Optimal Product Design of Wheat Straw Polypropylene Composites

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Abstract

The objective of this study is to develop robust statistical models that can be used to predict the flexural properties and specific gravity of wheat straw polypropylene composite (WSPPC). Constrained mixture design methodology is applied to design a set of optimum experimental design with a three-component mixture: low-impact polypropylene (polymer matrix), ground wheat straw (natural fiber filler) and maleic acid grafted polypropylene as a coupling agent. The D-optimality criteria, the leverage values of design points and Fraction of Design Space graph are used to evaluate the design of experiment. The structural property models of WSPPC are then constructed by analyzing the obtained data and applying fitting model technique of least square regression and backward model term reduction. Unlike some previous similar works on statistical modeling of natural plant fiber thermoplastic composite, this work provides not only the summary of the Analysis of Variance (ANOVA) test, but also provides complete diagnostics case statistic reports which can be used to properly describe the model predictions to meet the standard properties of response surface models.

Keywords
Composite structural modeling, wheat straw, polypropylene composite, mixture design, response surface model

1. Introduction
The use of natural plant fibers (NPFs) as fillers or reinforcement materials in thermoplastic composites has become of increased interest in recent years due to various economic and environmental advantages they offered. Many research works have been done to study the various NPFs compounded to various thermoplastic polymer matrices along with various chemical and mechanical treatments to overcome the fiber-matrix incompatibility due to their hydrophilic and hydrophobic nature of polymer and NPFs respectively (Gassan and Bledzki 1999; Sain et al. 2005, Shibata et al., 2005). However, expansion and establishment of the technology of NPFs reinforced compounds is only possible if database and software solutions have been developed which can simulate the structural and processing properties of these materials (Bos et al. 2006).

Traditionally, modeling a composite system is carried out by decomposing the system into three main parts: composition selection, processing condition and final properties. Following this system decomposition, three different kinds of modeling strategies are then conducted. First, the final composite properties are modeled as a function of composition selection. The resulted models are commonly called structural property models. Second, the final composite properties are modeled as functions of the processing conditions. The resulted models are called processing property models. And finally, based on the fact that some properties strongly correlated to other 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 combined to simulate the composite system (Zhang and Friedrich, 2003).

Many researchers have attempted to use a theoretical approach to model the structural properties of NPFs Polymer composites. The focus of those studies is to model the mechanical properties as function of fiber loading, fiber orientation and fiber properties (i.e., fiber length), fiber length distribution and fiber aspect ratio. This approach, however, seem to fail to give proper models due to the complexity of the composite systems. Among of the sources of complexity are the fiber-matrix compatibility and fiber degradation during the compounding process. The degree of complexity is even higher in short fiber with orientation uncertainties within the composite structure (Mittal, 2008).

Alternatively, statistical modeling approaches have been used by many researchers to attempt to develop models that can be used to accurately predict mechanical properties of composite (Esfandiari, 2007). But, only few used response surface methodology and mixture design experiment, despite many successful works have been reported on mixture and mixture-process design experiments in the area of chemical product designs (Mittal 2008; Costa 2010).

Of the NPFs, agricultural residues such as wheat straw and soy stem have become of interest due to their nature as "pure" residues and their abandoned availability to secure feedstock with competitive, stable, and low price. Wheat straw has been proven to increase the flexural modulus of polypropylene and polyethylene. The presence of small amount of coupling agents such as maleic acid grafted polypropylene (MAPP) and maleic acid grafted polyethylene (MAPE) have increased the fiber matrix compatibility which resulted in better reinforcement mechanism (Karakus and Kahramanmaras, 2008).

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

2. The Design of Experiment

Three-component mixture design of experiment is chosen for the study. The input variables are the proportion (in weight percentage) of mixture components: polypropylene, wheat straw and the coupling agent (MAPP). The response variables of interest: 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 a 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).

$$\begin{aligned} 0.46 \le x_1 \le 0.70 \\ 0.30 \le x_2 \le 0.50 \\ 0 \le x_3 \le 0.04 \end{aligned} \qquad (1)$$

where x_1, x_2 and x_3 are weight fractions of polypropylene (A), wheat straw (B) and MAPP (C) respectively. A good design is desired in this work – that is, a design that will produce reliable results under a wide variety of possible circumstances, not designs that are optimal under a fairly restrictive and idealized set of conditions and assumptions. The Design Expert Software is used to generate, to construct and to pre-evaluate the properties of the proposed set of design points by considering the leverage values, the D-optimality and Fraction of Design Space graph. The constrained L-Pseudo Simplex design region as well as the 15 design points constructed can be seen in Figure 1 .

The design consists of one centroid and four vertices and are replicated twice to provide lack-of-fit test, three centre-edge points and two axial-check-blend points. The coordinates of the design points and the leverage values of each design points can be seen in Table 1. To fit the design points in calculating the parameter estimates of scheffe canonical model terms, the standard L-pseudo simplex lattice coordinates x' are applied, with the following transformation formula (Kruger 2007):

$$x_1' = \frac{x_1 - 0.46}{0.24}, \quad x_2' = \frac{x_2 - 0.3}{0.24}, \quad x_3' = \frac{x_3 - 0}{0.24} \qquad (2)$$

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 throughout the entire design space.
The Fraction of Design Space graph of the proposed design is presented in Table 1. The design points cover 0.93 fraction of design space with predicted Mean of Standard Error of 0.663 or lower. These values meet the suggested values of 0.8 and 1.0 for fraction of design and standard error respectively.

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

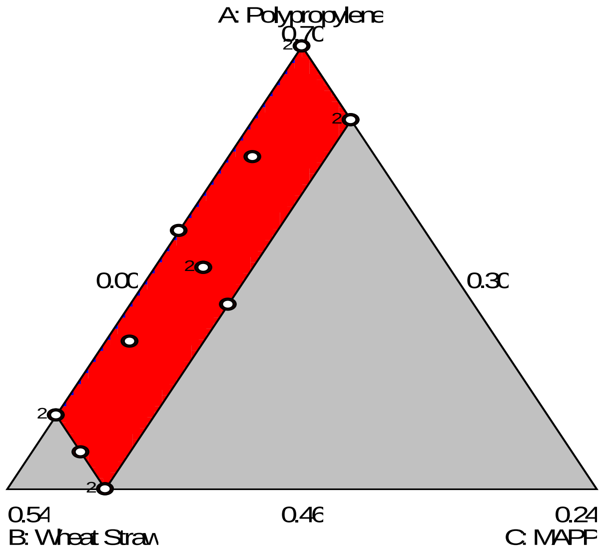

Figure 1: Constrained L-Pseudo Simplex Design Region of Wheat Straw-MAPP-Polypropylene Mixture.
(The values are real values; the dots are the design points; mark #2 indicated points are replicated twice.)

Table 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

3. Materials and Response Measurement Method

Homo polypropylene 6301 with a melt flow index of 12g/10 min (230 oC, 2.16 kg, ASTM D 1238) in form of powder was donated by A. Schuman Inc., Ontario, Canada. Wheat straw used in this study was soft white winter harvested in late 2007 in the Ontario region. The straw was first cut into approximately 3-5 cm length pieces using

Wheel Byend cutter and later grounded into a fine powder using rotary hammer mill. Prior to use for compounding, the ground wheat straw was passed through a sieve with mesh sizes of 35. The coupling agent used is Fusabond MD-353D, a maleic anhydride grafted polypropylene from DuPont. Two antioxidants, namely Irganox 1010 and Irgafos 168 purchased from Ciba Inc. Both antioxidants are phenol based and used to avoid the degradation of polypropylene during melt compounding.

Wheat straw polypropylene composites 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% 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 in the form of strands. The strands were cut into smaller pieces proper for the next processing step.
The resulting pellets were then injection molded using Ray-Ran injection molding machine to get ASTM standard samples 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 100psi. 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 10min 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.

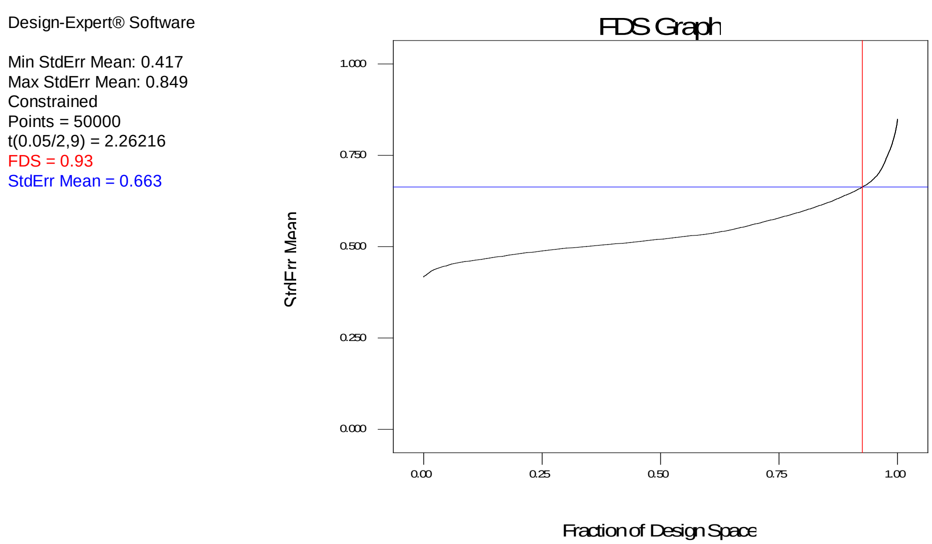

Figure 2: Fraction of design space graph of the proposed design

4. Results and Analysis

The results of WSPPC flexural properties and density measurements can be seen in Table 2. Analysis of the results is conducted by using Design Expert software. The following steps of standard statistical modeling and analysis are applied to each response variable: model fitting, analysis of Variance (ANOVA) Test, Model Diagnostics and model graphs. Initially, the fittest model is chosen by first comparing various coefficient of determination R's value between linear, quadratic, special cubic and cubic model. The model is chosen based on the maximum value of Adjusted-R^2 and Predicted-R^2 values. The number of model terms is then can be reduced by applying backward elimination technique to get the model term combination which gives highest coefficient of determination values. The model diagnostic case is then carried out to examine the influence of each design point on the model.

Table 2: Measured Flexural Properties and Density of WSPPC

Std #	Composition,			Flex. Modulus		Flex Strength		Offset Yield		Density (g/mL)	
	PP	WS	MAPP	Mean	Std.	Mean	Std.	Mean	Std.	Mean	Std. Dev.
1	50	50	0	2323	148	40	1.43	65	1.29	1.0505	0.006979
2	46	50	4	2803	265	72	2.45	122	5.44	1.0740	0.019949
3	60	40	0	1930	195	48	1.88	74	2.14	1.0423	0.010838
4	48	50	2	3025	56	69	2.13	112	4.44	1.0636	0.011012
5	70	30	0	2012	100	53	1.13	72	2.18	0.9747	0.00722
6	66	30	4	2140	101	72	1.58	102	5.15	0.9724	0.001727
7	54	45	1	2588	112	67	1.29	109	4.69	1.0380	0.004612
8	64	35	1	2172	116	66	1.64	102	2.07	1.0011	0.004424
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	0.010097
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	-	-

4.1 Flexural Modulus

The model summary statistics for Flexural Modulus show that a quadratic canonical model is better than the other models (Table 3). Special cubic model has higher adjusted R^2 value which means that the model is able to describe the response variations for all design points better than a quadratic model. However, special cubic model has much lower value of Predicted R^2 which means that the over fitting problem occurs in this model; the model will "fail" to predict the response value for any given points excluded from the dataset for model construction.
After backward elimination of quadratic model, the fittest model obtained is as follows:

$$\mathit{Flexural\ Modulus} = \underset{(102)}{1778\, x_1'} + \underset{(128)}{2435\, x_2'} - \underset{(11652)}{43996\, x_3'} + \underset{(13980)}{57397\, x_1' x_3'} + \underset{(14066)}{57207\, x_2' x_3'} \tag{3}$$

Table 3: Design Expert Output for Flexural Modulus Model Summary Statistics

Source	**Std.**	**R-**	**Adjusted**	**Predicted**	**PRESS**	
Linear	238.8356	0.608517	0.54327	0.411036	1029805	
Quadratic	168.0736	0.854596	0.773817	0.573251	746171.8	Suggested
Special	152.2576	0.893933	0.814382	0.35432	1128973	
Cubic	108.2941	0.966464	0.906099		+	

Where x_1', x_2' and x_3' are proportions 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.

Applying the formulas, in terms of actual components where the value of component proportions are real values in weight percentage, the model becomes:

$$\mathit{Flexural\ Modulus} = 9.57\, x_1 + 36.94\, x_2 - 9461\, x_3 + 99.65\, x_1 x_3 + 99.32\, x_2 x_3 \tag{4}$$

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 ; while the Adjusted R-Squared value is in reasonable agreement with predicted R-Squared value. The suggested difference of the two is less than 0.2.

The ANOVA-test summary statistics for the proposed model is presented in Table 4.

Table 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				

The model p-value of 0.0003 means that there is only 0.03 % chance that the F-Value of the model is due to noise. The significance of model and model terms can be statistically assured if the p-value is less than 0.0500. All of p-values of the model and model terms are less than 0.0500. 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 use the model.

Table 5 provides the report of diagnostic case statistics for 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 that the assumption of constant variance of the model is not rejected thus the model is reliable. The leverage values range from 0.171 to 0.439. These values are very good. In general, a leverage value of 1 for a data point means that the residual will be zero. In other words, all errors in experimentation are brought to the model. Lower leverage values are favored; and as a general rule, the 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 point is not rejected since all internally studentized residuals are within the range of -3 to +3. Furthermore, there is no indication of any outliers in dataset since all externally studentized residuals are within the range of -3.5 to +3.5. The same is true for DFFITS and Cook's distance values which are within the suggested values; indicates that all data points constitute the model evenly. Those properties of diagnostic case statistics show that the model has met most criteria for good response surface model as suggested by Myers et.al. (2009).

Table 4: Design Expert Report of Diagnostic Case Statisitcs for Flexural Modulus Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values	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

4.2 Flexural Strength

The second flexural property being examined in this study is flexural strength. The same data analysis technique is applied to the flexural strength of WSPPC. Similar to the flexural modulus, 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 percentage x_i are as follows:

$$Flexural\ Strength = 51.799\ x_1' + 42.158\ x_2' - 1222\ x_3' + 1670\ x_1'x_3' + 1749\ x_2'x_3' \quad (5)$$
$$(1.52) \quad (1.90) \quad (174) \quad (208) \quad (209)$$

$$Flexural\ Strength = 63.85\ x_1 + 23.68x_2 - 27694\ x_3 + 29000\ x_1x_3 + 30359\ x_2x_3 \quad (6)$$

The model significance, model parameter significance as well as insignificance of lack of fit are clearly proven by the ANOVA test as can be seen in Table 6. Table 7 provides the report of diagnostics case statistics for the proposed model. Again, similar to the model for flexural modulus, the constant variance assumption used in developing this statistical model are not rejected, each data point contribute to the model evenly, and the model meets the common criteria for response surface model.

Table 5: 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 6: Design Expert Report of Diagnostic Case Statisitcs for Flexural Strength Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values	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

4.3 Yield Strength

The last flexural property being modeled is yield strength of composite. The obtained models, the summary of ANOVA test and the report of case diagnostic statistics are presented below. Similar to flexural modulus and flexural strength models, the proposed model gives very good coefficient of determination, meets the assumption of constant variance and equal influence of design points. The model meets the criteria of good model for response surface models that can be used to predict the yield strength of composite as function of component proportions.

$$Yield\ Strength = 72.925\ x_1' + 69.340\ x_2' - 2355\ x_3' + 3138\ x_1'x_3' + 3293\ x_2'x_3' \quad (7)$$
$$(3.25) \quad (4.06) \quad (367) \quad (444) \quad (447)$$

$$Yield\ Strength = 77.41\ x_1 + 62.47\ x_2 - 52247\ x_3 + 544778\ x_1x_3 + 57168\ x_2x_3 \quad (8)$$

Table 7: 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 8: Design Expert Report of Diagnostic Case Statisitcs for Yield Strength Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values	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

4.4 Density

As strongly expected based on the common “rule of mixture”, the density of WSPPC is a linear function of the weight proportion of each component. The building process of the model, however, is slightly different from the previous three models and data analysis. There is one data point which is considered as an outlier. And the proposed model is developed from a dataset without this outlier. But still, the proposed model gives good coefficient of determination and meets the criteria for good response surface model. 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 percentage x_i are as follows:

$$\underset{}{Density} = \underset{(0.0045)}{0.9711\, x_1'} + \underset{(0.0048)}{1.0761\, x_2'} + \underset{(0.0294)}{1.0162\, x_3'} \tag{9}$$

$$Density = 0.8397\, x_1 + 1.2775\, x_2 + 1.0280\, x_3 \tag{10}$$

The ANOVA test results summary table and Diagnostic Case Statistics report are presented in Table 10 and Table 11, respectively:

Table 9: 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				

Table 10: Design Expert Report of Diagnostic Case Statisitcs for Density Model

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Values	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 (*)

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

Table 11: Models Summary and Their Coefficients of Determination

Properties	Models	R^2	$R^2_{Adjusted}$	$R^2_{Predicted}$
Flexural Modulus	$9.57\,x_1 + 36.94\,x_2 - 9461\,x_3 + 99.65\,x_1x_3 + 99.32\,x_2x_3$	0.854289	0.796004	0.703629
Flexural Strength	$63.85\,x_1 + 23.68x_2 - 27694\,x_3 + 29000\,x_1x_3 + 30359\,x_2x_3$	0.971582	0.960215	0.945566
Yield Strength	$77.41\,x_1 + 62.47\,x_2 - 52247\,x_3 + 544778\,x_1x_3 + 57168\,x_2x_3$	0.958989	0.942585	0.921964
Density	$0.8397\,x_1 + 1.2775\,x_2 + 1.0280\,x_3$	0.978227	0.97097	0.932099

4.5 The Optimum Ratio of MAPP/Wheat Straw

Since the main role of MAPP is a coupling agent, the composition of MAPP that gives maximum benefit of reinforcement should depend on the ratio of filler-matrix composition. By knowing the best recipe of MAPP composition as function of wheat straw proportion, one can easily determine how much MAPP should be added to composite mixture for any different filler-matrix composition. Another advantage of the fixed recipe of MAPP is reduced number of mixture components from three to two components. This reduction will simplify the composite system and would be a great benefit when we are trying to combine the mixture design with process variables to carry out process-mixture experimental design.

The Latest version of Design Expert software is also featured with optimization tools. However, one should be aware that the software doesn't provide options on optimization method to solve the optimization problems. The software only uses the direct search method in finding optimum objective functions which can be easily set up by users. Even if the software provides options on the number of initial points for searching optimum points, the direct search method still has great potential to end up with local optima instead of global optima.

Figure 3 shows the results of Design Expert optimization tools for optimum weight percentage of MAPP which gives maximum benefit of each flexural property. Only flexural modulus data point series that give reasonable result; not for the other three objective functions. 4 shows the optimum weight percentage of MAPP which give maximum benefit of each flexural property. The data points were obtained by solver tools in Microsoft Excel spreadsheet. Those results are much more reasonable than the results of Design Expert Optimization Tools. Figure 3 gives a rough understanding of how the MAPP proportion changes differently for maximum effects of each flexural properties. Relatively constant value of 2.4% MAPP gives maximum flexural modulus for any weight percentage of wheat straw within the range of 30%-50%. Meanwhile, the optimum MAPP compositions for maximum flexural strength and yield strength increase as the wheat straw content increases; from 2.7% to 3.2% and 2.85% to 3.3% for yield and flexural strength respectively. This kind of information would be very important for engineers when optimizing costs for different products with different specifications for different properties.

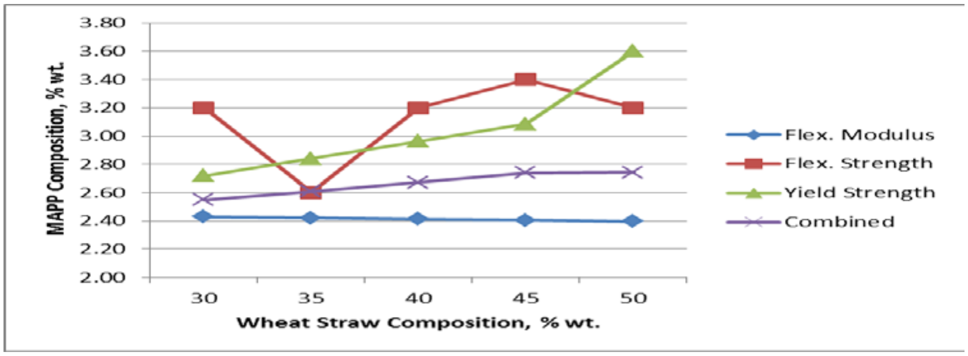

Figure 3: MAPP Composition for Maximum Flexural Properties of WSPPC (Design Expert result)

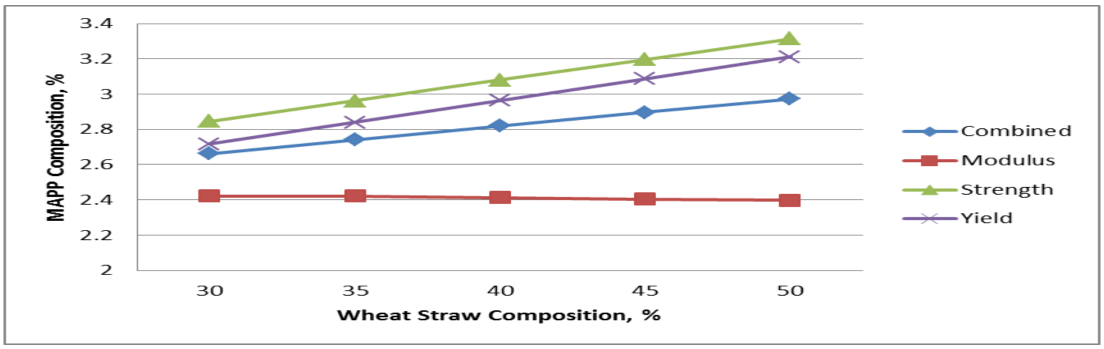

Figure 4: MAPP Composition for Maximum Flexural Properties of WSPPC (Microsoft Excel Solver Tools Result)

5. Conclusion

Mixture design of experiment is successfully implemented in modeling flexural properties and specific gravity of wheat straw polypropylene composite. The models correlate the responses as function 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, reports of case diagnostic 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 an engineering perspective, the models are reliable enough to be used to design composite products. However, this initial work is done without considering process variables; the variables which are not related to component proportion. Included in this kind of variables are matrix properties, fiber properties, as well as composite processing modes and processing conditions. When the process variables are included in the design of experiment, the so-called process – mixture design of experiment is applied. Works on process-mixture design of experiment of wheat straw polypropylene composite are underway and will be communicated in a future publication.

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