Experimental Design methodology have been applied to develop response surface models that can be used to correlate input properties of a wheat straw polypropylene composite system to the final properties of the composite. The models obtained can then be inverted to predict the required properties and compositions of fiber,

matrix, and additives for specified composite product properties. The prediction includes the fiber grading (type and size) and fiber classification in order to maximize fiber utilization for different needs of composite products.

Technically, the research has been done by performing series of three main tasks:

1. Organizing and analyzing the existing data provided by previous works in our group,
2. Designing and performing mixture design of experiments, and
3. Designing and performing process-mixture experimental design.

Finally, based on the results of the tasks, a general framework for designing natural plant fiber thermoplastic composite product is proposed in this thesis.

1.4 Thesis Overview

Following the general introduction of the research explained in this Chapter, the literature review section is presented in **Chapter 2**. The history and current progress of natural plant fiber plastic composite, especially the wheat straw polypropylene composite is presented. It is followed by a brief literature review on product design, mixture design, and process-mixture design as subclasses of the response surface methodology (RSM). Statistical and mechanistic modelings of natural-fiber thermoplastic composite are also discussed in Chapter 2.

Chapter 3 presents the approach for this research. The three main tasks mentioned in the research approach section are discussed. Analysis of the previous studies on wheat straw polypropylene composites especially those were done in our research group is presented in this chapter, followed by detailed methodology of the mixture and process - mixture design of experiments.

Chapter 4 presents the work on mixture design of experiment of the composite. Response surface models for the flexural properties and density of the composite as function of component proportions were developed based on the carefully designed experiment of three primary components of the composite: polypropylene as the matrix, ground wheat straw as the fiber and polypropylene maleic anhydride as coupling agent. One of the important finding

of this work was the optimum proportion of coupling agent to maximize a set of physical properties of the composite.

Chapter 5 presents the work on process-mixture design of experiment of the composite. Fiber length and aspect ratio are two process variables of great interest in this work. Wheat straw was ground to produce fibers and those were fractionated into different fiber fractions to create grades with distinct fiber length and aspect ratio. These grades of fibers were used to evaluate the performance of those fractions as grades of straw fiber with respect of performance in the final thermoplastic composites. The composite samples were made from each fiber grade at two different fiber loadings: 30 wt-% fiber and 50 wt-% of fiber. One of the important finding of this work is "mapping" the fiber attributes and quality in terms of the properties of composite. This "map" can be used to correlate and to optimize the utilization of grades of straw fiber for different applications in thermoplastic composites.

Chapter 6 presents the application of experimental mixture design of composite with higher level of complexity compared to the previous work presented in Chapter 4. In some practical automotive applications there is a requirement (need) to maintain the toughness (measured by impact strength) at a certain level without sacrificing the stiffness (measured by modulus). This can be done by blending homopolypropylene and high-impact polypropylene copolymer at certain compositions. Meanwhile, adding wheat straw fiber will increase the flexural modulus of the polymer blend at the expense of decreasing impact strength. It is expected that a composite material consists of homopolypropylene/impact copolymer polypropylene blending as polymer matrix and wheat straw as filler would have both toughness and stiffness increased. A set of mixture experiments has been designed and carried out in order to develop response surface model of impact and flexural properties of wheat straw – homopolypropylene/impact copolymer polypropylene (WS-PP/ICP) composite. A case study has been done to demonstrate that the model can be used to design a WS-PP/ICP composite formulations meeting or exceeding targets of practical product specifications.

Chapter 7 presents the proposed systematic methodology applied to product design of plant fiber thermoplastic composites. The methodology developed here is based on the research done on wheat straw-polypropylene composites and can be applied to the similar thermoplastic composites containing plant fiber.

Chapter 8 summarizes the research conclusions and contributions, and it discusses the suggestions for the future work.

2 Literature Review

2.1 Natural Fiber Plastic Composites

2.1.1 History and Current Market Situation

The use of natural fibers as reinforcement in composite materials dates back to thousands of years ago; 3000 years ago ancient Egyptian used clay reinforced with wheat straw as materials to build walls of their houses. In the automotive industry, Henry Ford developed the first prototype composite car made from hemp fibers in 1942. Due to economic constraints at that time, however, the car was not commercially produced. Since then, numerous attempts have been made to incorporate natural fibers into automotive components. The pressure to produce fuel-efficient, low-polluting vehicles has become the major driving force for the increasing use of natural fiber in automotive parts. The inclusion of natural fibers will be able to reduce the utilization of petroleum-based polymeric materials. It will also increase the mileage due to the decreased cars' total weight, and will result in an easier product end-of-life management (Suddell & Evans, 2005). Today, several car manufacturers are using natural fiber composites in their products. Some examples of the applications are presented in Table 2-1

Both thermoplastic and thermoset resins were being used in automotive industries. However, since thermoplastic resins are easily recyclable they exhibit less environmental impact than the thermoset resins. The automotive industry is using more thermoplastics than thermosets. The key advantage of thermoplastics is that they can be reprocessed or recycled, thus reducing the amount of scrap material during manufacturing and allowing easy recover and recycling of material at the end-of-life cycle. Due to the lower thermal stability of natural fibers, the number of thermoplastics which can be used to make composite materials is limited to those thermoplastics with processing temperature that does not exceed the temperature for degradation or burning the plant fibers (typically below 210 ^{o}C). Polypropylene and polyethylene are the most commonly used thermoplastic polymer matrix with plant natural fibers (Bledzki, Faruk, & Sperber, 2006).

Table 2-1 Automotive Manufacturers, Model, and Components Using Natural Fibers (Bledzki, Faruk, & Sperber, 2006)

Manufacturer	Model and Application
Audi	A2, A3, A4, A4Avant, A6, A8, Roadstar, Coupe: Seat back, side and back door panel, boot lining, hat rack, spare tire lining
BMW	3, 5 and 7 series and others: Door panels, headliner panel, boot lining, Seat back
Daimler-Chrysler	A, C, E, S class: Door panels, windshield/dashboard, business table, piller cover panel; A class, Travego bus: exterior under body protection trim; M class: Instrumental panel (Now in S class: 27 parts manufactured from bio fibres, weight 43 kg)
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156
Ford	Mondeo CD 162, Focus: Door panels, B-piller, boot liner
Opel	Astra, Vectra, Zafira: Headliner panel, door panels, pillar cover panel, instrumental panel
Peugeot	New model 406
Renault	Clio
Rover	Rover 2000 and others: Insulation, rear storage shelf/panel
Saab	Door panels
SEAT	Door panels, seat back
Volkswagen	Golf A4, Passat Variant, Bora: Door panel, seat back, boot lid finish panel, boot liner
Volvo	C70, V70
Mitsubishi	Space star: Door panels; Colt: Instrumental panels

There are various natural fibers with broad ranges of sizes and properties available to be used as fibers in composites, such as cotton, jute, flax, hemp, sisal, coir, bamboo, wood, pineapple, ramie, coconut leaves, and so on. The choice of fibers depends much on the final composite product specifications and particular applications. However, flax, hemp, and kenaf fibers are favored because they have excellent combinations of economic and functional properties (Suddell & Evans, 2005).

2.1.2 Technical issues and current research progress

The basic rule of reinforcement is that stresses to the material must be transmitted from the polymer matrix to the fiber. To get the optimum reinforcement to the polymer matrix, a fiber must have some attributes. The length of the fiber and the aspect ratio (length/diameter) of the fibers should be controlled to each specific type of resin and application. Much of the

research in the area of fiber reinforced plastics has been done using glass fiber. Glass fiber have uniform diameter and can be made to any required length, therefore the length and aspect ratio are easily controlled in the case of glass fiber. The fiber alignment is also a significant factor for composite strength. Fibers randomly oriented will lose their reinforcement effect up to 80%. For processing that prohibits the use of continuous fiber, discontinuous fibers are used. In this case, stress cannot be transmitted from the matrix polymer to the fibers across the fiber ends. Fibers with size longer than a critical minimum length *lc* are required for these discontinuous fibers (Rudin, 1999).

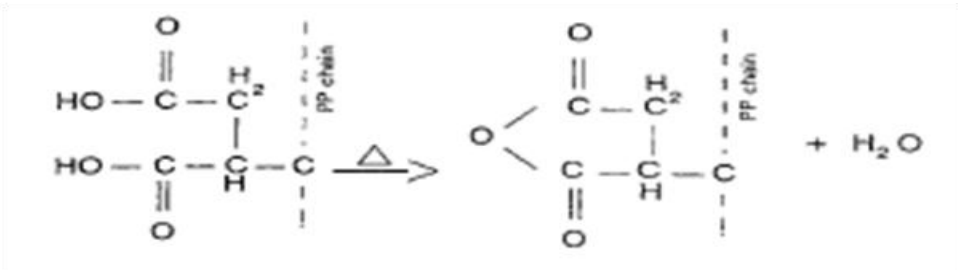
Since stresses must be transmitted across the boundaries between polymer matrix and the fiber, the properties of fiber-polymer composites are influenced by the strength of the bond between the phases (interface). Some problems have been encountered in providing strong interfacial bonds because it is not easy to wet hydrophilic natural fiber surfaces with generally hydrophobic viscous (molten) polymers. Coupling agents play an important role to bind the matrix and the fibers together at the interface.

Coupling agents for more inert polymers like polyolefins are often acid-modified versions of the matrix polymer, with maleic anhydride grafted polypropylene (MA-*g*-PP) as a prime example. MA-*g*-PP is widely used as a coupling agent in composites reinforced with cellulose fibers. The treatment of cellulose fiber with hot MA-*g*-PP copolymers provides the covalent bonds across the interface.

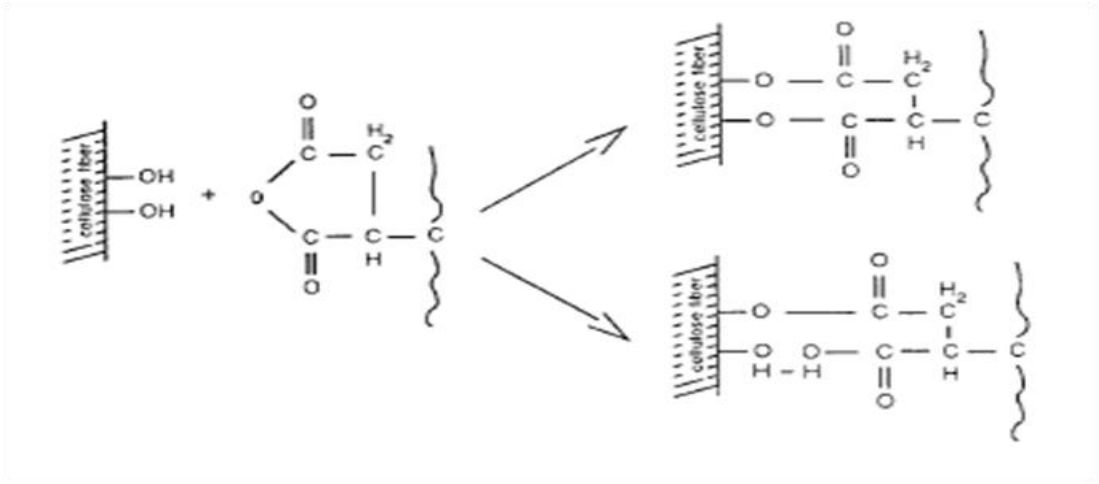
The mechanism of the reactions, which is basically divided into two steps: activation of the copolymer by heating, and esterification of cellulose, is illustrated in Figure 2-1. After this treatment the surface energy of the fibers is changed to a level much closer to the surface energy of the matrix. Thus, a better wettability and a higher interfacial adhesion are obtained. The polypropylene (PP) chain permits segmental crystallization and cohesive coupling between the modified fiber and the PP matrix (Gassan & Bledzki, 1999).

Some recent research publications show that one of the focuses of the on-going research activities is to find out the effect of coupling agents on polymer blends and composites. With the aid of Scanning Electron Microscopy (SEM), the coupling or dispersion mechanism and the fracture behavior can be evaluated by observing the morphology of the fractured surface

of the composite. Differential Scanning Calorimetry (DSC) is usually applied to examine the crystallization behavior (Girones & co-workers, 2008), (Araujo, 2008), (Bera & Kale, 2008).



(a)



(b)

Figure 2-1 Illustration of Coupling Mechanism of Cellulose Fiber and Maleic Acid grafted Polypropylene; (a) Copolymer Activation, (b) Cellulose Esterification (Gassan & Bledzki, 1999)

However, to the best of my knowledge, no literature exists discussing the optimum proportion of such coupling agents in system containing polypropylene and wheat straw which give maximum benefits of composite mechanical properties. The precise information related to the optimum proportion is absolutely needed when we want to commercially produce the natural fiber plastic composite.

Another important issue that has to be addressed is the fiber quality. Compared to mineral and synthetic fibers, natural fibers have a broader range of fiber size and mechanical properties. That is because of the differences in variety and maturity of the plant, handling

the straw before processing the fiber (bales, storage) and the method for manufacturing the straw fiber by grinding and sieveing. There is a real need for a quality assurance protocol for natural fibers to be established; especially when fibers are to be used in technical applications like the automotive parts (Bos, Mussig, & Van den Oever, 2006).

2.2 Wheat Straw Polypropylene Composites

The use of wheat straw as a filler in plastic composites has received considerable attention in recent years. Many factors have caused this interest, such as the limited supply of wood fibers, environmental issues, and government policies. However, the main attractiveness of using wheat straw in plastic composites comes from its potential to become a serious competitor to the other natural fibers: its lower price and feedstock stability. The estimated world-wide production of wheat straw is approximately 540 million tons in 2007 (Reddy & Yang, 2007). The price of wheat straw in 2008, in Ontario, based on the annual average was around US$ 0.20-0.30/kg (Ng, 2008). In August 2010, the price of raw jute in India was about US$ 0.65 – 0.80/kg (The Jute Baler's Association, 2010).

Currently, the major application of wheat straw in Ontario is for horse bedding or mushroom composting. Wheat straw fiber is also used to make panel and other building system components such as walls and roofs. Extensive efforts are still in progress to exploit the potential application of wheat straw in sectors which need highly engineered, structured materials such as the automotive industry (Xiaoqun, Wang, & Sun, 2005).

The studies of wheat straw polypropylene composites (WSPPC) have been done by many researchers from many disciplines. Despite the different objectives, focus, and scales of observations, all of the studies followed typical approaches in composite science. In general, the study of composite materials involves three aspects: composition selection, manufacturing process and property investigation. The summary of the studies of wheat straw polypropylene composite system is presented in Table 2-2.

Various mechanical (Sain, Law, Suhara, & Boullioux, 2005), chemical (Digabel, Boquillon, Dole, Monties, & Averous, 2004), thermo-mechanical (Halvarsson, Edlund, & Norgren, 2008), chemo-mechanical (Alemdar & Sain, 2008), (Sain, Law, Suhara, & Boullioux, 2005), and biological (Schirp, Loge, Aust, Swaner, Turner, & Wolcott, 2006) techniques have been used to pre-treat wheat straw fiber before they are compounded with polypropylene matrices from different types and grades.

Table 2-2 Examples of Variables in the Formulation and Manufacturing of Wheat Straw Polypropylene Composites

Composition Selection			**Manufacturing Process**	**Property Investigations**
Matrix System	**Filler System**	**Additives**		
Polypropylene (Properties) • Various grades (melt flow index, MFI) • Blends (mixtures of grades) • combined with recycled PP	Wheat Straw (Properties) *Chemical properties - composition* • cellulose • hemicelluloses • lignin • waxes *Physical properties:* • fiber length • aspect ratio *Fiber pre-treatment:* • Mechanical: Ground fiber, Long fiber • Chemical: Acid hydrolysis, chemical pulping • Thermo-mechanical: Steam explosion • Chemo-mechanical • Biological: Fungi, enzymes	*Product - Structure purpose:* • Coupling agent: *Product-Manufacturing purpose:* • Anti oxidant • Lubricant *Product - Usage purpose* : • UV stabilizer • Colorant • Heat stabilizer	*Processing Techniques* • Extrusion • Injection molding • Compression Molding • Thermoforming *Fiber Architecture* • Fiber Orientation • Web / woven Fiber	*Mechanical* • Tensile strength • Flexural strength • Flexural Modulus • Impact strength *Thermal* • Deflection Temp. • Crystallization temp. • Melting temp. • Degree of Crystallization *Other* • Rheological • Water absorption • Dimensional stability • Acoustical
Components' proportion: volume percentage, weight percentage			Processing variables	Various methods and standards

In general there are three types of polypropylene: PP homopolymer, PP random copolymer, and PP impact copolymer. The choice of polypropylene types depends on many factors such as the process to be used, the aesthetic and mechanical function of the final product, and special additive requirements. Homopolypropylene suitable for injection molding was the most used type of polypropylene reported in literatures, with Melt Flow Index ranges from 3 to 30.

Polypropylene matrix was also combined with other polymer matrices for a specific purpose, such as recycled polypropylene for environmental purposes (Kruger, 2007) and polyethylene terephthalate (PET) for technical purposes (Bera & Kale, 2008). Extrusion and injection molding is the most frequently used method for making the composites, while compression molding was also reported (Zou, Huda, & Yiqi, 2010). Most studies used fibers with length of 0.5 – 5 mm. However, the use of flour wheat straw with particle size < 0.5 mm (Mengeloglu & Karakus, 2008) or mechanically-split wheat straw fiber resulting in up-to-10 cm long fiber have also been reported (Zou, Huda, & Yiqi, 2010).

Many kinds of additives have been added to maintain or to improve composite structural, processing and usage properties. The type of additives depends primarily on the requirement of final applications. For example, applications exposed to sun light require UV-stabilizer and applications exposed to high temperatures require heat stabilizers.

Despite the extensive studies resulting in better understanding of WSPPC system and its potential application in sectors which need highly engineered materials, only a few successful applications has been reported. This is probably due to the lack of systematic database and reliable property models needed in manufacturing processes. Product Design approach and computer aided product design methods is probably one of the best solutions to overcome this problem.

2.3 Product Design and Computer Aided Product Design

There were major changes in the chemical industry during the last two decades. The dominance of commodity chemicals has been eroded by a newer emphasis on products such as specialty chemicals (Cussler & Moggridge, 2001). Chemical process industries have always launched successful new products. However, the dynamic and demanding markets

require companies to adopt a more systematic approach to bring the new product to the market faster and cheaper to guarantee competitiveness. Chemical Product Design and Engineering is becoming more important as a consequence of this change.

Costa, et. al. (2006) defined chemical product design (CPD) as a systematic procedure or framework of methodologies and tools whose aim is to provide a more efficient and faster design of chemical products able to meet market demands. Chemical product engineering is the whole science and art of creating chemical products, a much larger concept encompassing chemical product design. In other words, chemical product engineering can be seen as the general background of knowledge and practice supporting the concrete task of designing chemical products and their manufacturing processes.

From the practical stand point, Cussler and Moggridge (2001) simply defined product design as a procedure consisting four steps: (1) defining the needs; (2) generating ideas to meet the needs; (3) selection of the best ideas; and (4) manufacturing the product. Generating ideas and selection of the best ideas are the most time-consuming steps. These two steps traditionally involved an exhaustive search by trial and error methods which often ended up with no significant results. One way to overcome this problem is by using computer-aided techniques to identify very quickly a set of promising candidates and select a subset of likely final products, from which the desired properties can be identified through experiments.

The first step is considered as pre-design, or problem formulation step. Steps 2 and 3 represent respectively two types of product design problems: molecular design and mixture/blend design. In the molecular design, the objective is to find a chemical product that exhibits certain functional properties. The invention of new fuel additives and solvents in organic synthesis are examples of this type of design. In the mixture/blend design, the objective is to find a formula of chemical ingredients which give desirable final product properties. Examples of this type of design are the design of oil blends and polymer blends, including polymer composites and additives. The associated computer-aided designs for the two chemical product designs are called Computer-Aided Molecular Design (CAMD) and Computer-Aided Mixture/Blend Design (CAM^{b}D) (Gani R. , 2004a).

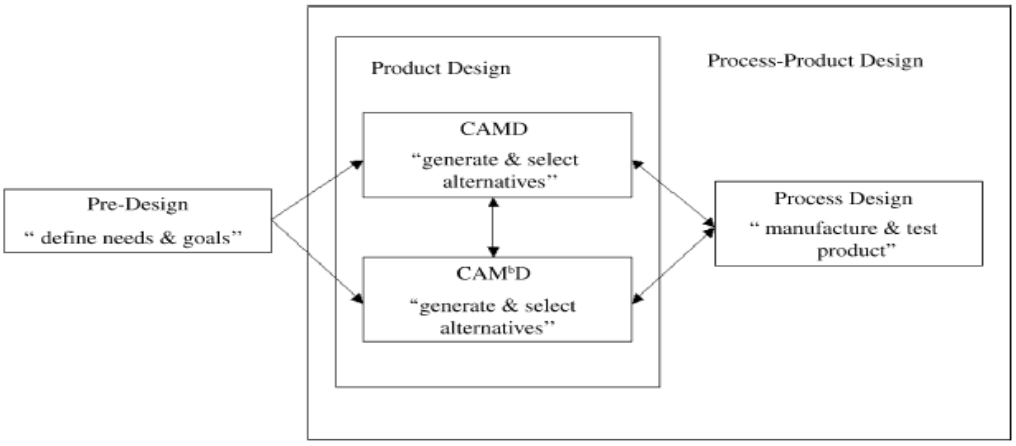


Figure 2-2 The Design Process for Product Design (Gani R. , 2004b)

Chemical products are judged by consumers not from their technical specifications but rather by the functional and performance attributes which are usually described by a set of performance indices. These indices are determined by three factors: (1) the composition and physicochemical properties of materials that constitute the product; (2) product structure, which is dependent on the manufacturing process; and (3) product usage conditions. The relationship between performance indices and product composition, product ingredients' properties and product structure has been mathematically systematized through the concept of property function (Costa, Moggridge, & Saraiva, 2006).

In generic terms, the chemical product design can be defined as: given a set of desired (target) needs, determine a chemical product (molecule or mixture) that satisfy these needs. Based on this definition and the concept of property function, the chemical product design problem can be described as "reverse property prediction", as illustrated in Figure 2-3 , where the needs are defined through product properties (Gani R. , 2004b).

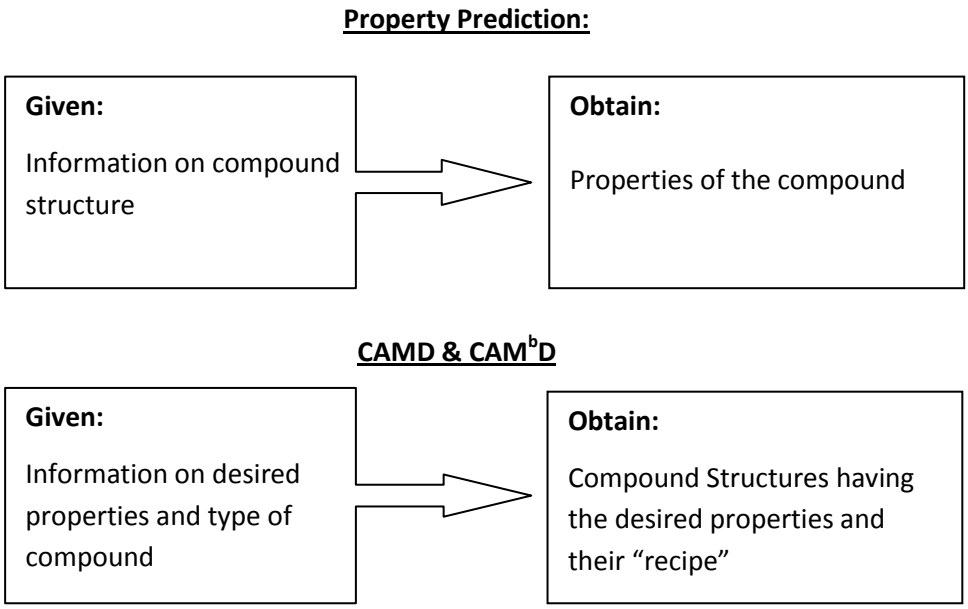


Figure 2-3 Chemical Product Design (CAMD, CAM^{b}D) are "reverse" of Property Prediction Problems

A simple framework for *chemical product design* (CPD) is illustrated in Figure 2-4. Different aspects of CPD are represented by methods for CAMD, CAM^{b}D, analysis and model validation; while different calculation options are represented by tools of process simulation, pure component property estimation, mixture property estimation and search engines for data retrieval from databases. Although the two-directional arrows in Figure 2-4 show the connection between two adjacent methods or tools, they are meant to indicate that all the tools and methods are connected to each other.

In any CPD problem, property functions and property models play important roles. While the framework is flexible enough to handle a large range of chemical product design problems, the currently available methods and tools can only solve a relatively small percentage of these problems. This is because the property models that are currently available are unable to predict the needed properties within an acceptable limit of uncertainty.

The framework, however, is able to give a great contribution in creating property models and database development in a systematic way. This will reduce time and effort in the early

stages of the product design process and subsequently bring the product to the market cheaper and faster.

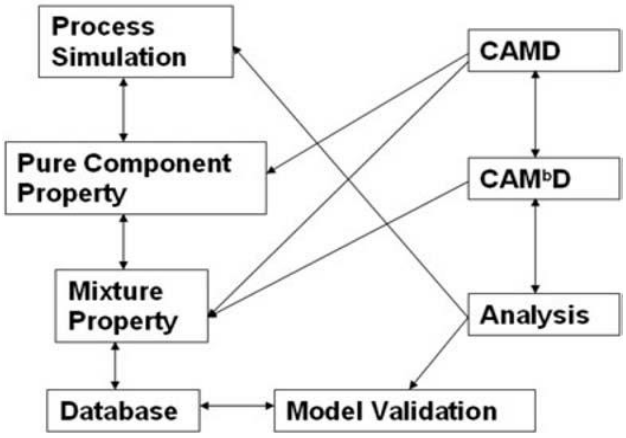


Figure 2-4 A Simplified Frameworks for Computer-Aided Chemical Product Design (Gani R. , 2004a)

2.4 Modeling Natural Fiber Polymer Composites

Traditionally, modeling a composite system is carried out by dividing the system into three main parts: composite composition selection, processing condition and composite final properties. Following this framework, three different kinds of modeling strategies are conducted as illustrated by Figure 2-5.

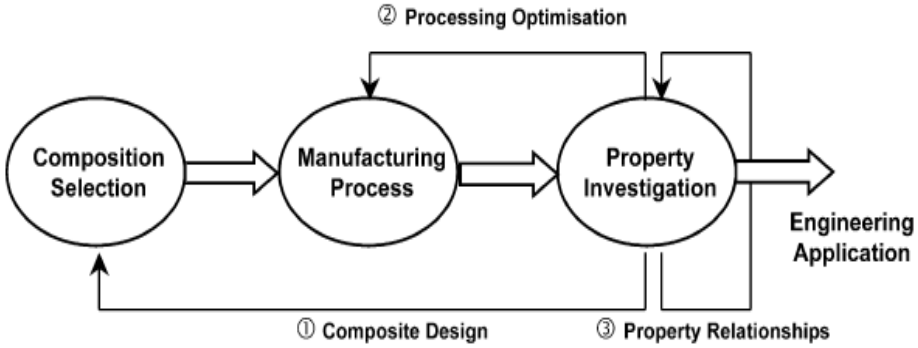


Figure 2-5 Schematic Presentation of Composite System and Composite Modeling Strategy (Zhang & Friedrich, 2003)

First, the final composite properties are modeled as a function of composition selection. These obtained models are commonly called structural property models. Second, the final composite properties are modeled as a function of the processing conditions. These models

are called processing property models. And finally, based on the fact that some properties strongly correlate to the other properties, such as a trade-off relationship between strength and toughness of composites, the final composite properties are investigated to develop models that correlate the properties each other. Once the various models were constructed, they can be manipulated and then be combined to simulate the composite system (Zhang & Friedrich, 2003).

Despite the well-established mechanistic modeling in composite science, researchers seem to face many difficulties in using the mechanistic approach to model natural fiber polymer composites. There are several issues where the composite theories are difficult to be applied in natural fiber plastic composite, as summarized in Table 2-3.

Table 2-3 Discrepancies between Theory and Experimental Work in Natural Fiber Composite (Fornes & Paul, 2003).

Issue	Theory	Experimental
Fiber shape and size	– Uniform shape – Constant Dimensions	– Non-uniform shape – Distributions of length and thickness
Fiber orientation	– Unidirectional, or – Isotropy (random orientation)	– Some degree of misalignment, or – Not completely isotropic
Fiber interface	– The fiber and matrix are well bonded	– Imperfect bonding between the fiber and matrix – Introduction of coupling agent is difficult to be mechanically modeled
Fiber modulus	– Assume fiber modulus is the same in all directions	– Fiber or filler are anisotropic
Matrix considerations	– Assume matrix is isotropic	– Polymer chain orientation – Presence of polymer crystallites
Fiber concentration effects	– Ignores particle-particle interactions – Ignores change in viscosity – Ignores agglomerations	– Particle-particle interactions and agglomerations – Changes in viscosity can alter morphology during injection molding – Changes in crystalline morphology

A few modifications of available composite models have been proposed to overcome these problems. Shibata and coworkers proposed a method to calculate the fiber orientation coefficient in modeling flexural properties of polypropylene with kenaf and bagasse fiber (Shibata, Cao, & Fukumoto, 2005). The Kelly-Tyson Modified Rule of Mixture and the Bowyer–Bader model was used to introduce a model that can take into consideration the super-critical and sub-critical length distributions of fibers in a hemp fiber polypropylene composite (Beckermann & Pickering, 2009).

A geometrical approach of cuboidal shape has been used to model the epidermal surface and parenchyma surface of wheat straw compounded in a polypropylene matrix (Thamae, 2008). Those modifications, however, only covered the individual issue of the complex natural fiber plastic composite system.

Alternatively, some researchers used experimental design methods to develop statistical models of natural fiber plastic composites. Adapting previous work of statistical experimental design of glass fiber mat polypropylene composite (Lee & Jang, 1997), Costa and co-workers used a $2^2 \cdot 3^1$ factorial design to develop statistical models of flexural properties as functions of the amount of coupling agent, the type of polypropylene matrix and the components' proportion of polypropylene-wood fiber composites (Costa T. H., 2000).

The use of semi-empirical models and artificial neural network (ANN) has also been reported. ANNs were considered by many as a powerful tool in composite property prediction and composite design (Zhang & Friedrich, 2003). Neural network-based analysis was applied to fiber-length's probability density estimations. The estimates were combined with Griffith Theory (the effectiveness of natural fibers) and Halpin-Tsai model to predict the flexural properties of polypropylene natural fiber composites (Esfandiari, 2007).

To the best of my knowledge, however, there were only a few reports of the work on statistical modeling of natural fiber plastic composite and none of those covered the combination of polypropylene and wheat straw.

2.5 Mixture Design of Experiments

Mixture Design of Experiments, or Experimental Design of Mixtures, is a subclass of response surface methodology (RSM). RSM is used to study relationships between measured dependent variables (responses) and independent/explanatory variables (factors). The main idea of RSM is to use a sequence of designed experiments to obtain optimal response(s). The optimum desired response(s) can be found by a regression analysis of data collected from designed experiments called response surface designs. Factorial design, fractional factorial design and composite design are examples of response surface designs.

In mixture design, the measured response is assumed to depend only on the **proportions** of ingredients in the mixtures; not on the **amounts** of the mixture. The Experiment of Lemonade is a famous example to show how the conventional response surface design does not apply well to experiments with mixtures (Anderson & Whitcomb, 1998). In this kind of experiment, the objective is to find the composition of water and lemonade which give the optimum taste. A 2^2 factorial design of experiment was carried out as presented in Table 2-4. It can be seen that run #4 is a replication of run #1. Both actually have the same proportion of water and lemonade. In addition, the design only covered approximately 1/3 of the design space. In other words, factorial design requires more experiments for less information when it was applied to experiments with mixtures.

Table 2-4 A 2^2 (two factors – two levels) Factorial Design of the Lemonade Experiment

Run #	Lemons Level	Water Level	Taste
1	Low (-)	Low (-)	Good
2	High (+)	Low (-)	Sour
3	Low (-)	High (+)	Weak
4	High (+)	High (+)	Good

The unique feature of mixture experiments is that the sum of all of q components proportion must equal to 1; meaning that all independent variables x_i correlate to each other, i.e.,

$$\sum_{i=1}^{q} \boldsymbol{x_i} = \boldsymbol{x_1} + \boldsymbol{x_2} + \cdots + \boldsymbol{x_q} = \mathbf{1.0} \tag{2.1}$$

$$x_i \geq 0, \quad i = 1, 2, \ldots, q \tag{2.2}$$

The experimental region for a mixture experiment with *q* components is called *simplex*, which is regularly a sided figure with q vertices in q-1 dimensions. The coordinate system for mixture proportions is a *simplex* coordinate system. The simplex coordinate system for a three-component mixture is presented by Figure 2-6 (Myers, Montgomery, & Anderson-Cook, 2009).

To accommodate a polynomial equation to represent response surface over the entire simplex region, an arrangement consisting of evenly distributed points called *lattice* has to be constructed. A [*q*,*m*] *simplex lattice design*, therefore, is a design of points for a *q* components mixture to accommodate an m^{th} degree polynomial of a response surface. Examples of *simplex lattice* designs are shown in Figure 2-7 .

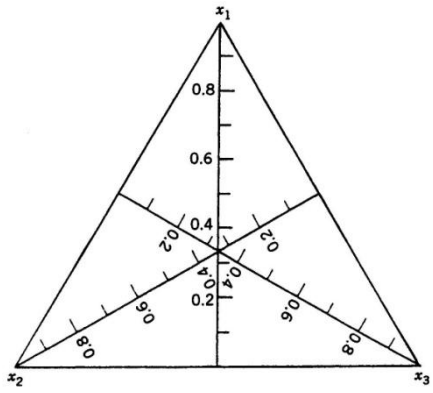


Figure 2-6 Simplex Coordinate System for a Three-component Mixture (Myers, Montgomery, & Anderson-Cook, 2009)

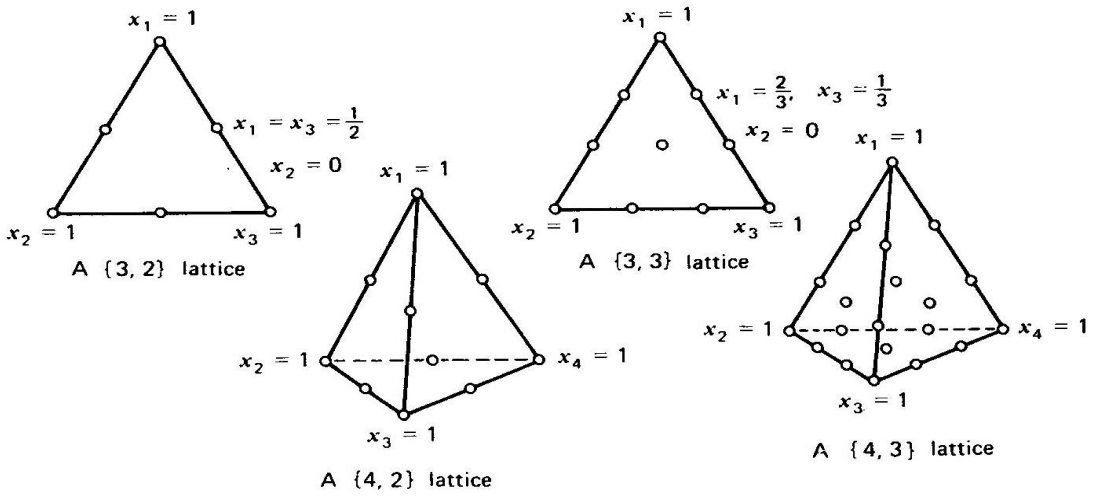


Figure 2-7 Examples of a (q,m) Simplex Lattice Design (Cornell, 2002)

Because the independent variables *x* are not unique, the standard polynomial model has been modified to become a *canonical* mixture polynomial model. In general, the canonical or Scheffe forms of the mixture models are as follows:

Linear:
$$E(y) = \sum_{i=1}^{q} \beta_i x_i \tag{2.3}$$

Quadratic:
$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<}\sum_{j=2}^{q} \beta_{ij} x_i x_j \tag{2.4}$$

Full Cubic:
$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<}\sum_{j=2}^{q} \beta_{ij} x_i x_j + \sum_{i<}\sum_{j=2}^{q} \delta_{ij} x_i x_j \left(x_i - x_j\right) + \sum_{i<}\sum_{j<}\sum_{k=3}^{q} \beta_{ijk} \beta_i \beta_j \beta_k \tag{2.5}$$

Special Cubic:
$$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}\sum_{=2}^{q} \beta_{ij} x_i x_j + \sum_{i<j}\sum_{=2}^{q} \delta_{ij} x_i x_j + \sum_{i<}\sum_{j<}\sum_{k=3}^{q} \beta_{ijk} \beta_i \beta_j \beta_k \tag{2.6}$$

The models can be used to construct a response surface and a contour plot as illustrated in Figure 2-8.

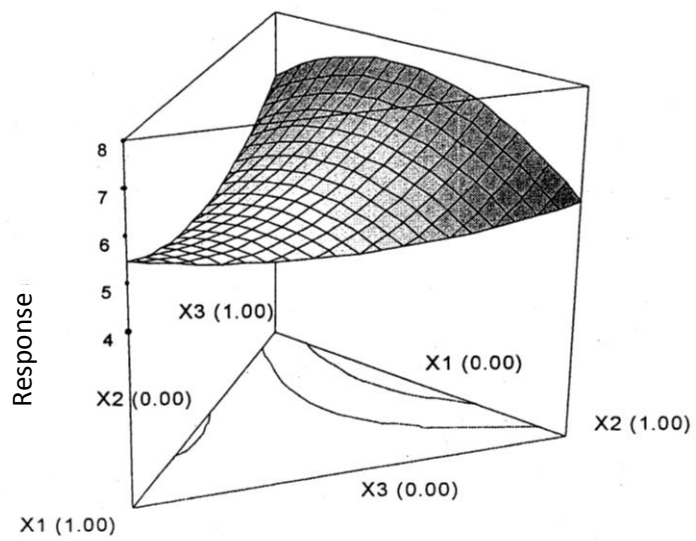


Figure 2-8 Response Surface and Contour Plot of a Response over a Three-component Simplex Region (Anderson & Whitcomb, 1998)

The response surface of a linear polynomial model is a planar surface over the simplex region. The quadratic polynomial model consists of linear blending terms and quadratic blending terms. Therefore, the response surface of a quadratic polynomial model is a curved surface which consists of a planar surface plus a curvature surface representing the quadratic term. Figure 2-9 illustrates the response surfaces of linear and quadratic canonical polynomial model of a three component mixture (Cornell, 2002).

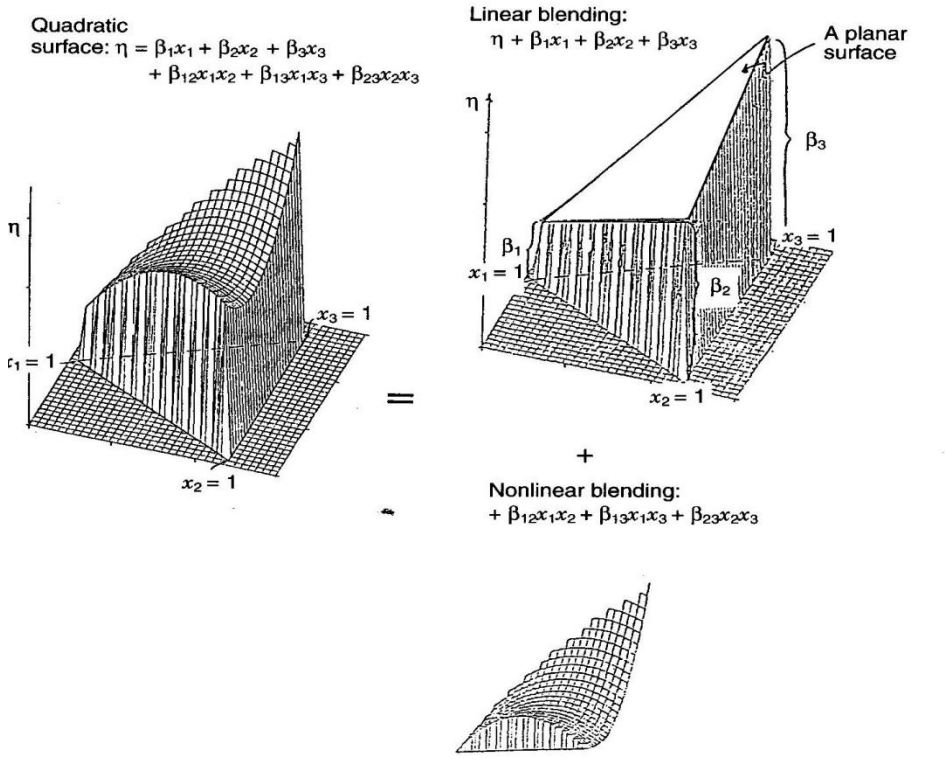


Figure 2-9 Response Surface for Quadratic Canonical Polynomial Model of a Three-component Mixture (Cornell, 2002)

There are many variations of mixture design problems. One of the variations is the addition of upper and lower bounds on some of the component proportions. Constrained mixture design and *pseudo-simplex* design are examples of design strategies for such problems. Various types of mixture designs for various mixture design problems, as well as data analysis and model building techniques are discussed by Cornell (2002).

In some cases, non-mixture variables are involved in the problem and affect the responses. These variables are called as *process variables z*. One possible strategy to tackle this case is through the use of Process-Mixture Design. This design combines the standard mixture design with factorial or fractional factorial design for process variables as illustrated in Figure 2-10 .

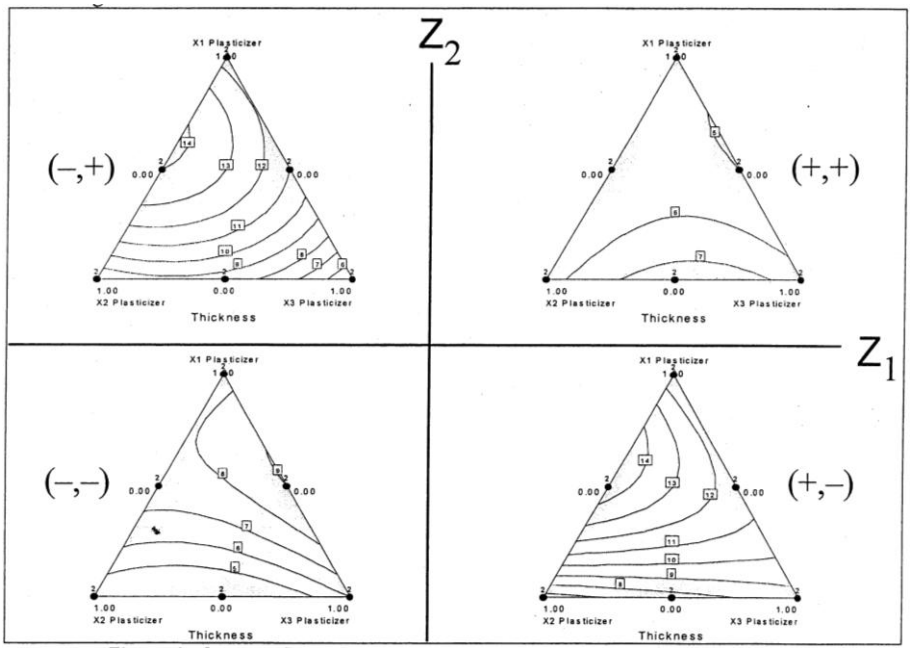


Figure 2-10 A Process-Mixture Designs with a Three-component Mixture Design and a 2^2 Factorial Design of Process Variables z_1 and z_2 (Anderson & Whitcomb, 1998)

The standard canonical polynomial model is combined with the process model to constitute a response surface model. For instance, the overall response model of problem with a three-component mixture and three process variables may follow this equation:

$$E(y) = \sum_{i=1}^{3} \gamma_i^0 x_i + \sum \sum_{i<j}^{3} \gamma_{ij}^0 x_i x_j + \sum_{l=1}^{3} \left[\sum_{i=1}^{3} \gamma_i^l x_i + \sum \sum_{i<j}^{3} \gamma_{ij}^l x_i x_j \right] z_1 + \sum \sum_{l<m}^{3} \left[\sum_{i=1}^{3} \gamma_i^{lm} x_i + \sum \sum_{i<j}^{3} \gamma_{ij}^{lm} x_i x_j \right] z_1 z_m + \left[\sum_{i=1}^{3} \gamma_i^{123} x_i + \sum \sum_{i<j}^{3} \gamma_{ij}^{123} x_i x_j \right] z_1 z_2 z_3 + \epsilon \quad (2.7)$$

A common application of mixture design of experiment is product formulation; where a product is formed by mixing several components together. Successful applications have been found in formulation of gasoline, soaps, shampoo, detergent, pharmaceutical products, as well as foods and beverages. However, only few applications have been reported in composite studies. One of the few is the study of mechanical behavior of polymer-layered silicate nanocomposite (Mittal, 2008).

3 Research Methodology

3.1 Organizing and Analyzing the Existing Data Provided by Previous Works

The objective of this task was to understand the current subject matter and to extract as much as information from the existing data provided by previous works in our laboratory and other research groups that have worked with wheat straw polypropylene composites. The information would be very critical in designing an experiment, especially in determining the factors, i.e., the independent variables of the experiments; and the levels, i.e., the values of the factor(s) for which we wish to observe the response variables (Canavos & Koutrouvelis, 2009) .

Recent studies of WSPPC system in our laboratory conducted by Kruger (2007) and Ng (2008) are summarized in Table 3-1 and Table 3-2, respectively. Among the key findings of these works are the optimum operating-conditions of compounding and injection molding process, and the range of fiber loading that give acceptable results of the composite flexural properties.

Table 3-1 Summary of WSPPC System Studied by Kruger (2007)

Composition Selection	**Manufacturing Process**	**Properties Measured/Observed**	**Testing Methods/Standards**
Fiber loading (%wheat straw) 0, 10, 20, 30, 40, 50, 60	Batch Extrusion: Different operating temperatures: 160, 190, 230 Celsius	Thermal • Melting Temperature • Crystal Temperature • % Crystallinity	Differential Scanning Calorimetry (DSC)
Additives: • MAPP 2% • MAET 2% • Lubricant 3%		Water absorption • Diffusivity of water	Water immersion
		Mechanical • Flexural Modulus • Yield Strength	ASTM D-790-03
		Morphology • Fiber length • Aspect ratio	Scanning Electron Microscopy (SEM)

Table 3-2 Summary of WSPPC System Studied by Ng (2008)

<table>
<tr><th>Composition Selection</th><th>Manufacturing Process</th><th>Properties Measured/Observed</th><th>Testing Methods/Standards</th></tr>
<tr><td>Polypropylene
• Virgin PP (vPP)
• Recycled PP (rPP)</td><td rowspan="4">• Batch – Extrusion
60% plastics
5 combinations : 0, 25, 50, 75, 100 % rPP
40% filler (4 types of filler)
• Extrusion – Orientation
(80% plastics and 20% gWS)</td><td>Thermal properties
• Melting Temperature
• Crystal Temperature
• % Crystallinity</td><td>• Differential Scanning Calorimetry (DSC)
• X-Ray Diffraction (XRD)</td></tr>
<tr><td rowspan="3">Ag-Filler
• Wheat Straw - ground
• Soy Hull
• Soy Hull - ground
• Soy Stem – ground</td><td>Chemical</td><td>FTIR</td></tr>
<tr><td>Mechanical
• Flexural Modulus
• Yield Strength</td><td>ASTM D-790-03</td></tr>
<tr><td>Filler properties
• Fiber length
• Aspect ratio</td><td>Scanning Electron Microscopy (SEM)</td></tr>
</table>

Following those two studies, Sardashti (2009) introduced clay as another additive and studied the effects of different fiber sizes and coupling agent proportions to the composite properties (Table 3-3).

Sardashti (2009) studied the flexural properties of WSPPC made of different sizes of ground wheat straw. He used three different ground wheat straw populations obtained from the grinding process of a raw wheat straw, namely: fine, mid, and large. Those three different sizes were obtained from screening the ground wheat straw through two sieves with mesh size of 16 and 35. The WSPPC samples were prepared from each size of wheat straw with 30% fiber loading. The flexural properties of the composite samples were obtained by carrying out a set of measurements according to the ASTM standard.

Despite the variation of fiber sizes, no significant differences found in flexural properties of WSPP composites. To investigate the effect of fiber size on composite flexural properties, measurements of fiber size have been done for both before and after the compounding process by extrusion. It was found that the differences of fiber length distribution of three different sizes (grades) of wheat straw decreased after the extrusion (compounding) process, as can be seen in Figure 3-1 and Figure 3-2, respectively. The similar trend was also found in

the aspect ratio distribution, as can be seen in Figure 3-3 and Figure 3-4, respectively. In summary, the preparation of the composites by extrusion and injection molding decreased the size and the aspect ratio of the straw fiber.

Table 3-3 Summary of WSPPC System Studied by Sardashti (2009)

Composition Selection	**Manufacturing Process**	**Properties Measured/Observed**	**Testing Methods/Standards**
Polypropylene Ground Wheat Straw • Different fiber sizes Additives Clay (0-5%) MAPP (0-4%)	• Extrusion At 190 Celsius	Thermal properties • Melting Temperature • Crystal Temperature • % Crystallinity	• Differential Scanning Calorimetry (DSC) • X-Ray Diffraction (XRD)
		Morphology	SEM Analysis
		Mechanical • Flexural Modulus • Water Absorption	 ASTM D-790-03 ASTM D-570-01
		Filler properties • Chemical composition (cellulose, hemi-cellulose and lignin) • Fiber density • Thermal degradation • Fiber length and Aspect ratio	 • Neutral Detergent Fiber and Acid Detergent Fiber Tests • Gas Picnometer • TGA Analysis • Leica MZ6 Digital camera and ImageJ Data Analysis Software

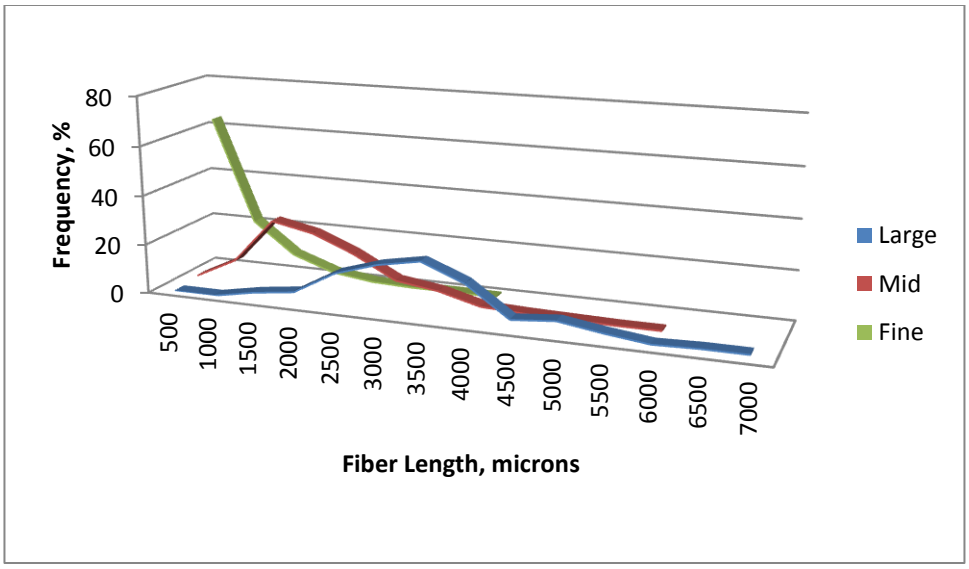


Figure 3-1 Fiber Length Distributions of Wheat Straw Fibers before Compounding Process.

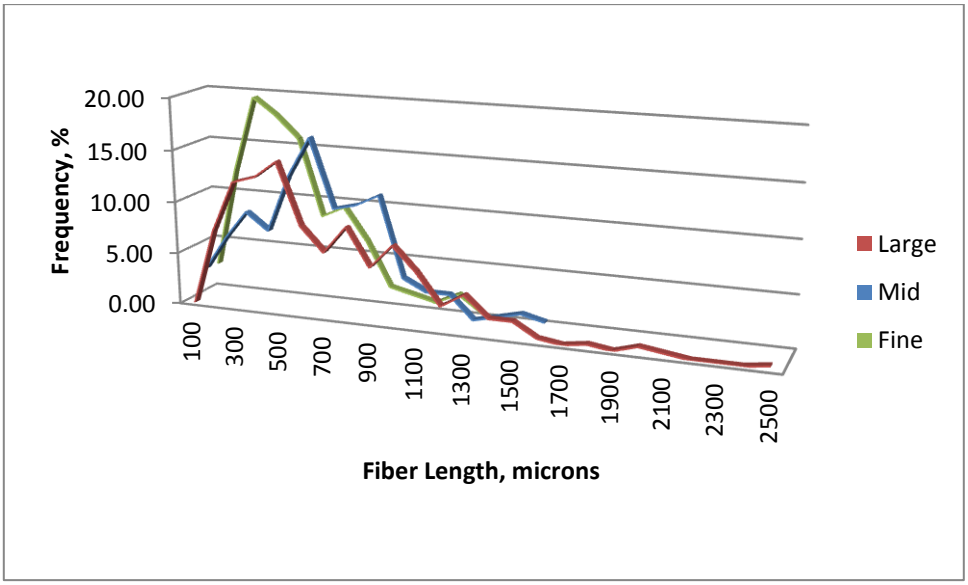


Figure 3-2 Fiber Length Distributions of Wheat Straw Fibers after Compounding Process.

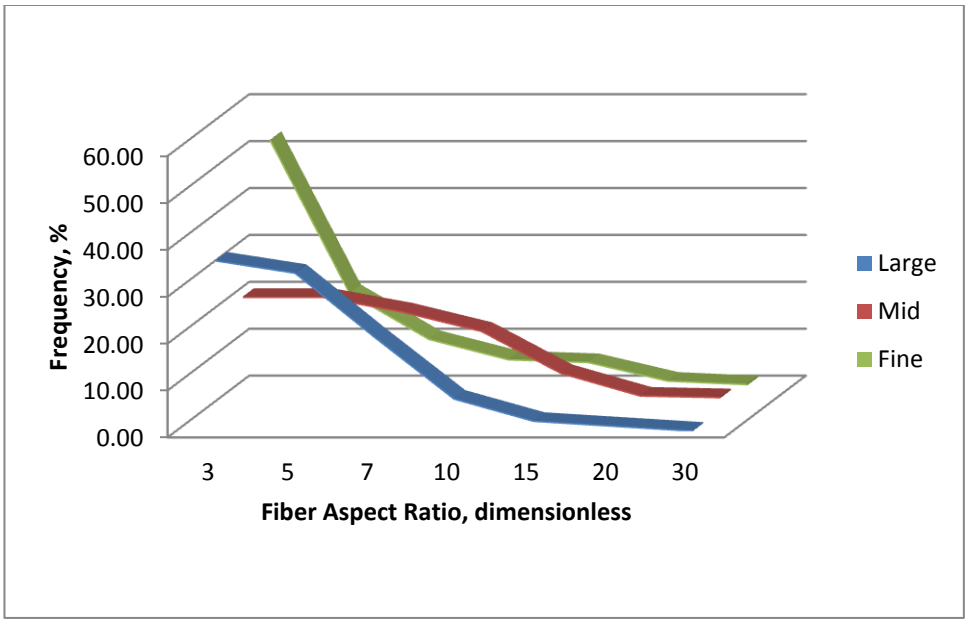


Figure 3-3 Fiber Aspect Ratio Distributions of Wheat Straw Fibers before Compounding Process

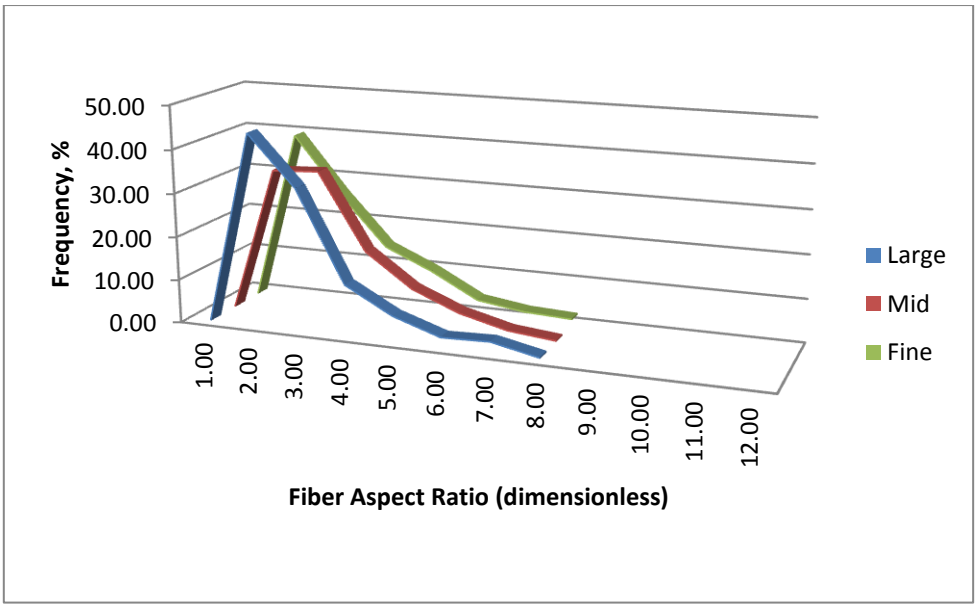


Figure 3-4 Fiber Aspect Ratio Distributions of Wheat Straw Fibers after Compounding Process

It can be seen in those Figures that after the compounding process, the fiber would have similar aspect ratio distributions regardless their various initial distributions before the compounding process. Also, the fiber length distributions after compounding process only

showed a small difference in the distributions between the three fiber populations (large, medium and small).

It was concluded that the lack of differences in flexural properties of the composites from difference fiber size were influenced by the similarities of the fiber length and aspect ratio distributions in the actual composites, regardless the initial fiber size before compounding process.

Therefore, to further investigate the effect of fiber size on composite flexural properties, a third study was carried out by Sardashti on the separation of different types (grades) of fiber using a screening process that resulted in 18 fractions of ground wheat straw with different sizes and aspect ratios. Sardashti recommended as future work to prepare WSPPC samples from each of those 18 fractions and to investigate their flexural properties.

3.2 Designing and Performing Mixture Design of Experiments

The objective of this task was to apply Mixture Experimental Design to develop robust, reliable statistical models that can be used to construct the operating window (based on the input variables and required properties) and to perform response surface optimization for the design of wheat straw polypropylene composite.

A three-component mixture design of experiment was chosen for the study. The input variables are the proportion (in weight percentage) of the major components: polypropylene, ground wheat straw, and a coupling agent (MAPP). The response variables in this study are: Flexural Modulus, Flexural Strength, Yield Strength, and Density of the composite.

The levels of all process variables (i.e. variables not related to the component proportions such as components' properties and processing variables) should be kept as constant as possible.

Based on the results of previous studies in our laboratory (Sardashti, 2009), (Kruger, 2007), it was found that there were significant improvements on mechanical properties of wheat straw polypropylene composite in the presence of Maleic anhydride-grafted-polypropylene (MAPP) as the coupling agent. One of the important results of those previous results was the ranges of composition of each component which give acceptable results. The ranges can be

used to set up a constrained *l-pseudo simplex* design of a three-component mixture design (Cornell, 2002).

The Design Expert Software was used to generate, to construct, and to evaluate the properties of the proposed set of design points by considering the leverage values, the D-optimality and the Fraction of Design Space graph.

The composite samples with the composition specified by the design are then prepared by a laboratory work consisting of two main processes: 1) melt-blending method of the components using a co-rotating conical twin-screw extruder followed by pelletization of the extrudates and 2) injection molding of the pellets by using a laboratory injection molding machine to make ASTM-standard samples for flexural testing and density measurement.

The flexural property models of wheat straw polypropylene composites will be constructed by analyzing the obtained data. The least square regression and backward model term reduction techniques will be applied to the model fitting processes.

Unlike some previous similar works on statistical modeling of natural plant fiber thermoplastic composite, this study provides not only the summary of the Analysis of Variance (ANOVA) test, but also provides a complete diagnostics case statistics report. The report can be used to evaluate the model properties according to the standard properties of response surface models.

A second study of mixture design of experiment to better illustrate the application of mixture design of experiments in WS-PP composite product design was also performed. A wheat straw polypropylene/impact copolymer polypropylene composite system was studied in order to provide composite products that meet typical specifications of automotive parts application.

3.3 Designing and Performing Process-Mixture Experimental Design

The objective of this task was to apply the process-mixture experimental design in order to investigate the effects of fibers sizes and fiber loading on several properties of wheat straw polypropylene composite.

Mixture Design of Experiments only allows the using of *component proportions* as independent variables. In designing WSPCC, however, we are dealing with several variables which are not related to component proportions, such as type of polypropylene matrix (grades with different properties) and the type of wheat straw fibers (shape, size, and aspect ratio) . These variables were called *process variables*; a term used to differentiate the variables from components' proportion variables. Process variables are not mixture variables. Process-Mixture Design of experiment accommodates both mixture variables and process variables in a systematic way.

Understanding how those process variables – together with the component proportion variables – can influence the composite properties and developing models to describe the influence will contribute to the product design and optimization of WSPPC.

The main *process variables* being studied in this task were the type particles of wheat straw fiber. The main attributes of the fiber are length and aspect ratio because they have direct effect on the mechanical properties. Another important attribute is the thermal stability, since degradation of the fibers at high temperatures (> 200 ^{o}C) may contribute to poor mechanical performace.

Recalling one possible design discussed in the end of Section 2.5 where a three-component mixture design is combined with a factorial design involving two process variables as illustrated in Figure 2-10, the design will consist of a set of mixture design in each four combinations of high level and low level of fiber size and high level and low level of fiber aspect ratio. Two-stage technique of fiber separation is used to provide fibers with different sizes based on the design.

Furthermore, during the compounding and molding process, the shape and the size of fibers are changing. In fact, it is the shape, size, and orientation of the fibers after compounding and molding process that actually constitute the final properties of WSPPC product; not the fiber properties before the compounding process. To investigate the change in fiber size during the compounding process, fibers are extracted from the sample and the size measurement is performed.

4 Modeling the Flexural Properties of Wheat Straw Polypropylene Composite by Using Experimental Mixture Design

4.1 Introduction

The use of natural plant fibers (NPFs) in thermoplastic composites as fillers (to reduce cost or density when compared with mineral fillers) or as fibers (to improve mechanical properties when compared to the polymer matrix) has become an interest to researchers in recent years due to various economical and environmental advantages they offer. Many research works have been done to study the various NPFs compounded to different thermoplastic polymer matrices. Various types of chemical and mechanical modifications are usually applied on the natural fibers to overcome the hydrophilic nature of the fiber and make it compatible with the hydrophobic polymers. (Gassan & Bledzki, 1999), (Sain, Law, Suhara, & Boullioux, 2005) , (Shibata, Cao, & Fukumoto, 2005). However, there is an absolute need of database and software solutions which can simulate the structural and processing properties of these materials to open the possibility for further expansion and establishment of the technology of NPFs reinforced compound. (Bos, Mussig, & Van den Oever, 2006)

The need for this database is particularly important when a new type of fiber is conceived. There are two main reasons for this: a) plant fibers are heterogeneous because of conditions associated to their chemical compositions (affecting thermal stability) and structure (affecting strength), which are associated with growth, species and harvest, for example; b) plant fibers are heterogeneous because of conditions associated with the manufacturing of the fiber, which depend on the processing methods used to produce grades of fibers (specified by size, shape and aspect ratio).

Traditionally, modeling a composite system is carried out by dividing the system into three main parts: composite composition selection, processing condition and composite final properties. According to this division, three different kinds of modeling strategy are then conducted. Firstly, the final composite properties are modeled as a function of composition selection. These obtained models are commonly called structural property models. Secondly, the final composite properties are modeled as a function of the processing conditions. These

obtained models are called processing property models. And finally, based on the fact that some properties strongly correlated to other properties, such as tensile and flexural properties, the final composite properties are investigated to develop models that correlate each property to other properties. Once the various models are constructed, they can be manipulated and then be combined to simulate the composite system. (Zhang & Friedrich, 2003)

Many researchers have attempted to use mechanical and theoretical approaches to model the structural properties of NPFs polymer composite. The focus of those studies was to model the mechanical properties as a function of natural fiber loading, natural fiber orientation and natural fiber properties i.e. fiber length, fiber length distribution and fiber aspect ratio. These approaches, however, failed to give proper models due to the complexity of the composite system such as fiber-matrix compatibility and fiber degradation during compounding process. The degree of complexity is even higher in short fiber with different types of orientation within the composite structure. (Mittal, 2008)

Alternatively, statistical modeling approach has been used by many researchers in attempt to develop models that can be used to accurately predict mechanical properties of these composites. (Esfandiari, 2007) It should be noted that only few of these models use response surface methodology and mixture design experiment, despite the fact that many successful works have reported on mixture and mixture-process design experiments in the area of chemical product designs. (Mittal, 2008), (Costa, Carvalho, Souza, Coutinho, Pinto, & Kokta, 2000)

Among NPFs, agricultural residues and byproducts such as wheat straw, soy stem, and soy hulls for example, have become of interest due to their abundant availability, relatively low cost, and the fact that there are sustainable sources of feedstock. Wheat straw has been proven to increase the flexural modulus of polypropylene. The presence of small amount of coupling agents such as maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted polyethylene (MAPE) have shown to increase the fiber matrix compatibility which resulted in better reinforcement mechanism. (Karakus, 2008), (Panthapulakkal, Zereshkian, & Sain, 2006)

The objective of this study is to apply the mixture design experiment technique as a subclass of response surface methodology in order to develop statistical models that can be used to predict the mechanical properties of wheat straw polypropylene composite. The product design approach and technique are applied to determine the variables and responses to be studied.

4.2 The Design of Mixture Experiment

A three-component mixture design of experiment is chosen for the study presented here. The input variables are the proportion (in weight percentage) of composite components: polypropylene, wheat straw and the coupling agent (MAPP). The response variables measured in this study are: flexural modulus, flexural strength, yield strength and density of the composite.

Based on the results of previous works it was found that there were significant improvements on mechanical properties of wheat straw polypropylene composite in the presence of maleic anhydride-grafted-polypropylene (MAPP) as coupling agent. One of the important results of those works was the range of composition of each component which gives acceptable results (Kruger, 2007). The ranges can be used to set up a constrained L-pseudo simplex design of three component mixture design (Cornell, 2002) :

$$\begin{aligned} 0.46 \leq x_1 \leq 0.70 \\ 0.30 \leq x_2 \leq 0.50 \\ 0 \leq x_3 \leq 0.04 \end{aligned} \qquad (4.1)$$

where x_1, x_2 and x_3 are weight fraction of polypropylene (denoted as A), wheat straw (denoted as B), and MAPP (denoted as C) respectively.

Design Expert Software was used to generate, to construct and to evaluate the properties of the proposed set of design points. Since the objective of the experiment is to develop models with good predictive capability, the D-optimality criterion was chosen to find the optimal design. The D-optimal design minimizes the variance of model parameters and increases the confidence region of the models. (Myers, Montgomery, & Anderson-Cook, 2009) The

constrained l-pseudo simplex design region as well as the 15 design points constructed can be seen in Figure 4-1.

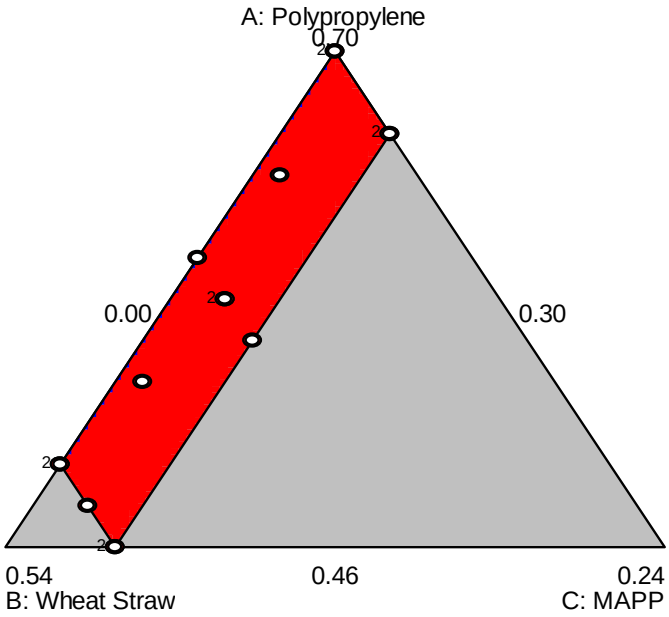


Figure 4-1 The Constrained l-Pseudo Simplex Design Region of Wheat Straw-MAPP-Polypropylene Mixture. (The proportions are in real values; the dots are the design points; "2" indicates the points are replicated twice).

The proposed design consists of: 1) one *centroid*; 2) four *vertices*, which are being replicated (twice) to provide lack-of-fit test; 3) three *centre-edge points*; and 4) two *axial-check-blend points*. The coordinate of the design points and the leverage values of each design points can be seen in Table 4-1 .

To fit the design points in calculating the parameter estimates of *scheffe's canonical* model, the standard *l-pseudo simplex lattice* coordinates x' are applied, with the following transformation formula (Cornell, 2002) :

$$x_1' = \frac{x_1 - 0.46}{0.24}, \quad x_2' = \frac{x_2 - 0.3}{0.24}, \quad x_3' = \frac{x_3 - 0}{0.24} \tag{4.2}$$

The design evaluation shows that the average leverage value is 0.4. This low average value and the uniformity of the leverage value among design points are highly desired in an experimental design, since the influence of design points is distributed evenly within the

design space. This distribution will allow us to remove any outliers of the measured response without losing the robustness of the models. (Cornell, 2002)

Table 4-1 Design Points of the Proposed Mixture Design with design point types and leverage values

Point #	L-Pseudo simplex coordinates			Original Composition, wt. fraction			Type	Leverage
	X'_1	X'_2	X'_3	X_1	X_2	X_3		
1	1/6	5/6	0	0.50	0.50	0.00	Vertex	0.431255
2	0	5/6	1/6	0.46	0.50	0.04	Vertex	0.440698
3	7/12	5/12	0	0.60	0.40	0.00	Centre Edge	0.461845
4	1/12	5/6	1/12	0.48	0.50	0.02	Centre Edge	0.509808
5	1	0	0	0.70	0.30	0.00	Vertex	0.450155
6	5/6	0	1/6	0.66	0.30	0.04	Vertex	0.472674
7	1/3	5/8	1/24	0.54	0.45	0.01	Axial CB	0.182782
8	3/4	5/24	1/24	0.64	0.35	0.01	Axial CB	0.211144
9	5/12	5/12	1/6	0.56	0.40	0.04	Centre Edge	0.486307
10	1/2	5/12	1/12	0.58	0.40	0.02	Center	0.279275
11	1/2	5/12	1/12	0.58	0.40	0.02	Center	0.279275
12	0	5/6	1/6	0.46	0.50	0.04	Vertex	0.440698
13	1/6	5/6	0	0.50	0.50	0.00	Vertex	0.431255
14	5/6	0	1/6	0.66	0.30	0.04	Vertex	0.472674
15	1	0	0	0.70	0.30	0.00	Vertex	0.450155

Another criterion for design evaluation is Fraction of Design Space (FDS) graph. The FDS graph of the proposed design is presented in Figure 4-2. The graph shows that the proposed design points are able to cover 0.93 fraction of design space with predicted Mean of Standard Error of 0.663 or lower. These figures meet the suggested values of 0.8 and 1.0 for fraction of design and mean standard error, respectively.

The main advantage of the design evaluation step is to measure the effectiveness of proposed design of experiments in modeling the response surface even before the experiments are being carried out. This good practice will minimize the excessive and unnecessary experiments which could be very costly and time-consuming (Myers, Montgomery, & Anderson-Cook, 2009).

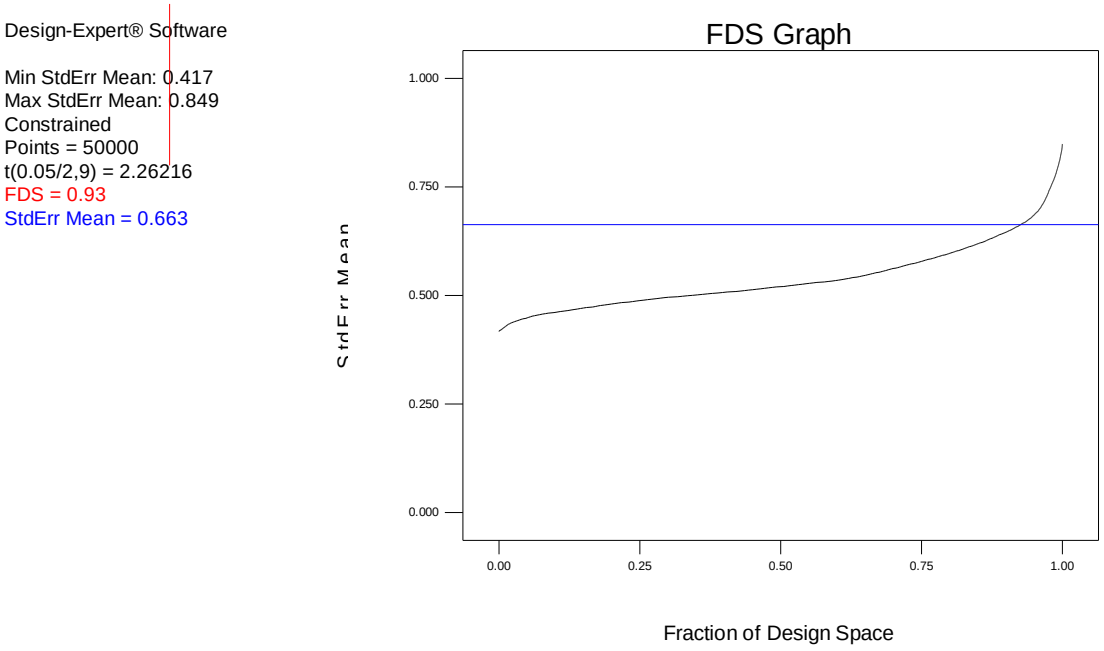


Figure 4-2 Fraction of Design Space Graph of the Proposed Design

4.3 Materials and Response-Measurement Method

Homopolypropylene 6301 with a melt flow index of 12 g/10 min (230 ^{o}C, 2.16 kg, ASTM D 1238) in the form of powder was donated by A. Schuman Inc. Wheat straw used in this study was a soft white winter wheat straw (AC Mountain) harvested in late 2007 from the Ontario region.

Straws were first fed to a flywheel by end cutter to reduce their sizes approximately to 3-5 cm. The cut wheat straw was then fed to a directly coupled, rotary hammer mill for grinding. Grinding was performed at 60 minutes intervals followed by 15-20 min cooling cycles. Prior to use for compounding, the ground wheat straw was passed through a sieve with mesh sizes of 35 to select the grade of straw fibers used here. The ground wheat straw was supplied by OMTEC Inc.

The coupling agent used was Fusabond MD-353D, a maleic anhydride grafted polypropylene (MAPP) from DuPont. Two antioxidants, namely Irganox 1010 and Irgafos 168 were purchased from Ciba Inc. and were used in order to avoid thermal degradation caused by the processing conditions as well as increase the shell life of the final product.

Wheat straw polypropylene composites were prepared by the melt-blending method using a Haake Minilab Micro-compounder (Minilab), a co-rotating conical twin-screw extruder. The operating conditions of extruder such as temperature and screw rotation rate were set at 190 ^{o}C and 40 rpm, respectively. The components of composite, polypropylene, wheat straw, and MAPP and antioxidants were hand-blended to get a uniform mixture before feeding into extruder. Both antioxidants were used in equal amounts maintained at a total of 0.5 wt-% with respect to polypropylene content.

As the mixture of components of composite are conveyed through the screws of twin-screw extruder, melting and mixing took place and a homogenized extrudate came out through the flush orifice (die) in the form of strands. The extrudate strands were cooled by air contact (no water). The strands were cut into smaller pieces proper for the next processing step.

The resulting pellets from compounding process were then injection molded using Ray-Ran Laboratory injection molding machine (RR/TSMP) to get samples (ASTM standard) for flexural testing and density measurement. The injection molding was performed keeping the barrel temperature at 190 ^{o}C and mold tool temperature at 50 ^{o}C with injection periods of 15 seconds at 100 psi.

Flexural properties of the samples were investigated on sample specimens prepared by injection molding. Conditioning the sample and analysis procedure followed are as per ASTM D790-07. Prior to conditioning, injection molded samples were annealed at 150 ^{o}C for 10 min and then were cooled down at a rate of 10^{o}C/min to have a homogenized crystallinity for all the samples and to erase any thermal history taken place during the injection molding.

The density measurement was conducted according to ASTM D792-07.

4.4 Results and Discussions

The results of flexural properties and density measurements on the composite samples are presented in Table 4-2. The analysis of the results was conducted by using the Design Expert software. The following steps were applied to each response variable: (1) model fitting; (2) analysis of variance (ANOVA) test; (3) model diagnostics; and (4) response surface graphs. The fittest model was chosen by first comparing various coefficients of determination R^2 values between linear, quadratic, special cubic and cubic canonical polynomial model. The model was chosen based on the maximum value of *Adjusted*-R^2 and *Predicted*-R^2 values. The number of model terms was reduced by applying backward elimination technique to get the model term combination which gives highest R^2 values. The model diagnostic case was then carried out to examine the influence of each design points to the model.

Table 4-2 Measured Flexural Properties and Density of WSPPC

Std #	Composition, (weight %)			Flex. Modulus (MPa)		Flex Strength (MPa)		Offset Yield (MPa)		Density (g/mL)	
	PP	WS	MAPP	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.
1	50	50	0	2323	148	40	1.43	65	1.29	1.0505	0.0070
2	46	50	4	2803	265	72	2.45	122	5.44	1.0740	0.0199
3	60	40	0	1930	195	48	1.88	74	2.14	1.0423	0.0108
4	48	50	2	3025	56	69	2.13	112	4.44	1.0636	0.0110
5	70	30	0	2012	100	53	1.13	72	2.18	0.9747	0.0072
6	66	30	4	2140	101	72	1.58	102	5.15	0.9724	0.0017
7	54	45	1	2588	112	67	1.29	109	4.69	1.0380	0.0046
8	64	35	1	2172	116	66	1.64	102	2.07	1.0011	0.0044
9	56	40	4	2545	126	73	2.50	115	4.31	1.0190	0.0063
10	58	40	2	2335	140	69	2.52	108	4.69	1.0180	0.0101
11	58	40	2	1903	159	63	2.42	115	7.03	-	-
12	46	50	4	2560	155	72	2.12	125	6.03	-	-
13	50	50	0	2173	152	45	1.73	71	3.40	-	-
14	66	30	4	1974	144	72	1.82	106	3.58	-	-
15	70	30	0	1867	107	51	1.38	69	4.61	-	-

4.4.1 Flexural Modulus

The summary of statistics for the flexural modulus model shows that the quadratic canonical model is better than the other models (Table 4-3). The special cubic model has higher adjusted R^2 value, meaning that the model is able to describe the response variations for all design points better than quadratic model do. However, special cubic model has much lower value of *Predicted- R^2* which means that the over-fitting problem occurs in this model. Therefore the special cubic model will "fail" to predict the response value for any given points excluded from the dataset for the model construction.

Table 4-3 Design Expert Output for Flexural Modulus Model Summary Statistics

Source	Std. Dev.	R^2	*Adjusted- R^2*	*Predicted- R^2*	PRESS	
Linear	238.8356	0.6085	0.5433	0.4110	1029805	
Quadratic	168.0736	0.8546	0.7738	0.5733	746171.8	Suggested
Special Cubic	152.2576	0.8939	0.8144	0.3543	1128973	
Cubic	108.2941	0.9665	0.9061		+	

After the backward elimination was applied to the quadratic model, the fittest model obtained is as follows:

$$Flexural\ Modulus = \underset{(102)}{1778}\, x_1' + \underset{(128)}{2435}\, x_2' - \underset{(11652)}{43996}\, x_3' + \underset{(13980)}{57397}\, x_1' x_3' + \underset{(14066)}{57207}\, x_2' x_3' \quad (4.3)$$

Where x_1', x_2' and x_3' are weight fractions of polypropylene, wheat straw, and MAPP, respectively. The numbers in the parenthesis are the standard error for the parameter coefficients. It is important to note that the model is for *l-pseudo component* coding with transformation formula as previously described. Transforming the formula into the actual components where the values of component proportions are the real values in weight fractions, the model become:

$$Flexural\ Modulus = 957\, x_1 + 369.4\, x_2 - 9461\, x_3 + 996500\, x_1 x_3 + 993200\, x_2 x_3 \quad (4.4)$$

The model gives good prediction of the flexural modulus with R^2= 0.8543, *Adjusted*-R^2 =0.7960 and *Predicted*-R^2 = 0.7036. The *Adjusted*-R^2 value of 0.796 is higher than suggested *Adjusted*-R^2 value for response surface model: 0.7. Also, the *Adjusted*-R^2 value is in reasonable agreement with *Predicted*-R^2 value. The difference of the two is 0.096; less than the suggested maximum difference of 0.2.

The summary of ANOVA-test for the proposed model is presented in Table 4-4. All of p-values of model and model terms are less than 0.05. On the opposite of that, the p-value of lack of fit of 0.1056 shows that the hypothesis of significance of lack of fit is rejected. We need insignificant lack of fit to be able to use the model.

Table 4-4 Design Expert output for Flexural Modulus Model ANOVA-test Summary Statistics

Source	Sum of Squares	df	Mean Square	F value	p-value prob > F	remark
Model	1493727	4	373432	14.65723	0.0003	significant
Linear Mixture	1063994	2	531997	20.88094	0.0003	
AC	429470	1	429470	16.85675	0.0021	
BC	421404	1	421404	16.54014	0.0023	
Residual	254776	10	25478			
Lack of Fit	196138	5	39228	3.344895	0.1056	not significant
Pure Error	58638	5	11728			
Cor Total	1748503	14				

Table 4-5 provides the summary of the diagnostic case statistics for the flexural modulus model. It can be seen that the residuals between predicted value and actual value is scattered throughout the data points within the range of -158.9 to 259.2. This means the assumption of constant variance of the model is not rejected, meaning that the model is reliable.

The leverage values range from 0.171 to 0.439. Lower leverage values are favored; and as a general rule, maximum leverage value is equal to 1/k where k is the number of replication for each particular data point.

The assumption of constant variance of each data points is not rejected since all internally-studentized residual values are within the range of -3 to +3. Furthermore, there is no indication of any outliers in dataset since all externally-studentized residual values are

within the range of -3.5 to +3.5. The same is true for the calculated values of DFFITS and Cook's distance values which both are within the suggested ranges of values; indicating all data points constitute the model evenly.

The plots for the residuals can be seen in Appendix E

Table 4-5 Design Expert Report of Diagnostic Case Statistics for Flexural Modulus Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values DFFITS	Cook's Distance
1	2390.174	2325.488	64.68615	0.422396	0.533233	0.513218	0.438881	0.041587
2	2638.063	2641.875	-3.81196	0.435191	-0.03178	-0.03015	-0.02646	0.000156
3	1902.519	2051.881	-149.362	0.192248	-1.04117	-1.04606	-0.51033	0.0516
4	2957.223	2882.274	74.94918	0.307804	0.564381	0.544156	0.362865	0.028328
5	1885.447	1778.273	107.1736	0.411458	0.875224	0.864064	0.72247	0.107106
6	2196.591	2121.067	75.52361	0.439068	0.631754	0.611665	0.541159	0.062481
7	2788.047	2568.376	219.671	0.170831	1.511373	1.632314	0.740909	0.094123
8	2327.298	2298.07	29.22876	0.207871	0.205747	0.195603	0.100202	0.002222
9	2640.672	2381.471	259.2006	0.199139	1.814587	2.101967	1.048154	0.163751
10	2505.98	2615.269	-109.289	0.252942	-0.79217	-0.77627	-0.4517	0.042494
11	2462.933	2615.269	-152.335	0.252942	-1.10419	-1.11789	-0.65048	0.082563
12	2501.003	2641.875	-140.872	0.435191	-1.17434	-1.19988	-1.05324	0.212518
13	2234.369	2325.488	-91.1193	0.422396	-0.75113	-0.73358	-0.62732	0.082518
14	1962.14	2121.067	-158.928	0.439068	-1.32943	-1.39001	-1.22978	0.276683
15	1753.557	1778.273	-24.7163	0.411458	-0.20184	-0.19188	-0.16043	0.005696

All of the diagnostic case statistics show that the model has met most criteria for good response surface model as suggested by Myers et.al. (2009).

The response surface and the contour plot based on the model for flexural modulus are presented in Figure 4-3 and Figure 4-4 respectively.

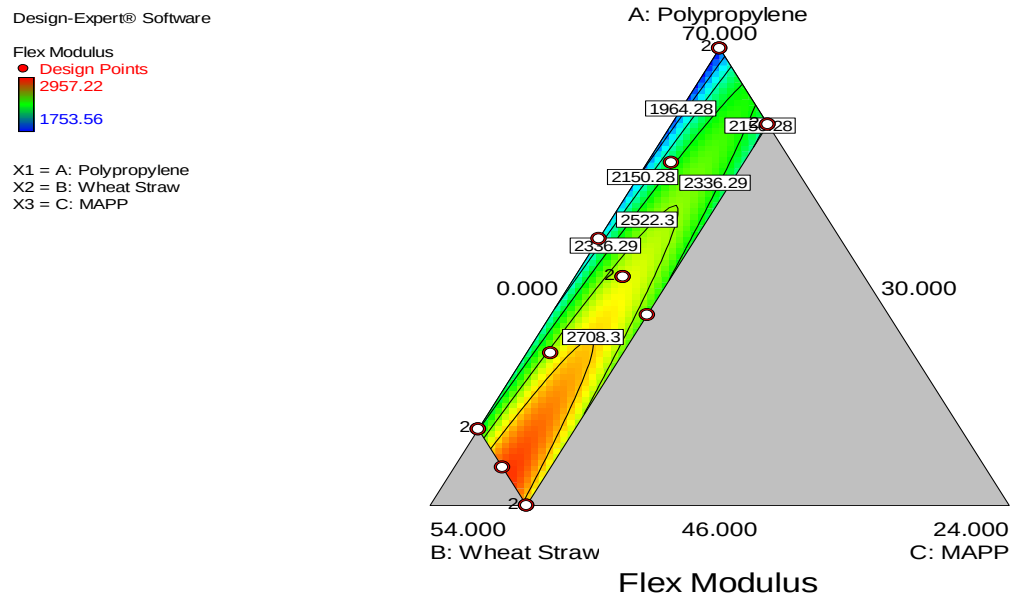


Figure 4-3 Contour Plot of Flexural Modulus

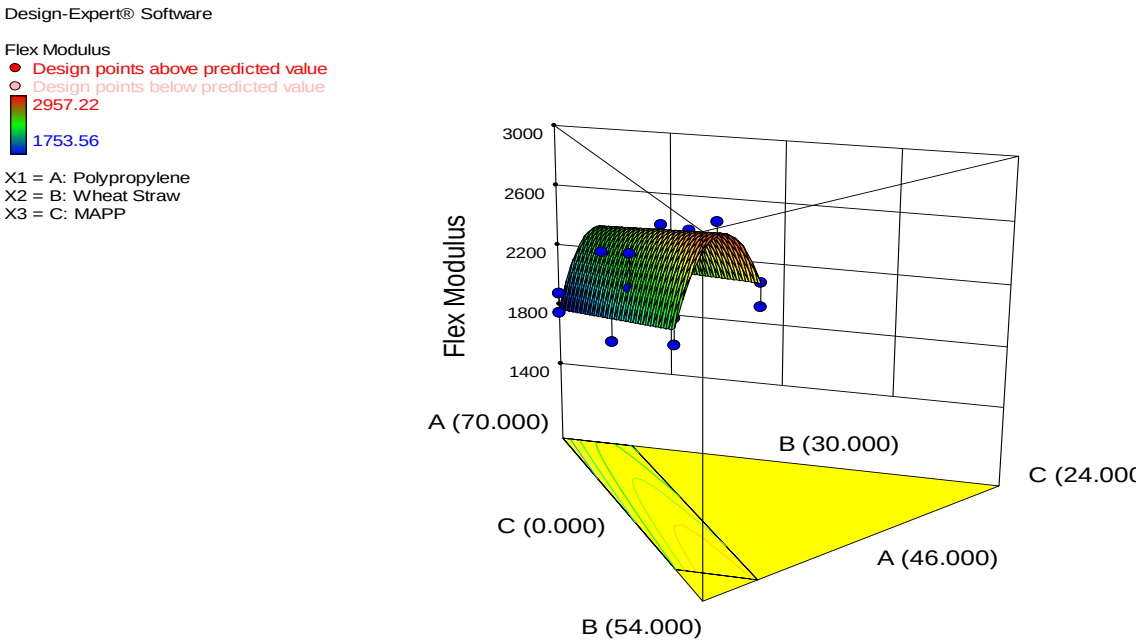


Figure 4-4 Response Surface Graph of Flexural Modulus

4.4.2 Flexural Strength

The second flexural property being studied is flexural strength. The same technique of data analysis was applied to the flexural strength of the composite. Similar to the flexural modulus, the reduced quadratic canonical model gives the best coefficient of determination values of 0.9590, 0.9426 and 0.9220 for R^2, *Adjusted-*R^2 and *Predicted-*R^2 respectively. The models for both l-pseudo-component coding x_i' and real component mixture weight fractions x_i are as follows:

$$Flexural\ Strength = \underset{(1.52)}{51.799}\, x_1' + \underset{(1.90)}{42.158}\, x_2' - \underset{(174)}{1222}\, x_3' + \underset{(208)}{1670}\, x_1'x_3' + \underset{(209)}{1749}\, x_2'x_3' \quad (4.5)$$

$$Flexural\ Strength = 63.85\, x_1 + 23.68 x_2 - 27694\, x_3 + 29000\, x_1x_3 + 30359\, x_2x_3 \quad (4.6)$$

The model significance, model terms significance and insignificance of lack-of-fit are shown by the summary of ANOVA test statistics (Table 4-6).

Table 4-6 Design Expert output for Flexural Strength Model ANOVA-test Summary Statistics

Source	Sum of Squares	df	Mean Square	F value	p-value prob > F	remark
Model	1931.928	4	482.9821	85.47312	< 0.0001	significant
Linear Mixture	1507.132	2	753.5658	133.3582	< 0.0001	
AC	363.7606	1	363.7606	64.37455	< 0.0001	
BC	393.7338	1	393.7338	69.67888	< 0.0001	
Residual	56.5069	10	5.65069			
Lack of Fit	41.71831	5	8.343661	2.820979	0.1398	not significant
Pure Error	14.78859	5	2.957719			
Cor Total	1988.435	14				

Table 4-7 provides the report of diagnostics case statistics for the proposed model. Again, similar things to the model for flexural modulus happen: 1) the assumed constant variance in developing the statistical model was not rejected; 2) each data points constituted the model evenly; and 3) the model met the common criteria for response surface model. The response surface and the contour plot based on the model for flexural strength are presented in Figure 4-5 and Figure 4-6 respectively.

Table 4-7 Design Expert Report of Diagnostic Case Statistics for Flexural Strength Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values DFFITS	Cook's Distance
1	40.67795	43.76467	-3.08672	0.422396	-1.70857	-1.92625	-1.64724	0.426956
2	73.68441	74.23086	-0.54645	0.435191	-0.30588	-0.29155	-0.25592	0.014418
3	47.40143	47.782	-0.38058	0.192248	-0.17814	-0.16926	-0.08258	0.00151
4	69.29285	70.59811	-1.30525	0.307804	-0.65998	-0.64021	-0.42692	0.038738
5	52.06401	51.79933	0.264674	0.411458	0.145135	0.137832	0.115245	0.002945
6	70.63763	71.4042	-0.76657	0.439068	-0.43057	-0.41232	-0.36479	0.029023
7	66.77024	61.41131	5.358936	0.170831	2.475746	3.775146	1.713542	0.25256
8	65.22689	64.07097	1.155915	0.207871	0.546358	0.526234	0.269574	0.015667
9	74.24237	72.81753	1.424843	0.199139	0.669789	0.650168	0.324209	0.02231
10	69.06289	71.90011	-2.83722	0.252942	-1.38091	-1.45623	-0.84735	0.12913
11	71.15644	71.90011	-0.74367	0.252942	-0.36195	-0.34565	-0.20113	0.008871
12	74.53569	74.23086	0.304826	0.435191	0.170628	0.162108	0.142296	0.004487
13	45.35839	43.76467	1.593724	0.422396	0.88216	0.871487	0.745256	0.113819
14	71.8019	71.4042	0.397699	0.439068	0.223383	0.21245	0.187961	0.007812
15	50.96517	51.79933	-0.83417	0.411458	-0.45742	-0.43856	-0.36669	0.029255

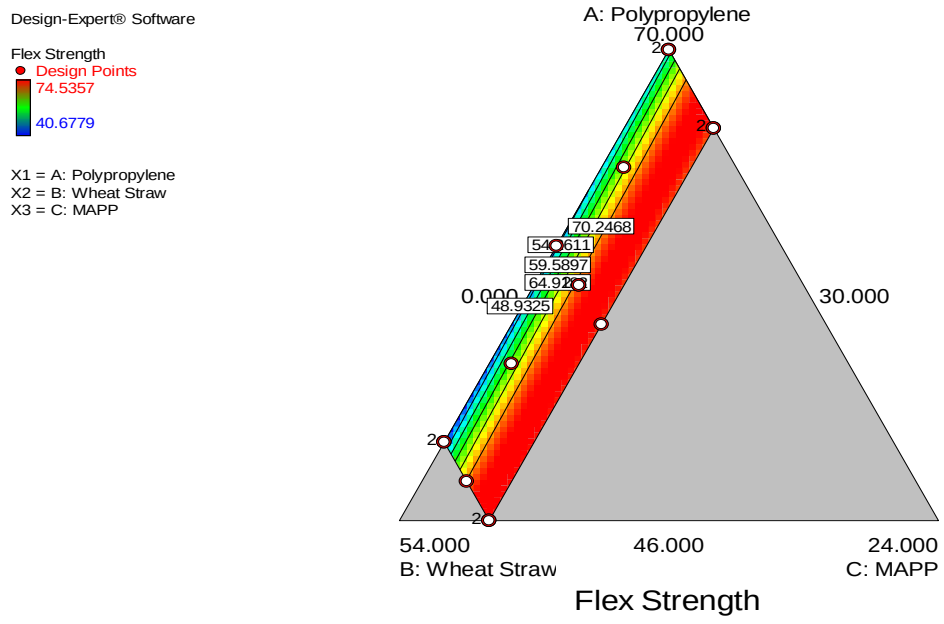


Figure 4-5 Contour Plot of Flexural Strength

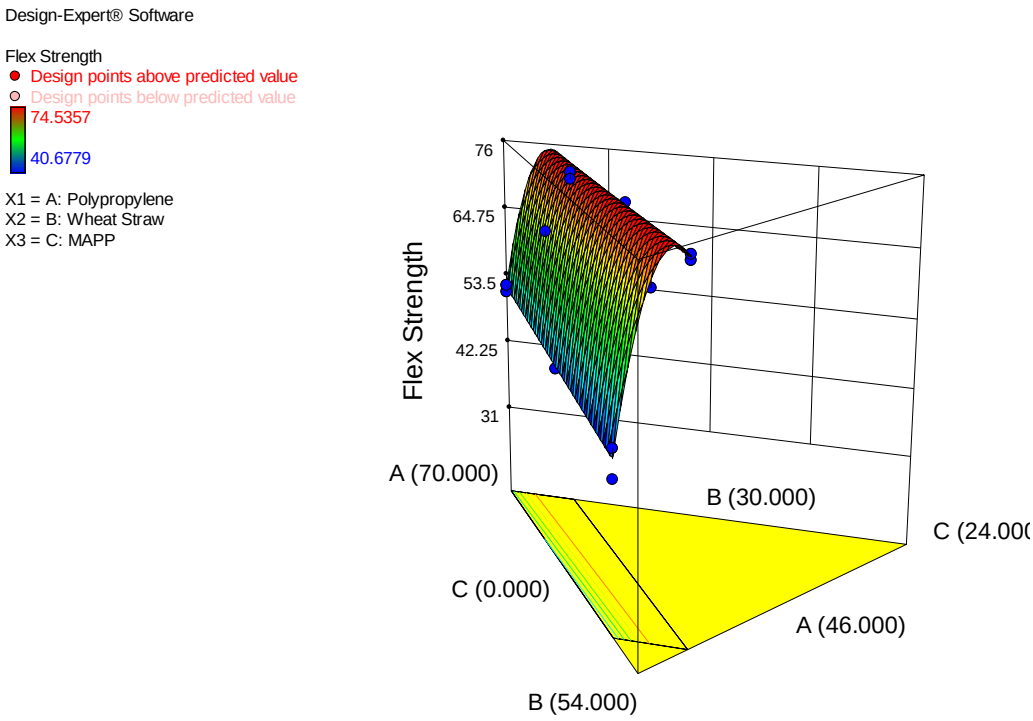


Figure 4-6 Response Surface Graph of Flexural Strength

4.4.3 Yield Strength

The last flexural property modeled is the yield strength of composite. The obtained models, the summary of ANOVA test and the report of diagnostics case statistics are presented in Table 4-8 and Table 4-9 respectively. Similar to the flexural modulus and the flexural strength models, the proposed model for the yield strength gives very good coefficient of determination, meets the assumption of constant variance and equally influence of design points. The model met the criteria of good model for response surface models and can be used to predict the yield strength of composite as function of component proportions.

$$Yield\ Strength = \underset{(3.25)}{72.925\ x_1'} + \underset{(4.06)}{69.340\ x_2'} - \underset{(367)}{2355\ x_3'} + \underset{(444)}{3138\ x_1'x_3'} + \underset{(447)}{3293\ x_2'x_3'} \quad (4.7)$$

$$Yield\ Strength = 77.41\ x_1 + 62.47\ x_2 - 52247\ x_3 + 544778\ x_1x_3 + 57168\ x_2x_3 \quad (4.8)$$

Table 4-8 Design Expert output for Yield Strength Model ANOVA-test Summary Statistics

Source	Sum of Squares	df	Mean Square	F value	p-value prob > F	remark
Model	6005.516	4	1501.379	58.45922	< 0.0001	significant
Linear Mixture	4482.465	2	2241.233	87.2669	< 0.0001	
AC	1283.605	1	1283.605	49.97976	< 0.0001	
BC	1396.206	1	1396.206	54.36407	< 0.0001	
Residual	256.825	10	25.6825			
Lack of Fit	201.7107	5	40.34213	3.659855	0.0904	not significant
Pure Error	55.11439	5	11.02288			
Cor Total	6262.341	14				

Table 4-9 Design Expert Report of Diagnostic Case Statistics for Yield Strength Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values DFFITS	Cook's Distance
1	65.14236	69.93778	-4.79542	0.422396	-1.24507	-1.28496	-1.09884	0.226728
2	121.6243	122.7078	-1.08358	0.435191	-0.28451	-0.27101	-0.23788	0.012474
3	74.34167	71.4314	2.91027	0.192248	0.638963	0.61894	0.301953	0.019434
4	112.4391	118.1139	-5.67478	0.307804	-1.34591	-1.41102	-0.94093	0.161104
5	72.3798	72.92502	-0.54522	0.411458	-0.14024	-0.13317	-0.11135	0.00275
6	101.8776	104.1716	-2.29405	0.439068	-0.60441	-0.58416	-0.51682	0.057189
7	109.4609	98.8752	10.5857	0.170831	2.293925	3.161603	1.435055	0.216826
8	101.5323	97.67839	3.853961	0.207871	0.854458	0.841927	0.431294	0.038319
9	115.0146	113.4397	1.574878	0.199139	0.347256	0.33144	0.165274	0.005997
10	108.3277	114.2266	-5.8989	0.252942	-1.34671	-1.41205	-0.82165	0.122814
11	114.9706	114.2266	0.743942	0.252942	0.169841	0.161358	0.093891	0.001953
12	124.9044	122.7078	2.196584	0.435191	0.576737	0.556474	0.488465	0.051258
13	70.72712	69.93778	0.78934	0.422396	0.204942	0.194834	0.166614	0.006143
14	105.5828	104.1716	1.411132	0.439068	0.371787	0.355171	0.314231	0.021639
15	69.15118	72.92502	-3.77384	0.411458	-0.97068	-0.96758	-0.80902	0.131744

The response surface and the contour plot based on the model for yield strength are presented in Figure 4-7 and Figure 4-8, respectively.

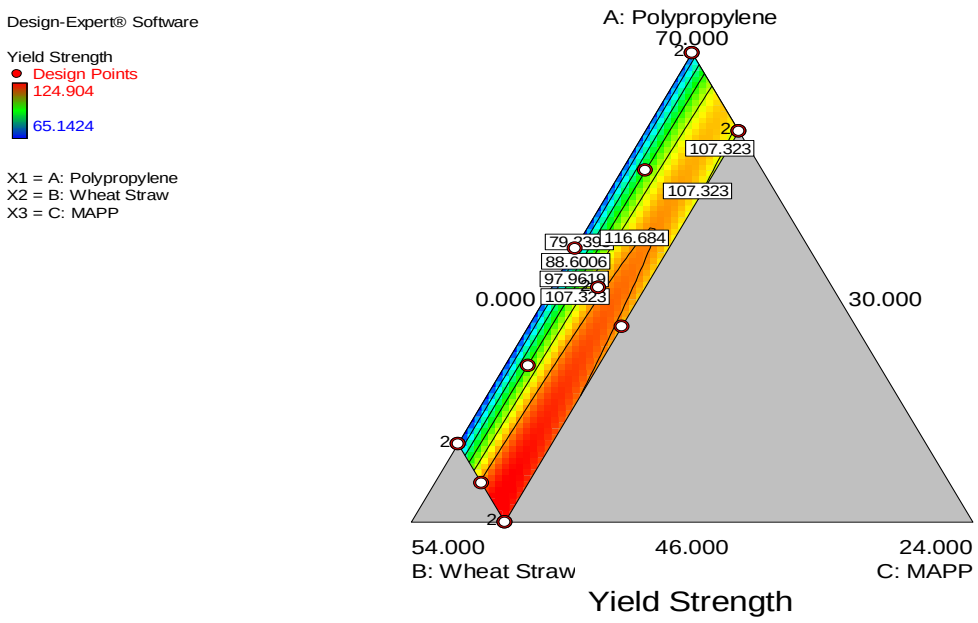


Figure 4-7 Contour Plot of Yield Strength

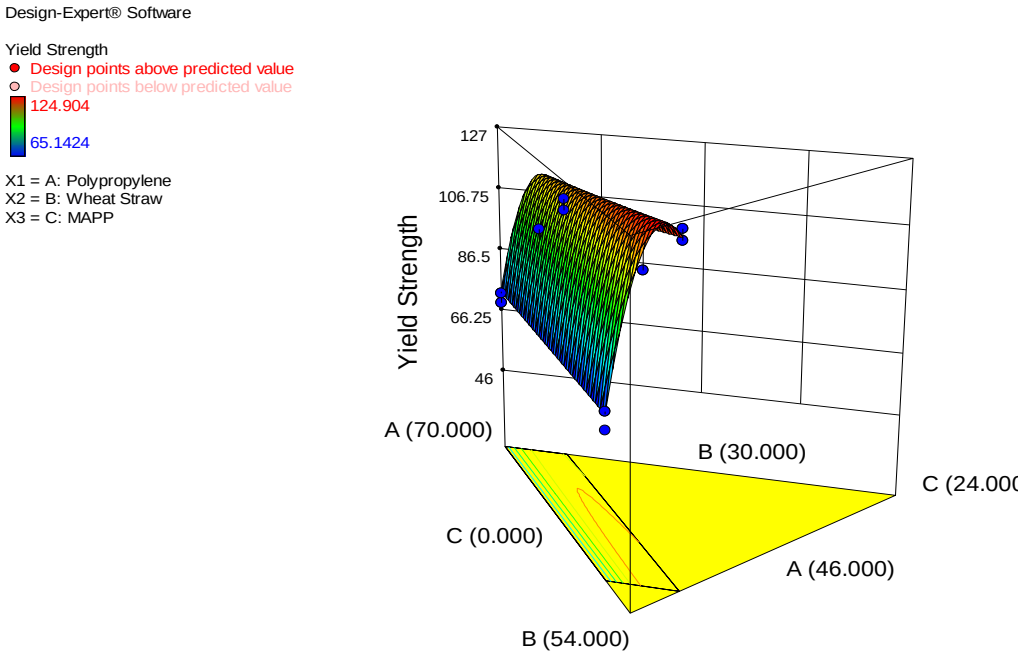


Figure 4-8 Response Surface Graph of Yield Strength

4.4.4 Density

The density of composites was a linear function of the weight proportion of each component. This is the expected behavior according to the rule of mixture, since the matrix (polypropylene) and the dispersed (straw) represent the vast majority of the components and they are immiscible. Furthermore, the nature of crystallization of the polypropylene phase is not expected to change when the amount of that phase is change; consequently the density of the polypropylene phase is expected to remain constant.

The development of the density model is slightly different from the previous three models and the data analyses. There is one data point which is considered as an outlier. Therefore, the model was developed from a dataset excluding the outlier data point.

The Diagnostic Case Statistics report and ANOVA test results summary table are presented on Table 4-10 and Table 4-11, respectively

Table 4-10 Design Expert Report of Diagnostic Case Statistics for Density Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values DFFITS	Cook's Distance
1	1.050492	1.058627	-0.00814	0.43955	-1.74881	-2.27998	* -2.02	* 0.80
2	1.074019	1.066158	0.007861	0.43955	1.689963	2.131175	1.887361	0.746629
4	1.06359	1.062392	0.001197	0.257732	0.223616	0.204989	0.120791	0.005788
5	0.974697	0.97106	0.003637	0.522024	0.8467	0.823702	0.86082	0.260989
6	0.972448	0.97859	-0.00614	0.522024	-1.42974	-1.6074	-1.67984	0.744185
7	1.037999	1.038618	-0.00062	0.18463	-0.11036	-0.10085	-0.04799	0.000919
8	1.001071	0.994834	0.006237	0.225867	1.140804	1.176829	0.63567	0.126572
9	1.018965	1.022374	-0.00341	0.29522	-0.65335	-0.61885	-0.40053	0.059603
10	1.01798	1.018609	-0.00063	0.113402	-0.10736	-0.0981	-0.03509	0.000491

Note: Exceeds limits (*)

The proposed model gives the best coefficient of determination values of 0.9782, 0.9800 and 0.9321 for R^2, *Adjusted-*R^2, and *Predicted-*R^2, respectively. The models for both *l-pseudo-component* coding x_i' and real component mixture weight fractions x_i are as follows:

$$Density = \underset{(0.0045)}{0.9711\, x_1'} + \underset{(0.0048)}{1.0761\, x_2'} + \underset{(0.0294)}{1.0162\, x_3'} \quad (4.9)$$

$$Density = 0.8397\, x_1 + 1.2775\, x_2 + 1.0280\, x_3 \quad (4.10)$$

Figure 4-9 and Figure 4-10 are the contour plot and response surface graph for the density, respectively.

Table 4-11 Design Expert output for Composite Density Model ANOVA-test Summary Statistics

Source	Sum of Squares	df	Mean Square	F value	p-value prob > F	remark
Model	0.010409	2	0.005204	134.7863	< 0.0001	significant
Linear Mixture	0.010409	2	0.005204	134.7863	< 0.0001	
Residual	0.000232	6	3.86E-05			
Cor Total	0.01064	8				

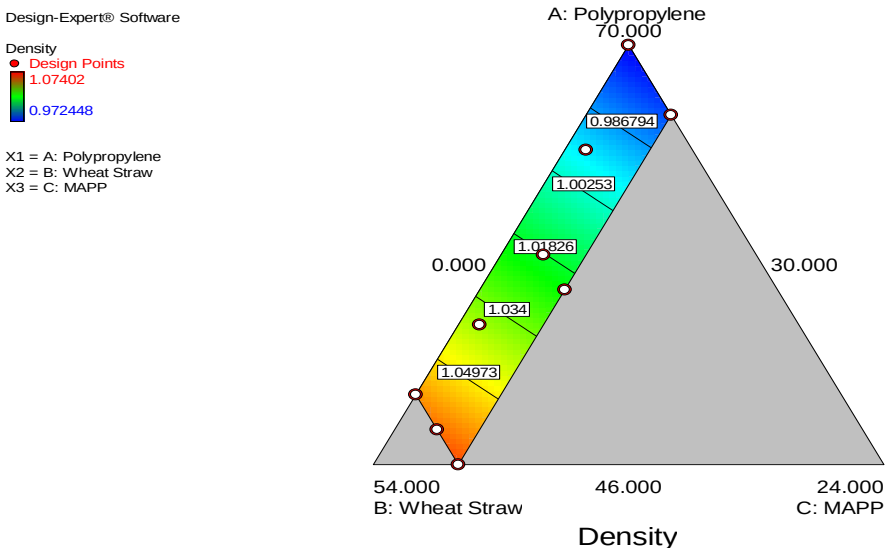


Figure 4-9 Contour Plot of Density

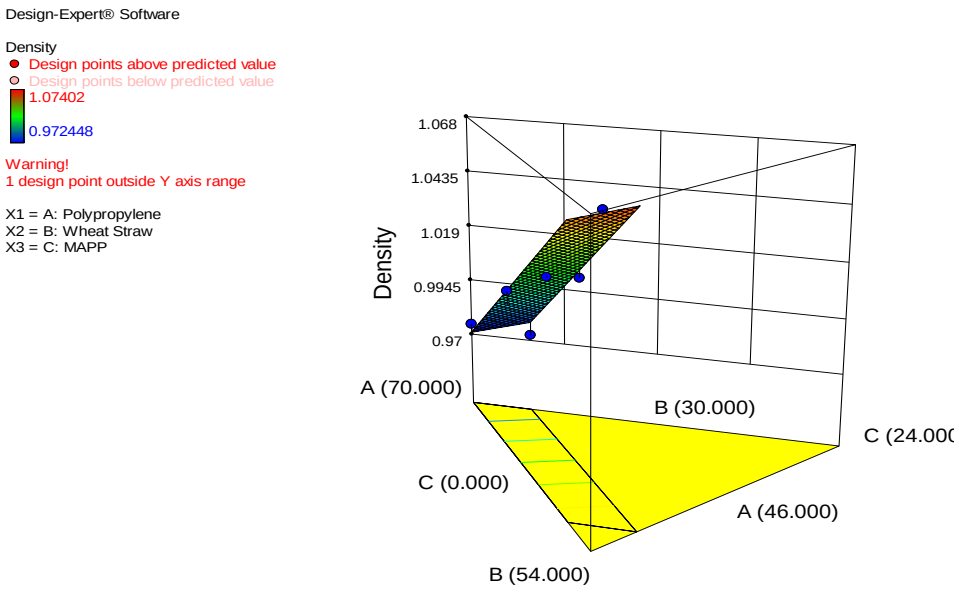


Figure 4-10 Response Surface Graph of Density

Table 4-12 provides the summary of proposed structural property models for WSPPC flexural properties and density.

Table 4-12 Summary of the Models and Their Coefficients of Determination

Properties	Models	R^2	$R^2_{Adjusted}$	$R^2_{Predicted}$
Flexural Modulus	$957\,x_1 + 3694\,x_2 - 946100\,x_3 + 996500\,x_1x_3 + 993200\,x_2x_3$	0.8542	0.7960	0.7036
Flexural Strength	$63.85\,x_1 + 23.68x_2 - 27694\,x_3 + 29000\,x_1x_3 + 30359\,x_2x_3$	0.9715	0.9602	0.9455
Yield Strength	$77.41\,x_1 + 62.47\,x_2 - 52247\,x_3 + 544778\,x_1x_3 + 57168\,x_2x_3$	0.9589	0.9425	0.9219
Density	$0.8397\,x_1 + 1.2775\,x_2 + 1.0280\,x_3$	0.9782	0.9709	0.9320

4.4.5 The Optimum Ratio of MAPP/Wheat Straw

The main role of MAPP is to increase the interfacial strength between the polypropylene and wheat straw in order to maximize the reinforcement benefit of wheat straw fiber to the polypropylene matrix. The presence of MAPP, on the other hand, will decrease the mechanical properties of polypropylene itself. That is because the presence of MAPP may affect the type and the degree of crystallinity of polypropylene when the dispersed phase (straw fibers) is not present. Therefore, there must be an optimum proportion of MAPP that gives maximum benefit of reinforcement.

By knowing the optimum weight percentage of MAPP as a function of wheat straw proportion, one can easily determine how much MAPP should be added to the formulation of composite mixture for any different filler-matrix composition. Once we were able to fix the recipe of MAPP, the number of mixture variables is reduced from three to two variables. This reduction will simplify the composite design problem and would be an advantage when the mixture design is combined with *process variables* to carry out *process-mixture* experimental design.

The optimum weight percentage of MAPP which give maximum benefit of each flexural property is shown in Figure 4-11. The graph shows that the optimum MAPP proportion increases by increasing the fiber loading within the range of 30%-50%. The optimum MAPP composition giving the maximum flexural strength increases from 2.7% to 3.2% as the wheat straw contents increases. The same is true for the maximum yield strength, where the

optimum MAPP proportion is increasing from 2.85% to 3.3% as the fiber loading is increasing from 30% to 50%. However, the optimum MAPP proportion for the maximum flexural modulus is relatively constant at 2.4%. This kind of information would be very important for engineers in product design and optimization of wheat straw polypropylene composites.

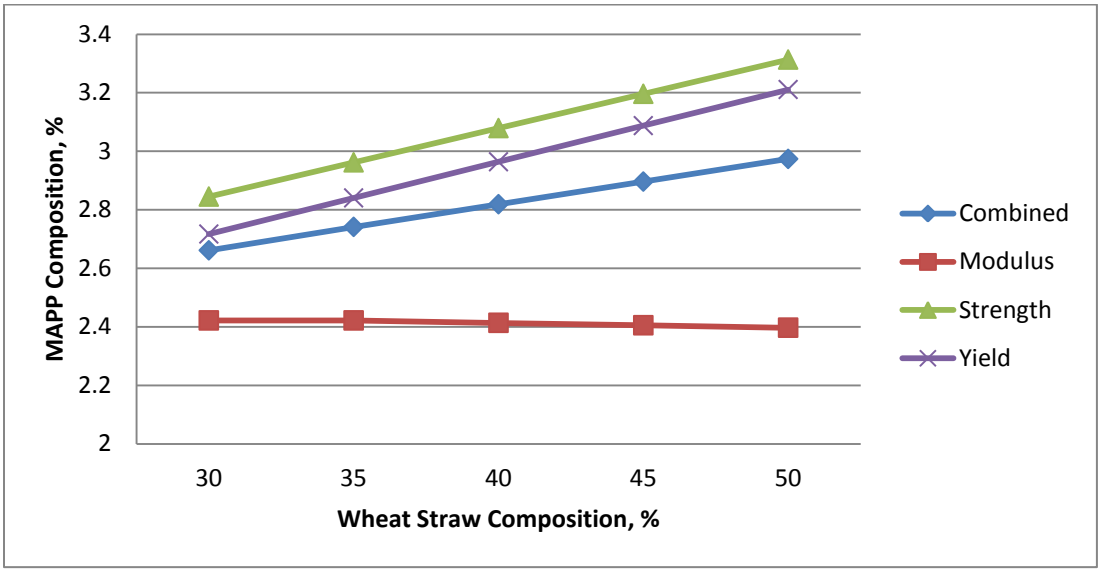


Figure 4-11 Optimum MAPP Compositions for Maximum Flexural Properties of WSPPC

4.5 Chapter Summary

Mixture design of experiment was successfully implemented in modeling flexural properties and specific gravity of wheat straw polypropylene composite. The models correlate the responses as functions of component proportions in weight percentages. The ANOVA test summary statistics show that the models are able to describe most variability of the response as function of component proportions.

Furthermore, the diagnostic case statistics show that the assumption of constant variance and dispersed influence of design points are not rejected. In terms of sensitivity analysis, the models are also accompanied by the standard error of model term parameters. From

engineering perspective, the models are reliable enough to be used to design composite products.

One of the important finding in this study is the optimum proportion of coupling agent for any proportion of fiber within the design space. This information can be used to simplify further experiments by fixed-recipe of the coupling agent proportion, thus reducing the number of independent variable.

5 The Effects of Fiber Sizes on Mechanical Properties of Wheat Straw Polypropylene Composite

5.1 Introduction

The benefit of fiber reinforcement on polymer matrix in a composite material depends on how well the load is transferred from the matrix to the fiber. As described in Chapter 2, fiber length and aspect ratio play important role in this load-transfer process; together with other factors such as fiber orientation, fiber dispersion, and fiber-matrix interface. The objective of the work presented here is to study the effect of fiber sizes, i.e. fiber length and aspect ratio on mechanical properties in the thermoplastic composite with polypropylene. Two previous similar studies on ground wheat straw thermoplastic composites showed that there is little or no significant difference on mechanical properties when different fiber sizes were used to constitute the composites.

Sardashti (2009) studied the flexural properties of WSPPC made of different sizes of ground wheat straw with 30% of fiber loading. The author used three different sizes of ground wheat straw obtained from the grinding process of a raw wheat straw, namely: fine, mid, and large. Those three different sizes were obtained from screening the ground wheat straw through two sieves with mesh size of 16 and 35.

Thamae (2008) investigated the tensile and flexural properties of wheat straw polyethylene composite made of different sizes of wheat straw with 10% to 40% fiber loadings. The author used two different sizes of ground wheat straw obtained from milling process of a raw wheat straw, namely: large and small. Those two different sizes were obtained from screening the ground wheat straw through two sieves with pore sizes of 2000 micrometers and 250 micrometers.

The critical length theory requires a minimum length of fiber in order to establish maximum benefit of fiber reinforcement on polymer matrix. Composites made of longer fibers, therefore, will have better mechanical properties because they have fibers with length greater or near to the critical length. On the other hand, fiber-matrix bonding theory requires higher surface area of fiber in order to get better reinforcement of composite. Composites

made of smaller fiber, therefore, will have better mechanical properties due to higher surface area they have.

Both those studies in the literature used only one “parameter” to differentiate the variable of fiber size, i.e. the size of sieves used in fiber preparation. Despite the difference of fiber length among all fiber sizes, there are no differences in aspect ratio among the fibers. All sizes of fiber have the similar aspect ratio. It is very difficult to avoid interdependency between fiber length and surface area in this method. That is probably one of the reasons of why both studies reported no significant differences of composite mechanical properties that can be attributed directly to the difference of fiber sizes. One good attribute acquired by a certain size of fiber has been “neutralized” by another attribute it had. Composites with larger sizes of fiber have better length but poorer dispersion due to smaller surface area. Meanwhile, composites with smaller sizes of fiber have larger surface area and better dispersion but they have shorter fiber, shorter than the needed critical length.

In this study, different fiber sizes were prepared by considering both length and surface area. It is believed that fibers with greater length and greater aspect ratio (ratio of fiber length to fiber width) will give significant effects of reinforcement on composite materials. Two steps of separation were used in order to prepare fibers with distinct fiber length and aspect ratio. In the first step, the fibers were separated based on their width. In the second step, the fibers were separated based on their length. Since aspect ratio is defined as the ratio of fiber length to fiber width, different fiber lengths among the fibers with the same width would give different fiber aspect ratios.

Composite samples were then produced by using those fibers to investigate the effects of fiber size on several properties of the composites. This type of work has never been reported in the literature. It is expected that this work will contribute to a better understanding of how the particle size and shape contributes to reinforcement of the composites. A practical application of this work would be in the manufacturing of grades of fiber for specific applications.

5.2 Materials and Methods

5.2.1 Materials

Homopolypropylene 6301 with a melt flow index of 12 g/10 min (230 ^{o}C, 2.16 kg, ASTM D 1238) in the form of powder was donated by A. Schuman Inc. Wheat straw used in this study was a soft white winter wheat straw (AC Mountain) harvested in late 2009 from the Ontario region. The coupling agent used was Fusabond MD-353D, a maleic anhydride grafted polypropylene from DuPont. Two antioxidants, namely Irganox 1010 and Irgafos 168 were purchased from Ciba Inc. and were used in order to avoid thermal degradation caused by the processing conditions as well as increase the shell life of the final product.

5.2.2 Fiber Preparation and Size Measurement

The coarse-ground wheat straw obtained from OMTEC Inc. was fed into Ultra-Centrifugal Mill ZM200 running at 8000 rpm. The milled wheat straw came out from the mill through the 0.5 mm ring sieves. The milled straw was then manually screened by using sieves in order to get wheat straw fractions with distinct fiber length and aspect ratio. This was done by two steps of screening. The first step was fiber separation based on fiber width. After separated into fractions with different width, the second step of length-based screening was performed on each fraction. Since aspect ratio is defined by length divided by width (l/w), separating fibers with the same width based on their length would result in fractions with different length and aspect ratio.

The measurement of fiber size was done by using ImageJ Java-based image processing program on images of wheat straw. The images were taken by stereomicroscope Leica MZ6 which uses two illumination techniques: transmitted light and incident light. Wheat straw fibers were well spread on a glass slide in a way that none would overlap each other.

To analyze the particles, the software automatically counts and measures the objects of interest by scanning across the image. When a boundary of an object is found the program draws an ellipse that best fits the object and then redraws the dark object in a different gray level, so that it becomes invisible to the scanning process. For each wheat-straw fraction, a sample of approximately 200 particles was analyzed.

Length and width of the fibers were obtained from the length of major axis and length of minor axis, respectively, of the best fitting ellipse drawn by the ImageJ analysis software for each particle available in the field of view of the microscope. Aspect ratio of the fibers was calculated by dividing the length by the width of each fiber.

5.2.3 Fiber Thermal and Chemical Analysis

Thermal and chemical analyses were performed to each fiber fraction before the compounding process.

Thermogravimetric analysis was determined in a Q500 TGA controlled by a TA processor connected to a computer for data analysis. The experimental conditions were as follows: Initial temperature 40° C; Final temperature 800° C; heating rate of 10° C min^{-1}; sample size close to 5 mg. Purging gas in this analysis is air with the flow-rate of 50 mL/minute.

Chemical analysis of acid detergent fiber (ADF), neutral detergent fiber (NDF), and lignin content test were performed at Agri-Food Laboratories based in Guelph, Ontario. Values of ADF and NDF are used to calculate the amount of cellulose and hemi-cellulose in the sample. These test as they sound are basically consist of soaking the wheat straw in either neutral or acid detergents followed by proper filtering. These methods are based on single extraction of soluble components. The residue left from the filtration process is then analyzed and correlated to straw components. Lignin content test was also performed in order to investigate the amount of lignin in each fraction.

5.2.4 Composite Sample Preparation and Properties Measurement

Wheat straw polypropylene composite samples were prepared for each fiber fraction with 30% and 50% fiber loadings.

The samples were prepared by melt-blending method using a Haake Minilab Micro-compounder (Minilab); a co-rotating conical twin-screw extruder. The operating conditions of extruder such as temperature and screw rotation rate were set at 190^{o} C and 40 rpm, respectively.

The components of composite namely wheat straw, polypropylene, coupling agent and antioxidants were hand-blended to get a uniform mixture before feeding into extruder. Both

antioxidants were used in equal amounts maintained at a total of 0.5 wt-percent with respect to polypropylene content.

As the mixture of components of composite were conveyed through the screws of twin-screw extruder, melting and mixing took place and a homogenized extrudate came out through the flush orifice in the form of strands. The extrudate strands were cooled by air contact (no water). The strands were cut into smaller pieces proper for the next processing step.

The resulting pellets from compounding process were then injection molded using Ray-Ran Laboratory injection molding machine (RR/TSMP) to get samples (ASTM standard) for flexural testing and density measurement. The injection molding was performed by keeping the barrel temperature at 190^{o} C and mold tool temperature at 50^{o} C with injection periods of 15 seconds at 100 psi.

Flexural and impact properties of the samples were investigated on sample specimens prepared by injection molding. Conditioning the sample and analysis procedure followed are as per ASTM D790-07. Prior to conditioning, injection molded samples were annealed at 150^{o} C for 10 min and then were cooled down at a rate of 10^{o} C/min to have a homogenized crystallinity for all the samples and to erase any thermal history taken place during the injection molding.

In order to obtain the specific properties of the composites, i.e. the ratio of mechanical properties per mass, the density of the composite is needed. The density measurement was conducted according to ASTM D792-07.

To investigate the fiber size reduction during the compounding process (extrusion and injection molding), fibers were extracted from the samples and their sizes were measured. The extraction was carried out using boiling xylene in a round-bottom flask according to ASTM D2765 (with a minor difference of using a 41 screen ashless filter paper). The size measurement was performed by using the same method of fiber measurement performed before the compounding process.

5.3 Results and Discussions

5.3.1 Fiber Fractionation and Size Measurement

The fractionation of wheat straw resulted in 7 fractions of fibers. It is important to note that the initial objective of fiber fractionation was to provide four fiber fractions in order to perform a 2^2 (two-level, two-factor) factorial design. This design of experiment needs four different fiber sizes consisting of low level and high level of two variables: fiber length and aspect ratio. Therefore, the first step of separation (i.e. width-based separation) is focused to prepare fibers with two different widths which were subsequently separated in the second step of separation (i.e. length-based separation) to obtain those four fractions. During the preparation there were also obtained three other fractions from milled wheat straw. Because one of the main objectives of the research is to obtain enough information to optimize wheat straw utilization, it was decided to use all fiber fractions in this study instead of only 4 fractions.

The first step of separation, i.e. width-based separation, resulted in four fiber fractions with four different widths, namely: F, A, B and C. The median values of the width of those fractions are 40 µm, 240 µm, 350 µm, and 650 µm, respectively. Fraction F is the smallest fraction resulted from the smallest size of sieve. The letter code F stands for "fine". The other three fractions were named after letters A, B, and C which represent the order of the width in ascendant order. Fraction B and C both have relatively uniform width distributions compared to fraction A. That is because the focus of separation is to produce fractions B and C. Fraction A and F were the "by-product" during the preparation of fraction B and C. Each fraction was then separated based on their length; resulted in AS and AL, BS and BL, and CS and CL. S stands for "short", while L stands for 'long". Due to its small size, fraction F could not be further separated.

The size measurement of each fraction has been done, and the summary of the measurement results can be seen in Figure 5-1. It can be seen that Fraction BS and BL have similar width distribution with the median of around 350 µm. Fraction CS and CL have similar width distribution with the median of around 650 µm. The two pairs of fractions are the main fractions obtained during the first step of fiber separation process. It can also be seen that

Fraction BS and BL have significant difference of fiber length distribution. Fraction BS and BL has the median length of about 1800 µm and 2300 µm, respectively. Fraction CS and CL have different fiber length distribution as well; with the median length of 1750 µm and 3150 µm, respectively. Since each pair of fractions has similar width, the difference in length would lead to difference in aspect ratio, as can be seen in Figure 5-2.

Figure 5-3 is the picture of 7 fractions of fibers. The summary statistics of individual fiber measurement for each fraction are provided in Appendix A.

Fisher's Least Significant Difference method was used to detect significance of size differences among fiber fractions. The mean values of fiber width, fiber length and fiber aspect ratio for each fiber fractions, along with the mean standard error values, are presented in Table 5-1. The Table also shows the results of LSD test. The superscript letters on each data points in the Table indicate significance values. It can be seen that each pair of Fiber BS and BL and Fiber CS and CL have the statistically same width.

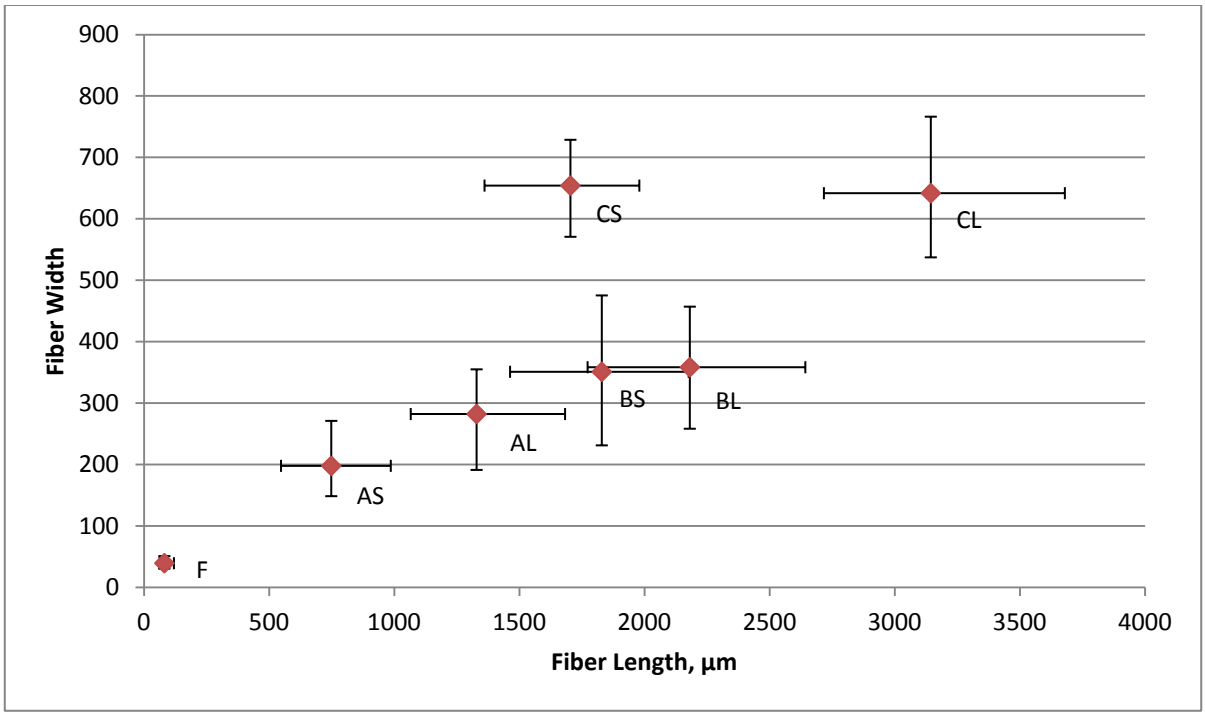


Figure 5-1 Results of fiber length and width measurements of fiber factions. The dots represent the median; the error bars represent the inter-quartiles.

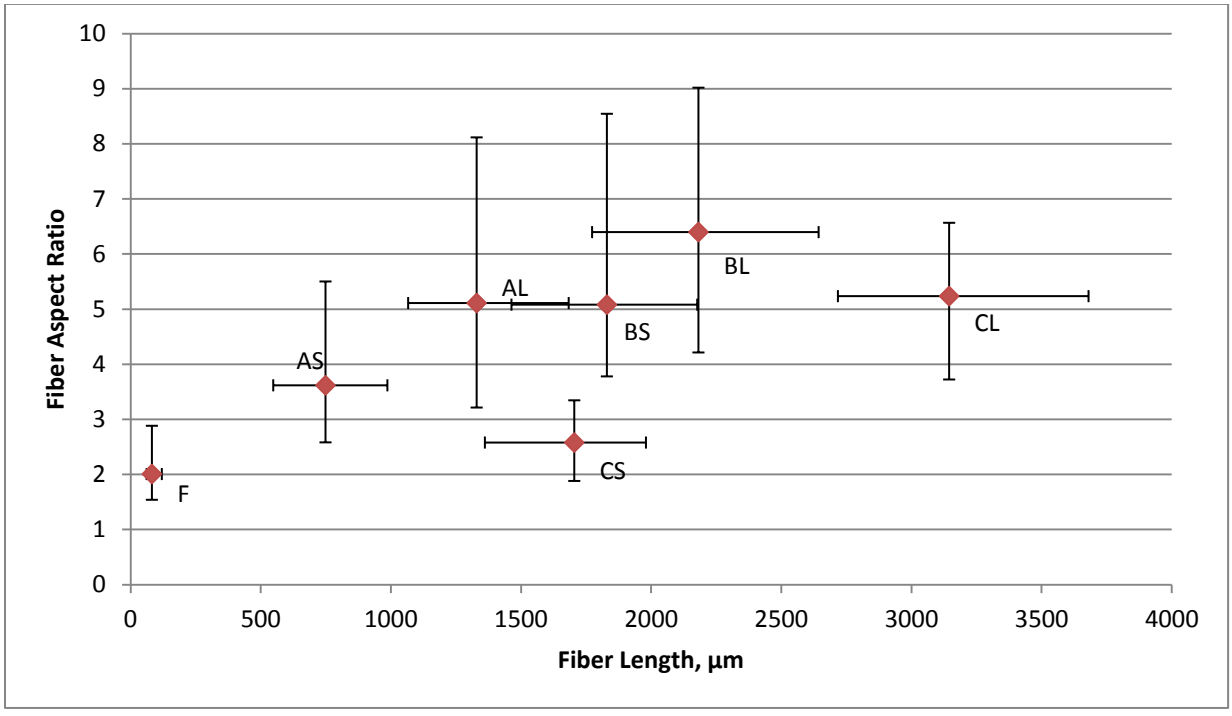


Figure 5-2 The summary of size measurements of fiber fractions. The dots represent the medians; error bars represent the inter-quartiles.

Table 5-1 The Mean Values of Fiber Width, Fiber Length, and Fiber Aspect Ratio.

Fraction ID#	Fiber Width, µm	Fiber Length, µm	Fiber Aspect ratio
F	44 ± 1 [a]	96 ± 3 [a]	2.4 ± 0.09 [a]
AS	210 ± 6 [b]	788 ± 23 [b]	4.7 ± 0.24 [b]
AL	284 ± 8 [c]	1395 ± 35 [c]	6.0 ± 0.26 [c]
BS	361 ± 12 [d]	1884 ± 41 [d]	6.9 ± 0.36 [d]
BL	362 ± 10 [d]	2227 ± 54 [e]	7.5 ± 0.37 [e]
CS	654 ± 11 [e]	1706 ± 33 [f]	2.9 ± 0.12 [f]
CL	645 ± 12 [e]	3204 ± 54 [g]	5.5 ± 0.19 [g]

Note: The values are accompanied by the mean standard errors. The superscript symbols indicate the statistical significance difference values. Within each column, any values with the same symbols are statistically the same.

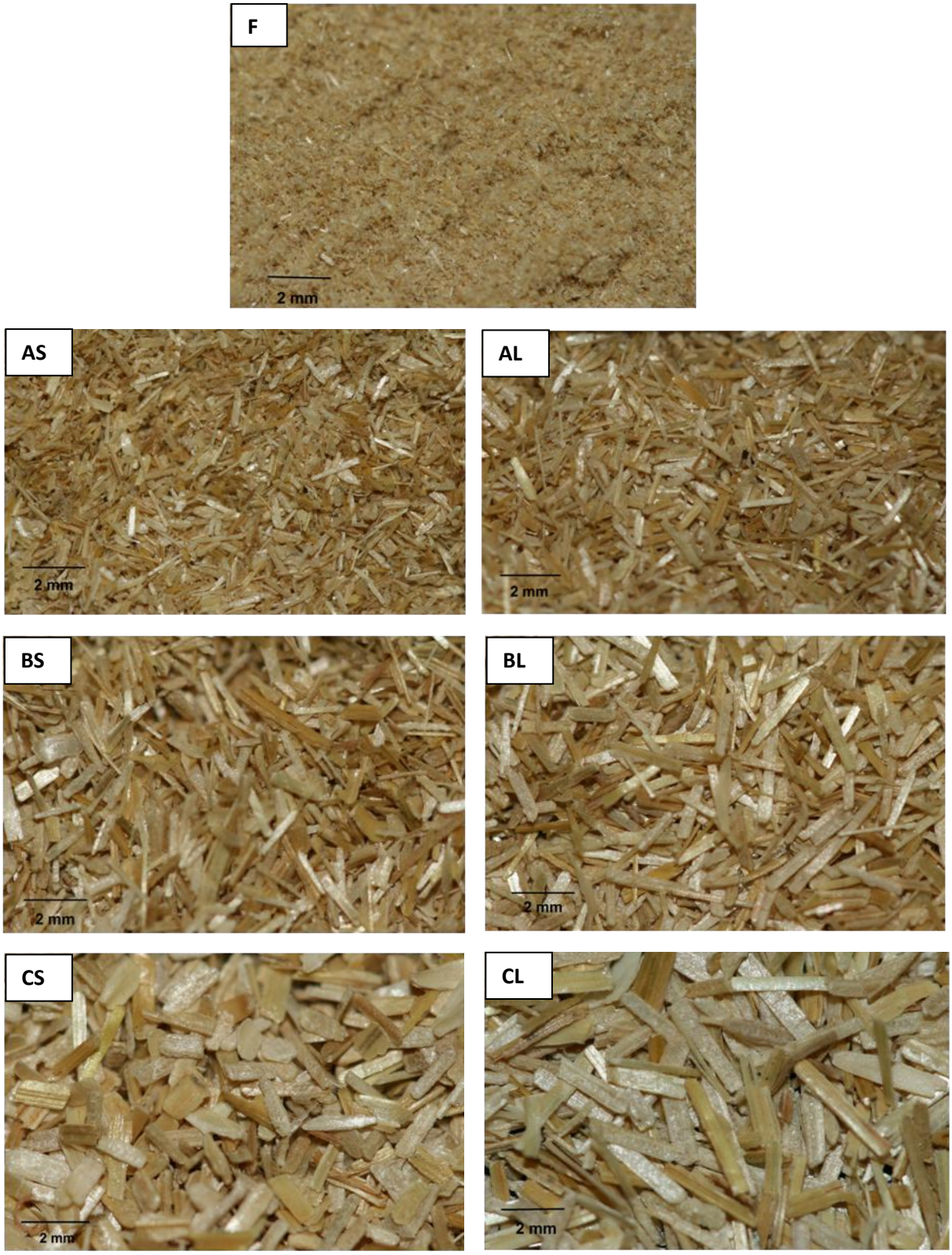


Figure 5-3 Pictures of Fiber Fractions.

5.3.2 Fiber Thermal and Chemical Analysis

The summary of TGA analysis and ADF/NDF analysis of fibers are presented in Table 5-2 and Table 5-3, respectively. The graphical representation of those analyses is presented in Figure 5-4 and Figure 5-5. It can be seen that all fractions have similar degradation temperatures, with the exception of Fraction F which has lower degradation temperature. It also can be seen that despite the variation of lignin, cellulose, and hemicelluloses contents of the fibers, all fractions exhibit similar thermal stability character.

Table 5-2 TGA Analysis Summary of Fiber Fractions

Fiber ID#	Temperature, °C			
	Onset Degradation	Peak Degradation	1%wt loss	5%wt loss
F	258.5	306.0	183.2	235.4
AS	263.4	308.0	195.9	245.9
AL	264.9	311.5	196.9	247.4
BS	265.2	314.0	199.4	248.7
BL	267.0	315.0	202.1	251.8
CS	264.3	311.0	196.6	246.6
CL	265.0	311.5	199.0	248.1

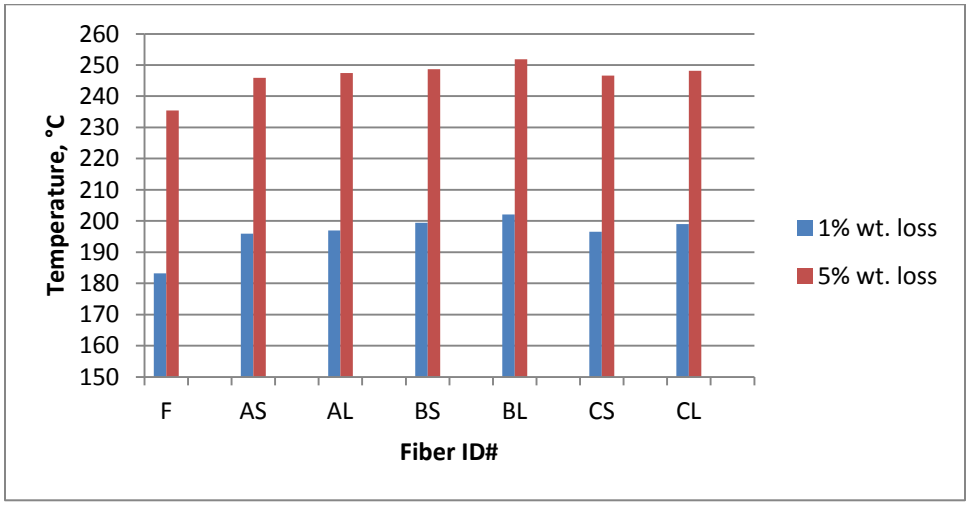


Figure 5-4 Degradation Temperatures of Fiber Fractions.

Even though cellulose is known to be more thermally stable compared to hemicelluloses and lignin, it appears that thermal degradation characteristics of the fibers is more related to their sizes rather than their cellulose-lignin contents. Fraction F has much smaller size compared

to the other fractions. Smaller size results in larger surface area which gives more exposure to the heat. This would subsequently lead to lower degradation temperature.

Table 5-3 Chemical Analysis Summary of Fiber Fractions

Fiber ID#	% Weight					
	Lignin	Cellulose	Hemicellulose	Ash content	Moisture content[#]	Estimated extractables and others[*]
F	6.91	37.99	28.80	4.55	2.84	18.91
AS	8.04	40.06	14.90	3.75	2.63	30.62
AL	8.82	42.88	29.90	3.53	2.56	12.31
BS	9.03	43.67	29.00	3.57	2.38	12.35
BL	8.87	45.13	28.50	3.37	2.33	11.80
CS	8.66	32.64	11.40	3.77	2.43	31.10
CL	9.05	43.65	10.30	3.77	2.43	30.80

[*] *The balance to 100% is made of extractables and others.*[#]*Moisture obtained from TGA.*

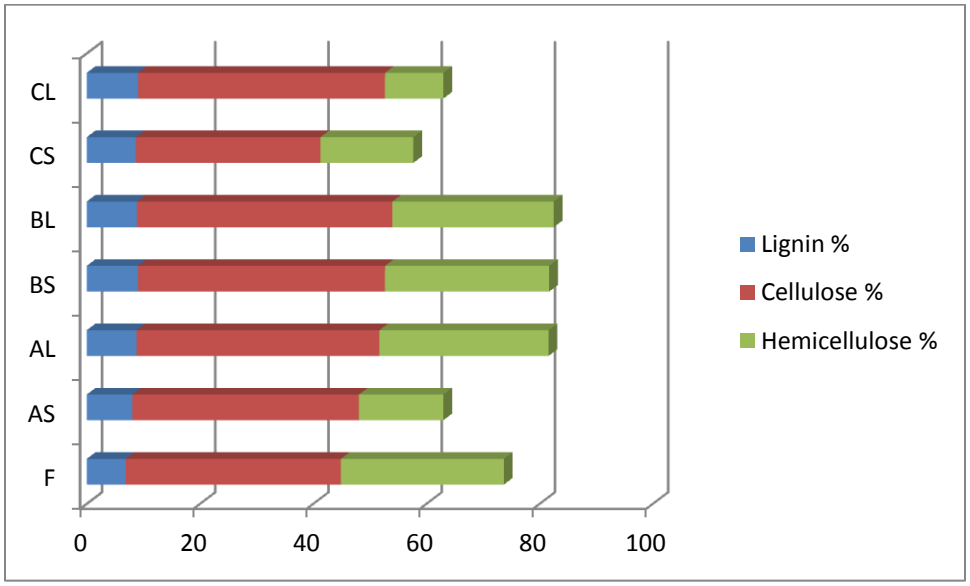


Figure 5-5 Cellulose, Hemicelluloses and Lignin Content of Fiber Fractions.

5.3.3 Fiber Size Reduction during Compounding Process

The extraction of fibers from composite samples and the measurement of the extracted fibers were done to evaluate the effect of particle break up during extrusion and injection molding. The summary of measurements is presented in Table 5-4. Figure 5-6 shows the mean plot of fiber length and fiber width. In order to investigate any pattern of fiber size reduction, the mean plot of fiber length and width before compounding process is also presented in this figure, along with the fiber length and width extracted from 30% and 50% fiber-loaded composites. The similar plot for fiber length and fiber aspect ratio can be seen in Figure 5-7.

In general, it can be seen that there is major reduction in fiber length. Despite the large different of fiber length before the compounding process ranging from 800 µm (AS) to 3300 µm (CL), all fibers were shortened to the range of 700 µm (AS) to 1300 µm (CL) at 30% fiber loading, and the range of 400 µm (AS) to 950 µm (CL) at 50% fiber loading. The longer fiber underwent higher degree of length reduction. It can also be seen that the order of fiber length after compounding is the same as the order of fiber length before compounding.

The width reduction of fibers follows the similar pattern of length reduction of fibers. The wider fiber underwent higher degree of width reduction. They also kept the same width order before and after compounding, with the exception of Fraction CS at 30% fiber loading.

Even though the length and the width reduction follow the similar pattern, the two have slightly different degree of reduction. The degree of reduction of fiber width is not as high as the degree of reduction of fiber length, especially for the larger fiber. As a result, this difference affected the pattern of fiber aspect ratio after compounding. As can be seen in Figure 5-7, the aspect ratio of fibers after compounding did not follow the same order of aspect ratio before the compounding. At 30% fiber loading, fraction AL and AS have higher aspect ratio compared to the larger fiber (Fraction B and C). Before the compounding, the two were ranked at the lowest in fiber ratio among other fibers. At 50% fiber loading, all fractions have relatively the same aspect ratio.

The pattern of size reduction mentioned above will be used to discuss the properties of composites in the following sections.

Table 5-4 The Mean Values of Fiber Width, Fiber Length and Aspect Ratio of Fibers Before and After Composite Compounding.

Fraction ID#	Fiber Width, µm			Fiber Length, µm			Fiber Aspect ratio		
	Initial	*30%*	*50%*	*Initial*	*30%*	*50%*	*Initial*	*30%*	*50%*
F	44 ± 1 [a]	n/a	n/a	96 ± 3	n/a	n/a	2.4 ± 0.09	n/a	n/a
AS	210 ± 6 [b]	237 ± 7	195 ± 7	788 ± 23	700 ± 17	413 ± 13	4.7 ± 0.24	3.3 ± 0.11 [a]	2.4 ± 0.08 [a]
AL	284 ± 8 [c]	265 ± 9	225 ± 9	1395 ± 35	834 ± 22	534 ± 18	6.0 ± 0.26	3.6 ± 0.11 [b]	2.6 ± 0.08 [b]
BS	361 ± 12 [d]	401 ± 13	304 ± 12	1884 ± 41	983 ± 31	742 ± 24	6.9 ± 0.36	2.7 ± 0.08 [c]	2.7 ± 0.08 [b]
BL	362 ± 10 [d]	327 ± 8	299 ± 10	2227 ± 54	1056 ± 24	732 ± 22	7.5 ± 0.37	3.5 ± 0.10 [a,b]	2.8 ± 0.09 [b]
CS	654 ± 11 [e]	317 ± 11	372 ± 13	1706 ± 33	895 ± 27	867 ± 30	2.9 ± 0.12	3.2 ± 0.11 [a]	2.5 ± 0.07 [a,b]
CL	645 ± 12 [e]	591 ± 17	411 ± 17	3204 ± 54	1247 ± 30	909 ± 33	5.5 ± 0.19	2.4 ± 0.08 [d]	2.5 ± 0.08 [a,b]

Note: The values are accompanied by the mean standard errors. The superscript symbols indicate the statistical significance difference values. Within each column, any values with the same symbols are statistically the same.

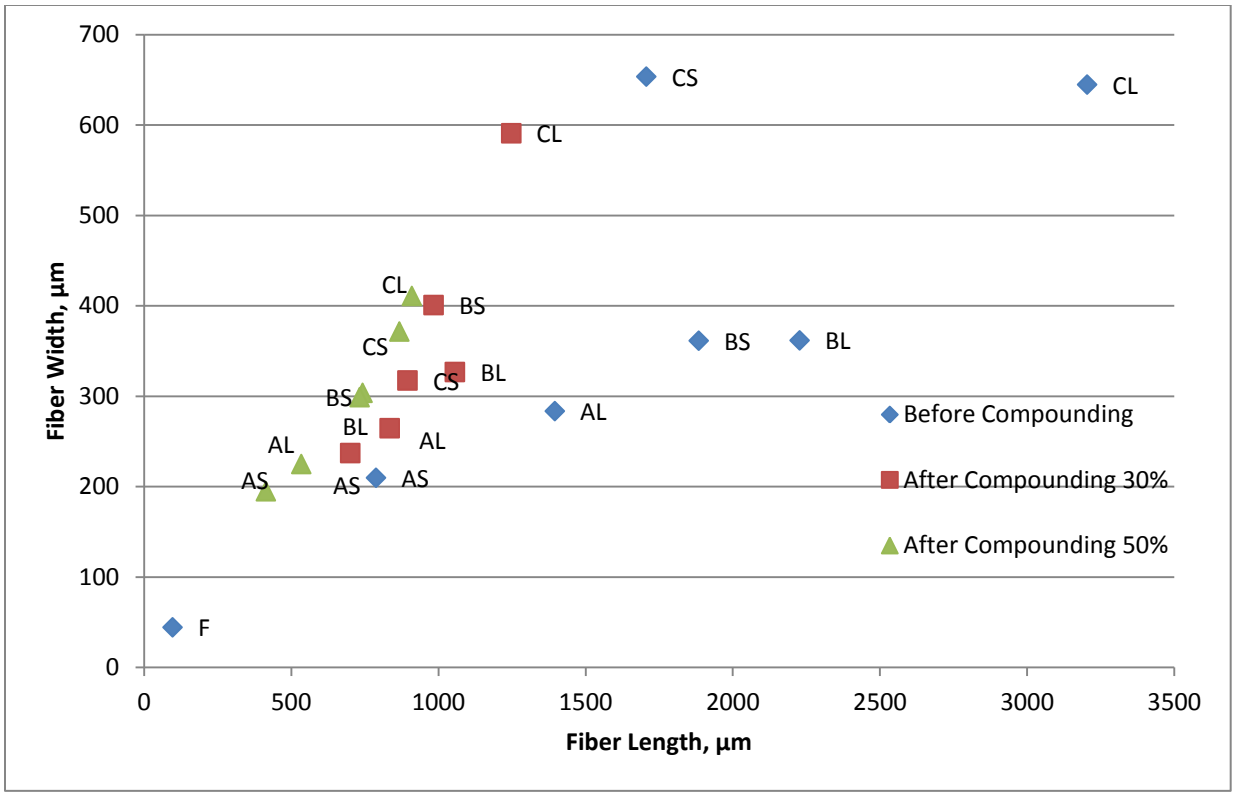


Figure 5-6 Mean Plot of Fiber Length and Fiber Width Before and After Compounding Process.

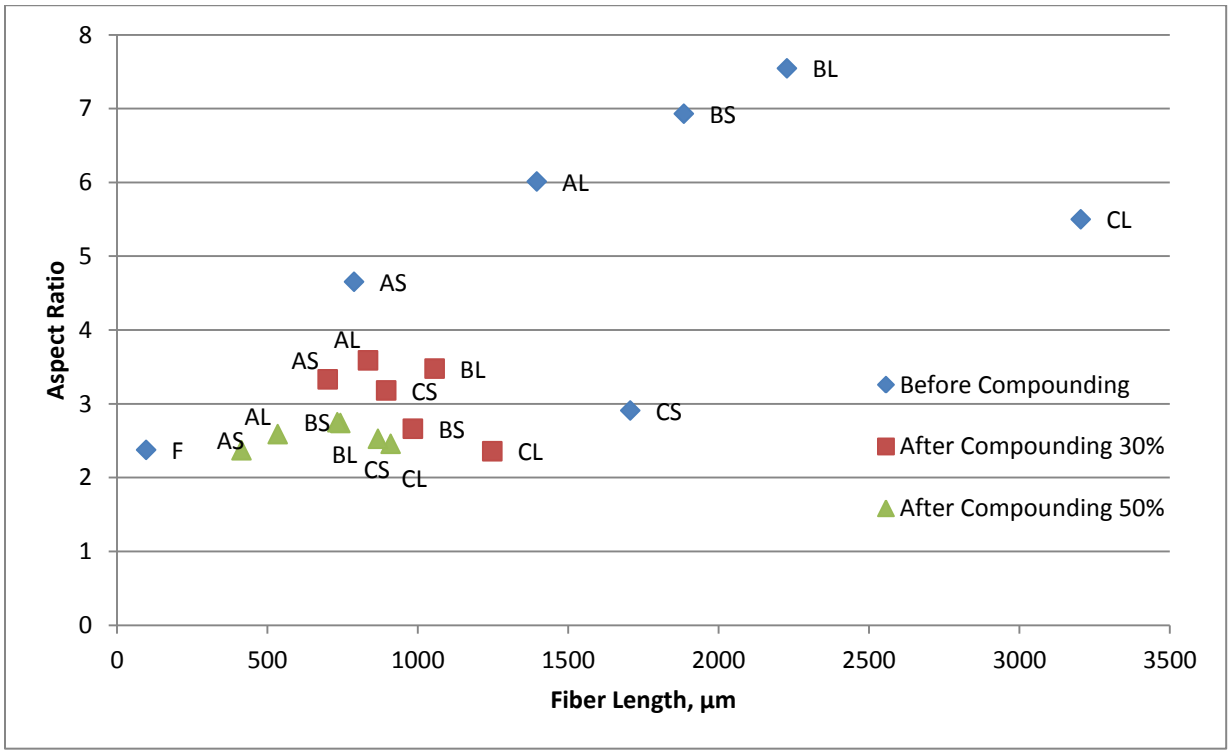


Figure 5-7 Mean Plot of Fiber Length and Aspect Ratio Before and After Compounding Process

5.3.4 Composite Flexural Properties

The flexural modulus of WS-PP composite samples made of seven different sizes of fiber at 30% and 50% fiber loadings is presented in Figure 5-8. At 30% fiber loading, the flexural modulus of the composite samples for all fiber sizes is relatively the same at values about 2000 MPa. At 50% fiber loading, however, the modulus values varies between 2300 MPa to 3000 MPa.

The error bars on the graph represent the mean standard errors. Fisher's Least Significance Difference method was used to investigate the significance difference of measured flexural modulus. The superscript letters indicate the statistically distinctive values of measured flexural modulus. At 30% fiber loading there are differences of flexural modulus between composites made with different fibers (with the exception of composite made with fiber AL and CL which have the same flexural modulus). The difference, however, is not as high as of composite samples at 50% fiber loading.

It was expected that composites made of fibers with higher aspect ratio such as fiber fractions AL, BL, and CL would have higher flexural modulus. The results confirmed this expectation. Each of them has higher flexural modulus compared to their pairs (AL compared to AS, BL compared to BS, and CL compared to CS) at both 30% and 50% fiber loading.

It was also expected that composites made of fibers with higher length would have higher flexural modulus. However, the results did not conform to this expectation. At 30% fiber loading, the flexural modulus of composites made with AS and AL fibers are close to flexural modulus as composite made of CS and CL fibers despite that AS and AL are much shorter than CS and CL. Even at 50% fiber loading, composites made of AS and AL fiber have higher flexural modulus.

That is because all fibers underwent size reduction during compounding process; and larger fibers have had higher degree of reduction and failed to maintain both their length and aspect ratio. The smaller fiber, on the other hand, only exhibited lower percentage of fiber shortening while maintained their aspect ratio; higher than the aspect ratio of larger fibers.

The composite made of fiber Fraction BL has the highest flexural modulus among other fibers for both 30% and 50% fiber loading. This is in accordance with the expectation that fiber with both higher length and aspect ratio will give maximum reinforcement effect on composite. Fraction BL is better than Fractions AL and AS because they have relatively the same aspect ratio but Fraction BL is longer than AL and AS. Fraction BL is better than CL and CS because even though CL and CS are longer than BL, their aspect ratio is lower than BL's aspect ratio.

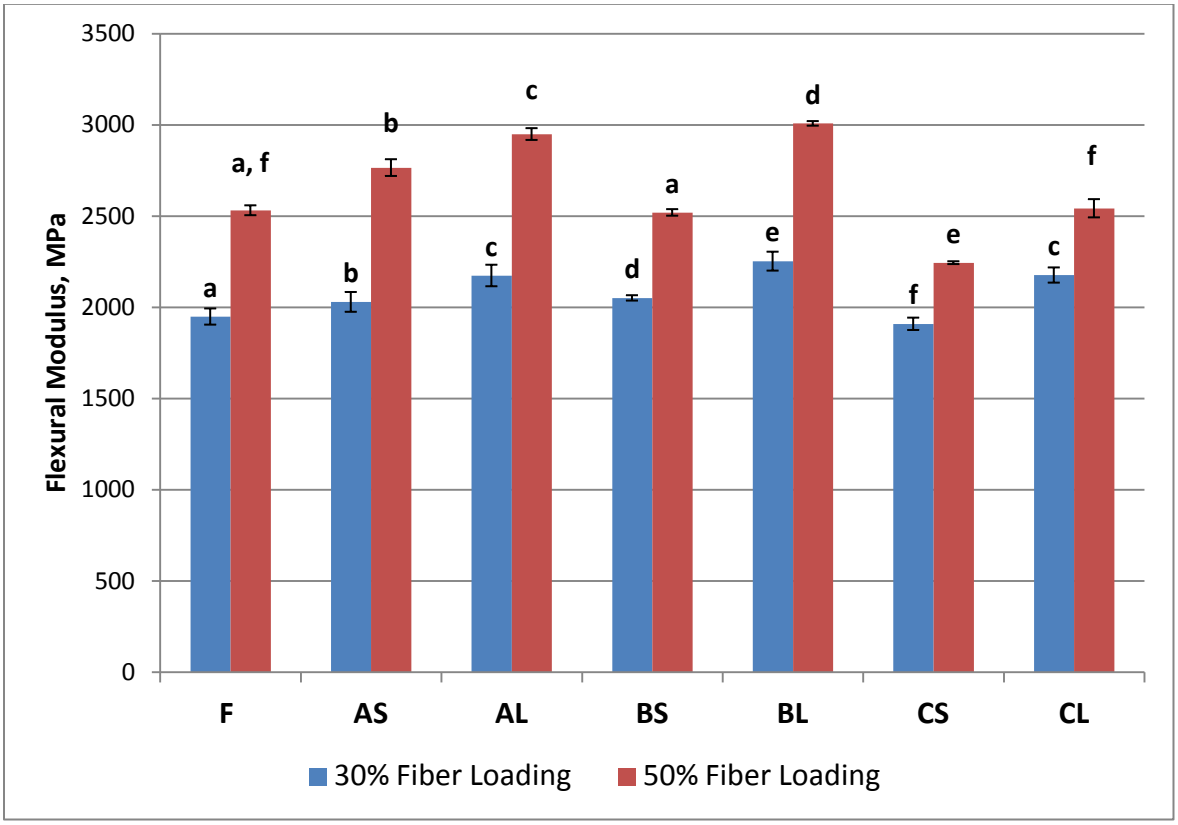


Figure 5-8 Flexural modulus of WS-PP composite samples made of different sizes of fiber with 30% and 50% fiber loading. The error bars represent standard errors. [a,b,c,d,e,f] If any bars within the same labels has the same letters, their values are statistically the same.

5.3.5 Composite Impact Properties

The results of impact strength measurement of composite samples can be seen in Figure 5-9. The error bars on the graph represent the mean standard errors. Fisher's Least Significance Difference method was used to investigate the significance difference of measured impact strength. The superscript letters indicate the statistically distinctive values of measured impact strength. At 30% fiber loading the impact strength of composite samples made with AS and AL fibers are statistically the same. The same is true for composite samples made with BS and BL fibers. However, the impact strength of BS and BL composites are higher than AS and AL composite. At 50% fiber loading the impact strength of composite samples categorized into two significant groups: composite made with fiber F, AS and AL in one group and composite made with fiber BS, BL, CS and CL.

It was expected that inserting wheat straw into polypropylene would increase the flexural modulus and decrease impact strength. The more the fiber content, the more flexural modulus increase and the more impact strength decrease. The results confirmed those expectations. At 30 % fiber loading, the impact strength of composites made of different fibers decrease from 4 % to 29 % compared to the impact strength of pure polypropylene. As the fiber content increases to 50% fiber loading the decrease become higher: ranging from 12 % to 29 %. (See Table 5-5).

However, the inverse pattern of increasing flexural modulus and decreasing impact strength does not apply to the fiber size. It can be seen that composites made of Fractions BS and BL fiber have the lowest percentage of impact strength decrease; while their flexural modulus increase were also high compared to the others. It can be concluded that when it is necessary to increase the flexural modulus without decreasing the impact strength, fibers with 350 μm of width (Fractions BS and BL) are the best choice.

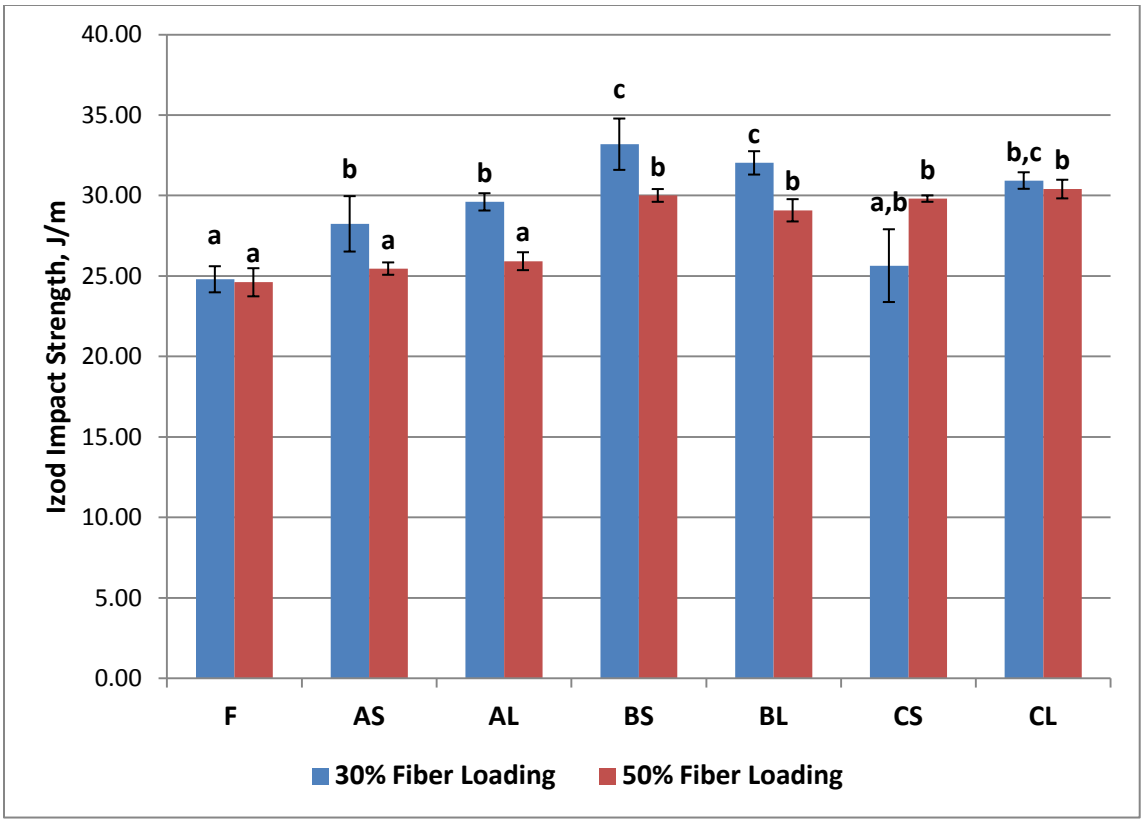


Figure 5-9 Impact test results of composite samples made of different fiber sizes. Error bars represent standard errors. [a,b,c] if any bars within the same series has the same letters, their values are statistically the same.

Table 5-5. The results of impact strength measurement of composites made of different fiber sizes.

Fiber ID#	30% Fiber Loading			50% Fiber Loading		
	Impact Strength, J/m	Std. Dev.	Decrease to Pure PP, %	Impact Strength, J/m	Stdv	% Decrease
F	24.80	1.81	28	24.61	1.95	29
AS	28.24	3.85	18	25.46	0.86	26
AL	29.61	1.20	14	25.92	1.24	25
BS	33.19	3.57	4	30.01	0.89	13
BL	32.03	1.62	7	29.08	1.55	16
CS	25.64	5.06	26	29.81	0.45	14
CL	30.93	1.15	10	30.40	1.30	12

5.3.6 Composite Specific Properties

One of the most important properties of composite materials is specific modulus. Specific modulus is defined as modulus divided by the density. Materials with higher specific modulus are highly favorable in automotive application because they can save material cost and energy. To obtain the specific modulus of WS-PP composite, the density of composite samples was measured according to ASTM D792. The results can be seen in Figure 5-10. At 30% fiber loading, the densities of composite slightly decrease as the fiber size increase. At 50% fiber loading, the densities are relatively the same, with exception of composite made of F fiber.

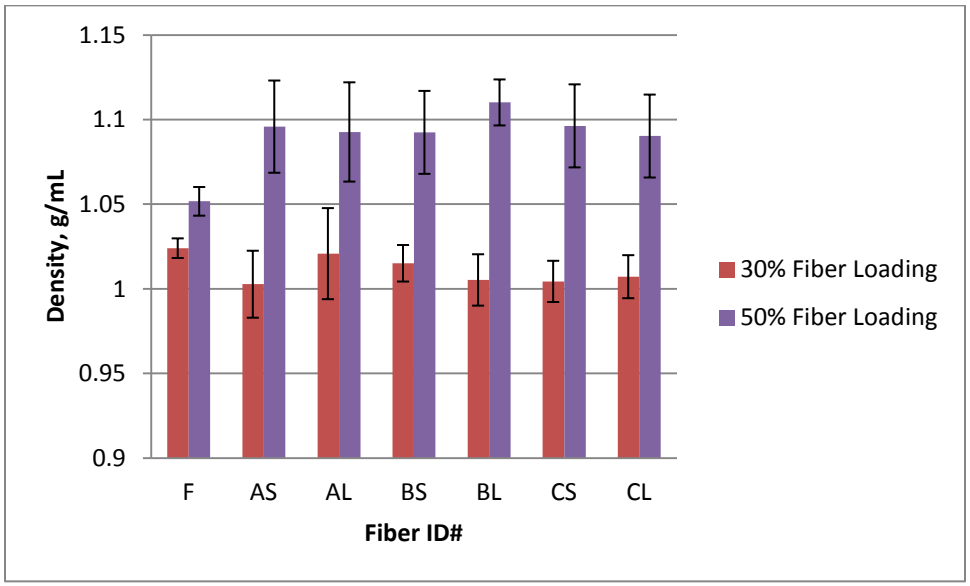


Figure 5-10 The Density of Composite Made of Different Fiber Sizes.

Note: The bars represent the standard deviation. Each value was calculated from 8 samples.

The specific modulus of the composite samples is presented in Figure 5-11 with the relative ratio to the specific modulus of pure polypropylene (considered as 1). Due to the relatively the same values of density among the composite samples, the pattern of specific modulus of composite made of different fiber sizes is identical with the pattern of flexural modulus discussed in the previous section.

Figure 5-12 shows the graph plot of specific modulus vs. impact strength of composite samples made of different fiber sizes at 30% and 50% fiber loading. The plot also includes the specific modulus and impact strength of pure polypropylene. It can be seen that BS and

BL fiber are the best fiber. Fraction BS is preferred when the impact strength is more relevant than the specific modulus, and Fraction BL is preferred when the specific modulus is more relevant than the specific modulus.

The chemical analysis results suggest that the superiority of Fraction BL is in accordance with its cellulose and ash content. Fraction BL has the highest content of cellulose and the lowest content of ash. However, there is not enough support to draw a conclusion about the relationships between cellulose and ash content and mechanical properties of WS-PP composites. Further investigations are suggested to follow up this information.

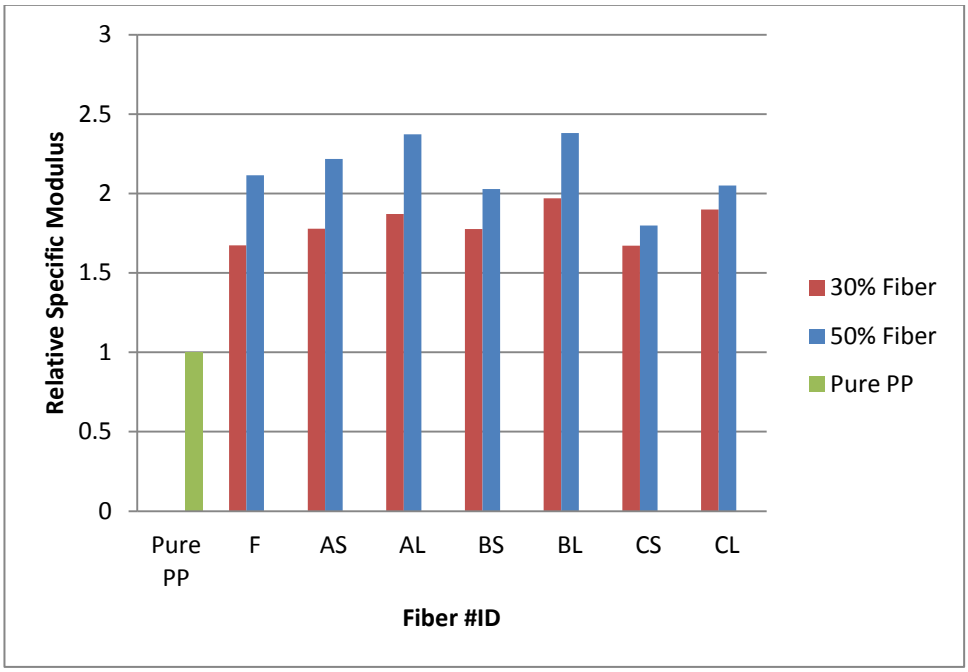


Figure 5-11 Relative Secific Modulus of Composite Samples Compared to Pure Polypropylene.

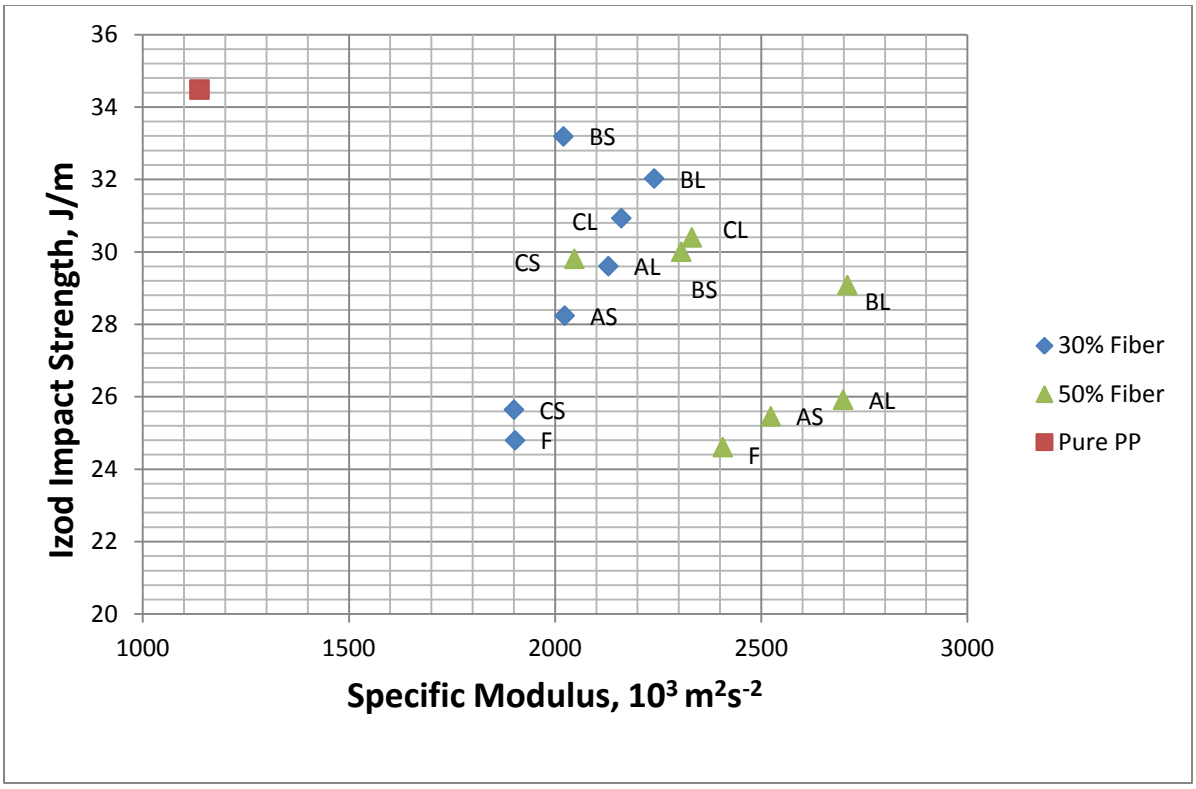


Figure 5-12 The Graph Plot of Specific Modulus vs. Impact Strength of WS-PP Composites Made of Different Fiber Sizes.

It can also be seen that if a penalty of approximately 30% on the impact strength is allowed, a 50% fiber loading of Fraction AL fiber would give increased specific modulus at the same level as the Fraction BL fiber. And even smaller fibers, i.e. Fractions AS and F fiber would also give higher specific modulus of composite.

This information is very useful for optimizing the wheat straw utilization. All fraction of ground wheat straw can be used for producing grades with improved value when producing composites for different needs and specifications.

5.4 Chapter Summary

The study of the effect of fiber size on some properties of thermoplastic composites of polypropylene and wheat straw fiber was completed. Different sizes of fibers were prepared by two-stage separation, i.e. width-based separation and length-based separation, in order to obtain fibers with distinct fiber width and aspect ratio.

The measurement of fiber sizes before and after processing the fiber with the thermoplastic by extrusion and injection molding showed different patterns of length reduction and width reduction among different fiber sizes. Fibers with smaller initial width were able to maintain their aspect ratio. Fibers with greater initial width underwent length reduction and aspect ratio reduction. Fibers with medium initial width also had a decrease in their length but they were able to maintain their aspect ratio during the composite processing stage. Therefore, fibers with medium initial width are the best fibers to be used to produce thermoplastic composites when a balance of flexural and impact properties are needed.

The investigation of flexural modulus of composites made with different fiber sizes shows that there are significant differences of flexural modulus among different composites, especially between the composites made with fibers which have the same fiber width and different fiber length. The differences at 30% fiber loading are not as high as the differences at 50% fiber loading.

The investigation of impact strength of composites made with different fiber sizes shows the inverse pattern of increased flexural modulus by increasing fiber loading. Increasing fiber loading decreases the impact strength. Specific pattern of the effect of fiber sizes on impact strength was not found, but it was shown that fibers with medium width are the best choice when it is necessary to increase the flexural modulus with minimum decrease of the impact strength.

6 Response Surface Models for Optimization of Wheat Straw – Polypropylene/Impact Copolymer Polypropylene Composite Formulation

6.1 Introduction

The insertion of wheat straw fiber in polypropylene matrix is able to increase the stiffness of the composite at the expense of decreasing its impact strength. While for some product specifications this decrease in impact strength is acceptable to a certain degree, other specifications require maintaining the impact strength at certain level or even improving it significantly above the level of the impact strength of the homopolypropylene.

Apart from the above mechanical properties issues, the addition of wheat straw into polypropylene increases the apparent viscosity of the materials. The increasing viscosity may cause problems in compounding and molding process. Higher viscosity means greater torque and higher operating cost in compounding process. Higher viscosity can also lead to higher processing time and or temperature in molding process.

In order to maintain the impact resistance level in the final composite product properties and to meet the rheological properties requirements in composite processing facilities, high-impact copolymer polypropylene (ICP) is added to a less viscous, high melt flow index polypropylene matrix. Compounding this polymer blend matrix with wheat straw fiber will produce wheat straw polypropylene/impact copolymer polypropylene (WS-PP/ICP) composite with higher flexural modulus while maintaining high impact resistance and low viscosity for easier processing.

The objective of this study is to develop response surface models for WS-PP/ICP blend composite which correlate composite properties to its formulation (component proportion). These models can be used to design formulations of wheat straw PP/ICP blend composite with properties which meet product specifications for automotive applications. Three case studies of composite formulation optimization problems are performed to demonstrate the usefulness of the models.

6.2 The Design of Mixture Experiment

The WS-PP/ICP blend composite system consists of four major components: homopolypropylene (PP) and impact copolymer polypropylene (ICP) as matrix, wheat straw (WS) as fiber and maleic anhydride polypropylene as coupling agent. The coupling agent proportions were fixed according to the suggested proportions from previous results presented in Chapter 4. This left the composite system with three components variables (PP, ICP and WS).

The desired wheat straw content range is 20% to 40%. The results of preliminary experiments on the PP/ICP blend properties measurements suggested the reasonable percentage of impact copolymer (ICP) is 10% to 40%. Those ranges lead to a constrained pseudo-simplex mixture design with the following constraints:

$$\begin{aligned} 0.2 \leq x_1 \leq 0.4 \\ 0.3 \leq x_2 \leq 0.7 \\ 0.1 \leq x_3 \leq 0.4 \end{aligned} \tag{6.1}$$

where x_1, x_2 and x_3 are weight proportions of wheat straw (A), polypropylene (B), and impact copolymer polypropylene (C), respectively.

The complete lists of 12 design points of the design of experiment are presented in Table 6-1. Figure 6-1 illustrates the plot of design points and design space on pseudo-simplex lattice coordinates. The degree of percentage of each component follows the lines parallel to each edge. Along the edge line, the proportion of a component is at its minimum. As the lines move away from the edge, the proportion values increase and reach the maximum value at the vertex which opposites to the edge. For instance, wheat straw percentage value is 20% at the bottom edge, 30% at the first horizontal line parallels to the edge, and 40% at the next line. At any point in the simplex lattice coordinate, the sum of components' proportion is 1. The red-shaded area of the pseudo-simplex *lattice* coordinate shown in Figure 6-1 is the design space of the experiment.

Among those design points, 8 of them were replicated twice. This replication is aimed to provide better characteristics of the design, such as the evenly distributed standard error of

design; and to provide sufficient data points for statistical analysis in model building process. Figure 6-2 shows the plot of standard error of the design. It can be seen that the standard error is relatively the same thorough the design space at relatively low value of 0.4 to 0.5.

Table 6-1 The Design Points of WS-PP/ICP Mixture Experimental Design.

Design Point ID#	Component's proportion (weight fraction)		
	Wheat Straw (A) x_1	Polypropylene (B) x_2	Impact Copolymer Polypropylene (C) x_3
1*	0.20	0.70	0.10
2*	0.20	0.60	0.20
3*	0.20	0.50	0.30
4*	0.20	0.40	0.40
5	0.30	0.60	0.10
6	0.30	0.50	0.20
7	0.30	0.40	0.30
8*	0.30	0.30	0.40
9*	0.40	0.50	0.10
10	0.40	0.40	0.20
11*	0.40	0.30	0.30
12*	0.40	0.20	0.40
Note: Asterisk symbol represents replicated design points.			

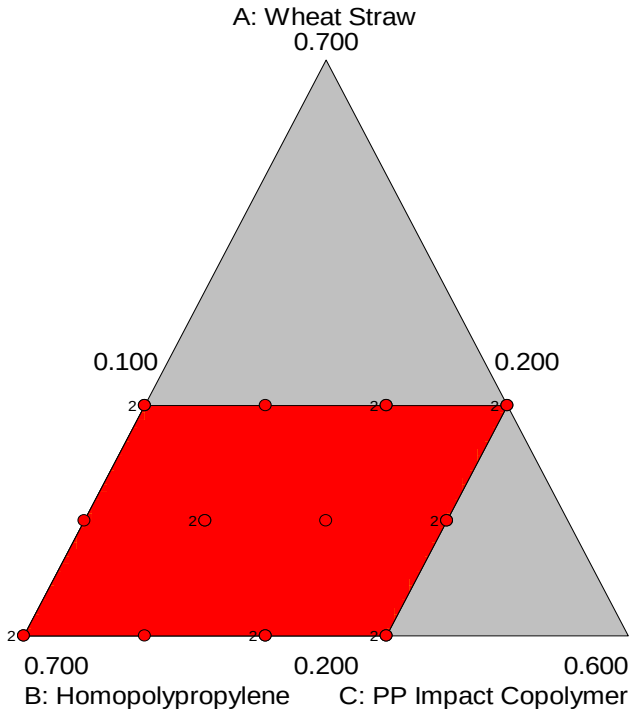


Figure 6-1 Plot of Design Space and Design Points on Pseudo-simplex Lattice Co-ordinate of WS-PP/ICP Mixture Experiments.

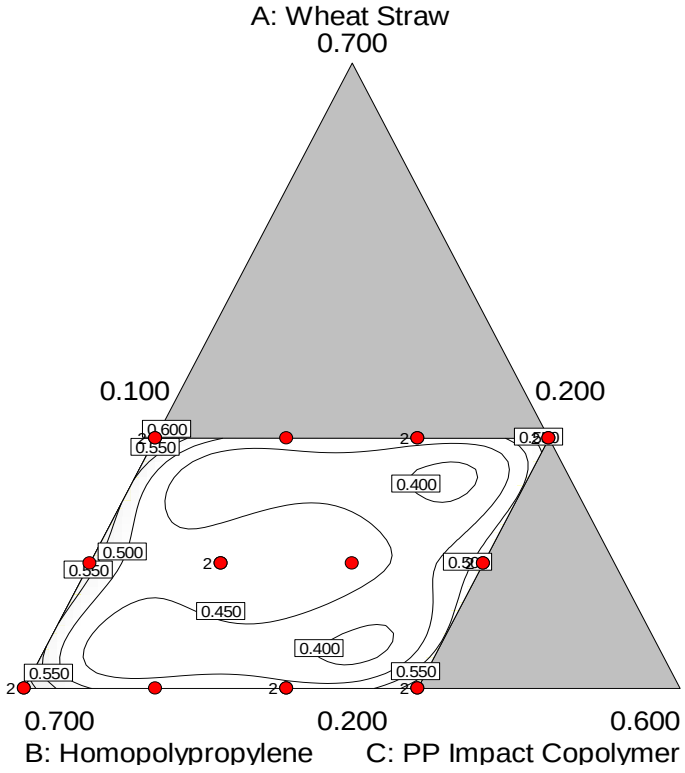


Figure 6-2 Contour Plot of Standard Error Design of the Design of Experiment.

The composite samples were produced according to the design points and response variables of the composite samples were measured. The results of the measurements were used to calculate the parameter estimates of *scheffe* canonical models for each response variable. Design Expert software was used in model structure selection, model fitting, and model evaluation as well.

The response variables measured were: flexural modulus and flexural strength, elastic modulus and tensile strength, elongation at break, impact strength, density and apparent shear viscosity.

6.3 Materials and Methods

Commercial grade homopolypropylene with a melt flow index of 36 g/10 min (230 ^{o}C, 2.16 kg, ASTM D 1238) and impact copolymer polypropylene with melt flow index of 24 g/10 min (230 ^{o}C, 2.16 kg, ASTM D 1238) within the form of pellets was donated by A. Schuman Inc. (Due to the confidentiality required by the reserach sponsor, further information regarding these materials cannot be provided here).

Wheat straw used in this study was a soft white winter wheat straw (AC Mountain) harvested in late 2009 from the Ontario region, the wheat straw was donated by Omtec Inc. The coupling agent used was Fusabond MD-353D, a maleic anhydride grafted polypropylene purchased from DuPont. Two antioxidants, namely Irganox 1010 and Irgafos 168 were purchased from Ciba Inc. and were used in order to avoid thermal degradation or polypropylene caused by the processing conditions.

Before the compounding, homopolypropylene and impact copolymer polypropylene pellets were ground into fine powder by using laboratory blender. Prior to the grinding process the pellets were immersed into liquid nitrogen, cooled to below the glass transition temperature, making the pellets easier for grinding.

The Fraction BL of ground wheat straw obtained during fiber fractionation explained in Chapter 5 was used in this study. The mean width and mean length of the fibers are 350 μm and 2300 μm, respectively. As discussed in Chapter 5, this is the fiber fraction that gives the best improvements and balance on both stiffness and impact strength for the composites.

The composite samples for mechanical properties measurement were prepared according to the standards used in testing methods. The standards are ASTM D790, ASTM D256, and ASTM D792 for flexural test, izod impact test, and density measurement, respectively. The method and procedure of sample preparation are the same as described in Chapter 5.

To investigate the rheological properties of the composite, the melt flow index (MFI) and the apparent shear viscosity of the samples were measured. The MFI measurement was performed according to ASTM D1238.

The measurement of apparent shear viscosity was performed by pressure drop approximation method by using the Haake Minilab micro compounder. Five grams of sample was fed into the extruder operating at the same operating conditions used during the sample bars preparation for mechanical testing. The extruder was set to "cycle" mode, such that all material was directed into the slit channel illustrated in Figure 6-3. The pressure drop was measured using two pressure transducers indicated in Figure 6-3 as P_1 and P_2. The pressure drop displayed on the screen was monitored and was recorded when it showed steady values..

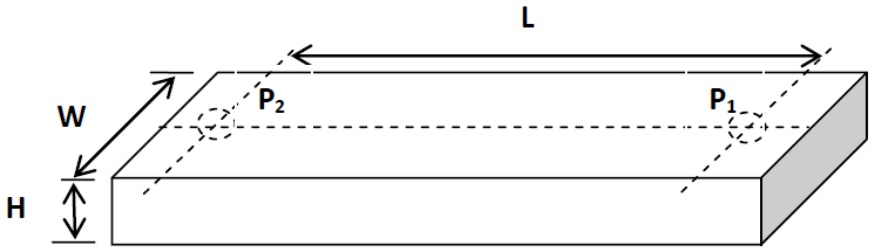


Figure 6-3 Illustration of Rectangular Slit Channel in Apparent Shear Viscosity Measurement.

The resultant shear stress across the channel is determined by the following formula:

$$\tau = \frac{\Delta P \cdot H}{2L} \tag{6.2}$$

Where

$\Delta P = P_1 - P_2$

H = Height of the channel (1.5 mm)

L = Length between pressure transducers in the channel (64 mm)

W = Width of the channel (10 mm)

The shear rate is calculated as :

$$\dot{\gamma} = \frac{6Q}{WH^2} \tag{6.3}$$

where Q is volumetric flow rate.

Due to limited equipment specifications, Q could not be definitely determined. To allow further analysis, it was assumed that the channel was fully filled at steady state during the

measurement of pressure drop. Therefore, Q was assumed to be constant regardless the type of material that is under testing, provided that the equipment was operated at the same operating conditions. Although the value of Q is expected to change with the different formulations measured here (specially the amount and the type of dispersed phase), it is beyond the scope of this thesis to make accurate measurements of Q.

This assumptions lead to representing shear viscosity (i.e. the ratio of shear stress to shear rate) as a function of a constant Q^{-1}:

$$\eta = \frac{\tau}{\dot{\gamma}} = \left[\frac{\Delta P \cdot W \cdot H^2}{12L}\right] \cdot \left[\frac{1}{Q}\right] \tag{6.4}$$

The relative shear viscosity of the composite is then calculated by comparing the measured pressure drop of each design points to PP/ICP blend consists of 30% ICP and 70% of PP.

6.4 Results and Discussions

The results of WS-PP/ICP composite properties measurements can be seen in Appendix 3. Analysis of the results is conducted by using Design Expert software. The following steps are applied to each response variable: (1) model fitting; (2) analysis of variance (ANOVA) test; (3) model diagnostics; and (4) plotting response surface graphs.

The fittest model is chosen by first comparing various coefficients of determination R^2 values between linear, quadratic, special cubic, and cubic canonical polynomial model. The model is chosen based on the maximum value of *Adjusted*-R^2 and *Predicted*-R^2 values. The number of model terms was reduced by applying backward elimination technique to get the model term combination which gives highest R^2 values. The model diagnostic case is then carried out to examine any violation against standard statistical assumptions and the influence of each design points to the model.

6.4.1 Flexural Modulus

The model summary statistics for Flexural Modulus model shows that quadratic canonical model is better than the other model structures. After backward elimination process, the model parameters were reduced and the response surface model for flexural modulus is:

$$FM = 2877\,x_1 + 1518\,x_2 - 3209\,x_3 + 10679\,x_1x_3 + 5037\,x_2x_3 \quad (6.5)$$

where *FM* is composite flexural modulus in MPa, while x_1, x_2, and x_3 are weight fractions of wheat straw (WS), polypropylene (PP) and impact copolymer polypropylene (ICP), respectively.

The model gives good prediction of the flexural modulus with R^2= 0.91, *Adjusted*-R^2 =0.89 and *Predicted*-R^2 = 0.84. The *Adjusted*-R^2 value of 0.89 is higher than suggested *Adjusted*-R^2 value for response surface model: 0.7. Also, the *Adjusted*-R^2 value is in reasonable agreement with *Predicted*-R^2 value. The difference of the two is 0.05; less than the suggested maximum difference of 0.2.

The values of model parameter estimates represent the levels of contribution from each component proportion to the flexural modulus. As it was expected, the increase of flexural

modulus came from wheat straw, while the presence of impact copolymer gave a negative contribution to the flexural modulus of the composite. The positive estimate values of parameter β_{13} and β_{23} means that there are positive blending effects between the wheat straw and impact copolymer and between polypropylene and impact copolymer on the flexural modulus of the composite. This effect is represented by the curvature contour plot shown in Figure 6-4.

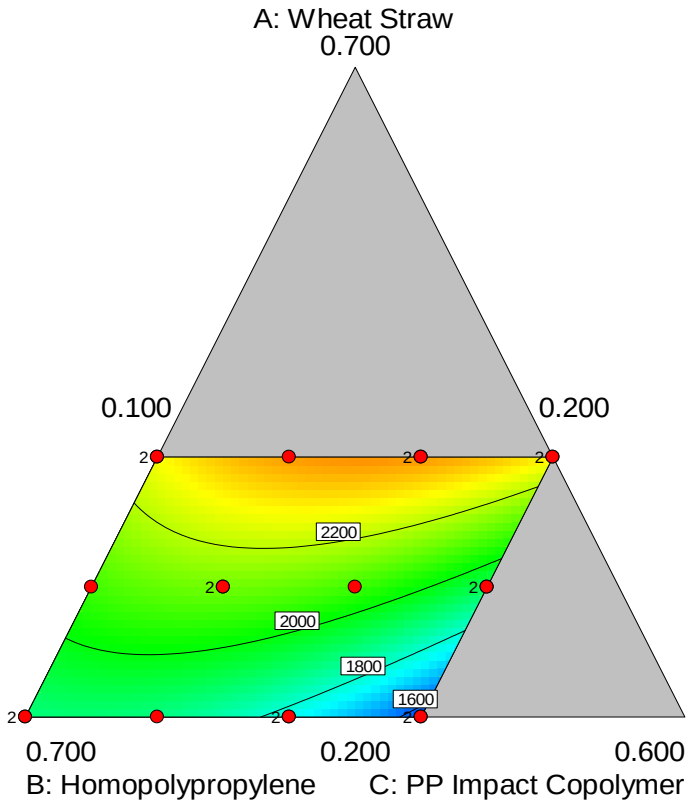


Figure 6-4 Contour Plot of Flexural Modulus (MPa) of WS-PP/ICP Composite within the Design Space.

6.4.2 Izod Impact Strength

The model summary statistics for impact strength shows that quadratic canonical model is the best among other model structures. After backward elimination process, the model parameters were reduced and the response surface model for flexural modulus is:

$$IS = 57.2\,x_1 + 13.8\,x_2 + 168.3\,x_3 - 275.3\,x_1x_3 - 67.7\,x_2x_3 \qquad (6.6)$$

Where *IS* is composite impact strength in J/m, and x_1, x_2, and x_3 are weight proportions of wheat straw, PP and ICP, respectively.

The model gives good prediction of composite izod impact strength with R^2= 0.97, *Adjusted-*R^2 =0.97 and *Predicted-*R^2 = 0.95. The *Adjusted-*R^2 value of 0.97 is higher than suggested *Adjusted-*R^2 value for response surface model: 0.7. Also, the *Adjusted-*R^2 value is in reasonable agreement with *Predicted-*R^2 value. The difference of the two is 0.01; less than the suggested maximum difference of 0.2.

The values of model parameter estimates represent the levels of contribution from each component proportion to the flexural modulus of composite. As it was expected, the impact copolymer (ICP) contributes the most to the impact strength of the composite. The negative estimate values of parameter β_{13} and β_{23} means that there are negative blending effects between the wheat straw and the impact copolymer and between the polypropylene and the impact copolymer on the impact strength of the composite. This effect is represented by the curvature contour plot shown in Figure 6-5

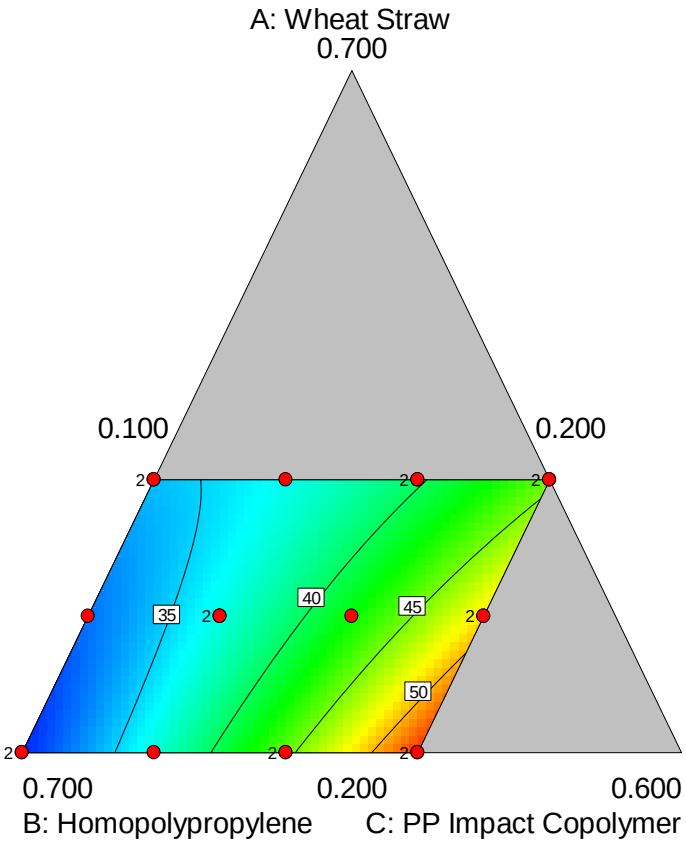


Figure 6-5 Contour Plot of Izod Impact Strength (J/m) of WS-PP/ICP Composite within the Design Space.

6.4.3 Apparent Shear Viscosity

The model summary statistics suggested linear model structure for the apparent shear viscosity of the composite during compounding process in the extruder. The obtained model to estimate the measured pressure drop in the slit chamber is:

$$\Delta P = 25.62\, x_1 + 1.87\, x_2 + 1.14\, x_3 \tag{6.7}$$

Where ΔP is pressure drop estimate in bar, and x_1, x_2, and x_3 are weight proportions of wheat straw, polypropylene and impact copolymer, respectively.

Again, the model gives good prediction of pressure drop with R^2= 0.96, *Adjusted*-R^2 =0.96 and *Predicted*-R^2 = 0.94. The contour plot of pressure drop for various component proportions of composite within the design space based on the obtained model can be seen in Figure 6-6. It can be seen that there is no curvature on the plot since the model is linear.

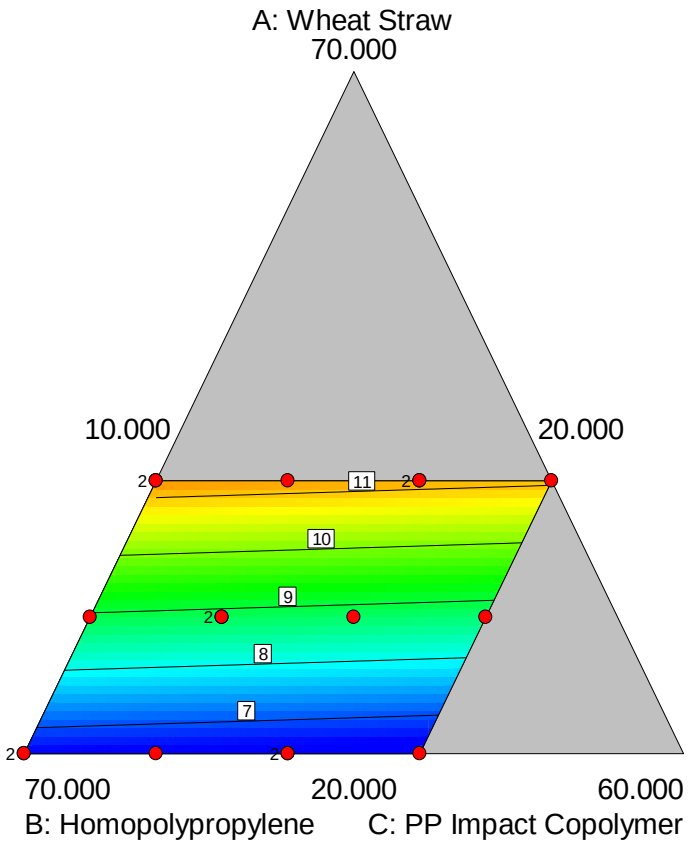


Figure 6-6 Contour Plot of Estimated Pressure Drop (bar) of WS-PP/ICP Composite during Compounding Process within the Design Space.

6.4.4 Other Properties

The models for other composite properties have also been obtained and were presented in Table 6-2. All models have the linear structure of standard canonical model. That means there is only linear blending effect between each component for those composite properties. The parameter estimate value for each component proportion indicates the level of contribution of each component for composite properties.

The linear structure of the model can also be interpreted that the property of the composite follows the "rule of mixture". For flexural strength, for example, the parameter estimate for each component proportion represents the flexural strength of each component. The flexural strength of composite will be equal to the density of one of the component when that component's proportion is 100%.

Table 6-2 Composite Property Models Obtained from the Designed WS-PP/ICP Experiments

Properties	Model Equations
Tensile Strength, MPa	$TS = 23.29\,x_1 + 36.18\,x_2 + 37.05\,x_3$
Elongation at break, %	$EL = 1.78\,x_1 + 15.08\,x_2 + 15.98\,x_3$
Flexural Strength, MPa	$FS = 74.90\,x_1 + 53.95\,x_2 + 30.94\,x_3$
Density, g/cm3	$D = 1.20\,x_1 + 0.91\,x_2 + 0.98\,x_3$
Elastic Modulus, MPa	$EM = 469\,x_1 + 253\,x_2 + 272\,x_3$

It is important to note that the above interpretation is only applied to a standard simplex design, where the component proportion variable x can take any values from 0 to 1. The model obtained in this study is based on constrained pseudo-simplex design with constrained design space. The interpretation, therefore, is only an approximation because a mixture with 100% component proportion is not included in the design space.

For some properties such as the composite flexural strength, the approximation is in agreement with the individual density measurement of each component. However, for some other properties such as the shear viscosity which was estimated by the pressure drop measurement during extrusion process, the parameter estimate of PP and ICP proportion is not in agreement with the results of the experiment. The measured pressure drop of PP/ICP blend with 20% and 30% ICP content is around 4 bar, while the parameter estimate for PP and ICP proportion in the model are 1.87 and 1.14, respectively.

The coefficients of determination of the models are given in Table 6-3. The results of model significance ANOVA-test are also presented in that Table.

It can be seen that all model were statistically significant to describe the relationship between the measured values of composite properties, with the exception of tensile strength. At significance level of 0.05, the model is not significant; and the tensile strength mean value of 32.54 MPa is the suggested value for all composite compositions.

Table 6-3 Summary of Calculated Model Coefficient of Determinations and Model Significance ANOVA -Test Results.

Model	R^2	$R^2_{Adjusted}$	$R^2_{Predicted}$	Model ANOVA-test result
Tensile Strength	0.26	0.18	-0.06	Not significant, p-value = 0.0735
Elongation at break	0.91	0.90	0.88	Significant, p-value < 0.0001
Flexural Strength	0.93	0.92	0.90	Significant, p-value < 0.0001
Density	0.61	0.56	0.43	Significant, p-value = 0.0004
Elastic Modulus	0.34	0.26	0.06	Significant; p-value = 0.0308

The ANOVA summary table and the diagnostic case statistics for each property model can be seen in Appendix C of this thesis.

6.4.5 Optimization of Composite Formulation

A set of typical target specifications for thermoplastic composites with applications in automotive parts were obtained from the industrial partner (Ford Motors). These targets were used to perform the optimization of composite formulation. After an extensive review on the specifications and the ranges of measured response values obtained from the experiments carried out here, three product specifications were chosen as the targets for optimization case studies (Products A, B and C). The lists of the selected specifications (properties) can be seen in Table 6-4.

Table 6-4 Lists of Product Specifications Used as the Targets of WS-PP/ICP Formulation Optimization

Properties	Product A	Product B	Product C
Flexural modulus, GPa	≥ 2.2	≥ 1.9	≥ 2.3
Tensile strength, MPa	≥ 29	N/A	≥ 25
Impact strength, J/m	≥ 39	≥ 40	≥ 23
Density, g/cm^3	≤ 1.08	≤ 1.10	≤ 1.06

Graphical simulations based on the response surface models obtained from the experiments and the constraints determined by specification of Product A, Product B, and Product C can be seen in Figure 6-7, Figure 6-8, and Figure 6-9, respectively. The overlay plots show that WS-PP/ICP composite was able to meet all three sets of target properties. The un-shaded area (represented in white) of each plot represents the range of compositions which meets each set of target properties.

To show the superiority of WS-PP/ICP composite system produced in this study over the other systems in catching up the targeted product specifications, a comparison matrix has been made between WS-PP/ICP composite, WS-PP composite and PP/ICP polymer blend. (Table 6-5)

The results of WS-PP study with different fiber size show that at 40% fiber loading, the flexural modulus of WS-PP composite ranges between 2.1 to 2.6 GPa. (see Figure 5-8 in

Chapter 5). Meanwhile, the required flexural modulus for product A, B and C are 2.2 GPa, 1.9 GPa, and 2.3 GPa, respectively. Therefore, flexural modulus of WS-PP composite has met those requirements. However, the maximum impact strength of the composite with 40% fiber content is only 32 J/m. (see Figure 5-9 in Chapter 5). The only product which requires impact strength below that value is product C. Therefore, WS-PP composite can only meet the specification of product C.

Table 6-5. Flexural and Impact Properties Comparison Matrix between Composite Systems against Product Specifications

Product	Specification	WS-PP/ICP Composite	WS-PP Composite	PP/ICP Polymer Blend
Flexural modulus range, GPa		1.5 – 2.5	2.1 – 2.6	≤ 1.3
Impact strength range, J/m		30 - 54	≤ 32	30 - 70
A	Flexural Modulus ≥ 2.2	✓	X	X
	Impact Strength ≥ 39	✓	X	✓
B	Flexural Modulus ≥ 1.9	✓	✓	X
	Impact Strength ≥ 40	✓	X	✓
C	Flexural Modulus ≥ 2.3	✓	✓	X
	Impact Strength ≥ 23	✓	✓	✓

The measurements of the flexural modulus and impact strength of PP/ICP polymer blend samples with various ICP proportion have been done. The results of those measurements are summarized in Figure 6-10. The impact strength of about 40 J/m as required by all product specifications can be achieved by adding 30% of ICP. However, the maximum flexural modulus of PP/ICP blend is only 1.3 GPa; much less than the required specifications for all products (1.9 to 2.5 GPa). Therefore, none of product specifications would be met by PP/ICP polymer blend.

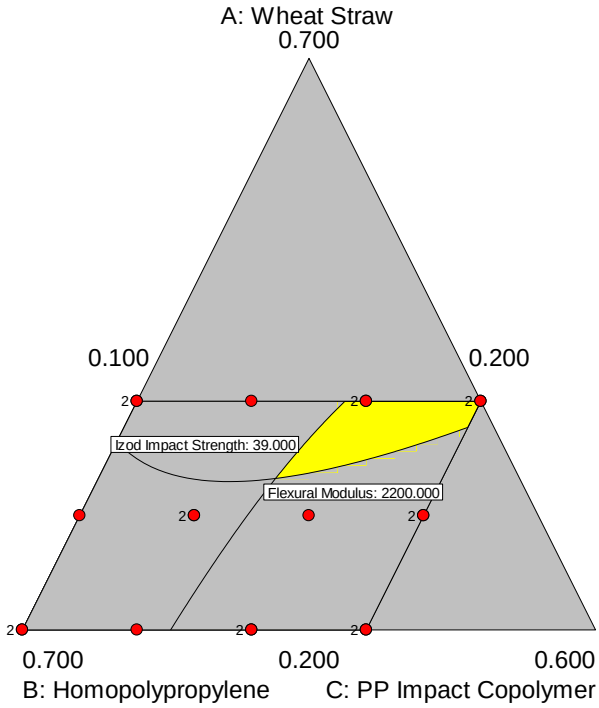


Figure 6-7 Overlay Plot of Model Simulation with Constraints Required by Specifications of Product A.

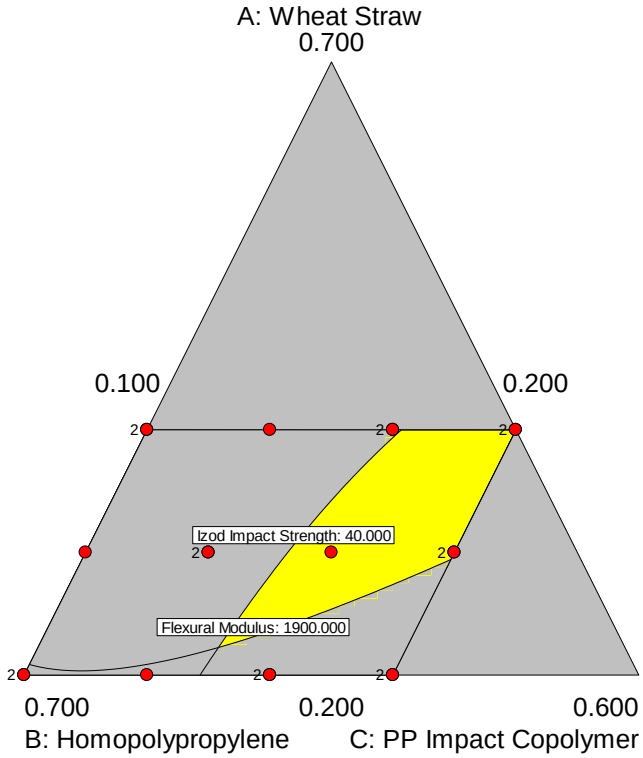


Figure 6-8 Overlay Plot of Model Simulation with Constraints Required by Specifications of Product B.

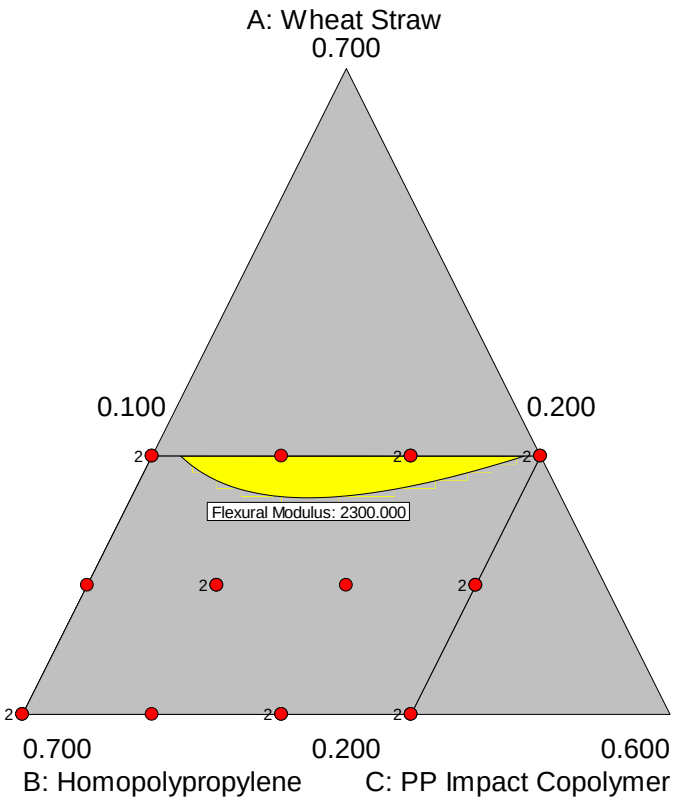


Figure 6-9 Overlay Plot of Model Simulation with Constraints Required by Specifications of Product C.

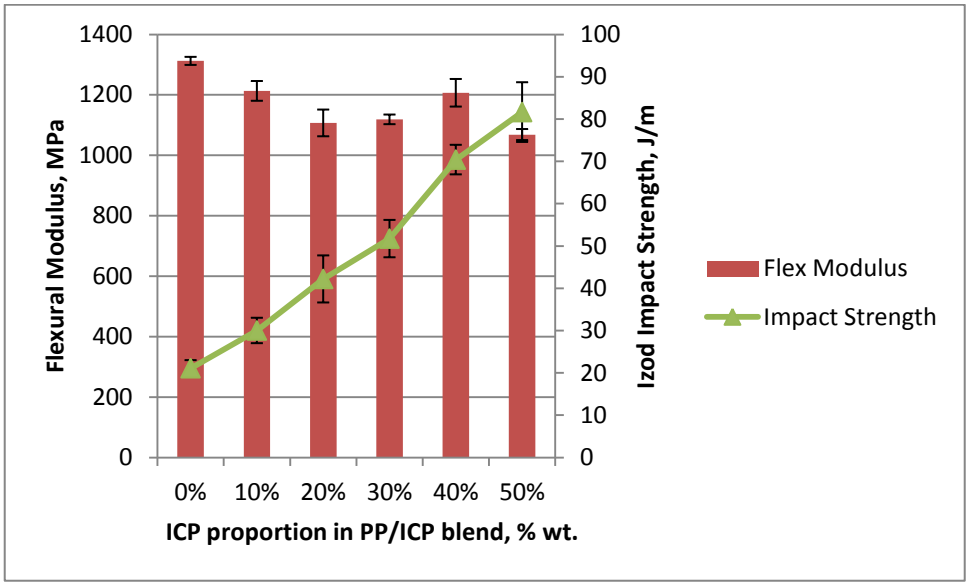


Figure 6-10 Flexural Modulus and Izod Impact Strength of PP/ICP Blend Samples at Various ICP Proportions. Error bars represent standard deviations of measurements.

For optimization case study, the objective function to be minimized is the material cost per unit volume when all products have to be produced.

The optimization problem can be described as follows:

The estimated value *y* of WS-PP/ICP composite property *k* of can be modeled as a function of component proportions *x* which follows the quadratic structure of *scheffe's* canonical polynomial form:

$$y_k = \sum_{i=1}^{3} \beta_{ik} x_i + \sum_{i<}^{} \sum_{j=2}^{3} \beta_{ijk} x_i x_j \quad (6.8)$$

Where subsets *i* and *j* are 1, 2, 3 and represents wheat straw, PP and ICP, respectively.

Since *x* is mixture variable, for each product *l*, the total component proportions *x* must equal to 1.

$$\sum_{i=1}^{3} \boldsymbol{x_{i,l}} = \mathbf{1} \quad (6.9)$$

The proportion limits stated in equation 6.1 was also applied in this problem formulation.

The parameter estimate β of the models were obtained from the designed experiments, and are summarized in Table 6-6

Table 6-6 The Value of Parameter Estimates β for Composite Property Models

Composite Property *k*	β_1	β_2	β_3	β_{13}	β_{23}
Flexural Modulus (FM)	*2877*	*1518*	*-3209*	*10679*	*5037*
Tensile Strength (TS)	*23.29*	*36.18*	*37.05*	-	-
Impact Strength (IS)	*57.17*	*18.33*	*168.29*	*-275.3*	*-67.7*
Density (D)	*1.20*	*0.91*	*0.98*	-	-

For all product *l*, the value of composite property *k* must satisfy constraint value *C* in product specifications given in Table 6-4. Equation 6.7 was reformulated to become composite quality constraints expressed by:

$$C_{k,l} \leq \sum_{i=1}^{3} \beta_{i,k} x_{i,l} + \sum_{i<} \sum_{j=2}^{3} \beta_{ij,k} x_{i,l} x_{j,l} \tag{6.10}$$

And objective function total material cost per unit volume is formulated as:

$$f_{obj} = \sum_{l} \sum_{i} (c_i x_{i,l}) \cdot \left[\sum_{i=1}^{3} \beta_{i,D} x_{i,l} + \sum_{i<} \sum_{j=2}^{3} \beta_{ij,D} x_{i,l} x_{j,l} \right] \tag{6.11}$$

The component price per mass unit *c* is given in Table 6-7

Table 6-7 Unit Price of Composite Components Used in WS-PP/ICP Composite Formulation Optimization.

Materials	Price*, $/lb	Price, $/kg
Homo PP	0.63	1.39
Impact Copolymer PP	2	4.41
Wheat Straw	0.2	0.44

(The price of polymer was obtained from http://www.ides.com/resinpricing/Secondary.aspx; accessed on March 10, 2011. The price of wheat straw was obtained from industrial partner)*

The graphical representation of objective function values (material cost per unit volume) are presented in Figure 6-11.

The above optimization problem has been coded in GAMS software. (Appendix D). The component proportion unit was changed to percentage, and the parameter estimates has been adjusted accordingly. The CONOPT3 solver was chosen to solve the non linear programming (NLP) with the objective function of minimizing the total cost. The optimum solution was found, but there was an indication that the solution was local optima. This indication was confirmed by visual inspection on the graphical simulation provided by DESIGN EXPERT software. The CONOPT3 solver was replaced by MINOS solver, and the

optimal solution was found and the component proportion which gives minimum material cost per unit volume for each product is presented in Table 6-8.

.

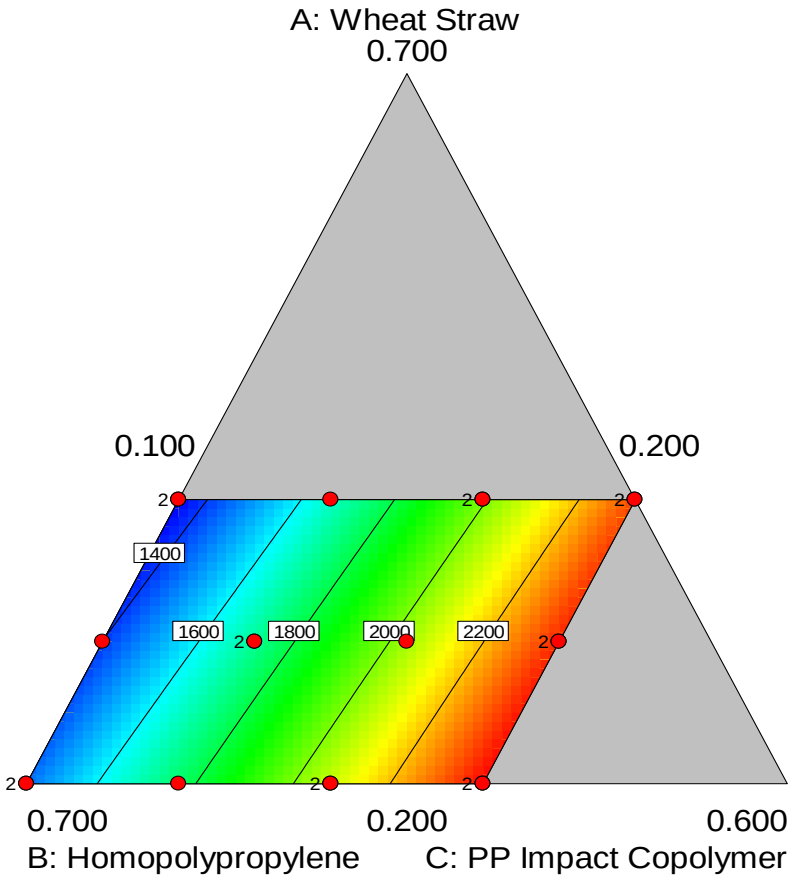


Figure 6-11 Contour Plot of Objective Function Values (in $/m^3)

Table 6-8 Optimum Proportions of WS-PP/ICP Composite Which Give Minimum Cost per Unit Volume.

Product	Optimum component proportion *x*, wt. %		
	Wheat Straw	PP	ICP
A	33	41	26
B	22	53	25
C	40	47.5	12.5

6.5 Chapter Summary

This chapter shows the successful application of product design approach and mixture design methodology in developing property models of wheat straw polypropylene composite in a relatively advanced level.

Real product specifications of automotive parts have been used as the targets for new composite product. Relevant information systematically obtained from the previous works has been used to design the experiments. The objective of the experiments is to develop response surface models of composite properties as the function of composite's component proportion.

The models obtained have met the required standard properties of response surface models and can be used to simulate and to optimize the composition formulation of WS-PP/ICP composite which meet the targeted product specifications. A case study was conducted by formulating the optimization problem with minimizing total material cost as objective function. The problem formulation was coded in GAMS software, and the optimal solution was found by using MINOS solver.

7 Framework for Product Design of Wheat Straw Polypropylene Composite

7.1 Introduction

The use of wheat straw and other agricultural by-product materials as a filler in plastic composites has received considerable attention in recent years. Many factors have caused this interest, but the main attraction is their potential to compete with mineral fillers (they are lighter than mineral fillers) and with cultivated, natural plant fibers (they are lower in price and more environmental-friendly).

The studies of wheat straw polypropylene composites have been done by many researches from many disciplines with the different objectives, focus, and scopes of observations. Some significant results such as better understanding of fiber-matrix reinforcement mechanisms has led to the better and easier product manufacturing of the composite. Recently, wheat straw polypropylene composite has been introduced in market as one of interior part in a commercial car.

The introduction of wheat straw polypropylene composite in the automotive application mentioned above has brought the studies of this composite into the next level. A systematic research approach needs to be applied to incorporate *i)* market needs, *ii)* manufacturing processes, and *iii)* economic considerations in order to increase the utilization of this composite.

Product design methodology has been successfully applied in developing and manufacturing new chemical products driven by consumer needs, and it was expected that that this methodology can also be applied in wheat straw polypropylene composite (Costa, Moggridge, & Saraiva, 2006) (Gani R. , 2004b) (Edwards, 2006).

This chapter presents a *product design framework* for wheat straw polypropylene composite. This framework was based on the series of methodologies and tasks that were developed in this research work and are presented in the previous chapters. It is expected that this framework can also be applied to other natural fiber thermoplastic composites.

This chapter is organized as follows. First, a review of product design and wheat straw polypropylene composite system is presented in Section 7.2. The description of the proposed framework is discussed in Section 7.3 and followed by a case study illustration in Section 7.4.

7.2 Product Design and Wheat Straw – Polypropylene Composite

The wheat straw polypropylene composite was discussed in Section 2.2. In general, the study of composite materials can be seen as the combination of three aspects: composition selection, manufacturing process and property investigation. The study of wheat straw polypropylene composite system can be systematically represented by those aspects as presented in the diagram shown in Table 7-1.

Table 7-1 Systematic Representation of the Study of Wheat Straw Polypropylene Composite System

<table>
<tr><th colspan="3">Composition Selection</th><th>Manufacturing Process</th><th>Property Investigations</th></tr>
<tr><td>Matrix System</td><td>Filler System</td><td>Additives</td><td rowspan="3">Processing modes

Processing variables</td><td rowspan="3">Mechanical

Thermal

Rheological

Others</td></tr>
<tr><td>Polypropylene:
Various grades
Blends (mixtures of grades)</td><td>Wheat Straw:
Chemical properties
Physical properties
Fiber pre-treatment</td><td>Purposes:
Product - Structure
Product - Manufacturing
Product - Usage</td></tr>
<tr><td colspan="3">Components’ proportions</td></tr>
</table>

Composition selection of WS-PP composite consists of choices of matrix system (polypropylene), filler system (wheat straw) and additives with different component’s compositions of product formulation. The matrix system can be chosen from various grades of polypropylene or blending of two or more different grades of polypropylene, including recycled polypropylene or even other thermoplastic polymers. The choice of wheat straw can be seen as selecting from grades with different attributes; a rational similar to choice of matrix when selecting from grades of polypropylene. The choice can be determined by considering chemical compositions (due to the different species of origin plant), different physical properties (due to different method of fiber preparation process), and different

options of fiber pre-treatment such as chemical treatment to increase (the mechanical or thermal) properties of fibers. The choice of additives generally was based on the purpose of adding additive materials. The purposes can be categorized, for example, into a) product-structure, b) product-manufacturing, or c) product-usage issues.

There are also choices in the manufacturing process of composite, based on processing modes or techniques during composite production process and processing variables for the process. The examples of processing techniques are injection molding, compression molding, and thermoforming. The choice also includes fiber architecture and fiber orientation in composite product.

The main properties of final composite product to be investigated are mechanical properties, thermal properties, and rheological properties. The choice of property being investigated is based on product specifications of the desired application of the composite product.

A discussion addressing the progress of research works on wheat straw polypropylene composite in our research group was presented in Section 3.1. The choice of variables of WS-PP composite studies in this research was based on the previous results, with a set of automotive parts specifications as the target of composite product application.

A brief introduction to product design was discussed in Section 2.3. Practically, product design is defined as a procedure consisting of four steps: (1) defining the needs; (2) generating ideas to meet the needs; (3) selection of the best ideas; and (4) manufacturing the product. In generic terms, the chemical product design can be defined as: given a set of desired (target) needs, determine a chemical product (molecule or mixture) that satisfy these needs.

Several product design frameworks for different applications of product design and development have been proposed by some researchers. (Smith & Ierapetritou, 2009), (Omidbakhsh, Duever, Elkamel, & Reilly, 2010), (Goos & Donev, 2007). The proposed frameworks basically follow the four-step procedure of product design mentioned above; with some modifications depend on the scope and specific issues that had to be addressed in each product design problem.

Omidbakhsh and co-workers (2010), for example, proposed a product design framework for a peroxide based disinfectant product. In this framework, emphasis was given to the utilization of the past data of disinfectant product formulation. The main focus of that framework, therefore, was analyzing the past data set and augmenting the historical data in order to design and perform experimental design. The properties of the final product were estimated by the models obtained from the experiments. The optimum product formulation that met the product specification was able to be found with less time and experiment costs, because only few additional data points were required to be performed in the experiments.

Smith and Ierapetritou (2009) proposed a product design framework for an under eye cream product. In that framework, the focus was given to how to define product specifications which were derived from customer preferences on several product attributes and product performance and how to find product formulation for the best product according to those specifications. The experiments were designed and performed to develop the attribute-based models. The optimum product formulation was found by performing multi-objective optimization. Several product attributes were combined in the objective function. In this function each attributes was "weighted" based on customer preferences.

Both frameworks mentioned above do not apply well in the product design problem of wheat straw polypropylene composite in this research for two main reasons. First, both frameworks dealt with single-product design and formulation optimization. Secondly, the ingredients of each product in both frameworks were materials with highly homogeneity in their properties.

Meanwhile, the product design problem in this research is how to increase the utilization of wheat straw polypropylene composite in several products which already have a well-defined specification, but using the wheat straw that is very heterogeneous in its properties. A framework that can handle those problems is proposed in this research.

7.3 Product design framework for WS-PP composite

The proposed framework presented here offers a comprehensive decision support for a systematic research of WS-PP composite with a set of product specifications as consumer needs that has to be met by the designed WS-PP composite product. It specifically emphasizes the use of mixture design and process mixture design in order to develop the response surface models of composite product properties. Furthermore, the framework specifically incorporate the multiple-product specifications which not only can be used to maximize the number of new products to fulfill the consumer needs, but also opens up the possibility of increasing competitiveness of WS-PP composite product by maximizing the utilization of wheat straw fibers. The framework is illustrated in Figure 7-1. It consists of seven steps listed as follows:

Step 1: Defining Customer Needs

The customer needs in this framework consists of various products with similar set of properties in their product specifications. In this multiple-product customer needs, product specifications are viewed as constraints rather than objective functions; thus giving more flexibility in formulating objective function in product design optimization problem. Car parts are one of good example in this case, and illustration of the application of this framework will take automotive parts as a case study.

Step 2: Organizing and Analyzing Relevant Data and Information from Previous Work

Step 3: Variable Screening of Composite System

This step consists of determining critical properties of final products and selecting variables in composite system which are relevant to those properties. The systematic representation of WS-PP composite system, as illustrated in Table 7-1, can be used as a framework for this screening step. Previous data and information plays important roles in this process, and step 2 and step 3 should be performed simultaneously.

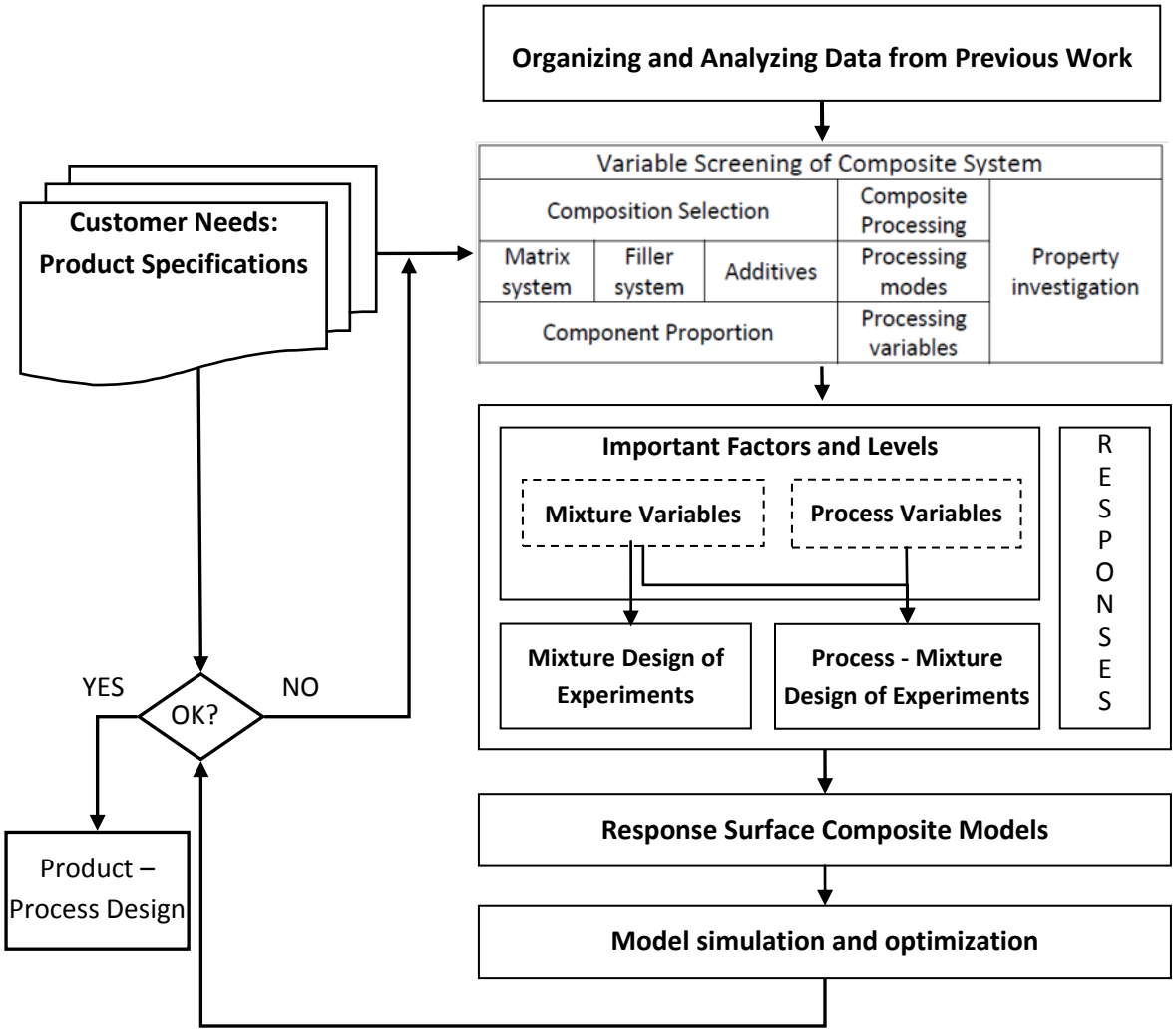


Figure 7-1 Illustration of Product Design Framework for Wheat Straw Polypropylene Composite

Step 4: Designing and performing mixture and/or process-mixture experiments.

In this step, the important factors and their reasonable levels as well as the important responses are determined. Independent variables (factors) of composition selection are categorized into mixture variables and process variables. Mixture variables are independent variables that are expected to affect the measured response (affecting performance) in a way that the influence on the response depends on proportions, not the

amounts of the variables. Non-mixture variables such as the properties of the materials are called *process* variables.

The separation of mixture variables and process variables in designing experiments can reduce the number of experiments that subsequently reduce time and costs in performing experiments. Statistical software which provides design of experiment feature can be used in the designing experiments to find optimal design of experiments which best support response surface models development.

Step 5: Developing Response Surface Composite Property Models

Response surface models of composite properties are developed by regression analysis of data collected from the designed experiments. Statistical software is used as a tool in developing the model, obtaining model parameters, and evaluating the properties of the models.

For models with mixture variables as independent variables, *scheffe's* canonical polynomial models are chosen as candidates of model structure. The fittest model is chosen by first comparing various coefficients of determination R^2 values between linear, quadratic, special cubic and cubic canonical polynomial model.

The choice of model structure is based on the maximum value of *Adjusted-*R^2 and *Predicted-*R^2 values. The number of model terms is then reduced by applying backward elimination technique to get the model term combination which gives highest R^2 values.

The model diagnostic case is carried out to evaluate the model properties, such as model adequacy checking, violation of statistical assumptions, and the influence of each design points to the model.

Step 6: Model Simulation and Optimization

Model simulation and optimization are performed by using the obtained set of composite property models and set of multiple-products property specifications. Model simulation is performed to construct an operating window to locate the targeted product specifications on the design region.

There is a possibility that the targeted specifications are outside the design region but they are close to the design region. In this case, a new process of designing experiments is suggested either by changing the choice of matrix-filler-additive system, changing the factors and/or levels, or by augmenting the existing design space.

Once the targeted product specifications are fixed, the multiple-product optimization problem can be formulated and product design optimization can be performed.

Step 7: Result Confirmation

The results of optimum product design need to be confirmed to the product specifications before it goes to next stage of the product-process design. This confirmation step is especially needed when there are multiple optima from the optimization results.

7.4 Case study: Product Design of WS-PP Composite for Automotive Parts

To illustrate the applicability of the proposed framework, two case studies are summarized presented in this section: the first study highlights the application of mixture design of experiments, while the second study demonstrates how the proposed framework can be applied in multiple-product design of WS-PP composite.

7.4.1 Case Study #1: Optimizing Composite Formulation by Using Mixture Design of Experiment.

Previous results of WS-PP composite studies in our research group showed that the presence of maleic anhydride polypropylene (MAPP) as coupling agent can increase the flexural properties of wheat straw polypropylene composite. However, the results did not provide the quantitative relationship between the proportion of MAPP and the increasing value of the flexural properties. This relationship is needed in formulating WS-PP composite product with specified flexural properties. This relationship can be used to improve properties and to decrease costs.

A set of mixture design of experiments was designed and performed to obtain response surface models of WS-PP composite flexural properties as a function of the proportions of wheat straw, polypropylene and MAPP. The models show the optimum MAPP proportion that gives the maximum flexural properties for any proportion of wheat straw ranging from 30% to 50%. The models also show that the proportion of MAPP should be calculated as the proportion of the total weight of composite, not the proportion of polypropylene matrix. It is important to note that some previous studies using the percentage of MAPP as proportion to polypropylene matrix. The results of the increasing value of composite properties can be misleading because the difference of actual proportion of MAPP could be very high especially when higher proportion of wheat straw was used.

Since only flexural properties that have been investigated in this case study, there was no WS-PP composite product found to meet a set of product specifications. However, the successful application of mixture design of experiment for developing response surface models in this study plays significant role in the studies that follows.

7.4.2 Case Study #2: Multiple-product Design of Wheat Straw Polypropylene Composite.

A set of typical specifications for thermoplastic composites with applications in automotive parts were obtained from the industrial partner (Ford Motors) as a suggestion for the case study. The main properties of the target are flexural modulus, impact strength and density. The variable screening and the analysis of the results from previous studies suggested a composite with a blend of homopolypropylene and impact copolymer polypropylene as polymer matrix and wheat straw as filler. The presence of impact copolymer increases the impact strength of homopolypropylene, while the insertion of wheat straw increases the flexural modulus. The proportion of MAPP as coupling agent was fixed by the optimum formulation obtained from the previous case study.

A constrained three-component mixture design of experiment was designed, with wheat straw, homopolypropylene and impact copolymer polypropylene as the components. Initially, the design consisted of twelve design points, with the range of impact copolymer from 10 wt-% to 30 wt-%, and the range of wheat straw from 20 wt-% to 40 wt-%. The "operating window" constructed from the obtained response surface models showed that there were some target properties (product specifications) which were close to the design space. The design was then augmented by adding eight more design points to accommodate the increasing range of impact copolymer to 40 wt-%.

The simulation of the new response surface models showed that there were three products whose target specifications can be met by the composite product. Optimization of product design was then performed with the minimum material cost as the objective function. The optimal composite formulation for three target specified products which gave the minimum material costs was found with the aid of GAMS software. A further detail of this study was presented in Section 6.4.5.

7.5 Chapter summary

A product design framework for wheat straw polypropylene composite is presented in this chapter. The proposed framework followed the general four-procedure of product design with some modifications. The modifications were aimed to accommodate the main objective of this research, i.e., how to increase the utilization of wheat straw polypropylene composite in automotive applications. The main modifications are the accommodation of the framework for multiple-product design problem and the emphasizing of mixture design of experiments. The case studies were presented to illustrate the applicability of the framework, and to specifically highlight the main modifications mentioned above.

8 Conclusions and Suggestions for Future Work.

8.1 Conclusions

There is a large potential application of wheat straw polypropylene composite in automotive parts and other similar products. Product design methodology was systematically applied in the study of wheat straw polypropylene composite in order to increase the utilization of the composites. The results and the contributions of the study are highlighted as follows:

- Mixture design of experiments was successfully applied to develop response surface models that can be used to estimate WS-PP composite product properties as functions of component's proportion.

- The models can be used to predict and to optimize the composite formulation for products which met typical set of specifications of automotive parts application.

- Process – mixture design of experiments was performed to obtain fiber grading in terms of fiber sizes and their contribution to flexural modulus, impact strength and specific properties of WS-PP composite product at different composition.

- The application of the fiber grading would be in manufacturing fibers with different sizes for different product applications.

- A framework for WS-PP composite product design and development was proposed. The four-step general product design was modified to accommodate multiple-product design problem and to emphasize the application of mixture and process – mixture experimental design.

- It is expected that the proposed framework can be used in product design and development of other natural plant fiber thermoplastic composite products.

8.2 Suggestions for Future Work

Among the suggestions for future studies which arise from the obtained results are:

- Continuing WS-PP composite product design and development with different set of product specifications and applications. Thermal stability for product application in elevated temperatures and UV-light stability for product application with sunlight exposure are good examples of this work.

- Performing optimization study of WS-PP composite with multiple products and multiple fiber grades to increase the yield of wheat straw. The study presented in Chapter 6 only used one type of fiber fraction among seven fiber fractions obtained in the study presented in Chapter 5. The results indicated that one or two product specifications can be reached by using the other fiber fractions.

- The study of natural fiber thermoplastic with different matrix and filler system by using the proposed framework or similar approach.

References

Alemdar, A., & Sain, M. (2008). Biocomposites from wheat straw nanofibers: morphology, thermal and mechanical properties. *Composite Science and Technoology , 68*, 557–565.

Anderson, M., & Whitcomb, P. (1998, April). Find The Most Favorable Formulations. *Chemical Engineering Progres*.

Araujo, J. (2008). Thermal properties of high density polyethylene composites with natural fibres: Coupling agent effect. *Polymer Degradation and Stability , 93*, 1770–1775.

Beckermann, G., & Pickering, K. (2009). Engineering and evaluation of hemp fibre reinforced polypropylene composites: Micro-mechanics and strength prediction modelling. *Composites: Part A , 40*, 210–217.

Bera, J., & Kale, D. (2008). Properties of Polypropylene Filled with Chemically Treated Rice Husk. *Journal of Applied Polymer Science , 110*, 1271-1279.

Bledzki, A., Faruk, O., & Sperber, V. (2006). Cars From Biofibers. *Macromoecular. Mateials Engineering. , 291*, 449–457.

Bos, H. L., Mussig, J., & Van den Oever, M. J. (2006). Mechanical properties of short-flax-fiber reinforced compounds. *Composites: Part A , 37*, 1591-1604.

Canavos, G. C., & Koutrouvelis, I. A. (2009). *An Introduction to the Design & Analysis of Experiments.* Pearson Prentice Hall.

Cornell, J. (2002). *Experiments with Mixtures; Designs, Models, and the Analysis of Mixture Data.* New York: Wiley Inter-Science.

Costa, R., Moggridge, G., & Saraiva, P. (2006). Chemical Product Engineering: An Emerging Paradigm Within Chemical Engineering. *AIChE Journal , 52*, 1976-1986.

Costa, T. H. (2000). Statistical experimental design and modeling of polypropylene-wood fiber composites. *Polymer Testing , 19*, 419-428.

Cussler, E., & Moggridge, G. (2001). *Chemical Product Design.* Cambridge: Cambridge University Press.

Digabel, F., Boquillon, N., Dole, P., Monties, B., & Averous, L. (2004). Properties of thermoplastic composites based on wheat-straw lignocellulosic fillers. *Journal of Appied Polymer Science , 93*, 428–436.

Edwards, M. (2006). Product Engineering Some Challenges for Chemical Engineers. *Chemical Engineering Research and Design , 84(A4)*, 255-266.

Esfandiari, A. (2007). The Statistical Investigation of Mechanical Properties of PP/Natural Fibers Composites. *Fibers and Polymers , 9*, 48-54.

Ford Motor Company. (2009, November 11). *About Ford*. Retrieved September 7, 2010, from Ford Motor Company Web site: http://www.ford.com/about-ford/news-announcements/press-releases/press-releases-detail/pr-ford-teams-up-to-develop-wheat-31391

Fornes, T., & Paul, D. (2003). Modeling properties of Nylon 6/clay nanocomposites using composite theories. *Polymer , 44*, 4993-5013.

Gani, R. (2004a). Chemical Product Design: Challenges and Opportunities. *Computers and Chemical Engineering , 28*, 2441-2457.

Gani, R. (2004b). Computer-Aided Methods and Tools for Chemical Product Design. *Chemical Engineering Research and Design , 82*, 1494-1503.

Gassan, A., & Bledzki, J. (1999). Composites Reinforced with Cellulose Based Fibers. *Progress in Polymer Science , 24*, 221-274.

Girones, J., & co-workers. (2008). Blocked Di-isocyanates as Reactive Coupling Agents: Application to Pine Fiber Polypropylene Composites. *Carbohydrate Polymers , 74*, 106-113.

Goos, P., & Donev, A. N. (2007). Tailor-Made Split-Plot Designs for Mixtures and Process Variables. *Journal of Quality Technology , 39* (4), 326.

Halvarsson, S., Edlund, H., & Norgren, M. (2008). Properties of medium-density fibreboard (MDF) based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Ind. Crop. Prod. , 28*, 37–46.

Kruger, P. K. (2007). *Wheat Straw Polypropylene Composite.* Waterloo: University of Waterloo MASc Thesis.

Lee, N.-J., & Jang, J. (1997). Performance Optimisation of Glass Fiber Mat Reinforced Polypropylene Composite using Statistical Experimental Design. *Polymer Testing , 16*, 497-506.

M. Sain, S. L. (2005). Interface Modification and Mechanical Properties of Natural Fibre-Polyolefin Composite Products. *24 pp. 121-130*.

Mengeloglu, F., & Karakus, K. (2008). Thermal degradation, mechanical properties and morphology of wheat straw flour filled recycled thermoplastic composites. *Sensors, 8*, 500-519.

Mittal, V. (2008). Modeling the Behavior of Polymer-layered Silicate Nanocomposites using Factorial and Mixture Designs. *Journal of Thermoplastic Composite Materials , 21*, 9-26.

Myers, R. H., Montgomery, D. C., & Anderson-Cook, C. M. (2009). *Response Surface Methodology.* New York: Wiley Inter-Science.

Ng, Z. (2008). *Bulk Orientation of Agricultural Filler- Polypropylene Composites.* Waterloo: University of Waterloo MASc Thesis.

Omidbakhsh, N., Duever, T. A., Elkamel, A., & Reilly, P. M. (2010). Systematic Statistical-Based Approach for Product Design: Application to Disinfectant Formulation. *Industrial and Engineering Chemical Research* , 204 - 209.

Panthapulakkal, S., Zereshkian, A., & Sain, M. (2006). Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites. *Bioresources Technology, 97*, 265–272.

Reddy, N., & Yang, Y. (2007). Preparation and characterization of long natural cellulose fibers from wheat straw. *Journal of Agriculture and Food Chemistry , 55*, 8570–8575.

Resin Material Prices: Secondary Markets. (2012, March). Retrieved March 10, 2012, from IDES Prospector Web site: http://www.ides.com/resinpricing/Secondary.aspx

Rudin, A. (1999). *The Elements of Polymer Science and Engineering.* Toronto: Academic Press.

Sain, M., Law, S., Suhara, F., & Boullioux, A. (2005). Interface Modification and Mechanical Properties of Natural Fibre-Polyolefin Composite Products. *Journal of Reinforece Plastic Composite, 24* , 121-130.

Sardashti, A. (2009). *Wheat straw-clay-polypropylene hybrid composites.* Waterloo: University of Waterloo MASc Thesis.

Schirp, A., Loge, F., Aust, S., Swaner, P., Turner, G., & Wolcott, M. (2006). Production and characterization of natural fiber-reinforced thermoplastic composites using wheat straw modified with the fungus Pleurotus ostreatus. *Journal of Applied Polymer Science, 102*, 5191.

Shibata, S., Cao, Y., & Fukumoto, I. (2005). Study of the Flexural Modulus of Natural Fiber/Polypropylene Composites by Injection Molding. *Journal of Applied Polymer Science, 100*, 911-917.

Smith, B. V., & Ierapetritou, M. (2009). Framework for Customer-Integrated Product Design. *Industrial and Engineering Chemical Research*, 8566 - 8574.

Sperling, L. (2006). *Introduction to Physical Polymer Science.* Wiley-Interscience.

Suddell, B. C., & Evans, W. J. (2005). Natural Fiber Composites in Automotive Applications. In A. K. Mohanty, M. Misra, & L. T. Drzal, *Natural Fibers, Biopolymer and Biocomposites* (pp. 231-259). Boca Raton, Florida: Taylor and Francis.

Thais H.S. Costa, e. (2000). Statistical experimental design and modeling of polypropylene-wood fiber composites. *Polymer Testing, 19 (419-4258)*.

Thamae, T. M. (2008). *Developing and Characterizing New Materials Based on Natural Fibres and Waste Plastic.* Queen's University PhD Thesis.

The Jute Baler's Association. (2010, August 30). *Raw Jute Market Price August 30, 2010*. Retrieved September 7, 2010, from Tepcon International (Ltd) India: http://www.worldjute.com/jute_prices/prices_index.html

Xiaoqun, M., Wang, D., & Sun, X. S. (2005). Straw-Based Biomass and Biocomposites. In A. K. Mohanty, M. Misra, & L. T. Drzal, *Natural Fibers, Biopolymer and Biocomposites* (pp. 437-495). Boca Raton: Taylor and Francis.

Zhang, Z., & Friedrich, K. (2003). Artificial Neural Networks Applied to Polymer Composite: A review. *Composite Science and Technology, 63*, 2029-2044.

Zou, Y., Huda, S., & Yiqi, Y. (2010). Lightweight composites from long wheat straw and polypropylene web. *Bioresource Technology, 101*, 2026–2033.

Appendices

Appendix A. Summary Statistics of Individual Fiber Size Measurement Before Compounding Process.

Fiber Fraction ID	F			AS			AL		
	Length, µm	Width, µm	Aspect Ratio	Length, µm	Width, µm	Aspect Ratio	Length, µm	Width, µm	Aspect Ratio
Maximum	418	143	10.64	1779	506	21.01	3313	579	21.98
Minimum	37	12	1.03	160	47	1.09	115	47	1.14
Range	381	131	9.60	1619	459	19.92	3198	532	20.83
Median	82	39	2.01	749	198	3.62	1329	282	5.11
Q1	61	31	1.54	548	149	2.58	1066	191	3.21
Q3	120	51	2.88	986	271	5.50	1683	355	8.12
Mean	96	44	2.38	788	210	4.65	1395	284	6.01
Standard Deviation	49	21	1.30	322	92	3.39	493	111	3.71

	BS			BL			CS			CL		
	Length, µm	Width, µm	Aspect Ratio	Length, µm	Width, µm	Aspect Ratio	Length, µm	Width, µm	Aspect Ratio	Length, µm	Width, µm	Aspect Ratio
Max	4982	801	32.36	5032	852	35.59	2996	1085	13.07	5257	1044	23.34
Min	147	66	1.45	201	60	1.23	676	183	1.06	1123	196	1.45
Ran	4835	735	30.91	4832	792	34.36	2320	902	12.01	4133	848	21.88
Med	1830	351	5.08	2182	358	6.40	1704	654	2.58	3145	642	5.23
Q1	1463	231	3.78	1773	258	4.21	1361	571	1.88	2717	537	3.72
Q3	2177	475	8.54	2643	457	9.02	1980	729	3.34	3680	766	6.57
Mean	1884	361	6.93	2227	362	7.55	1706	654	2.91	3204	645	5.50
SD	576	164	5.16	767	137	5.17	460	151	1.68	759	167	2.72

Appendix B. Experimental Results of Mixture Design of Homopolypropylene – Wheat Straw – PP Impact Copolymer Composites

		Composition, %wt			Flexural Modulus	Flexural Strength	Impact Strength	Tensile Strength	Elongation at break	Elastic Modulus
Std#	Run#	Wheat Straw	Homo Poly-propylene	PP Impact Copolymer	MPa	MPa	J/m	MPa	%	MPa
15	1	20	60	20	1905	55.1	36.3	32.9	12.8	284
17	2	30	50	20	2200	57.8	34.3	30.0	11.4	292
14	3	40	50	10	2270	60.0	33.7	27.5	9.8	307
16	4	40	30	30	2201	55.0	41.9	31.7	11.0	313
13	5	30	40	30	2047	52.5	42.2	35.4	11.1	358
12	6	40	50	10	2188	60.7	34.7	33.7	9.9	372
11	7	20	50	30	1803	51.8	43.1	32.8	12.9	281
10	8	20	70	10	1751	54.5	32.7	34.2	12.2	301
9	9	20	50	30	1766	50.1	44.9	32.5	13.3	269
8	10	20	70	10	1925	55.1	29.8	37.4	12.1	352
7	11	30	60	10	2164	58.0	32.8	31.0	11.3	298
6	12	40	40	20	2523	57.0	36.3	33.2	9.6	383
5	13	40	30	30	2305	54.3	39.7	29.9	10.1	328
4	14	30	50	20	2114	56.2	38.4	31.7	11.5	304
3	15	30	30	40	2013	51.4	47.4	31.4	11.1	319
2	16	40	20	40	2315	52.5	44.3	31.1	9.7	359
1	17	20	40	40	1573	49.1	54.1	34.4	12.8	316
18	18	40	20	40	2339	54.3	44.2	32.9	10.0	362
20	19	30	30	40	1879	51.1	48.0	33.3	11.2	329
19	20	20	40	40	1487	48.7	54.3	34.0	12.7	317
Minimum		**20**	**20**	**10**	**1487**	**48.7**	**29.8**	**27.5**	**9.6**	**269**
Maximum		**40**	**70**	**40**	**2523**	**60.7**	**54.3**	**37.4**	**13.3**	**383**

Appendix C. ANOVA-test Results Summary Tables for WS-PP/ICP Property Models

Response : Flexural Modulus						
ANOVA for Reduced Quadratic Mixture Model						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	1292574	4	323143.5	39.99168	< 0.0001	significant
Linear Mixture	1180545	2	590272.3	73.05109	< 0.0001	
AC	111773	1	111773	13.83284	0.0021	
BC	50168.55	1	50168.55	6.208773	0.0249	
Residual	121204	15	8080.267			
Lack of Fit	79917.79	7	11416.83	2.21223	0.1442	not significant
Pure Error	41286.22	8	5160.777			
Cor Total	1413778	19				

Response : Tensile Strength						
ANOVA for Linear Mixture Model						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	23.46033	2	11.73017	3.055649	0.0735	not significant
Linear Mixture	23.46033	2	11.73017	3.055649	0.0735	
Residual	65.26039	17	3.838846			
Lack of Fit	34.07778	9	3.78642	0.971419	0.5218	not significant
Pure Error	31.1826	8	3.897825			
Cor Total	88.72072	19				

Response : Impact Strength						
ANOVA for Reduced Quadratic Mixture Model						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	904.9608	4	226.2402	132.8641	< 0.0001	significant
Linear Mixture	812.1346	2	406.0673	238.4712	< 0.0001	
AC	74.28668	1	74.28668	43.62634	< 0.0001	
BC	9.056281	1	9.056281	5.318483	0.0358	
Residual	25.54191	15	1.702794			
Lack of Fit	8.213274	7	1.173325	0.541681	0.7830	not significant
Pure Error	17.32864	8	2.16608			
Cor Total	930.5027	19				

Response : Density						
ANOVA for Linear Mixture Model						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	0.013059	2	0.006529	13.1252	0.0004	significant
Linear Mixture	0.013059	2	0.006529	13.1252	0.0004	
Residual	0.008457	17	0.000497			
Lack of Fit	0.003901	9	0.000433	0.76097	0.6555	not significant
Pure Error	0.004556	8	0.00057			
Cor Total	0.021516	19				

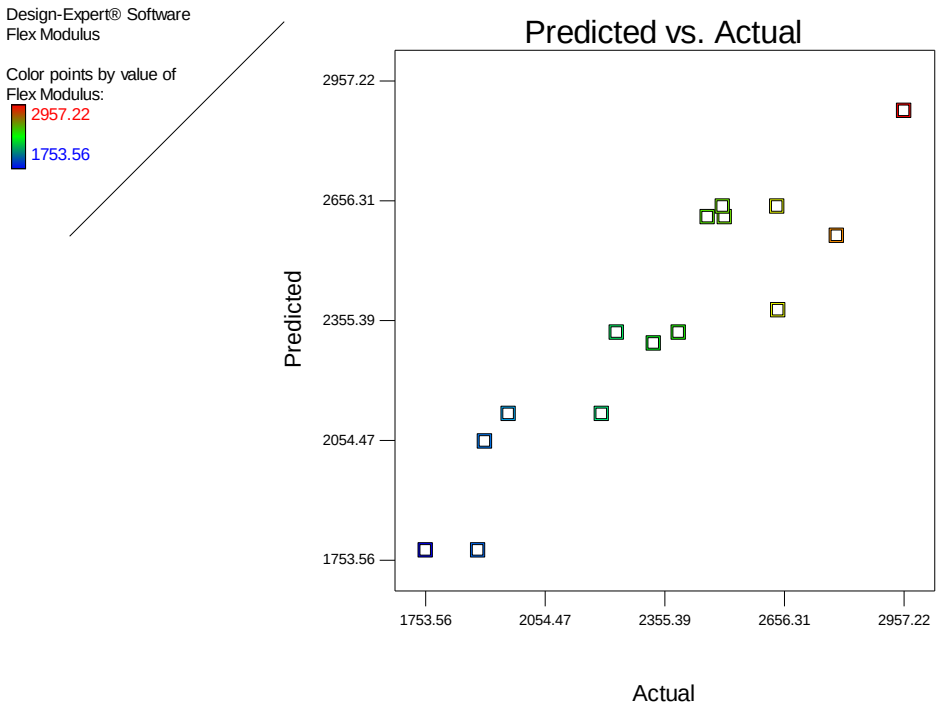
Appendix D. GAMS coding for WS-PP/ICP optimization

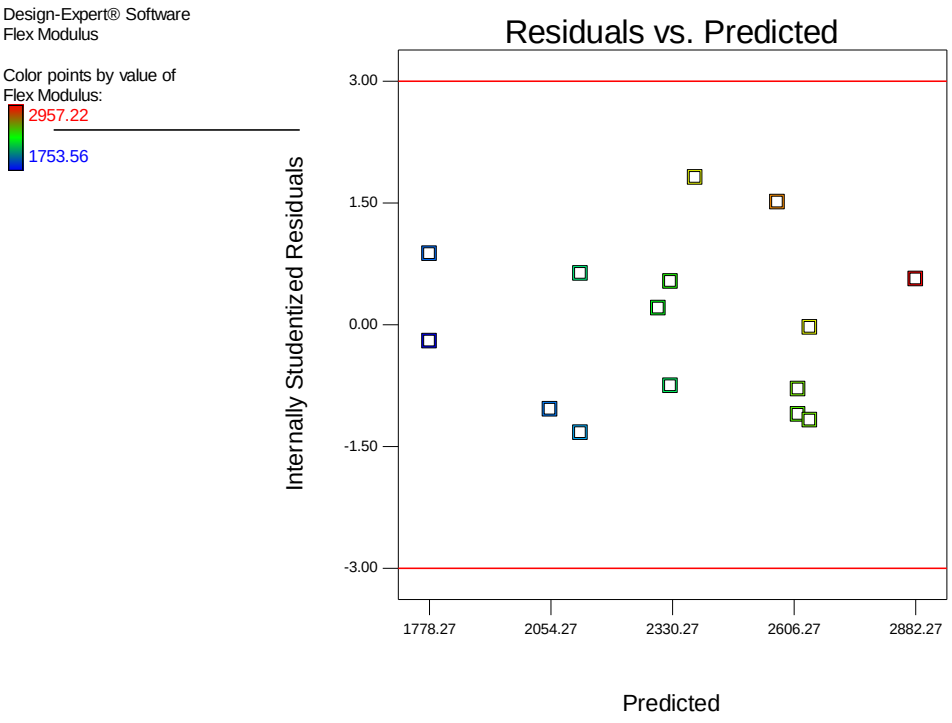
```
$Ontext
Optimization of WS-PP/ICP formulation
Section 6.4.5.PhD Thesis
Chemical Engineering, University of Waterloo, 2012
By : Rois Fatoni
$Offtext

sets
i /1,2,3/
j Composite Components WS - PP - ICP /1,2,3/
k Composite Properties  /FM,TS,IS,D/
l Composite Products    /A,B,C/;

variables
x(i,l) proportion of component i in product l
Cost(l) material cost of product l
Totalcost ;

positive variable x(i,l);
*Positive variable Cost(l);

Parameters
B(k,i)
B12(k)
B23(k)
C(k,l)
P(i) ;

Table data1(*,*)
         1       2       3       B12       B23      A       B       C
FM       28.77   15.18   -32.09  1.0679    0.5037   2200    1900    2300
TS       0.2329  0.3618  0.3705  0         0        29      25      25
IS       0.5717  0.1833  1.6829  -0.02753  -0.0067  39      40      23
D        0.0120  0.0091  0.0098  0         0        1.08    1.10    1.06 ;
```

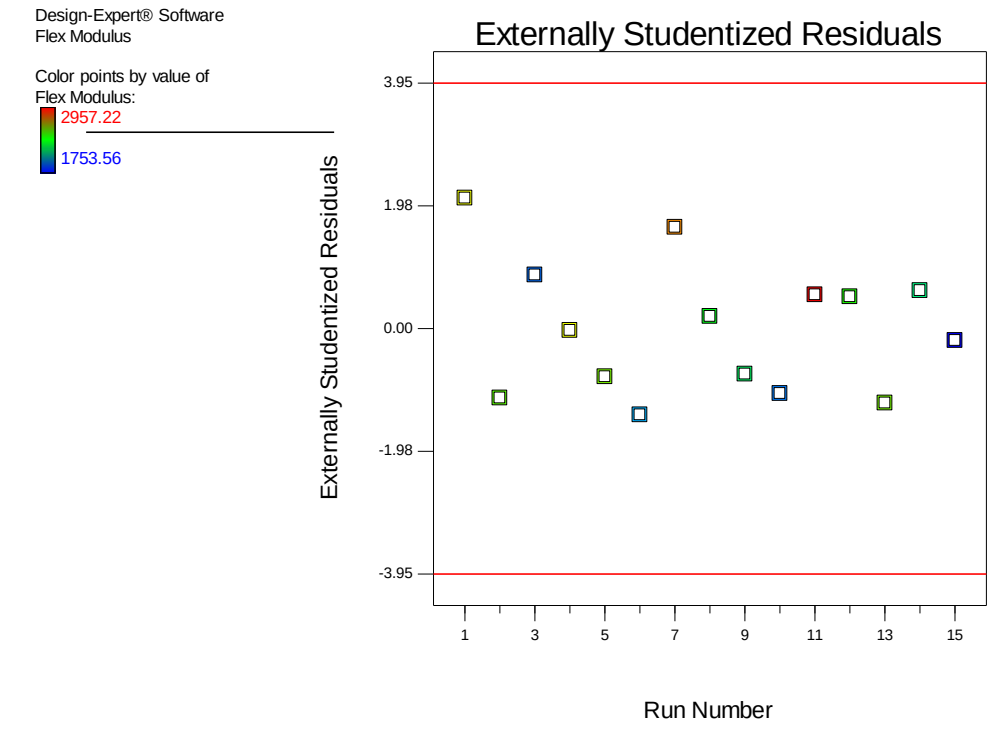
```
B(k,i)=data1(k,i);
B12(k)=data1(k,"B12");
B23(k)=data1(k,"B23");
C(k,l)=data1(k,l);

Table data2(*,*)
        Max        Min    Price
1         40        20       .4
2         70       20       1.39
3         40       10       4.41  ;

P(i)=data2(i,"Price");
x.up(i,l)=data2(i,"Max") ;
x.lo(i,l)=data2(i,"Min");
x.l(i,l)=10;
Cost.l(l)=(sum(i,(P(i)*x.l(i,l))))*10*(sum(i,(B("D",i)*x.l(i,l))));

Equations
Mixture(l)
ConstraintFM(l)
ConstraintIS(l)
ConstraintTS(l)
ConstraintD(l)
Costeq(l)
Objective ;

Mixture(l)..    sum (i, x(i,l))=e=100;

ConstraintFM(l)..
C("FM",l)=l=sum(i,(B("FM",i)*x(i,l)))+(B12("FM")*x("1",l)*x("2",l))+(B23("FM"
)*x("2",l)*x("3",l)) ;

ConstraintIS(l)..
C("IS",l)=l=sum(i,(B("IS",i)*x(i,l)))+(B12("IS")*x("1",l)*x("2",l))+(B23("IS"
)*x("2",l)*x("3",l)) ;

ConstraintTS(l).. C("TS",l)=l=sum(i,(B("TS",i)*x(i,l))) ;
```

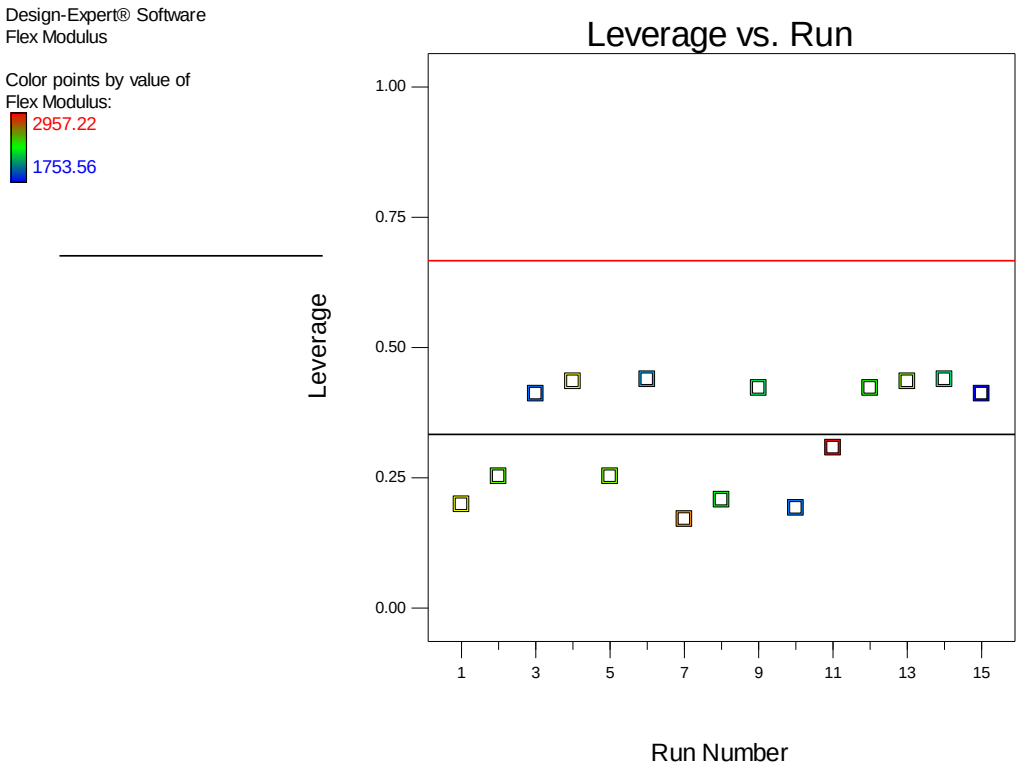
```
ConstraintD(l).. C("D",l)=g=sum(i,(B("D",i)*x(i,l)))    ;

Costeq(l).. Cost(l)=e=(sum(i,(P(i)*x(i,l))))*10*(sum(i,(B("D",i)*x(i,l)))) ;
Objective.. Totalcost=e=sum(l,Cost(l))  ;

Model WSPPICP /all/;
Solve WSPPICP minimizing Totalcost using NLP ;
Display x.l, x.m;
```

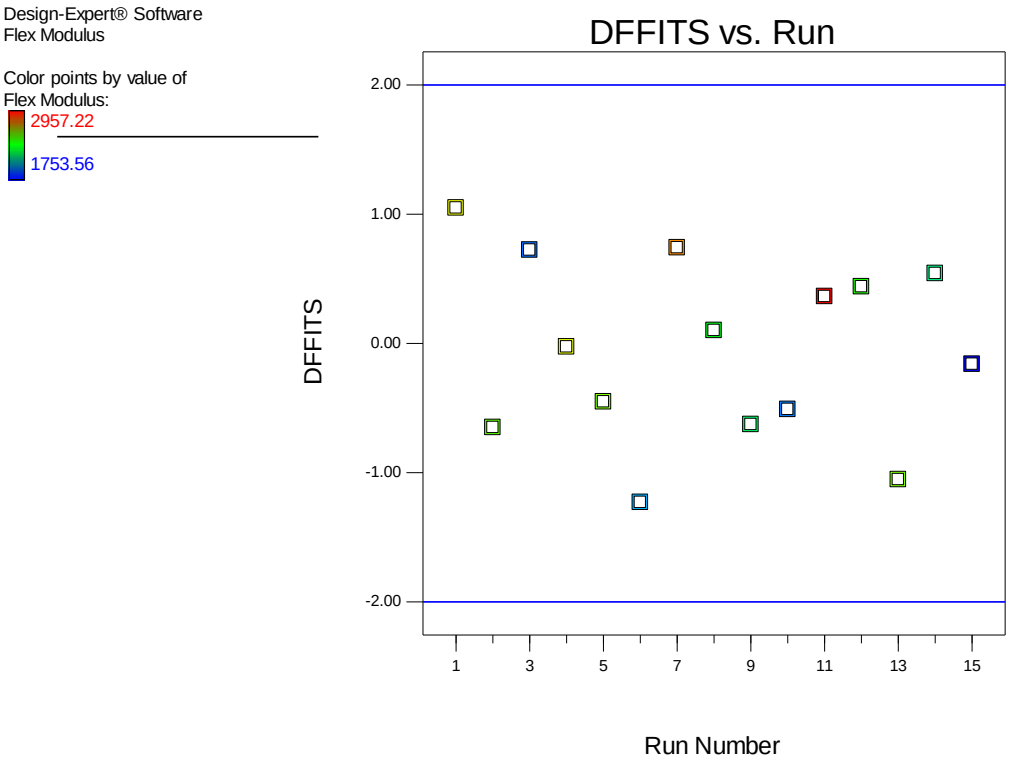
Appendix E. The plots of Diagnostic Case Statistics for Flexural Modulus Model (Chapter 4)

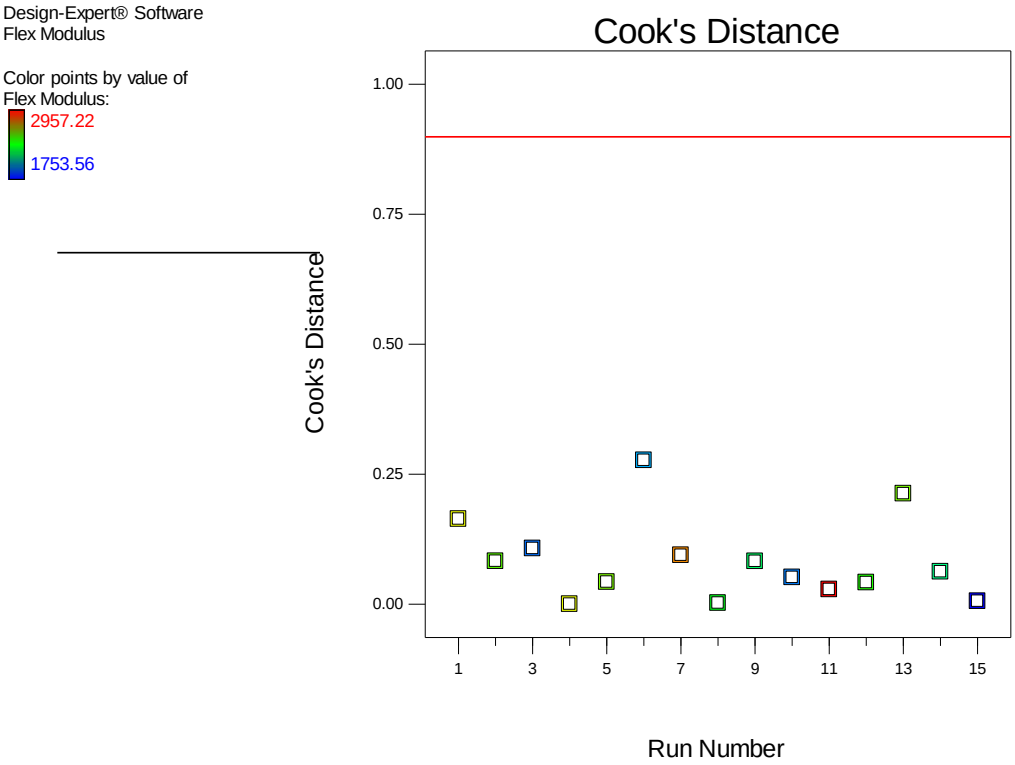





Design-Expert® Software
Flex Modulus
Color points by value of
Flex Modulus:
2957.22
1753.56
Externally Studentized Residuals
Externally Studentized Residuals
3.95
1.98
0.00
-1.98
-3.95
1
3
5
7
9
11
13
15
Run Number


Design-Expert® Software
Flex Modulus
Color points by value of
Flex Modulus:
2957.22
1753.56
Leverage vs. Run
Leverage
1.00
0.75
0.50
0.25
0.00
1
3
5
7
9
11
13
15
Run Number


Design-Expert® Software
Flex Modulus
Color points by value of
Flex Modulus:
2957.22
1753.56
DFFITS vs. Run
DFFITS
2.00
1.00
0.00
-1.00
-2.00
1
3
5
7
9
11
13
15
Run Number


Design-Expert® Software
Flex Modulus
Color points by value of
Flex Modulus:
2957.22
1753.56
Cook's Distance
Cook's Distance
1.00
0.75
0.50
0.25
0.00
1
3
5
7
9
11
13
15
Run Number