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Effect of Processing Variables on Tensile Modulus and Morphology of Polyethylene/Clay Nanocomposites Prepared in an Internal Mixer

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Abstract. A comparative study on effect of internal mixer on high density Polyethylene (HDPE)/clay nanocomposites preparation was done. Effect of temperature, rotor rotation (rpm), and mixing time, as well as rotor type (Roller and Banbury) on mechanical properties and morphology of HDPE/clay nanocomposites were studied using Box-Behnken experimental design. The model was developed according to secant modulus and confirmed to morphology analysis using Transmission Electron Microscopy (TEM). The finding suggests that there is different mechanisms occurred in each rotor to improve the mechanical properties. The mechanism in Roller is medium shear and medium diffusion, while Banbury is high shear and low diffusion. The difference in mechanism to disperse the clay particles attribute to the different optimum processing conditions in each rotor. The settings for roller samples are predicted around mid temperature, mid speed, and mid mixing time. There is no optimum setting for Banbury within the processing boundaries. The best settings for Banbury are at low, high, low settings. The morphology results showed a hybrid composite structure, with some exfoliations and some intercalations. There was a correlation between better mechanical properties and morphology with more exfoliation and thinner intercalated particles.

1. Introduction
Polyethylene (PE) is a commodity polymer that has low tensile modulus compared to most other commodity and engineering plastics. To improve this property, nanoclay is commonly added. However, the preparation of PE nanocomposites is challenging due to polarity difference between polymer and filler. In order to improve the filler-matrix interaction, a compatibilizer can be used. This material enables the polymer to penetrate into the clay interlayer galleries [1, 2] thereby enhancing interfacial adhesion and mechanical properties.

Melt intercalation is one popular method to produce nanocomposites due to wide availability of equipment in industry. A number of studies have shown that the dispersion and delamination degree of nanoparticle produced from this technique was influenced by equipment type [3, 4] and screw design [3, 5-7]. The internal mixer is one of the equipment types commonly used for preparing nanocomposites. It is a mixer which uses various rotor types such as Roller [8] and Banbury [2], with independent setting of temperature, speed and residence time. The Roller rotor is used to process polyolefins, while the Banbury is used to disperse common rubber fillers (such as carbon black, filler with nano scale) in highly viscous rubber blends [9, 10]. However, comparative studies on rotor design are limited. As other
studies have shown that polymer nanocomposite properties are influenced by screw design [3, 5, 7], it is of interest to better understand the role of rotor design in polymer nanocomposite preparation with an internal mixer.

Setting conditions are also considered as influencing factors to produce nanocomposites. However, most studies on polyethylene nanocomposites did not explain how processing condition was chosen. A single temperature point was set on mixer at 150 °C [11, 12] and 180 °C [2]. Range of temperature was applied from 130 °C to 190 °C on single screw extruder [13, 14] from 185 °C to 205 °C for twin screw extruder [15-18]. Residence time on extruder was not set because it depends on screw rotation. On the other hand, mixing time in the mixer equipment is independent factor. Lee et al. [2] set screw rotation at 50 rpm for 10 minutes, while another study set 60 rpm for 10 minutes with preheating at 30 rpm for 3 minutes [11, 12]. This fact suggests that the optimum processing condition on polyethylene nanocomposite is still unclear.

This research aims to analyze the effects of processing condition on PE/clay nanocomposites. Various temperatures, rotor rotations, and mixing times were applied in order to observe the effects of mixing conditions and their interactions on tensile modulus. The comparison between Roller and Banbury rotor was done by producing nanocomposites according to Box–Behnken experimental design. Sample morphology were analyzed using transmission electron microscopy (TEM).

2. Materials and Methods

2.1. Materials

All polymer used in this study was a commercially available blow molding grade high density Polyethylene (HDPE) HD5148 donated by QENOS Australia. Filler used in this research was Cloisite 93A (C93A) produced by Southern Clay Products. Maleic anhydride-grafted-polyethylene (HDPE-g-MA, Polybond® 3009) from Chemtura Singapore was used as compatibilizer. SongnoxTM 1010 (SX1010) and SongnoxTM 1680 (SX1680) supplied by SunAce Australia were used as processing stabilizers.

2.2. Nanocomposite preparation

Nanocomposite samples were fabricated according to three factors and three levels of Box–Behnken experimental design (DoE) shown in Table 1. The boundaries were chosen in order to melt the polymer without degrading the materials. Control sample was produced from neat HDPE produced at 180 °C, 30 rpm, and 4 minutes so that the samples have thermal history.

| Sample | temp (°C) | speed (rpm) | time (min) | Sample | temp (°C) | speed (rpm) | time (min) | Sample | temp (°C) | speed (rpm) | time (min) |
|--------|-----------|-------------|------------|--------|-----------|-------------|------------|--------|-----------|-------------|------------|
| 1      | 210       | 80          | 4          | 6      | 210       | 130         | 10         | 11     | 180       | 30          | 16         |
| 2      | 180       | 30          | 4          | 7      | 180       | 130         | 16         | 12     | 210       | 30          | 10         |
| 3      | 180       | 80          | 10         | 8      | 150       | 30          | 10         | 13     | 150       | 80          | 4          |
| 4      | 180       | 80          | 10         | 9      | 180       | 80          | 10         | 14     | 180       | 130         | 4          |
| 5      | 150       | 130         | 10         | 10     | 150       | 80          | 16         | 15     | 210       | 80          | 16         |

All samples were produced at 2 wt% of clay, 5 wt% of compatibiliser, and 0.05 wt% of SX1010 and SX1680, respectively. The clay was dried in the oven at 80 °C overnight prior to melt compounding. The clay was then hand mixed with HDPE, 5 wt% of HDPE-g-MA, and 0.05 wt% of SX1010 and SX1680, respectively. Haake Rheomix OS R600 equipped with Roller or Banbury rotors was used for mixing.

2.3. Characterizations

Tensile specimens were produced using compression molding at 180 °C according to ASTM D638 type II. Molten materials were pressed into specimen molds at 90 bar pressure, for 2 minutes preheating to obtain desired pressure, and followed by 5 minutes heating and 5 minutes cooling. All specimens were conditioned in a desiccator for 2 days prior to tensile modulus measurement.
The modulus measurements were carried out on minimum four specimens using an Instron 4467 equipped with extensometer. Crosshead rate was set at 5 mm/min for 2% secant modulus. The secant modulus was calculated because the neat HDPE samples did not exhibit any linear region.

Nanocomposite morphology was analyzed using TEM JEOL 1010. The degree of exfoliation was analyzed from 5 different sliced specimens per sample, with thickness ± 50 nm. The specimens were prepared using a Leica microtome with diamond knife at temperatures -110 °C for the specimen and -150 °C for the knife to produce very smooth surface and avoid specimen rolling and wrinkling. The pictures were captured using a Gatan Orius digital camera at 100 keV accelerating voltage.

3. Results and Discussions

3.1. Modelling on Tensile Modulus

Tensile modulus for all nanocomposites and control sample are presented in Table 2. All nanocomposite samples increased with addition of 2% clay in comparison with HDPE, as expected. The increase varied from 2 to 25%. The standard deviation for all nanocomposite samples is 6%. The modulus improvement in this study is similar to other studies in PE nanocomposites [14, 19, 20] with 2 wt% filler loading, but lower than another study which is attributed to different filler modification [21]. The results are also similar to improvements reported in other studies of PE nanocomposites with higher filler loadings, which range from 15% to 26% [1, 2, 22, 23]. These suggest that the mixing undertaken in this study was done effectively.

Table 2. Tensile modulus and strength for samples prepared by Roller or Banbury rotors

| Samples   | Filler [wt%] | Modulus Roller [MPa] | Modulus Banbury [MPa] |
|-----------|--------------|-----------------------|-----------------------|
| Control   | 0            | 745 ± 26              | 768 ± 22              |
| 1         | 2            | 897 ± 37 (+20%)       | 840 ± 23 (+9%)        |
| 2         | 2            | 761 ± 44 (+2%)        | 871 ± 9 (+13%)        |
| 3         | 2            | 917 ± 34 (+23%)       | 895 ± 21 (+16%)       |
| 4         | 2            | 913 ± 56 (+23%)       | 891 ± 44 (+16%)       |
| 5         | 2            | 777 ± 43 (+4%)        | 918 ± 27 (+19%)       |
| 6         | 2            | 787 ± 18 (+6%)        | 831 ± 15 (+8%)        |
| 7         | 2            | 802 ± 39 (+8%)        | 815 ± 28 (+6%)        |
| 8         | 2            | 820 ± 65 (+10%)       | 874 ± 16 (+14%)       |
| 9         | 2            | 881 ± 43 (+18%)       | 891 ± 33 (+16%)       |
| 10        | 2            | 860 ± 45 (+15%)       | 951 ± 33 (+24%)       |
| 11        | 2            | 808 ± 67 (+8%)        | 938 ± 25 (+22%)       |
| 12        | 2            | 861 ± 35 (+16%)       | 918 ± 41 (+19%)       |
| 13        | 2            | 806 ± 51 (+8%)        | 960 ± 46 (+25%)       |
| 14        | 2            | 821 ± 29 (+10%)       | 898 ± 39 (+17%)       |
| 15        | 2            | 773 ± 23 (+4%)        | 875 ± 28 (+14%)       |

Average 1-15       | 832 ± 52 (+12%) | 891 ± 42 (+16%) |
Average at mid-point | 904 ± 20 (+21%) | 892 ± 2 (+16%) |

The complete modulus data were analyzed and interpreted using Minitab 16 software. The data were regressed using a second order polynomial equation as follows:

\[ y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \]  \hspace{2cm} (1)

where \( y \) is the model response, \( x_i \) and \( x_j \) are independent variables, and \( \beta_0, \beta_i, \beta_{ii}, \beta_{ij} \) are the coefficients for the constant, linear and quadratic terms, and interactions, respectively. The responses were predicted from generated model using coded unit to (-1, 0, +1) to eliminate effects of measurement units [24]. The equations for each response are shown below:
\[ y_1 = 904 + 6.94 x_1 - 7.82 x_2 - 5.32 x_3 - 28.2 x_1^2 - 64.4 x_2^2 - 41.5 x_3^2 - 7.69 x_1 x_2 - 44.6 x_1 x_3 - 16.5 x_2 x_3 \]  
\[ y_2 = 892 - 29.9 x_1 - 17.4 x_2 + 1.25 x_3 + 9.46 x_1^2 - 16.5 x_2^2 + 4.71 x_3^2 - 32.8 x_1 x_2 + 11.0 x_1 x_3 - 37.5 x_2 x_3 \]

where \( y_1 \) is modulus for Roller and \( y_2 \) is modulus for Banbury. The variable \( x_1 \) represents temperature, \( x_2 \) for rotor rotation, and \( x_3 \) for mixing time.

Figure 1. Contour plots for modulus: (a) Roller at low temp, (b) Roller at medium temp, (c) Roller at high temp, (d) Response optimizer Roller, (e) Banbury at low temp, (f) Banbury at medium temp, (g) Banbury at high temp, and (h) Response optimizer Banbury.

Figures 1 show interacted factors to influence modulus and response optimizer plots developed from generated model. “A”, “B”, and “C” on the figures represents temperature, rpm, and time, respectively. The different effects of factors and their interactions in the various samples suggest there are several mechanisms influencing platelet dispersion, namely shear, diffusion, and degradation, and these sometimes work together and sometimes work against each other. Generally platelet dispersion is promoted by high shear [8] (low temperature and high speed), high diffusion [3] (long times at medium temperatures), and is reduced by clay surfactant degradation [1, 2, 25] (high temperature or speed for long times).

The contour plots show interactions between factors is complex. The Roller plots (Fig. 1 (a), (b) and (c)) show concentric circles with close contours and a dark green center. This indicates that a maximum modulus value occurs within the DoE boundary. On the other hand, the Banbury samples (Fig. 1 (e), (f), and (g)) show quite different behavior that there is no best modulus within boundaries conditions. That is the high and low modulus positions change with all process conditions.

The results from response optimizer (Fig. 1 (d) and (h)) show that the predicted modulus and corresponding processing conditions depend on rotor design. This shows that optimized processing conditions cannot be transferred from one rotor to another but should be identified for each rotor. The best conditions for Banbury suggested that the shear was a major factor to improve the modulus. This also suggested that Banbury rotor might be beneficial for processing thermal sensitive polymers, but not sensitive to shear. On the other hand, Roller rotor would be useful when it is used for longer mixing time due its consistency to time compare to the other one [26].

Table 3. Comparison of predicted and measured modulus

| Rotor  | Coded Unit | Actual Settings [°C, rpm, min] | Predicted Modulus [MPa] | Actual Modulus [MPa] | Error [%] |
|--------|------------|--------------------------------|-------------------------|---------------------|-----------|
| Roller | 0.27; -0.05; -0.19 | 188; 77; 9 | 906 | 873 ± 41 | -4% |
| Banbury | -1; 1; -1 | 150; 130; 4 | 982 | 949 ± 26 | -4% |
Confirmation experiments at best conditions were conducted to test the model accuracy. The results are summarized in Table 3. In general, measured modulus was lower than predicted values for both rotors. However, the optimized sample results are higher than the average values modulus by an average of 6% (±1 s.d to 2 s.d). This suggests that optimizing the processing conditions is worthwhile, as it is beneficial to improving modulus.

3.2. Morphology Analysis

TEM analysis was approached from qualitative and quantitative techniques. Quantitative analysis was carried out for 5 images per sample with Gatan Digital Micrograph software. The measurement areas were chosen in regions that show no agglomerates (particles over 100 nm) to maximize the number of exfoliated or intercalated structures in the image, thus improving accuracy. The particle thicknesses were divided into 2 (two) groups. All particles with thicknesses less than 10 nm are considered to have an exfoliated structure (that is, a single or double layer), while 10 to 30 nm are considered to be intercalated (that is, several layers). There were very few thicker particles as images without agglomerates were chosen for analysis.

![TEM micrographs for selected samples: (a) Roller-3, (b) Roller-13, (c) Banbury-3, (d) Banbury-13, (e) Number of particles thickness on analyzed samples, and (f) Modulus – Number of Particles Correlation](image)

Figure 2. TEM micrographs for selected samples: (a) Roller-3, (b) Roller-13, (c) Banbury-3, (d) Banbury-13, (e) Number of particles thickness on analyzed samples, and (f) Modulus – Number of Particles Correlation

Figure 2 (a – d) presents TEM micrographs for nanocomposite samples Run 3 and 13, representing the highest modulus prepared by each rotor. All TEM micrographs indicate a hybrid structure with some exfoliated and intercalated structures with particle thicknesses ranging between 0 and 30 nm. The Banbury sample run 13 has a higher number of thinner particles than other samples (Fig. 2 (e)). It was produced at high shear and low diffusion settings (150 °C, 80 rpm, and 4 minutes). Interestingly, this setting produced the least number of thinner particles in the Roller sample run 13. For the Roller samples, the highest number of exfoliated particles was produced in run 3 (Roller-3) with medium shear and medium diffusion (180 °C, 80 rpm, and 10 minutes). This further suggests that different dispersion mechanisms occur when different rotors are used.

Further analysis on correlations between number of thin particles and modulus (Fig. 2 (f)) show better linearity for exfoliated particles (<10 nm) than intercalated (10 – 30 nm). This suggests that the modulus improvement is more influenced by exfoliated structures which depend on the rotor type and mechanisms during mixing.

4. Conclusions

Analysis on effect of processing variables on PE/Clay nanocomposites prepared in an internal mixer was done. Analysis on the effects of different rotor design and setting parameters on tensile modulus showed significant improvement on modulus with additional of 2 wt% clay. The results showed that samples
produced in an internal mixer using a Banbury rotor had higher improvement compared to a Roller rotor. The modulus improvement in Banbury samples was influenced by high shear (low temperature, high rpm), while in Roller was especially at medium shear conditions (medium temperature, medium rpm). The TEM results showed that the exfoliated and intercalated structures were found in the nanocomposite system produced using either Roller or Banbury rotor at selected conditions. The effect of exfoliated particle was more significant to improve the modulus than the intercalated particles. TEM analysis showed different mechanism needed to produce the exfoliated structures. Medium shear and medium diffusion were the best for Roller rotor, while high shear and low diffusion for Banbury that confirm results from modulus measurements.

5. Recommendation for Future Works
Process variables were focused on this research as formulations have been reported by many studies. However, to minimize the cost and environmental impact, both process and material composition are important. Hence further work on synergy between process and material composition to produce economic material but less environmental effect is recommended.

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