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A Statistical Approach to Engineer a Biocomposite Formulation from Biofuel Coproduct with Balanced Properties

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ABSTRACT: A 3^2-full factorial design of experiment (DOE) and regression modeling were implemented together as a practical approach to attain a distillers' grains-filled biocomposite with balanced mechanical and physical properties. The effects of compatibilizer and lubricant on tensile strength, flexural modulus, impact strength and melt flow index of the biocomposites were studied. Analysis of variance (ANOVA) was implemented to develop least square regression models containing statistically significant main effects (linear and quadratic) and interaction effect. The developed models showed good predictability for the new measurements. The statistical approach adopted in this work including overlaying contour plots of the response surfaces in the studied level domain was effective in highlighting an optimized region that leads to balanced mechanical and physical properties. © 2014 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40443.

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INTRODUCTION

More than 10 billion people are expected to inhabit the globe in less than 40 years.[1] With this, the sustainability of the current depleting petroleum resources is a huge concern for satisfying the energy demand of the growing population. Thus for today's and the future generation, the energy resources have to be renewable in a reasonable period of time. The transportation sector is a main petroleum consumer. Biodiesel and biobased ethanol are the two candidates from renewable resources for substituting the petroleum-based fuels and the aim is to gradually reduce the contribution of the petroleum in transportation fuels.[2]

Corn and sugar are currently the major precursors for producing biobased ethanol. Having a higher energy return on investment (EROI) value, the lignocellulosic resources have been recently considered as future feedstock for the second generation biobased ethanol.[3] However, it is projected that by 2020 the lignocellulosic matter will only offer a 4% share to the biobased ethanol production whereas corn and sugar will still contribute the most (78%).[4] Therefore, the future of this industry is highly affected by the sustainability of the first generation biobased ethanol.

With the recent expansion in dry mill plants and corn ethanol production, the sustainability of this industry is critically tied with finding new revenue streams for it, especially from its coproducts, CO_2 and distillers' grains. These coproducts are produced as much as ethanol on a weight basis[5]; however, it is a challenge now to maximize the revenue of selling these coproducts. The raw CO_2 from corn ethanol plants cannot be utilized for the beverage and dry ice markets unless further refining steps of CO_2 are adopted.[6] Also, distillers' grains are only used as a low cost feed partially blended in livestock diet.[5]

With the low cost of distillers' grains, there is a great motivation to seek new applications for it with the aim of value addition. In this regard, distillers' grains have been compounded with several thermoset[7,8] and thermoplastic[9,10] polymers. The first few researches suggested that biocomposites of as-received distillers' grains are not satisfactory so far as the mechanical properties are concerned. Therefore like other fillers, pretreatment and/or compatibilization are two methods two enhance the performance, for which the composition of distillers' grains need to be investigated. Dried distillers grains with solubles (DDGS) mainly consist of protein, fiber (cellulose and hemicellulose),

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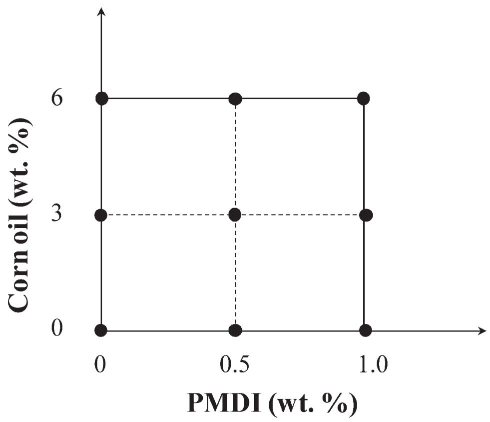

Figure 1. The schematic of the design of experiments in the present work.

lipid (oil), water-solubles and residual starch. The water-solubles need to be washed out for improved thermal stability of the biomass during composite melt processing.[11] The rigid fiber component of DDGS can contribute in modulus improvement while the protein and oil components may create a plasticized phase which decreases the stiffness. However, such a complex composition of DDGS contains several functional groups of O—H and N—H which are capable of chemical reaction with proper compatibilization.[12] By choosing such compatibilizer, crosslinks can form at the matrix–filler interface which can improve the mechanical properties significantly.

Aiming at an eco-friendly and biodegradable biocomposites, in our first attempt in producing DDGS biocomposite with biodegradable plastics, the DDGS filler showed promising results with utilization of compatibilizer. Although the produced DDGS biocomposite had a strength as high as that for the biodegradable matrix along with higher modulus, the impact strength and elongation of the material was drastically reduced.[13] In our previous work, a high-impact DDGS biocomposite was developed with improved modulus compared to the biodegradable matrix and a tensile strength very close to that of the matrix.[12] A bio-based lubricant was added to enhance the processability of the biocomposite together with the compatibilizer to enhance the mechanical performance of it. A synergistic effect of compatibilizer and lubricant on the impact strength was observed, while tensile properties were affected by compatibilizer and lubricant in different ways. On the other hand, the melt flow of the produced material was highly influenced by the compatibilizer only. The effects of compatibilizer and lubricant on different mechanical and physical properties were so complex that a more in-depth statistical approach seemed to be useful to draw an optimum region of the material's formulation and to realize the materials behavior for more practical applications.

For most engineering applications such as automotive interior parts, the polymeric material needs to satisfy the requirements of mechanical performance including rigidity, strength and toughness. At the same time, the physical properties such as flowability of the melt are important for manufacturing aspects. Therefore in the present work, we are trying to find the optimized formulation of the high-impact DDGS biocomposite with balanced rigidity, strength and melt flow properties. The interaction between the factors (compatibilizer and lubricant) is also examined with respect to different material properties. The approach here is a full factorial design of experiments (DOE) followed by statistical analysis of response surface methodology (RSM) using Minitab® software.

EXPERIMENTAL

Materials

The bioplastic matrix used in this research was a commercial biodegradable polymer marketed as Enmat Y5010P from TianAn Biologic Materials, China. The polymer was a blend of polyhydroxy(butyrate-*co*-valerate), PHBV, and poly(butylene adipate-*co*-terephthalate), PBAT. Dried distillers' grains with solubles (DDGS) were supplied by GreenField Ethanol, Chatham, Canada. Polymeric methylene diphenyl diisocyanate (PMDI) was used as the compatibilizer commercially named as RUBINATE® M from Huntsman Polyurethanes, Canada. Corn oil was purchased from the market and used as the processing aid lubricant for biocomposite processing.

Biocomposite Processing and Characterization

DDGS biocomposites with constant ratio of DDGS to bioplastic (hereinafter mentioned as Enmat), 20–80 (weight basis), with different levels of compatibilizer and lubricant were produced. The biocomposite processing was performed in a micro twin-screw extruder followed by injection molding in a micro injection molding machine, both from DSM Xplore. The processing

Table I. Mechanical and Physical Properties of Different Formulations (Data Adopted from Ref. 12)

Corn oil (wt %)	PMDI (wt %)	Tensile strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})	MFI (g/10 min)
0	0	16.3 ± 0.4	1090 ± 30	75 ± 6	20.9 ± 2.1
	0.5	22.7 ± 0.5	1350 ± 10	126 ± 8	3.9 ± 0.5
	1.0	22.7 ± 0.4	1250 ± 40	139 ± 21	0.4 ± 0.2
3	0	12.5 ± 0.7	930 ± 40	68 ± 5	26.3 ± 3.1
	0.5	20.3 ± 0.5	1080 ± 20	159 ± 15	7.5 ± 1.4
	1.0	20.5 ± 0.7	1110 ± 20	212 ± 13	0.5 ± 0.2
6	0	10.5 ± 0.3	820 ± 20	63 ± 7	27.7 ± 3.0
	0.5	17.5 ± 0.3	1020 ± 30	129 ± 6	3.8 ± 0.5
	1.0	18.0 ± 0.6	930 ± 50	200 ± 60	0.1 ± 0.0

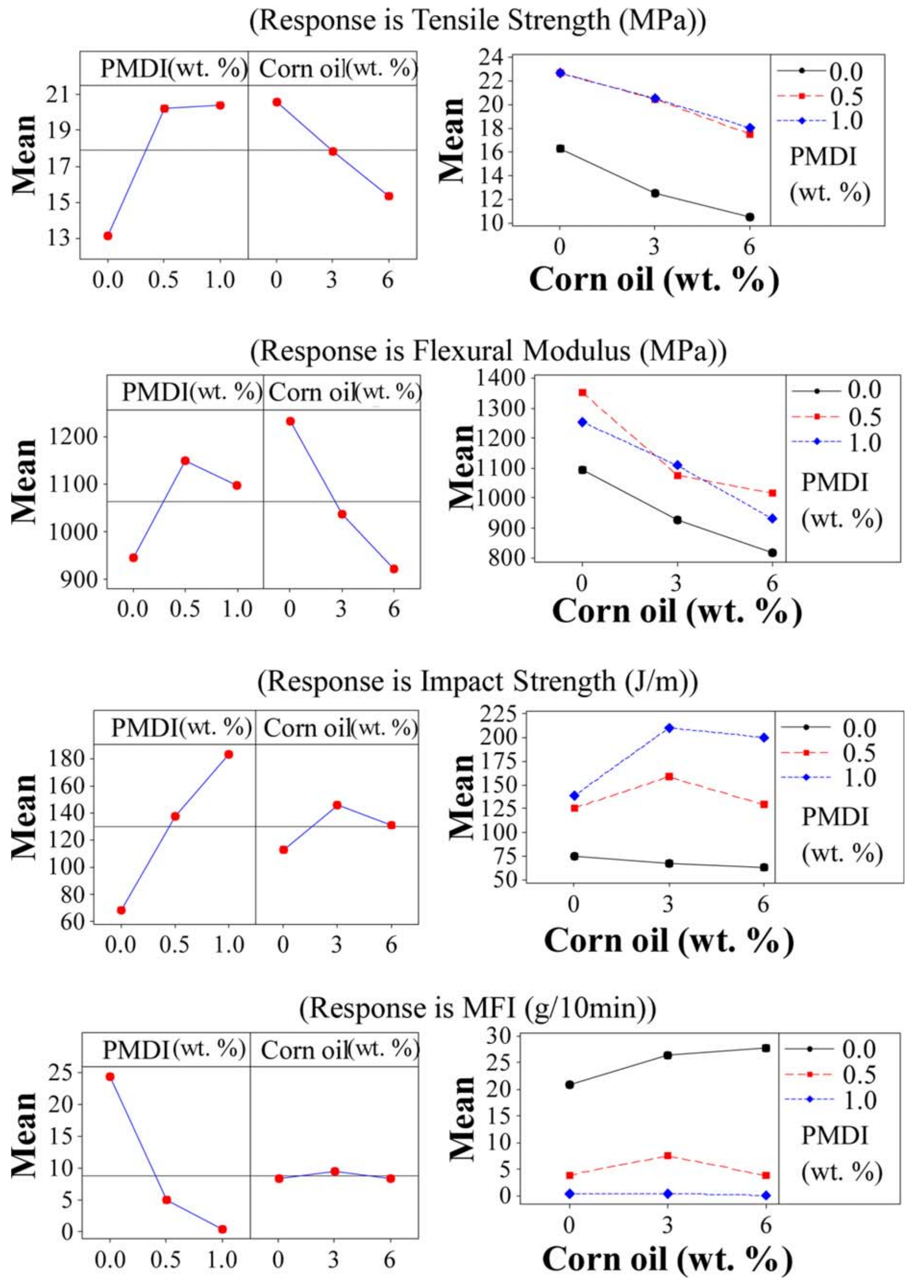

Figure 2. The main effects plots (left) and interaction plots (right) of the variable factors for all responses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conditions were kept constant for all samples. The processed biocomposites were characterized for their tensile strength, flexural modulus, impact strength and melt flow index (MFI). Detailed information about processing conditions and characterization method has been published in our previous work.[12]

Design of Experiments

The experiments were designed to investigate the effects of two variable factors on four measured responses. The variable factors are PMDI compatibilizer and corn oil lubricant amounts and the measured responses are tensile strength, flexural modulus, impact strength, and melt flow index of the biocomposites. The amount of PMDI compatibilizer was kept limited up to 1 wt % since higher amounts could result in occurrence of excessive crosslinking of the matrix and inhibit the flow of the molten material completely. Also, the excessive crosslinking in the matrix can make the microbial break-down of molecular chains more difficult which has an adverse effect on biodegradability of the final biocomposite.[14] The amount of corn oil was kept, by experience, not more than 6 wt % since higher amounts resulted in improper mixing of the corn oil with polymer matrix and DDGS filler.

Response surface methodology has been implemented here to find an optimized level of the independent variables (factors), PMDI and corn oil, while keeping a balance between mechanical

Table II. ANOVA Table for Full Model of All Studied Responses

	Analysis of variance for tensile strength						Analysis of variance for flexural modulus					
Source	DF	Seq SS	Adj SS	Adj MS	F	P	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	726.230	726.230	145.246	505.67	0.000	5	1082489	1082489	216498	132.23	0.000
Linear	2	603.936	256.471	128.236	446.45	0.000	2	902873	382699	191350	116.87	0.000
PMDI	1	401.136	219.568	219.568	764.42	0.000	1	174041	241193	241193	147.31	0.000
Corn oil	1	202.800	20.334	20.334	70.79	0.000	1	728833	104555	104555	63.86	0.000
Square	2	120.553	120.553	60.276	209.85	0.000	2	176736	176736	88368	53.97	0.000
PMDI × PMDI	1	120.409	120.409	120.409	419.20	0.000	1	160360	160360	160360	97.94	0.000
Corn oil × corn oil	1	0.144	0.144	0.144	0.50	0.483	1	16376	16376	16376	10.00	0.003
Interaction	1	1.741	1.741	1.741	6.06	0.018	1	2880	2880	2880	1.76	0.192
PMDI × corn oil	1	1.741	1.741	1.741	6.06	0.018	1	2880	2880	2880	1.76	0.192
Residual error	39	11.202	11.202	0.287			39	63855	63855	1637		
Lack-of-fit	3	2.970	2.970	0.990	4.33	0.011	3	28674	28674	9558	9.78	0.000
Pure error	36	8.232	8.232	0.229			36	35181	35181	977		
Total	44	737.432					44	1146344				

	Analysis of Variance for Impact Strength						Analysis of Variance for Melt Flow Index					
Source	DF	Seq SS	Adj SS	Adj MS	*F*	*P*	DF	Seq SS	Adj SS	Adj MS	*F*	*P*
Regression	5	137760	137760	27552.0	47.20	0.000	5	2547.97	2547.97	509.594	177.00	0.000
Linear	2	121263	12353	6176.3	10.58	0.000	2	2183.24	839.36	419.680	145.77	0.000
PMDI	1	118393	9869	9869.3	16.91	0.000	1	2173.28	771.84	771.839	268.08	0.000
Corn oil	1	2869	3581	3581.2	6.13	0.017	1	9.96	51.84	51.839	18.01	0.000
Square	2	8456	8456	4228.2	7.24	0.002	2	333.53	341.79	170.895	59.36	0.000
PMDI × PMDI	1	1729	1729	1728.8	2.96	0.092	1	309.91	323.66	323.663	112.42	0.000
Corn oil × corn oil	1	6728	6728	6727.6	11.53	0.001	1	23.62	21.47	21.472	7.46	0.013
Interaction	1	8041	8041	8041.0	13.78	0.001	1	31.20	31.20	31.196	10.84	0.004
PMDI × corn oil	1	8041	8041	8041.0	13.78	0.001	1	31.20	31.20	31.196	10.84	0.004
Residual error	48	28019	28019	583.7			19	54.70	54.70	2.879		
Lack-of-fit	3	4868	4868	1622.7	3.15	0.034	3	22.51	22.51	7.502	3.73	0.033
Pure error	45	23151	23151	514.5			16	32.20	32.20	2.012		
Total	53	165779					24	2602.67				

DF: Degree of freedom, Seq SS: sequential sums of squares, Adj SS: adjusted sums of squares, Adj MS: adjusted mean squares.

Table III. ANOVA Table for Reduced Model of Tensile Strength, Flexural Modulus, and Impact Strength

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Analysis of variance for tensile strength						
Regression	4	726.086	726.086	181.521	639.94	0.000
Linear	2	603.936	420.270	210.135	740.81	0.000
PMDI	1	401.136	219.568	219.568	774.07	0.000
Corn oil	1	202.800	100.572	100.572	354.56	0.000
Square	1	120.409	120.409	120.409	424.49	0.000
PMDI × PMDI	1	120.409	120.409	120.409	424.49	0.000
Interaction	1	1.741	1.741	1.741	6.14	0.018
PMDI × corn oil	1	1.741	1.741	1.741	6.14	0.018
Residual error	40	11.346	11.346	0.284		
Lack-of-fit	4	3.114	3.114	0.779	3.40	0.018
Pure error	36	8.232	8.232	0.229		
Total	44	737.432				
Analysis of variance for flexural modulus						
Regression	4	1079609	1079609	269902	161.78	0.000
Linear	2	902873	379847	189924	113.84	0.000
PMDI	1	174041	250445	250445	150.11	0.000
Corn oil	1	728833	129402	129402	77.56	0.000
Square	2	176736	176736	88368	52.97	0.000
PMDI × PMDI	1	160360	160360	160360	96.12	0.000
Corn oil × corn oil	1	16376	16376	16376	9.82	0.003
Residual error	40	66735	66735	1668		
Lack-of-fit	4	31554	31554	7888	8.07	0.000
Pure error	36	35181	35181	977		
Total	44	1146344				
Analysis of variance for impact strength						
Regression	4	136031	136031	34007.8	56.02	0.000
Linear	2	121263	22511	11255.7	18.54	0.000
PMDI	1	118393	21951	21950.8	36.16	0.000
Corn oil	1	2869	3581	3581.2	5.90	0.019
Square	1	6728	6728	6727.6	11.08	0.002
Corn oil × corn oil	1	6728	6728	6727.6	11.08	0.002
Interaction	1	8041	8041	8041.0	13.25	0.001
PMDI × corn oil	1	8041	8041	8041.0	13.25	0.001
Residual error	49	29748	29748	607.1		
Lack-of-fit	4	6597	6597	1649.2	3.21	0.021
Pure error	45	23151	23151	514.5		
Total	53	165779				

DF: Degree of freedom, Seq SS: sequential sums of squares, Adj SS: adjusted sums of squares, Adj MS: adjusted mean squares.

properties and MFI as the measured responses. Response surface methodology is usually coupled with a central composite design of experiment as an ideal design to study the curvature of the response function. However, a 3^2 full factorial design of two factors with three levels was adopted here due to the limitations on the levels of PMDI and corn oil and ease of processing. Such a design is also certainly a possible choice to investigate the curvature in response surfaces.[15] The schematic of the design is shown in Figure 1. The levels of both PMDI and corn oil are the ratio of the weight of each additive to the weight of the composite's load-bearing components (biopolymer plus DDGS).

Statistical Analysis

Minitab® statistical software, version 16, was used to analyze the significance of the effects of the factors via ANOVA.

Table IV. Regression Models and R^2 Statistic Obtained for Each Response

Response	Regression model	R^2 statistic
Tensile strength (MPa)	$TS = 16.0017 + 20.6033P - 0.9650C - 13.8800P^2 + 0.1967PC$	R^2= 98.46%; R^2_{adj} = 98.31%; $PRESS$ = 14.0084; R^2_{pred} = 98.10%
Flexural Modulus (MPa)	$FM = 1114.89 + 658.87P - 78.93C - 506.53P^2 + 4.50C^2$	R^2= 94.18%; R^2_{adj} = 93.60%; $PRESS$ = 84461.2; R^2_{pred} = 92.63%
Impact strength (J m^{-1})	$IS = 73.901 + 78.086P + 12.660C + 12.203PC - 2.631C^2$	R^2= 82.06%; R^2_{adj} = 80.59%; $PRESS$ = 37728.5; R^2_{pred} = 77.24%
MFI (g/10 min)	$MFI = 21.4923 - 51.3187P + 2.2377C - 1.1350PC + 30.1490P^2 - 0.2213C^2$	R^2= 97.90%; R^2_{adj} = 97.35%; $PRESS$ = 101.570; R^2_{pred} = 96.10%

This approach is used to: (1) generate the quadratic regression model for each response with least square method, (2) check the model adequacy using residual analysis, (3) plot the response surfaces and the respective contours, and (4) overlap the contour plots of different responses to find the optimized formulation region. A significance level of 0.05 was considered in this study.

RESULTS AND DISCUSSION

Effects of Compatibilizer and Lubricant on Mechanical and Physical Properties

Mechanical and physical properties of the different formulations investigated in this study are presented in Table I. These properties were selected for optimization analysis since tensile strength and flexural modulus are good measures of strength and rigidity of the resulting material, respectively. Moreover, impact strength and melt flow index (MFI) of a material represent its toughness and flowability/processability. These are typical properties of a commercial product for injection molding applications that are usually reported in materials' technical datasheet. Thus, the optimization of the formulation based on these criteria is adopted in our investigation to obtain a material with balanced mechanical performance and processability.

In Figure 2, the main effect plots (left hand side) and interaction plots (right hand side) of the two variable factors, compatibilizer (PMDI) and lubricant (corn oil), are illustrated. As also reported in our previous work,[12] PMDI had been used as the compatibilizer to enhance the mechanical performance of the DDGS bio-composite. Its positive effects on tensile strength, flexural modulus and impact strength can be observed by looking at the main effect

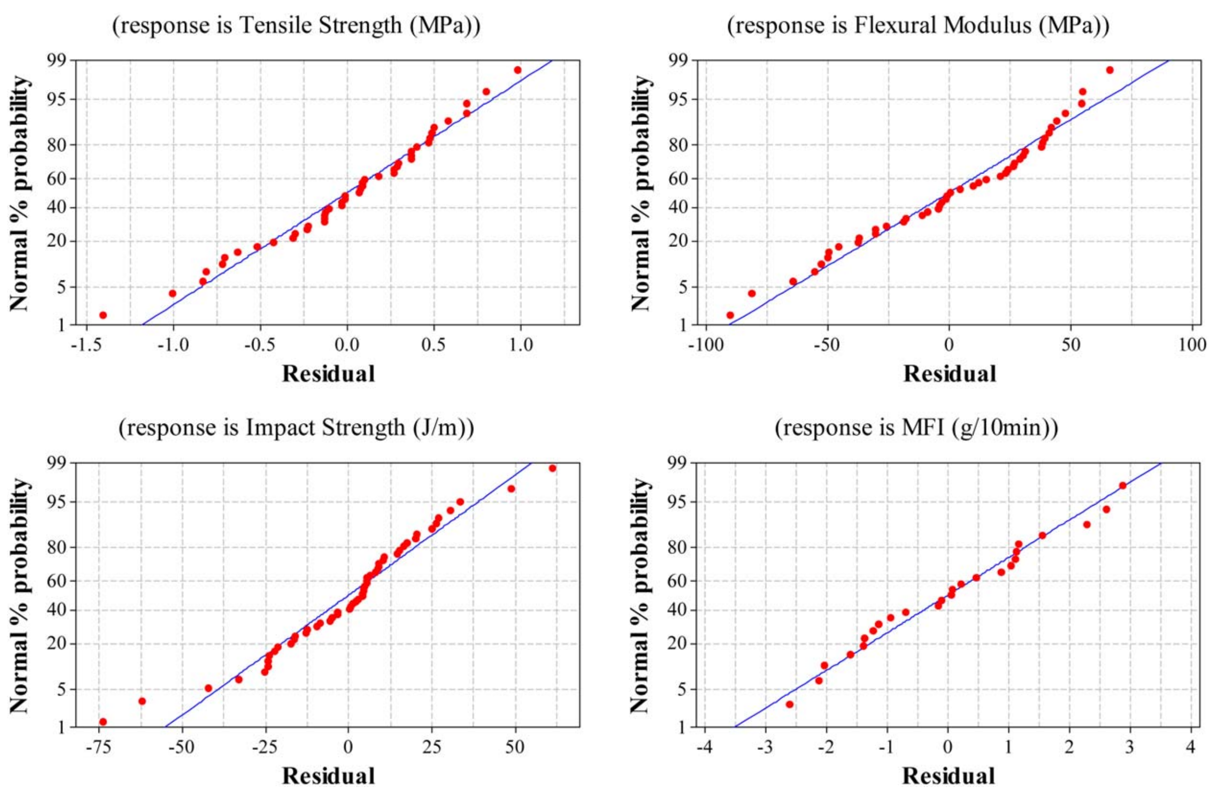

Figure 3. Normal probability plots of residuals for all responses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Experimental and Predicted Output of Responses for the DDGS Biocomposite Formulation with 0.75 wt % of PMDI and 3 wt % of Corn Oil

Source	Tensile strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})	MFI (g/10 min)
Experiment	19.8 ± 1.1	1090 ± 20	166 ± 13	2.2 ± 0.3
Regression model	21.2	1130	174	2.1
Deviation of predicted value from experimental value (%)	+7.1	+3.7	+4.8	−4.6

plots as well as the interaction plots with constant corn oil and varying PMDI amounts in Figure 2. On the other hand, it is obvious that the addition of PMDI drastically reduced the MFI. Moreover, we observed an increment of the mixing force with the addition of PMDI during processing of the biocomposites. Therefore, corn oil was introduced to this biocomposite system as the lubricant for the ease of processing and to increase the MFI of the final biocomposite. The interaction plot for MFI in Figure 2 shows enhancement of this measured response with the addition of corn oil alone (when PMDI level is zero).

It is also observed in Figure 2 that the two factors, PMDI and corn oil, affect the tensile strength in two different ways; same is observed for flexural modulus. No interaction between PMDI and corn oil is seen for tensile strength and flexural modulus. However, an interaction between the variable factors possibly exists with respect to the impact strength. This can be realized from the interaction plot for impact strength which shows a change in the plot's slope (from negative to positive slope) with the addition of PMDI within the 0–3 wt % of corn oil. Moreover, Figure 2 demonstrates that the MFI response is more influenced by PMDI factor than by corn oil. The complex effects the two factors and their interaction are studied in the following sections more in-depth.

Model Development via ANOVA Approach

The analysis of variance (ANOVA) is a useful tool to evaluate the significance of a factor and, in case of more than one factor, the interactions between the factors with respect to a specific response. The factors can be studied in two or more levels and the predictive capability of the regression model developed by ANOVA is dependent upon the number of levels chosen for the factors. In most preliminary studies, a linear model suits the requirements by changing the factors in two levels only (low and high levels). For more thorough investigations, the factors can be studied in more than two levels so that a regression of higher order can be developed, the factor interactions of higher degree can be evaluated and the curvature in the response plot can also be considered.[15]

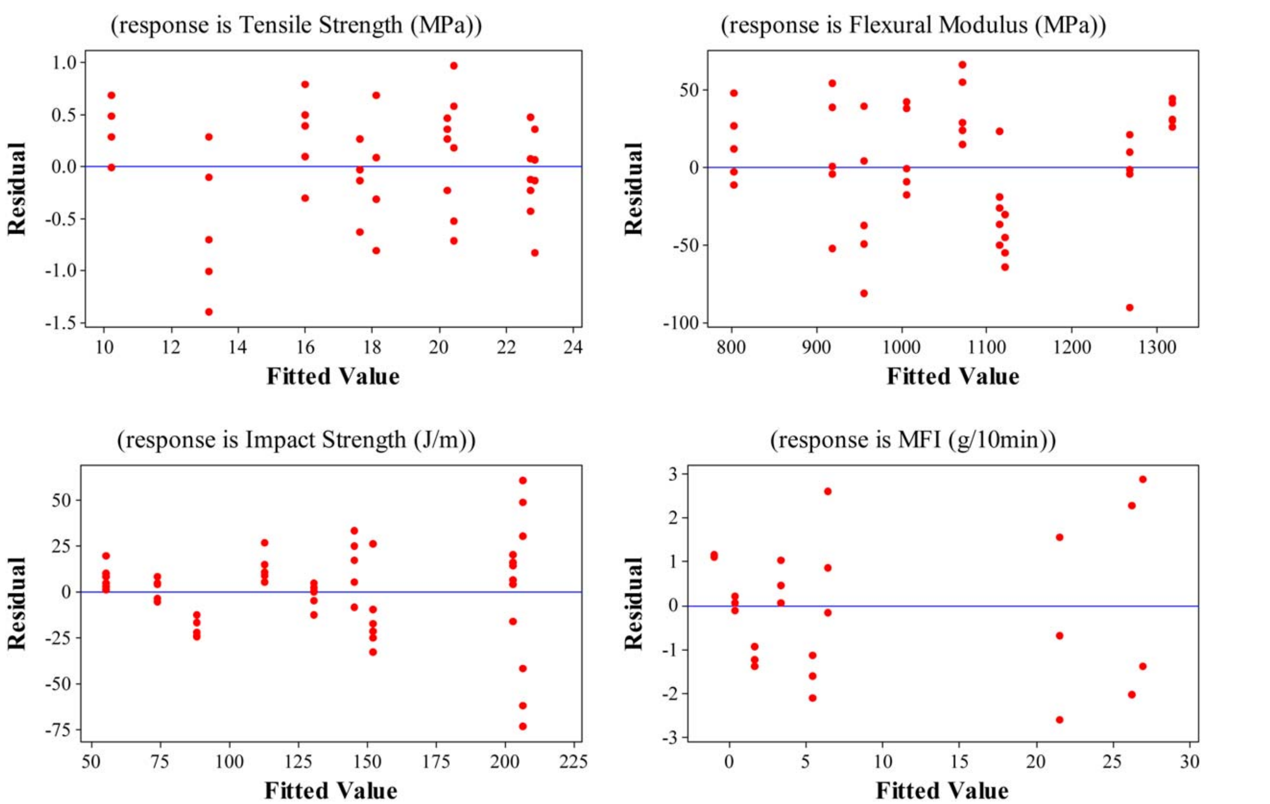

Figure 4. Residual plots versus fitted values for all responses. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In this work, a two-way ANOVA is implemented as two factors are studied. The factors were changed in three levels and a quadratic regression model is developed including the interaction of the two factors. The general format of the regression model for each response (R) would be:

$$R=a_0+a_1P+a_2C+a_3P^2+a_4C^2+a_5P\times C+\varepsilon \quad (1)$$

where P and C denote the PMDI and corn oil amounts in wt %, respectively, and a_i are equation constant and coefficients to be estimated by least square regression, and ε is the error term of the model.

Table II shows the ANOVA tables obtained for the all responses considering full model. The P-values for individual factor effects of first and second order as well as and their interaction are listed. This P value is an indication of whether the specific studied term is statistically significant or not. For the significance level of 5%, the P values of <0.05 indicate a statistically significant effect that has to be considered in the least square regression model. Referring to Table II, the quadratic corn oil effect on tensile strength, the PMDI-corn oil interaction effect on flexural modulus and the quadratic PMDI effect on impact strength are not statistically significant. Therefore, these effects were eliminated in generating the regression model of the respective responses. The ANOVA table for the reduced model of these three responses is presented in Table III.

The least square regression models developed from the three-level factorial design and (reduced) ANOVA tables are listed in Table IV. The models will be used to plot the response surfaces and find the optimized region with desired combination of response values. The R^2 statistics for the developed models are also presented. The results of the lack-of-fit test in Table III and R^2 statistic in Table IV are discussed in the following section.

Model Adequacy Check

The developed regression models with ANOVA approach needs adequacy check for at least three aspects, (i) the validity of assumption made in ANOVA about normal distribution of the errors, (ii) the lack-of-fit tests for the fitted model, and (iii) the R^2 statistic for variability in the data explained by the model.

The normal distribution assumption for the errors has been checked by illustrating the normal probability plots for the residuals resulted from each developed model. Figure 3 presents these plots. It is observed that all residual plots follow a straight line and confirm the validity of normal distribution assumption. In this method, the more emphasis is put on the middle part of the plot rather than the two extremes and small deviation from normality at these end points are of little concern.[15]

When replicates exist in the data points, the lack-of-fit test in ANOVA is one of the ways to check whether the developed model including the existing terms of effects (main effects and interaction) is fitting well the experimental data. In this test, the contribution of sum of squares for lack-of-fit toward the sum of squares of residual error is separated from the sum of squares of pure error. The lack-of-fit statistic is then calculated by dividing the mean square of lack-of-fit by that of pure error.[15]

The ANOVA results already presented in Tables II and III show that the lack-of-fit test statistic is significant in all cases. Several possibilities need to be considered here. First, it may suggest that the experimental data points are better described by a regression model with higher order, i.e., a 4^2 full-factorial design needs to be performed to obtain a more accurately fitted model. It may also be the result of occurrence of several data points with unusually large residual that cannot be explained by the existing fitted model. Moreover, it can also be partly because of that the mean square of the pure error is so significantly low that leads to a significantly high lack-of-fit statistic and this can sometimes happen as a result of precise measurements. Thus, it is recommended to consider the result from the lack-of-fit test along with R^2 statistic. The R^2 statistic is another informative approach to evaluate the applicability of the developed model. This information basically represents the variation about the mean values explained by the model and indicates an overall measure of the obtained fit.

The calculated values of the R^2 and R^2_{adj} show that the models reasonably fit the experimental data. Moreover, the PRESS (prediction error sum of squares) can measure how capable the model is to predict the responses in a new experiment, and

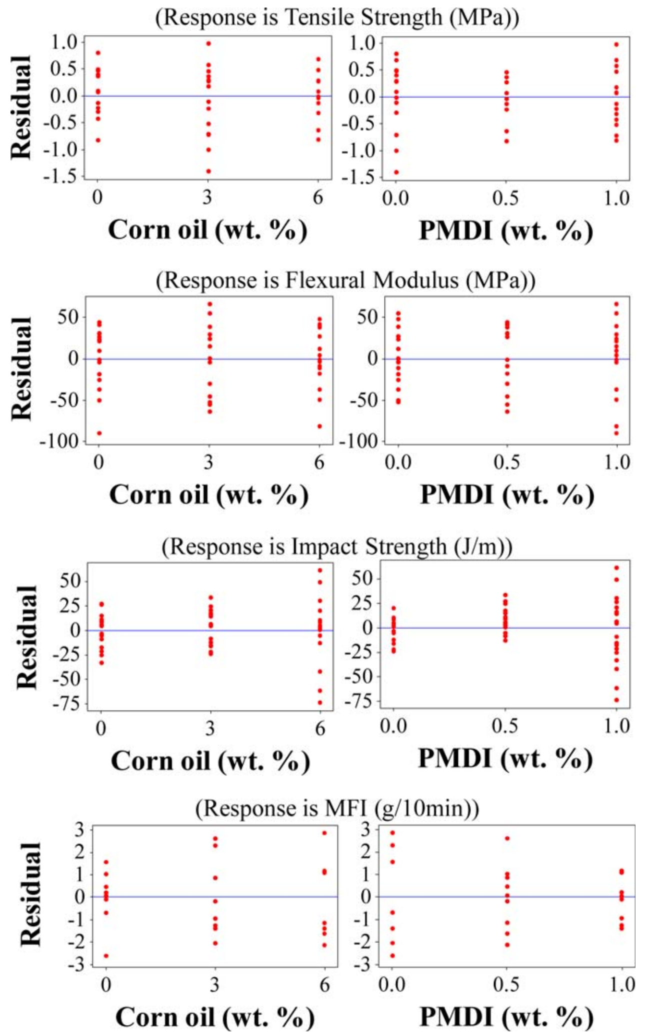

Figure 5. Residual plots versus variable factors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

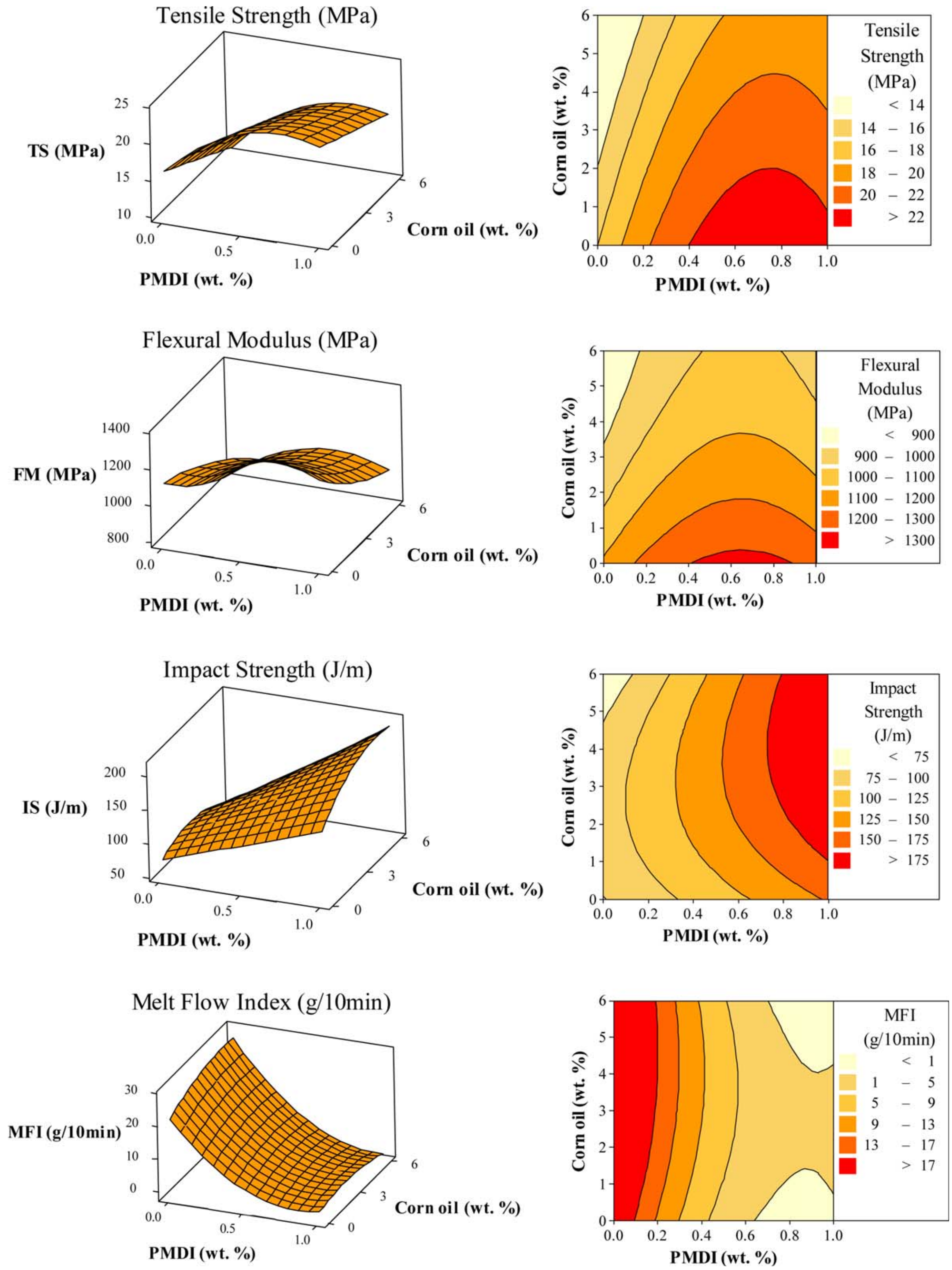

Figure 6. The 3D surface plots and 2D contour plots of all responses in the studied domain of the factors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

alternatively, R^2_{pred} (R^2 for prediction) can be calculated from the PRESS for the same purpose. The R^2_{pred} in Table IV indicate that the models can very well predict responses for new observations.

With these contradictory conclusions from lack-of-fit test and R^2 statistic, it is worth to note that when a large amount of data points are involved, a partially deficient model could be, nevertheless, applicable and sufficient to be used with proper caution.[16]

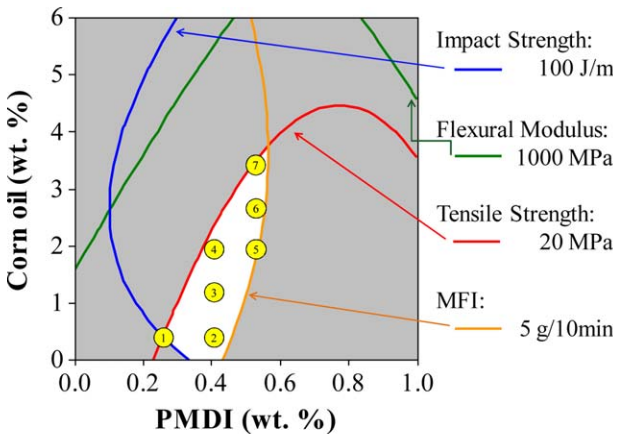

Figure 7. The overlaid contour plots of all responses highlighting the domain of the studied factors which attains the desired response values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, a new data point was experimentally tested. The DDGS biocomposite was formulated again from DDGS/bioplastic (Enmat), 20/80 (weight basis), and 0.75 wt % of PMDI and 3 wt % of corn oil. The experimentally measured physical and mechanical properties of this formulation are listed in Table V. The respective calculated values from the fitted model are also presented. The comparison between these two sets of data shows that there was a fairly good compliance between experimental and predicted values. The absolute difference between the predicted values and the experimental ones in worst case was not more than 7.1%. An important point to mention is that the pattern of the difference between predicted and experimental results among the responses does not follow the pattern of significance of the lack-of-fit statistic among them. Referring to Tables II and III, the lack-of-fit is the most significant for the flexural modulus > tensile strength > impact strength > MFI, while the absolute difference between predicted and experimental outputs is the higher for tensile strength > impact strength > MFI > flexural modulus (Table V). This confirms that both lack-of-fit statistic and R^2 statistic should be taken into account in order to examine the applicability of the fitted models.

Other Residual Plots

Apart from normal probability plot of residuals, other plots can be illustrated to obtain other useful information. By plotting the residuals versus fitted values, one can again check the normality assumption and/or whether the residuals follow any pattern with respect to a specific variable. Figure 4 shows the residual plots against the fitted values for all responses. Generally, the residual plots are structureless with respect to the fitted values except for the impact strength that shows large residuals at the extreme right hand side of the plot. This behavior is too mild to be considered as a heteroscedastic behavior for the residuals, especially that it is very outstanding only at fitted values of more than 200 J m^{-1}. This behavior can usually occur when the error of the experiment is a percentage of the magnitude of the response value.[15]

Moreover for impact strength, we found a correlation between the magnitude of the residual and the level of the variable factors (PMDI and corn oil). As illustrated in Figure 5, the residuals are the largest when PMDI and corn oil at their highest level. Such an obvious pattern was not observed for other responses. This suggest that extra caution needs to be considered when predicting the impact strength of formulations with PMDI and corn oil simultaneously close to their highest level (1 and 6 wt %, respectively), when using the developed regression model. As the level of PMDI and corn oil increases, their contribution toward the material formulation gets more prominent. In this case, it may be better to consider a mixture design of experiment in order to obtain a regression model with higher precision.

Response Surfaces, Contour Plots, and the Optimized Region

After developing regression models and analyzing strength and weakness points of them, a graphical method is a useful tool to find a region with desired properties within the studied level range of the variable factors. For this, the 3D surface plots of all responses have been demonstrated in terms of the factors in Figure 6. The 2D projections of the surfaces or the contour plots are also presented. The contour plots are more practical graphs to realize the pattern of the responses in the studied domain of factors. In Figure 6, it can be clearly observed that different patterns of responses are generated by the factors in the studied region. In this regard, finding a formulation with desired properties would be easier if taking advantage of these plots.

Given the desired values for responses, contour plot overlay method was adopted to find a formulation with balanced mechanical and physical properties. In the example in Figure 7,

Table VI. The Predicted Mechanical and Physical Properties for the Biocomposite Formulations Specified in Figure 7

Formulation no. in Figure 7	PMDI (wt %)	Corn oil (wt %)	Tensile strength (MPa)	Flexural modulus (MPa)	Impact strength (J m^{-1})	MFI (g/10 min)
1	0.26	0.4	20.1	1220	100	10.9
2	0.4	0.4	21.7	1270	112	6.5
3	0.4	1.2	21.0	1210	122	7.6
4	0.4	2	20.2	1160	130	8.5
5	0.53	2	21.3	1180	143	5.1
6	0.53	2.7	20.7	1140	148	5.6
7	0.53	3.5	20.0	1110	150	5.8

we have found an optimized formulation region where the tensile strength, flexural modulus and impact strength are at least 20 MPa, 1 GPa, and 100 J m^{-1}, respectively. This combination of mechanical properties gives acceptable tensile strength and flexural modulus balanced with a good impact strength which is normally expected to be achieved for a thermoplastic material in consumer products, automotive interior parts, etc. The MFI is the material property affecting the injection molding process and is usually decided by the size of the part. In this example, an MFI value of at least 5 g/10 min is specified for a medium to small size part. The domain of the factor levels that leads to the desired properties is highlighted in white color in Figure 7. The plot suggests that for such a combination of mechanical properties, flexural modulus is not a concern and it will be fulfilled as long as other three responses are met. Some examples points are specified in Figure 7 within the highlighted region for which the predicted responses are listed in Table VI. The values showed that a wide range of impact strength (from 100 to 150 J m^{-1}) and MFI (from 5 to 10.9 g/10 min) is achievable within the white feasible region of PMDI and corn oil levels in this example.

CONCLUSIONS

The combination of a 3^2-full factorial design of experiment (DOE) and analysis of variance (ANOVA) was implemented to predict the mechanical and physical properties of a DDGS-filled polymeric biocomposite. Tensile strength, flexural modulus, impact strength, and melt flow index were the measured responses after incorporation of compatibilizer and lubricant at low weight percentage levels in the material's formulation. Least square regression models were developed for each response to fit the data. The normal probability plot of residual admitted the validity of the normality assumption of the ANOVA. The R^2 statistic of the models demonstrated a good predictability of them. This approach was found to be very practical in the studied level domain of the factors. However, as analyzed with the residual plots versus the factors, it was noted that extra caution needs to be considered for predicting impact strength when the level of the factors increases simultaneously. The graphical methodology of the contour plots effectively helped in finding a level domain of the factors to obtain a formulation with balanced mechanical and physical performance.

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