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Polypropylene/clay nanocomposites prepared in an internal mixer: optimization of processing conditions to improve flexural modulus

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Abstract. Polypropylene (PP)/clay nanocomposites are usually processed by melt mixing. In this method, mixing conditions are important variables to improve nanocomposite properties. Some studies reported the effects of processing on mechanical properties of PP/clay, but there is no clear explanation on optimum conditions. This study aims to predict the optimum conditions of PP/clay nanocomposite prepared by an internal mixer using response surface methodology (DoE). The effect of mixing on flexural modulus and nanocomposite structures were analyzed. Temperature, rotation speed, and mixing time were varied. To improve interfacial bonding, polypropylene-graft-maleic anhydride (PP-g-MA) was added as a compatibilizer. PP/clay formulation was fixed at 88 wt% of PP, 9 wt% of PP-g-MA, and 3 wt% of clay. The results show that the optimum modulus was predicted at 222 ºC, 83 rpm and 5 minutes, giving 2085 MPa or 18% improvement compared to control sample. XRD diffractograms showed that nanocomposite peaks shifted to lower angles, suggesting the presence of some intercalated structures that supported the resulting increase in modulus.

1. Introduction

Polypropylene (PP) is one of the biggest commodity polymers in the world. Despite the vast applications of PP, the mechanical properties of PP are not good enough for some applications as building material. Therefore, fillers such as clay are needed to improve PP mechanical properties [1]. The clay is naturally a hydrophilic material, which has different polarity to PP. Therefore, a compatibilizer such as polypropylene-graft-maleic anhydride (PP-g-MA) is needed to facilitate the dispersion of clay layers in PP [2, 3].

The dispersion of clay layers also depends on the preparation process. Internal mixer is one of commonly used process that could facilitate the dispersion clay layers on nanocomposite [4]. The process parameters in internal mixer which can affect nanocomposite performance are process temperature, rotation speed, and time [5, 6]. The rotation speed will produce shear tension. A combination of low temperature and high speed rotation can produce a higher shear tension which can facilitate the dispersion process. However, a high shear tension can make the composite degraded [7]. Therefore, the optimum process condition is required.

Optimum process condition can be achieved by varying process parameters. Some studies showed that 190-240 °C processing temperature [6, 8, 9], 60-100 rpm rotation speed [8, 10, 11], 5-15 minutes mixing time [8, 11, 12] are the ranges that provide a chance of getting an optimum values for the mechanical properties. However, these varieties did not show optimum point directly. Therefore, a method, such as response surface methodology (DoE), to analyze optimum point is needed.

In this research, the effect of processing condition in PP/clay nanocomposite was studied. Various process temperatures, rotation speeds, and mixing times were used in our study. The optimum condition of PP/clay composite was analyzed using response surface methodology (DoE), based on flexural modulus results. The presence of intercalation or exfoliation of clay was also analyzed by X-ray diffraction.

2. Experimental method

2.1. Materials

PP (5169 MAS 2158) with 1.8 g/10min of MFI produced by P.T Politama was used as a matrix. PP-g-MA (Epolene Wax G 3015P) from Eastman Chemical Company were used as a compatibilizer, Southern Clay product, O-MMT clay (Cloisite 20A), was used as filler.

2.2. Preparation of nanocomposites

The nanocomposites were prepared using an internal mixer (Haake Rheomix 600) with various settings as planned in DoE (Table 1.). The clay was dried at 80 °C overnight. After that, the clay, PP-g-MA, and PP were dry mixed, followed by drying at similar conditions. The control sample, neat PP, was processed at 80 rpm, 10 minutes, and 220 °C, according to mid-setting shown in Table 1. The formula was fixed at 88/9/3 of wt% for PP/PP-g-MA/clay as resulted in the best mechanical property [13].

Table 1. Processing conditions used in an internal mixer.

Runs	Temp (°C)	Speed (rpm)	Time (minutes)	Runs	Temp (°C)	Speed (rpm)	Time (minutes)
Control	220	80	10	8	220	60	5
1	230	80	5	9	230	60	10
2	220	60	15	10	230	100	10
3	220	100	5	11	220	80	10
4	230	80	5	12	220	100	15
5	230	80	15	13	220	80	10
6	210	80	15	14	210	80	5
7	210	60	10	15	210	100	10

The specimen was produced by using compression molding, Collin P300P. According to some trials in our laboratory, all samples were compressed twice to produce smooth area. The conditions were shown in Table 2.

Table 2. Settings applied in compression molding.

Parameters	1st Compression					2nd Compression				
	1	2	3	4	5	1	2	3	4	5
Temperature (°C)	205	205	205	205	40	205	0	195	0	40
Pressure (bars)	0	1	1	0	0	0	0	0	0	1
Time (minutes)	10	5	5	0	15	10	0	3	0	15

3. Testings

Mechanical tests were performed according to flexural properties (ASTM D 790), using Universal Testing Machine, Shimadzu AGS 10 kNG. The support span was 25.4 mm. The flexural speeds were

set according to samples thickness as explained in the standard. All testing was conducted at 23 ± 2 °C, 50 ± 5% RH. The average of flexural modulus from five specimens was calculated for all samples.

Structural analysis of nanocomposites was done for selected samples namely PP, clay, optimized sample. The analysis was conducted using an X-ray diffractometer (XRD), Rigaku miniflex 600 with Cu Kα radiation. XRD scans were conducted at λ = 1.54 Å, with scan rate of 2.4°/min. The spectra were evaluated in the 2θ range from 2° to 10°.

4. Statistical analysis

The completed flexural modulus data was analyzed and interpreted using Minitab 17 software. The data was regressed using polynomial equation as follows:

$$y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (1)$$

Where y is the model response, x_i and x_j are independent variables, and βo, βi, βii, and βij are the coefficients for the constant, linear, quadratic terms, and interactions, respectively. Coded units (-1, 0, +1) were used in the calculation.

5. Results and discussion

5.1. Flexural modulus

Table 3 shows flexural modulus for all samples. In general, the average flexural modulus ranges from 1512 to 2248 MPa at various conditions. The average modulus of all nanocomposites is 2042 ± 168 MPa while mid-setting is 2096 ± 15MPa. The lowest is 1512 ± 55 MPa, while the highest is 2248 ± 180 MPa, giving -14% to 27% change on modulus. The improvement obtained in this research is higher than previous results reported by Yu Dong *et al.* (±20%) and H. Md. Akil *et al.* (±25%) [4, 14]. This suggests that mixing in this research was done properly.

Table 3. Flexural modulus of samples.

Sample	Temperature (°C)	Rotation Speed (rpm)	Time (minutes)	Average Flexural Modulus (MPa)
Control	220	80	10	1764 ± 86
1	230	80	5	2248 ± 180
2	220	60	15	2078 ± 71
3	220	100	5	2091 ± 99
4	220	80	10	2090 ± 158
5	230	80	15	1993 ± 76
6	210	80	15	2034 ± 121
7	210	60	10	1512 ± 55
8	220	60	5	2110 ± 167
9	230	60	10	2119 ± 57
10	230	100	10	2169 ± 105
11	220	80	10	2113 ± 205
12	220	100	15	2108 ± 94
13	220	80	10	2084 ± 184
14	210	80	5	1900 ± 87
15	210	100	10	1974 ± 131
Average modulus of all nanocomposites				2042 ± 168
Average modulus of mid-setting				2096 ± 15

5.2. Experimental design

Statistical model was developed from flexural modulus of nanocomposites. The model coefficient and

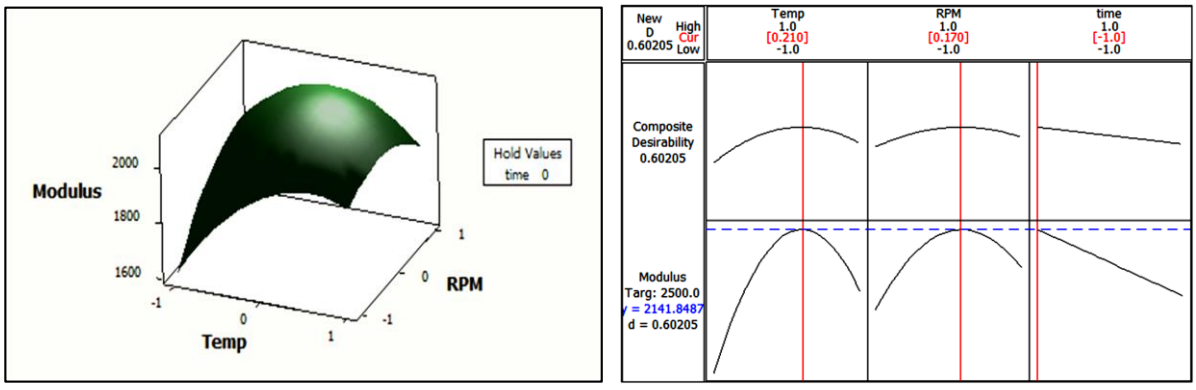
p-value is shown in Table 4. It is not showing all terms as significance consideration. The most significant factor is the quadratic effect of temperatures, giving p-value 0.034 suggests curvature region in the range of applied temperatures. P-values of rpm and time are higher than 0.05 for 95% confidence level suggests that these factors are not significant to influence the modulus.

Table 4. Model coefficient and p-value.

Term	Coefficient	P Value
Constant	2077	0.000
Temperature	80	0.087
RPM	52	0.241
Time	-52	0.241
Temp*Temp	-154	0.034
RPM*RPM	-90	0.174
Temp*RPM	-93	0.148

The effect of interacted factors is represented by surface plot shown in Figure 1 (a). There is no significant effect of mixing time in this research (p-value = 0.241 or > 0.1 for 90% confidence level). For this reason, further analysis will be done according to one setting of mixing time, namely at mid-setting.

Figure 1 (a) shows that the modulus increases by higher temperature and rpm in the range of low to medium settings. However, it decreases at higher conditions. This suggests that there might be a degradation mechanism occurred during mixing at extreme high conditions [15] or entropy loss during polymer penetration into clay galleries due to very low polymer viscosity [16]. Meanwhile, as temperature increases might reduce viscosity and facilitate diffusion mechanism, while rpm produces higher shear [6], the improvement on modulus at medium temperature and rpm might be caused by diffusion and shear that work together to disperse the platelets.



(a) (b)

Figure 1. (a) Surface plots at mid-setting of mixing time, (b) response optimizer analyzed plot.

The optimum conditions to produce the best modulus were predicted by response surface analyzer plot (Figure (b)). The plot shows that the optimum conditions are predicted at (0.21; 0.17; -1.00) in coded unit or 222 °C, 83 rpm, and 5 minutes in actual conditions. Applying these conditions would result in a flexural modulus of 2142 MPa. To validate the model and the predicted result, a verification experiment was carried out at optimized conditions. The flexural modulus value of verification sample was 2085 MPa. The value of the optimum prediction value as well as the verification result was lower than the maximum modulus (2248 MPa). This might be caused by the variations during the processing. However, the ranges of the maximum, optimum predicted, and verification are less than 1 standard

deviation of modulus (s.d = 168 MPa) for all nanocomposite samples. This suggests that the model is capable of predicting the modulus.

5.3. XRD analysis

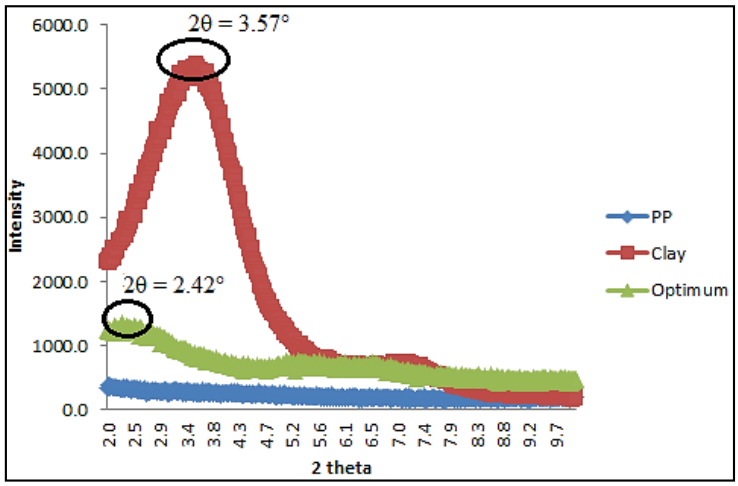


Figure 2. XRD diffractograms for selected sample.

Figure 2 presents XRD diffractograms of control, clay, and optimized nancomposite samples. The results showed that the clay peak of optimized nanocomposite sample shifted to the lower angle compare to peak of clay. It is shifted from 2θ = 3.57° (d_{001} = 2.47 nm) for original clay to 2θ = 2.42° (d_{001} = 3.65 nm), giving 48% increase of interlayer spacing. This supported the modulus results and proved that modulus improvement was achieved due to an increase of clay interlayer spacing.

6. Conclusion

Polypropylene (PP)/clay nanocomposites were prepared by an internal mixer. The effects of mixing conditions, namely temperature, rotation speed, and mixing time on flexural modulus were analyzed. The optimum conditions of PP/clay nanocomposite were predicted using response surface methodology (DoE). Nanocomposite with 2085 MPa flexural modulus (18% improvement compare to PP) was generated at 222 °C, 83 rpm, and 5 minutes as the optimum conditions. This improvement might be caused by existence of intercalated clay layers. This hypothesis was confirmed by XRD diffractograms that showed clay interlayer d-spacing increase from 2.47 nm to 3.65 nm.

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