Response Surface Models for Optimization of Wheat Straw-Polypropylene Composite Formulations

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Abstract

The insertion of wheat straw fiber in polypropylene matrix can increase the flexural properties of the thermoplastic composite. This increase, however, is accompanied by the decrease of impact strength. One of the common ways to increase the impact properties of homopolypropylene (HPP) is to blend it with polypropylene impact copolymer (PP-ICP). Therefore, it is expected that a wheat straw-HPP/PP-ICP blend composite will have both impact and flexural properties increased. The objective of this study is to develop response surface models which correlate the flexural and impact properties of the composite as functions of its formulation. Thereafter, the models can be used to optimize formulation for a set of specified target of properties. A constrained pseudo-simplex design of three component mixture was designed for the experiments. The design consists of 12 design points with 8 design points each replicated twice in experiments. The Design Expert software was used to construct the models based on our experimental data. Three case studies of composite formulation optimization problems are performed to demonstrate the usefulness of the models.

Keywords
Response surface models, natural fiber polymer composite, wheat straw polypropylene composite, optimum formulations.

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 (Kruger, 2007). 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 (Rudin, 1999). 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.

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 Elkamel, et al.(2012). This left the composite system with three components variables (PP, ICP and WS). Extensive review about the mixture design application in wheat straw polypropylene composite is given by Fatoni, et al. (2013).

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 (Cornell (2002) and Myers (2009)) with the following constraints:

$$\begin{aligned} 0.2 \le x_1 \le 0.4 \\ 0.3 \le x_2 \le 0.7 \\ 0.1 \le x_3 \le 0.4 \end{aligned} \qquad (1)$$

where x1, x2 and x3 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 1. **Error! Reference source not found.** 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 **Error! Reference source not found.** is the design space of the experiment.

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

Design Point ID#	Component's proportion (weight percentage)		
	Wheat Straw (A) x_1	Polypropylene (B) x_2	Impact Copolymer Polypropylene (C) x_3
1*	20	70	10
2*	20	60	20
3*	20	50	30
4*	20	40	40
5	30	60	10
6	30	50	20
7	30	40	30
8*	30	30	40
9*	40	50	10
10	40	40	20
11*	40	30	30
12*	40	20	40

Note: Asterisk symbol represents replicated design points.

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.

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, and density.

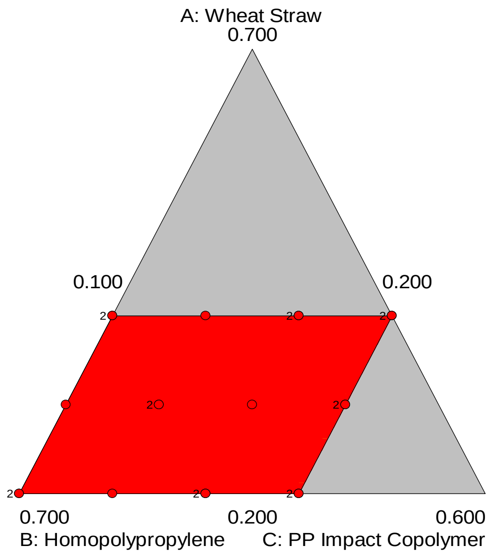

Figure 1: Plot of Design Space and Design Points on Pseudo-simplex Lattice Co-ordinate of WS-PP/ICP Mixture Experiments

3. Materials and Methods

Commercial grade homopolypropylene with a melt flow index of 36 g/10 min (230 oC, 2.16 kg, ASTM D 1238) and impact copolymer polypropylene with melt flow index of 24 g/10 min (230 oC, 2.16 kg, ASTM D 1238) within the form of pellets 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 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 ground wheat straw was obtained from fiber fractionation with the mean width and mean length of the fibers are 350 µm and 2300 µm, respectively.

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.

4. Results and Discussions

The results of WS-PP/ICP composite properties measurements were obtained. 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.

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:

$$FM = 2877\, x_1 + 1518\, x_2 - 3209\, x_3 + 10679\, x_1 x_3 + 5037\, x_2 x_3 \qquad (2)$$

where FM is composite flexural modulus in MPa, while x_1, x_2, and x_3 are weight proportions 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 (Cornell 2002).

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 **Error! Reference source not found.**.

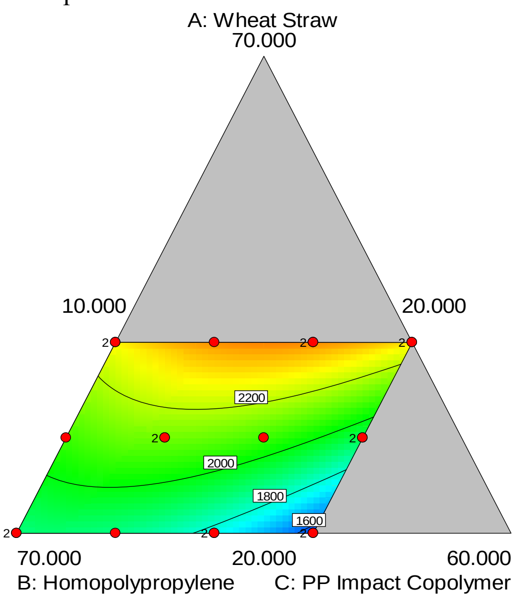

Figure 2: Contour Plot of Flexural Modulus (MPa) of WS-PP/ICP Composite within the Design Space

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:

$$IS = 57.2\, x_1 + 13.8\, x_2 + 168.3\, x_3 - 275.3\, x_1 x_3 - 67.7\, x_2 x_3 \qquad (3)$$

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 **Error! Reference source not found.**

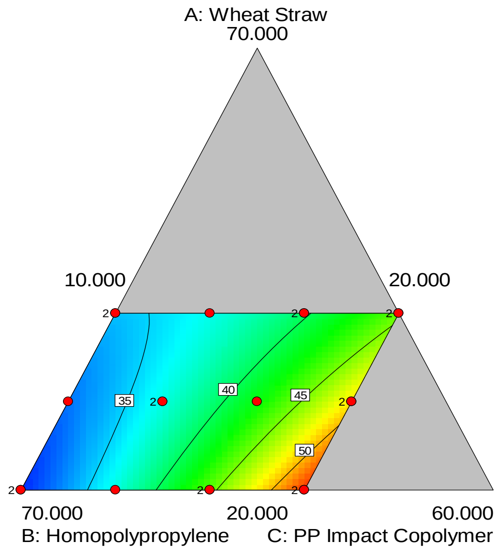

Figure 3: Contour Plot of Izod Impact Strength (J/m) of WS-PP/ICP Composite within the Design Space

4.3 Other Properties

The models for other composite properties have also been obtained and were presented in Table 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 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.

The coefficients of determination of the models are given in Table 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 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

However, the model p-value of 0.0735 is close to 0.05. At significance level of 0.1, the model is significant. For this reason, the model is still being used in the optimization case study described in the following section.

4.4 Models Simulation and 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 a model simulation and 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 simulation and optimization case studies (Products A, B and C). The lists of the selected specifications (properties) can be seen in Table 4.

Table 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/cm3	≤ 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 **Error! Reference source not found.**, **Error! Reference source not found.**, and **Error! Reference source not found.**, 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.

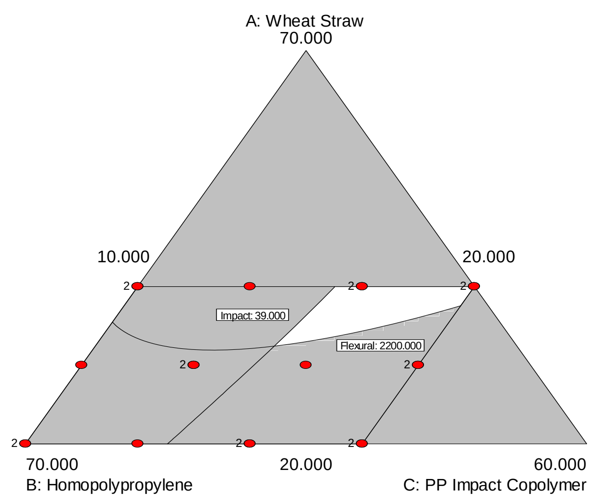

Figure 4: Overlay Plot of Model Simulation with Constraints Required by Specifications of Product A

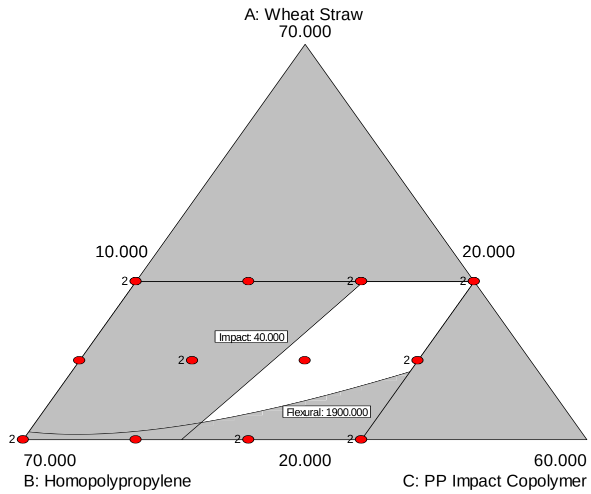

Figure 5: Overlay Plot of Model Simulation with Constraints Required by Specifications of Product B

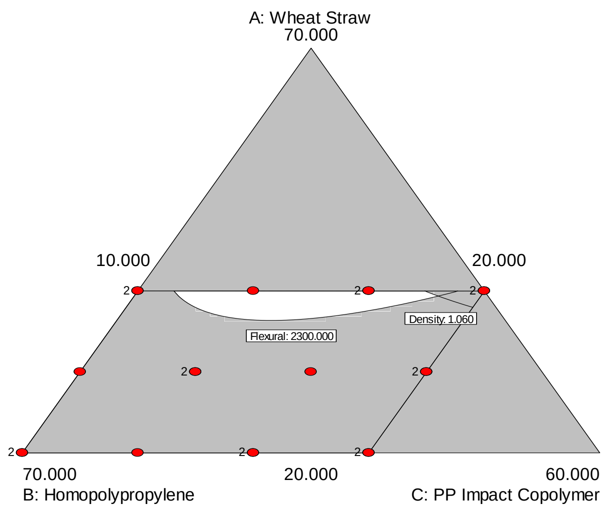

Figure 6: Overlay Plot of Model Simulation with Constraints Required by Specifications of Product C

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 5)

Table 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	OK	Not OK	Not OK
	Impact Strength ≥ 39	OK	Not OK	OK
B	Flexural Modulus ≥ 1.9	OK	OK	Not OK
	Impact Strength ≥ 40	OK	Not OK	OK
C	Flexural Modulus ≥ 2.3	OK	OK	Not OK
	Impact Strength ≥ 23	OK	OK	OK

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. 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. 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.

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 **Error! Reference source not found.**. 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.

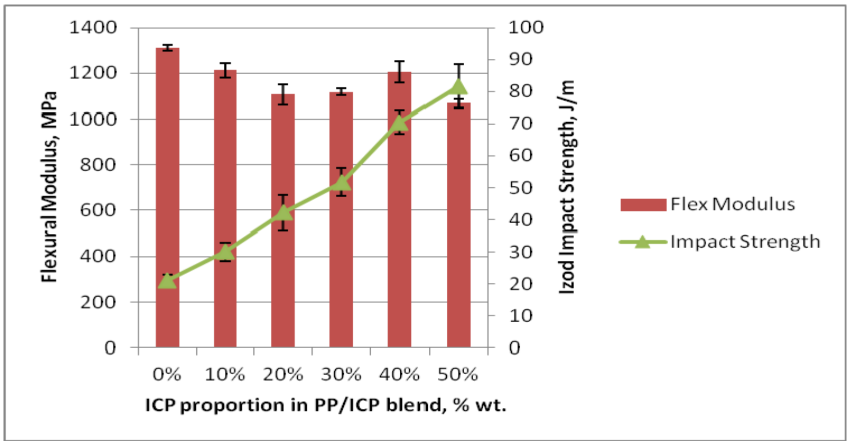

Figure 7: Flexural Modulus and Izod Impact Strength of PP/ICP Blend Samples at Various ICP Proportions. Error bars represent standard deviations of measurements

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:

$$y_k = \sum_{i=1}^{3} \beta_{ik} x_i + \sum_{i<} \sum_{j=2}^{3} \beta_{ijk} x_i x_j \quad (4)$$

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.

$$\sum_{i=1}^{3} x_{i,l} = 1 \quad (5)$$

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.

Table 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 4. Equation 6.7 was reformulated to become composite quality constraints expressed by:

$$C_{k,l} \le \sum_{i=1}^{3} \beta_{i,k} x_{i,l} + \sum_{i<} \sum_{j=2}^{3} \beta_{i,j,k} x_{i,l} x_{j,l} \qquad (6)$$

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

$$f_{obj} = \sum_{l} \sum_{i} (c_i x_{i,l}) \cdot \left[\sum_{i=1}^{3} \beta_{i,D} x_{i,l} + \sum_{i<} \sum_{j=2}^{3} \beta_{i,j,D} x_{i,l} x_{j,l} \right] \qquad (7)$$

The component price per mass unit c is given in Table 7.

Table 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 above optimization problem has been coded in GAMS software. 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 **Error! Reference source not found.**.

Table 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

5. Summary

This paper 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.

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Biography

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