Optimising Processing Conditions of PLA Nanocomposites Using Response Surface Methodology

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ABSTRACT

Numerous studies of polylactide nanocomposites have been conducted. However, the role and importance of processing conditions is the subject of very few papers. In this work, polylactide and a constant amount (2 %w/w) of organoclay Cloisite® 30B via melt intercalation technique were produced. It is generally believed that maximum benefits are achieved when organoclay is well dispersed in PLA matrix. It might be anticipated that melt processing conditions would have an important influence on the nanocomposites formed. Experimental design was carried out based on Box-Behnken methods, a response surface methodology (RSM) well suited to the goal of process optimisation. Three levels of processing temperature, rotor speed and mixing time were chosen in this study. The response was Young's modulus. The interaction effects with the most influence on the Young's modulus of these PLA/organoclay nanocomposites are temperature and speed. The maximum Young's modulus was predicted to be 1211 MPa at a temperature, speed, and time of 175°C, 100 rpm, and 7 min, respectively. Understanding the influence of processing conditions on the mechanical properties is needed for improving nanocomposites properties. Mathematical model and optimisations plot were used to illustrate the relationship between the parameters and mechanical properties considered. Results of the data analysis using Minitab software are presented.

Keywords: Box-Behnken, optimizing, organoclay, polylactide, response surface methodology

INTRODUCTION

In recent years, two major areas of study, namely nanocomposites and bio-related materials, have received much attention in industry and academia in the field of composite materials (Alexandre, Michael, & Dubois, 2000; Fischer, 2003; Ray & Okamoto,

2003). The area of nanocomposites has received considerable attention mainly because of the expectation that nanotechnology can lead to lighter and better material for engineering applications. Lately, studies based on bio-nanocomposites using clay as nano reinforcement in polylactic acid (PLA) have been a growing interest as one of the most promising materials with the brightest development prospect. PLA has attracted intensive research attention mainly because it is compostable polymer derived from renewable sources. Overall, PLA possesses the required mechanical and barrier properties desirable for a number of applications to compete with existing petroleum-based thermoplastics (Lim, Auras, & Rubino, 2008). However, PLA has inherent weaknesses in properties such as brittleness, low deflection temperature (HDT) and high price, which limit its widespread implementation (Nampoothiri, Nair, & John, 2010; Nyambo et al., 2010; Wu, 2005). On the other hand, layered silicate is naturally abundant, economic and more importantly, benign to the environment (Ray et al., 2003). Layered silicates such as organically modified montmorillonites (organoclays) appeared to be effective fillers (even at a low concentration, 1–5 wt%) for improving the overall performance of PLA/clay system (Pluta, 2006). Therefore, by producing this hybrid material, one not only obtains new biodegradable nanocomposites with improved properties in comparison with neat biodegradable polymers and enlarged application fields of biodegradable polymers, but the material would not affect the environment as well (Di et al., 2003).

Improvement of the nanocomposites properties should be dependent not only on the organoclay concentration but also on the degree of its dispersion (Pluta, 2006). Dispersion is a very important information because failure can be induced by agglomerates. In a general way, many of the properties associated with polymer clay nanocomposites are a function of the extent of exfoliation of individual clay sheets. The greatest improvement of benefits comes with exfoliated samples. This can be controlled by both the processing conditions and matching the interaction of organomodified clay to the polymer matrix (Pluta, 2006). The latter is well documented (Denault, Ton-That, & Bloch, 2006; Krishnamachari et al., 2009; Paul et al., 2003; Pluta, 2006). However, which processing factor imparts the better level of dispersion is still under discussion (Pogodina et al., 2008). Mixing is the key step in almost every polymer processing operation, affecting material properties, processability and cost (Manas-Zloczower, 1997). Therefore, its fundamental understanding is of prime importance.

PLA nanocomposites formed by melt blending have been described previously (Di et al., 2005; Pluta et al., 2002, 2006; Ray et al., 2003); however, these studies have not reported on how these conditions were chosen. Hence, this paper addresses the issue on how to predict the optimum processing condition of PLA organoclay nanocomposites using an experimental design to develop a model to obtain the desired mechanical properties. Processing temperature, rotor speed and mixing time were chosen because they were considered to have significant effects on the processing of nanocomposites in general (Hasook et al., 2008; Jollands & Gupta, 2010; Modesti et al., 2006; Pluta, 2006). Interaction between several factors greatly affects the performance of final products. Interactions cannot be determined by changing only one

variable at a time. If factors and the interactions between correlated factors are known, the optimum operating condition can be determined.

Design of Experiment (DOE) is widely used in research and development, where a large proportion of resources go towards solving optimisation problems. Statistical data and analysis can help researchers in predicting better processing conditions or better properties, leading to better outcomes of studies of materials such as nanocomposites. Process and property optimisation can save time, cost and energy. Application of DOE techniques by the engineering fraternity is limited; and research shows that when applied, they are often performed incorrectly (Antony & Kaye, 1995) because of the lack of skills in manufacturing and lack of statistical knowledge (Antony & Kaye, 1997).

The objectives of this study were to investigate the effects of temperature, speed and time on preparing nanocomposite composed of PLA with a constant amount of organoclay Cloisite® 30B (2 wt%), and construct models to predict the modulus of nanocomposite. The influence of operating conditions on the organoclay dispersion (nanostructure) on the modulus of the nanocomposites is discussed. The results of data analysis using Minitab software are presented.

MATERIALS AND METHOD

Materials

PLA 2002D from NatureWorks® was used as the matrix. Organically treated montmorillonite (MMT) Cloisite® 30B from Southern Clay Product was used as a filler. In order to remove water and other volatile components, PLA pellets and clays were dried in a vacuum oven at 90°C for 24 hours prior to processing.

Preparation of the nanocomposites. PLA pellets and a constant amount (2 %w/w) of organoclay Cloisite® 30B were melt-blended in a counter rotating Haake internal mixer. The samples were moulded by compression moulding at 190°C for 3 min before being subjected to mechanical measurements.

Characterisation

An Instron model 4465 Universal Testing Frame was used to perform the tests and measure Young's modulus. The test was conducted at a constant rate of 5 mm/min at room temperature according to ASTM D638. All the samples were stored in a desiccator prior to testing.

Experimental Design. The experimental design was carried out based on the Box-Behnken design, a response surface methodology (RSM) well suited to the goal of process optimisation. Ferreira et al. (2007) reported that the Box-Behnken design was much more efficient than the three-level full factorial designs. Three levels of processing temperature, rotor speed and mixing

time with a constant amount (2 wt%) of organoclay Cloisite® 30B were selected for the study. The output was Young's modulus. Young's modulus was used because the mechanical function is more sensitive to changes in the microstructure of nanocomposites. The experimental data were analysed using Minitab Statistical software. The software developed a 15-run design, which included 12 combinations of the factors plus three centre points (in which all factors are at their central values), and used for fitting a second-order response surface. The three centre point runs were added to provide as a measure of process stability and inherent variability (Dong et al., 2009). A significance level of 0.05 was used for all the statistical analyses. Table 1 presents the factors and levels identified for the experiment.

Table 1
List of control parameters and their level for the experiment

Control parameters	Parameter labels	Units	Low levels (-1)	High levels (+1)
Temperature	x_1	°C	175	195
Speed	x_2	rpm	60	100
Time	x_3	min	5	9

For predicting the optimal point, a second-order polynomial model was fitted to correlate the relationship between independent variables and response (Young's modulus). For the three factors, the equation is as follows:

$$Y = \beta_o + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \qquad [1]$$

Where Y is the predicted response; β_o is model constant; β_i is the coefficient of ith individual factor, β_{ii} is the coefficient of ith factor squared, β_{ij} is the coefficient of interaction between the ith and jth factors, and x_n ($n = i, j$) is the variable or factor value. The quality of fit of the polynomial model equation was expressed by the coefficient of determination R^2.

RESULTS AND DISCUSSION

Data Analysis and Interpretation

Upon obtaining the response values, the first step in the analysis involved finding the significant parameters. The results in Table 2 show the average values of four samples. The analysis was done using coded units. Use of coded units helps to eliminate any spurious statistical results due to different measurement scales of the factors, and makes them easy to interpret (Malik, Malik, Hussain, & Arain, 2011).

Table 2
The experimental design according to Box-Behnken method

Run	x_1	x_2	x_3	Young's Modulus (MPa)		Difference (%)
				Experimental	Predicted	
1	185	80	7	1,150	1,180	-2.2
2	175	100	7	1,210	1,210	0.3
3	195	60	7	1,190	1,190	0.0
4	175	60	7	1,140	1,150	-1.1
5	185	80	7	1,190	1,180	1.1
6	185	100	5	1,140	1,130	0.8
7	195	80	5	1,100	1,130	-2.6
8	175	80	5	1,150	1,130	1.9
9	175	80	9	1,120	1,130	-0.4
10	195	100	7	1,170	1,150	1.4
11	195	80	9	1,140	1,120	1.9
12	185	60	9	1,130	1,120	1.2
13	185	60	5	1,120	1,120	0.0
14	185	80	7	1,180	1,180	0.5
15	185	100	9	1,100	1,130	-2.6

Table 3
Estimated regression coefficients for modulus

Term	Coef	SE Coef	T	P
Constant	1173.75	11.637	100.866	0.000
Temperature	-4.24	7.126	-0.594	0.578
Speed	4.36	7.126	0.612	0.567
Time	-2.08	7.126	-0.291	0.783
Temperature*Temperature	3.96	10.489	0.378	0.721
Speed*Speed	0.11	10.489	0.010	0.992
Time*Time	-48.66	10.489	4.639	-0.006
Temperature*Speed	-26.17	10.078	-2.597	0.048
Temperature*Time	19.10	10.078	1.895	0.117
Speed*Time	-12.90	10.078	-1.280	0.257

From the analysis and output shown in Table 3, p-values for the estimated coefficients of quadratic terms (Time*Time) and interaction (Temp*Speed) are 0.006 and 0.048, respectively, indicating that they are significantly related to modulus at an α-level of 0.05. The adequacy of the model can be checked with R^2 and $R^2_{adjusted}$. $R^2_{adjusted}$ is considered rather than solely relying on R^2 value because the R^2 value can be easily increased by adding more variables, regardless of whether these factors are statistically significant or not (Montgomery, 2009). The R^2 and $R^2_{adjusted}$ values for the above regression model are 88% and 65%, respectively. These values

indicated that the model fits the data well. In general, the higher the R^2, the better the model will fit our data. The polynomial model for Young's modulus (Y) was regressed by considering only the significant terms, and this is shown below:

$$Y = -1291.8 + 10.0445x_1 + 24.4253x_2 + 170.290x_3 - 12.2377x_3^2 - 0.130850x_{12} \qquad [2]$$

Determination of the Optimal Conditions

The optimum conditions were determined using the Minitab Response Optimiser. Response optimisation is often useful in product development when determining the operating conditions, which results in desirable properties of a product. It helps to identify the combination of input variable settings that jointly optimise a single response or a set of responses. This is useful when evaluating the impacts of multiple inputs on a response.
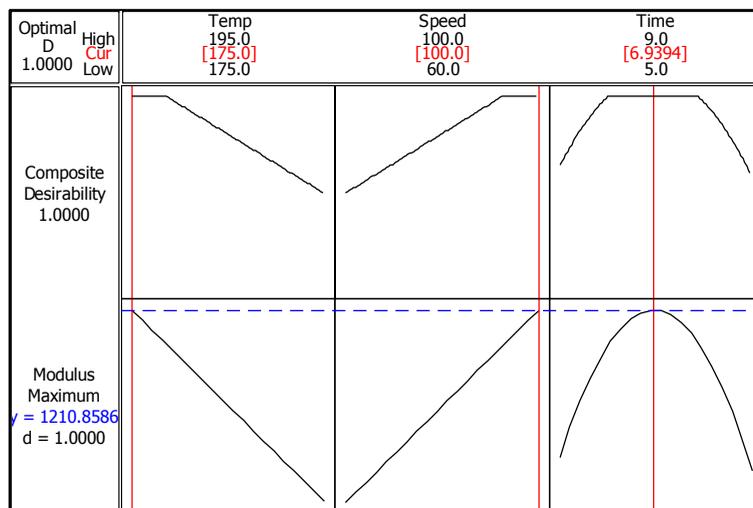

Figure 1. Optimisation plot

In Figure 1, the optimisation plot shows the effect of each factor (columns) on the response or composite desirability (rows). The vertical red lines on the graph represents the current factor settings. The numbers displayed at the top column (in red) show the current factor level settings. The horizontal blue lines and numbers represent the responses for the current factor level.

Temperature. Decreasing the temperature moves Young's modulus to its maximum because PLA undergoes thermal degradation at temperatures above 200°C (Garlotta, 2001). Since mixing increases the compound temperature, this suggests that it might be worthwhile to experiment with lower temperatures.

Speed. If we extrapolate the plots to higher values of speed, it appears that Young's modulus could be increased. This suggests that the experiment with high speed might be more desirable as it maximises the polymer–clay interactions, making the surface of layers ready for the polymer interaction. This should lead to the significant change in mechanical properties.

Time. In this model, Young's modulus depends on Time*Time, indicating that as time increases, Young's modulus increases quadratically with time. Increasing the time up to middle setting moves Young's modulus to its maximum, but a further increase in time will reduce Young's modulus. This result agrees with the previous data presented by Denault et al. (2006) who suggested that longer compounding time and higher compounding temperature would lead to organoclay degradation.

According to the best fit model to the data, the maximum Young's modulus was predicted to be 1211 MPa at a temperature, speed and time of 175°C, 100 rpm, and 7 min, respectively. The model was tested for robustness by making samples at the predicted optimum mixing condition, where the measured modulus was then compared with the prediction. The modulus of a sample made at the optimum condition was 1240 MPa, which is higher by 2.4% than what was predicted by the best fit model. Hence, the agreement between the measured and predicted response is considered to be reasonable and the model is considered as robust. The optimum modulus (1240 MPa) is also 7.8% higher than the average modulus for the BBD runs (1150 MPa), so it is significant at the 99% confidence level.

Although numerical optimisation along with graphical analysis can provide useful information, it is not a substitute for subject matter expertise. Relevant background information, theoretical principles and knowledge gained through observation or previous experimentation need to be considered when applying these methods (Minitab Inc., 2007).

It is important to note that determination of the optimum conditions is specific for this nanocomposite material in this mixing configuration. When different materials or mixers are used, the optimum condition will also change. This is in good agreement with the optimum process conditions reported by Dennis et al. (2001).

CONCLUSION

In order to optimise the processing conditions for preparing polylactide nanocomposites, the Box-Behnken design was applied to investigate three variables; processing temperature, rotor speed and mixing time, as highlighted in this study. The interaction effects with the most influence on the Young's modulus of these PLA/organoclay nanocomposites are temperature and speed. Young's modulus also increases quadratically with time.

The data were fitted with a simple mathematical model that was used to predict the condition to maximise Young's modulus. The maximum Young's modulus was predicted to be 1211 MPa at a temperature, speed and time of 175°C, 100 rpm, and 7 min, respectively. The model was found to be robust. Samples produced at the predicted optimum temperature, speed and time had a significant increase in modulus of 7.8% compared with the average readings for all the runs. Hence, making samples at optimised conditions improved the modulus significantly.

The application of Box-Behnken designs can provide answers to specific questions on the behaviour of a system using an optimum number of experimental observations. Thorough investigations into the nanocomposite morphology (transmission electron microscopy and small-angle X-ray scattering) are currently under investigation; the influence of nanoclay filler content is also being investigated. These will be the subject of a forthcoming article.

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