The Roles of Process Parameters on Structures and Mechanical Properties of Polypropylene/Clay Nanocomposites

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Abstract. Process parameters are crucial to produce targeted qualities in polypropylene (PP)/clay nanocomposites, due to their roles on the generation of shear and diffusion. Thus, this research aims to observe their effects on structures and properties of PP/clay nanocomposites. Samples were produced by mixing PP, PP grafting maleic anhydride (PP-g-MA), and Cloisite 20A at fixed compositions, 88/9/3 wt%, respectively, in an internal mixer with variations on temperatures (210, 220, 230 °C) and speeds (60, 80, 100 rpm). Effect of mixing parameters on nanocomposite structures and properties were investigated from XRD, SEM and flexural properties. The results showed that all samples had intercalated as well as agglomerated structures. Further analysis on XRD and SEM showed that samples produced at high conditions (230 °C or 100 rpm) had similar structures. In contrast, low setting sample (210 °C and 60 rpm), despite its similarity on dispersion level, had longer agglomerates than that of mixed at high settings. Correlated both increase of d-spacing and agglomerates length to flexural properties suggested that modulus was more influenced by dispersion level, while strength was affected by agglomerates. However, it was worth to note that improvement on d-spacing, with availability of long agglomerates might not guarantee modulus and strength improvement due to low interfacial bonding.

Keywords : Polypropylene, clay, internal mixer, XRD, SEM, flexural

1. Introduction
Polypropylene (PP) is widely applied to produce various applications as automotive, packaging, building component, etc. Due to its large applications, studies on enhancement properties of PP are still interesting field for many researchers. One possible technique that growth rapidly in the last two decades to improve PP properties as physical, mechanical, fire retardancy, and barrier is the addition of nanofiller as clay to PP matrix [1-5], due to its low loading. In order to mix this two different polarity materials, compatibilizer is needed [6, 7], and process parameters should also be considered as their contribution to disperse the fillers [8-11].

The processing parameters might provide shear, diffusion, and degradation mechanisms that influence clay exfoliation [12]. Our previous study on PP/clay nanocomposites showed that interaction
between temperature and mixing time was crucial to disperse nanoclay [13]. However, correlation between this interaction and structures and properties was still unclear. This study aimed to explore interaction effects of process temperatures and mixing speeds on clay dispersion and mechanical properties in Polypropylene matrix. Analysis on the role of mixing conditions was done according to flexural properties. The dispersion level was investigated from X-ray diffraction (XRD), while agglomerations were observed under Scanning Electron Microscopy (SEM).

2. Experimental method

2.1 Materials
Polypropylene (PP), 5169 MAS 2158 from PT. Politama Indonesia was used as matrix. It was PP with melt flow index (MFI) 1.8 g/10 min. Epolene Wax G 3015P, polypropylene-grafted-maleic anhydride (PP-g-MA), from Eastman Chemical Company was used as a compatibilizer. A commercial organophillic montmorillonite clay, Cloisite 20A (Southern Clay Product) was added as filler.

2.2 Nanocomposite preparations
Haake Rheomix 600 was used for mixing PP, PP-g-MA and clay according to process conditions presented in Table 1. All samples were produced at identical composition with 88% of PP, 9% of PP-g-MA, and 3% of clay to produce the best tensile strength [8]. Before mixing, overnight drying (80°C) was perform on clay to reduce its moisture. Nanocomposite specimens were prepared by compression molding (Collin P300P) with setting conditions shown in Table 2. Two steps of compression molding were applied to produce smooth surface as trials done in our lab.

Table 1. Setting Conditions used in an Internal Mixer.

| Samples | Temperature [°C] | Speed [rpm] | Time [min] |
|---------|-----------------|-------------|------------|
| Control | 220             | 80          | 10         |
| 1       | 210             | 60          | 10         |
| 2       | 210             | 100         | 10         |
| 3       | 220             | 80          | 10         |
| 4       | 220             | 80          | 10         |
| 5       | 220             | 80          | 10         |
| 6       | 230             | 60          | 10         |
| 7       | 230             | 100         | 10         |

Table 2. Setting Conditions used in Compression Molding.

| Parameters          | First Step | Second Step |
|---------------------|------------|-------------|
|                     | 1 2 3 4 5  | 1 2 3 4 5   |
| Temperature [°C]    | 205 205 205 205 40 | 205 0 195 0 40 |
| Pressure [Bar]      | 0 1 1 0 0 | 0 0 0 0 1   |
| Time [Min]          | 10 5 5 0 15 | 10 0 3 0 15 |

2.3 Characterizations
Flexural modulus and strength testing were performed using Shimadzu AGS 10 kN, Universal Testing Machine, according to ASTM D 790. Flexural speeds were calculating by considering samples thickness as stated in standard. The support span distance was set at 25.4 mm. At least five specimens were tested, and the average values were reported.

The structures of clay were observed from agglomeration analyzed using Scanning Electron Microscope (SEM) and d-spacing increase using X-Ray Diffraction (XRD). The agglomerations of clay
were observed to analyze the present of agglomerations in the mixtures using JEOL JSM-6510LA SEM with accelerated voltage of 15 kV. Measurement and analysis were done in 5 surface area of flexural sample number 1, 2, 6, and 7, with at least 1 measured agglomerate for each surface. Specimens were cooled with liquid nitrogen and cut. Specimens were sputter coated with Platinum to increase surface conductivity and reduce charging. The clay dispersions were analyzed using Simadzu X-Ray Diffractometer 7000 Maxima-X with Cu kα radiation. Analysis was performed at scan speed 2.4 deg/minute, λ = 1.54 A˚, 40 kV and 20mA. The intensity peak were integrated from 1° - 10° of 2 theta.

3. Results and discussions

3.1 Effects of processing parameters on flexural properties

Flexural modulus and strength of PP/clay nanocomposite samples are presented in Table 3. It is shown that the average modulus and strength increase about 12% and 6%, respectively, attributed to clay dispersion. However, despite the increase of flexural properties for most of samples, it is shown that there was one sample (sample 1, produced at low temperature and low rpm) experiencing decrease on both modulus and strength. These phenomena were also reported in another previous study [14]. The decrease might be produced by poor polymer - clay bonding due to availability of big agglomerates. These might be happened in case of very low generated shear applied to disperse the clay [15, 16] and very high polymer viscosity that difficult to penetrate clay galleries [17]. This suggested that setting combination between low temperature (210 °C) and low rpm (60 rpm) applied to mix sample 1 might not enough to disperse most of the clay in this nanocomposite system, and resulted in some big agglomerates.

### Table 3. Flexural modulus and strength of PP/clay nanocomposite samples.

| Sample | Temperatures [°C] | Speed [rpm] | Time [min] | Modulus [MPa] | Strength [MPa] |
|--------|-------------------|-------------|------------|---------------|---------------|
| Control | 220               | 80          | 10         | 1764 ± 86.0 (± 5%) | 49.15 ± 1.66 (± 3%) |
| 1      | 210               | 60          | 10         | 1512 ± 55.0 (± 4%) | 41.10 ± 2.05 (± 5%) |
| 2      | 210               | 100         | 10         | 1974 ± 131 (± 7%) | 53.20 ± 5.65 (± 11%) |
| 3      | 220               | 80          | 10         | 2090 ± 158 (± 8%) | 55.14 ± 1.13 (± 2%) |
| 4      | 220               | 80          | 10         | 2113 ± 205 (± 10%) | 56.46 ± 2.59 (± 5%) |
| 5      | 220               | 80          | 10         | 2084 ± 184 (± 9%) | 57.33 ± 2.60 (± 5%) |
| 6      | 230               | 60          | 10         | 2119 ± 57.0 (± 3%) | 50.70 ± 6.42 (± 13%) |
| 7      | 230               | 100         | 10         | 2169 ± 105 (± 5%) | 52.90 ± 7.89 (± 15%) |

Average all nanocomposites 1978 ± 123 (± 6%) 52.00 ± 3.75 (± 7%)
Average of mid setting 2096 ± 182 (± 9%) 56.31 ± 2.11 (± 4%)

![Figure 1. Effect of mixing speeds on flexural modulus and strength.](image1)

![Figure 2. Effect of mixing temperatures on flexural modulus and strength.](image2)
Figure 1 and 2 show the effects of processing parameters on flexural properties. In general, both modulus and strength increased as the higher settings. These improvements were clearly obtained especially at higher setting (either mixing speed (Figure 1) or temperatures (Figure 2)) when the other parameter was set at low condition. At low temperature and low mixing speed, polymer viscosity is still high so it difficult to penetrate the interlayer galleries. At the same time, low mixing speed might unable to disperse clay agglomerates effectively. Combination these two conditions resulted in low modulus and strength. In contrast, at low temperature, higher mixing speed generated higher shear that able to disperse the clay and improve modulus and strength. However, there were slight improvements at higher mixing speed when temperature was set at high setting, and vice versa. This suggested that the effect of shear and diffusion in these boundaries might not significant change flexural properties due to competing mechanisms between shear and diffusion that work simultaneously.

3.2 Effects of processing parameters on nanocomposite structures

The structures of PP/Clay nanocomposites are presented in Figures 3 to 7. In general, all nanocomposite samples have nanostructures as well as agglomerated structures. Nanostructures were observed from peaks shifted to lower angle compared to clay peak on XRD diffractogram, while agglomerated were analyzed from the length and width of microstructures available on SEM micrographs.

Figure 3 shown that all samples have peaks at lower degree suggested intercalated of some clay structures. The best improvement on the increase of interlayer spacing was obtained by samples 6 and 7 produced at high temperature (230 °C) and either at low or high mixing speed. The peaks were shifted from 3.26° represented 2.71 nm of d-spacing to 2.34° represented 3.77 nm of inter-gallery distance. The increase of intergallery spacing from 2.71 nm to 3.77 nm suggests that the nanocomposites structure is available on sample 6 and 7. In contrast, the lowest increase was produced by sample 1 prepared at low temperature and low mixing speed (210 °C and 60 rpm) that increase from 2.71 nm to 3.39 nm, and also suggests nanocomposite structures. However, this did not support to negative results of modulus and strength. So it was hypothesized that there were both nanostructures and agglomerates available on the system and competing each other. For this reason, further analysis on the size of agglomerates were done using SEM.
Figures 4 and 5 show selected surface area of microstructures available on each observed samples and agglomerate size. The length of microstructures ranges from 1.6 to 6.9 µm, while the width varies from 1.0 to 3.8 µm. The smaller agglomerates were available in samples 2 and 7 those were produced at high mixing speed. On the contrary, the bigger agglomerates found at low mixing speed samples (Sample 1 and 6). The size even more than twice for sample 1 (low mixing speed, low temperature) compare to another samples, attributed to limited shear in the process. This data explains the reason behind the decrease on modulus and strength for this sample compare to control, despite the
improvement on d-spacing. This finding also suggests that there is minimum ratio between level of dispersion and agglomerate size to improve both modulus and strength that is not covered in this research. For this reason, it is suggested that further experiment should be done in the future.

Combination analysis on XRD and SEM suggested that high dispersion level and small agglomerates can be achieved if there was minimum one parameter that be set at high condition (temperature or rpm). The fact that the high dispersion level was produced at high temperature or rpm, and small agglomerates were available on high rpm samples, suggested that there was synergism between shear and diffusion in order to produced desired nanostructures. The results of this research show that the shear is crucial to break the agglomerates, however this mechanism would not go further if there was no diffusion mechanism that runs simultaneously and need optimum viscosity to work.

3.3 Effects of nanocomposite structures on mechanical properties

![Figure 6. Effect of interlayer spacing increases on flexural modulus and strength.](image)

![Figure 7. Effect of agglomerate sizes on flexural modulus and strength.](image)

Structures and mechanical property of PP/clay nanocomposites are shown in Figure 6 and 7. In general, the increase on d-spacing and reduction on agglomerate length would improve modulus and strength. This is caused by the increase on aspect ratio that improves interfacial bonding between matrix and fillers. From the figures, it is also suggested that the d-spacing increase (Figure 6) has more influence to modulus ($R^2 = 0.88$) than to strength ($R^2 = 0.61$). In contrast, the reduction of agglomeration sizes (Figure 7) has more contribution to strength ($R^2 = 0.99$) than to modulus ($R^2 = 0.87$).

4. Conclusion

The roles of mixing conditions on structures and flexural properties of PP/clay nanocomposites have been explored. The samples were produced using an internal mixer with temperatures (210, 220, 230 °C) and mixing speeds (60, 80, 100 rpm) variations, and fixed composition. The structural of nanocomposites were investigated from XRD diffractograms and SEM micrograms, while mechanical properties were represented by flexural test.

The results showed that the average flexural modulus and strength of all nanocomposite samples increased by adding nanoclay on PP. These increases were influenced by the combination of intercalated structure and small agglomerate size. The samples produced at high conditions (230 °C or 100 rpm) had similar intercalated and agglomerate structures. On the other hand, bigger microstructures were found in the sample produced at low settings (210 °C and 60 rpm), despite its similarity on dispersion level. Analysis on structures and flexural property relationship shows that the intercalated structures have more contribution on modulus improvement, while agglomerates size contributes to strength. The findings of this research also suggest that the improvement on d-spacing might not successfully increase modulus and strength, if huge microstructures presents on the system.
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