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To cite this article: A. Chafidz *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **543** 012036

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Melt Rheological Properties of Polypropylene/Clay Nanocomposites Prepared from Masterbatch: Effect of Nanoclay Loadings and Reprocessing

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Abstract. In the present work, polypropylene (PP) and nanoclay in the form of masterbatch were melt compounded using a co-rotating twin screw extruder to fabricate polypropylene (PP)/clay nanocomposites. PP/clay nanocomposites samples with four different nanoclay loadings (i.e. 0, 5, 10, and 15 wt%) were prepared. Additionally, to study the effect of reprocessing on the properties of the nanocomposites, the melt compounding process was carried twice/recycle (i.e. 1st cycle and 2nd cycle). The surface morphological of the nanocomposites and their melt rheological behavior were investigated using a Scanning Electron Microscopy (SEM) and an oscillatory rheometer, respectively. The SEM micrographs showed that the nanoclay was well distributed in the polypropylene matrix for both 1st and 2nd cycles. While, the dispersion state of the nanoclay (either intercalated or exfoliated) could not be observed due to the limitation of the apparatus. Additionally, the melt rheological analysis results showed that the complex viscosity, $|\mu^*|$ of all nanocomposites samples (for both 1st and 2nd cycles) were higher than the neat PP and the $|\mu^*|$ also increased with the increase of nanoclay loadings. However, the 2nd cycle showed a slightly higher improvement of $|\mu^*|$ compared to the 1st cycle, and the improvement of $|\mu^*|$ was more prominent at lower angular frequencies (e.g. 0.1, 1, 10 rad/s) than at higher ones (e.g. 100, 500 rad/s).

1. Introduction

Nanotechnology has become a new trend of research in the world, which could solve problems of the world (e.g. energy, water, food, etc.), and thus affect the economies and societies of the world over the next decades. One of nanotechnology application is polymer nanocomposite (PNC). It is a relatively new class of composites materials that consist of nano-size materials incorporated in polymer matrix [1]. The PNCs have been widely investigated and developed for many applications in the last two decades [2, 3]. It was due to their improved mechanical (e.g. tensile modulus and strength), thermal stability, reduced gas permeability and flammability, etc. as compared to their conventional composites materials [4]. Among the various nanomaterials used for the preparation of nanocomposites, two of the widely investigated nanomaterials are carbon nanotubes (CNTs) and nanoclay or layered silicates, which are one- and two- dimensional nanomaterials, and therefore have a large aspect ratio [5]. The focus of the current work is the nanoclay materials, which has been found to be effective reinforcing nanomaterials due to their availability, economic competitiveness, high aspect ratio, low density, lamellar structure, high specific surface area, etc [6, 7]. Among various types of clay, montmorillonite



(MMT) type of clay has been extensively used in the fabrication of clay based polymer nanocomposites. The aspect ratio of the MMT clay approximately one nm thick and hundreds nm long [2].

Polypropylene (PP) is one of most important and widely used thermoplastic polymers for the production of versatile products in many applications, e.g. automotive, electronics, packaging, etc. It is due to its good mechanical properties, low density and cost, good processability and recyclability [4]. Therefore, fabrication of PP/clay nanocomposites has become an interesting topic of research. The work on these nanocomposites was first started at Toyota Research Laboratory, and until now, the studies about these nanocomposites have been carried out by many researchers [2]. In general, there are three methods to fabricate polymer nanocomposites, which are in-situ polymerization, solution intercalation, and melt compounding/blending [3, 4, 8]. The later one is the most favored and used method to fabricate polymer nanocomposites. It is because this method is simple, use no-solvent, and thus low cost and environmentally friendly. Moreover, this method is very compatible and suitable with existing industrial processes, such as extrusion and injection molding, and thus make the nanocomposites easy to be commercialized [3, 4].

Recently, the use of masterbatch has become an attractive alternative method to produce polymer nanocomposites via melt compounding compared with the use of bulk nanomaterials. Because, this method is a dust free, thus it has low health and safety risks compared to the use of bulk nanomaterials, as well as easy to handle. Additionally, the use of this method could eliminate the dispersion and formulation difficulties [5, 8]. Nevertheless, the number of literatures that studied the use of nanoclay based masterbatch to produce PP/clay nanocomposites were still limited, and thus it becomes an interesting topic of research. In the current work, PP/clay nanocomposites has been fabricated via melt compounding method using a commercial nanoclay based masterbatch. The prepared nanocomposites were characterized for their morphological and melt rheological properties. The objectives of this work was to effect of nanoclay loadings and reprocessing on the morphological and rheological properties of the prepared nanocomposites.

2. Experimental

2.1. Materials and nanocomposites fabrication

PP/clay nanocomposites were fabricated by melt compounding nanoclay masterbatch pellets (concentration of 50 wt% of nanoclay) with polypropylene (PP) pellets. The masterbatch (product name: NanoMax) was obtained from Nanocor, USA. Whereas, the PP (product name: PP570, MFI 8 g/10 min) was obtained from SABIC, Saudi Arabia. Based on the information provided by the supplier, the nanoclay material is organophilic montmorillonite (MMT) or organoclay, which has been modified with dimethyl-dihydrogenated tallow ammonium. The polymer carrier is PP, which has also been compatibilized with maleic anhydride (MA). The melt compounding process was done in a co-rotating twin screw extruder (TSE). Details about the extruder, preparation step, and processing conditions have been explained in our previous work [4]. The melt compounding process was carried out twice. The first melt compounding process was called 1st cycle, and the pellets obtained from the 1st cycle was then recycled/reprocessed again using the same procedure to get the 2nd cycle nanocomposites pellets. The nanocomposites obtained from the 1st cycle were referred to as NC-0-I, NC-5-I, NC-10-I, and NC-15-I for nanoclay loadings of 0, 5, 10, and 15 wt%, respectively. Whereas, the nanocomposites obtained from the 2nd cycle were referred to as NC-0-II, NC-5-II, NC-10-II, and NC-15-II. Afterward, all the nanocomposites pellets (i.e. 1st and 2nd cycle) from the extruder were molded into a set of ASTM standard samples for testing by using an injection molding machine. Details of the injection molding machine and processing conditions have been mentioned in our previous work [4].

2.2. Sample characterization

Morphological characterization is carried out by utilizing a Scanning Electron Microscopy (SEM). The SEM used in this work is a JEOL JSM-6360A, Japan. Molded bar samples were cryogenically-fractured

prior to SEM examination. To examine using SEM, first the fractured samples were finely coated with a gold. The coating can minimize the overcharging and overheating of the samples, and also can improve the signal as well as the surface resolution. All the samples were analyzed by the SEM at voltage of 15 kV. Additionally, an oscillatory rheometer instrument model AR G2 (TA Instruments, USA) was used to investigate the effect of nanoclay loadings and reprocessing on the melt rheological characteristic of the PP/clay nanocomposites. All the rheological analyses were done using frequency sweep procedure with parallel plates fixture (dia. 25 mm and gap 2 mm). The following test conditions were used: constant temperature of 260°C; oscillation stress of 500 Pa; angular frequency range of 0.1 - 628.3 rad/s. The samples used for this test were disk-disk like sample from the injection molding machine. Prior to the test, the sample was conditioned first at constant temperature of 260°C until the samples were completely melted. Afterward, the excess of the molten nanocomposites samples around the parallel plates was cleaned to ensure the validity of the analysis. One of the data generated and studied in the current work was complex viscosity $|\mu^*|$ vs angular frequency (ω). Figure 1 shows a photograph of an oscillatory rheometer with a parallel plates geometry. As seen in the figure, the excess of the molten nanocomposites samples is cleaned prior to the melt rheological test.

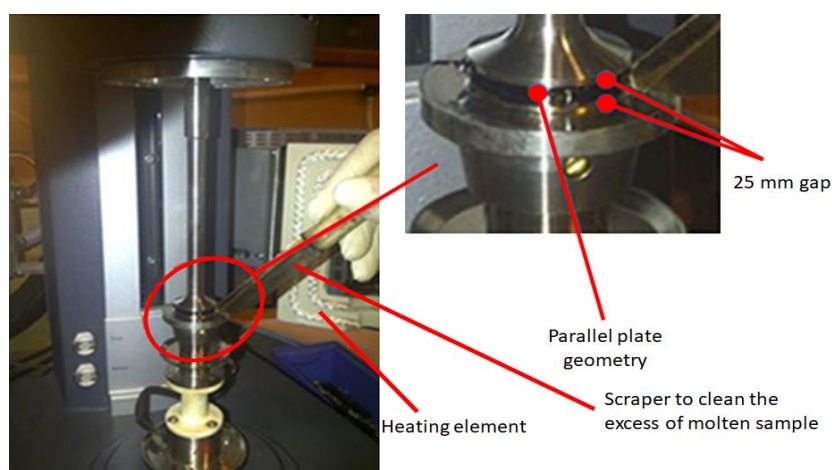


Figure 1. Photo of an oscillatory rheometer with a parallel plate fixture. (During cleaning proses of the excess molten sample prior to the frequency sweep test

3. Results and discussion

The surface morphology of the PP/clay nanocomposites samples for both 1st and 2nd cycle are shown by scanning electron microscopy (SEM) images depicted in Figures 2a-b and Figures 2c-d, respectively. The distribution of nanoclay platelets in the PP matrix could be analyzed by observing the SEM images. The SEM images shown in Figure 2 were only for nanocomposites samples with nanoclay loading of 5 wt%, i.e. NC-5-I (1st cycle) and NC-5-II (2nd cycle). In general, the nanoclay platelets were showed by the white needle-like in the dark area of PP matrix (as shown by the arrows). This has been confirmed by an EDX analysis of the SEM, which has been reported in our previous work [9]. As seen in Figure 2a (SEM magnification of 2,000X), the nanoclay platelets of the 1st cycle were fairly well distributed in the PP matrix. This distribution of nanoclay platelets were looked more clear at higher SEM magnification, i.e. 10,000X (see Figure 2b).

Whereas, for the nanocomposites 2n cycle, the distribution of nanoclay platelets in the PP matrix were quite better than that of the 1st cycle, which can be observed in Figures 2c and 2d. This results could be attributed to the fact that during the recycle or melt compounding of PP/clay nanocomposites (1st cycle), the nanoclay platelets that already distributed in the PP matrix were redistributed again by the shear stress induced by the twin screw extruder, and thus became much better distributed than the 1st cycle. Nevertheless, the dispersion state of the nanoclay (either intercalated or exfoliated) could not be

observed in these SEM images. To further study the dispersion state of the nanoclay, better microscopy technique such as Transmission Electron Microscopy (TEM) or Atomic Force Microscopy (AFM) are needed. Additionally, for the rest of the nanocomposites samples, i.e. NC-0, NC-10, and NC-15 for both 1st and 2nd cycle also showed the similar trend, but they were not presented in this paper.

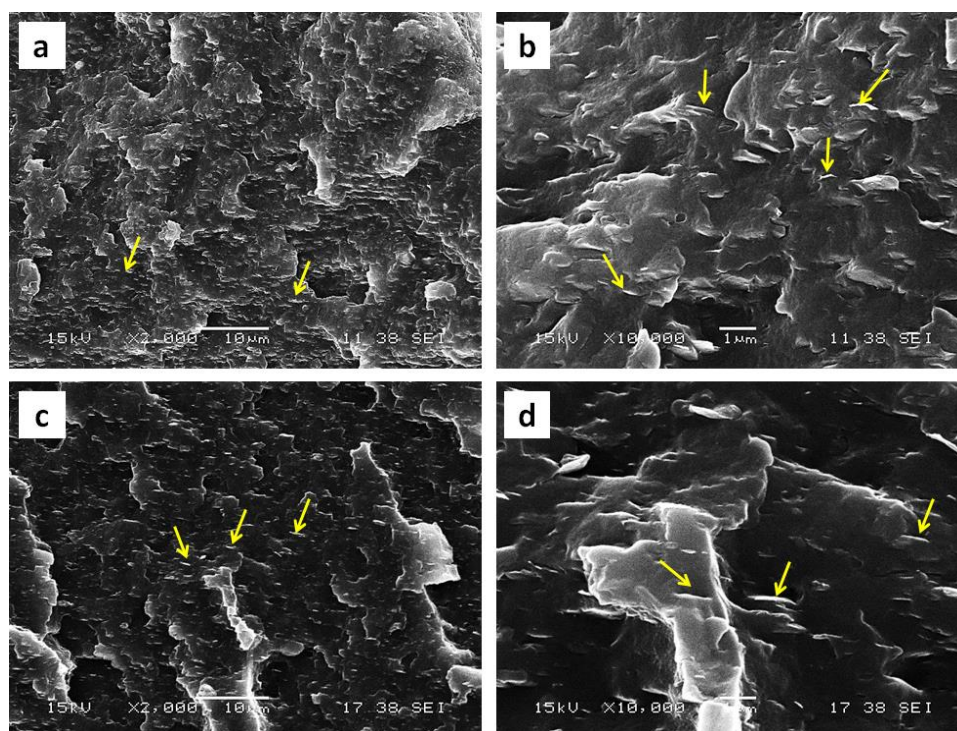


Figure 2. SEM micrographs of a) NC-5-I (2,000X); b) NC-5-I (10,000X); c) NC-5-II (2,000X); and d) NC-5-II (10,000X)

Additionally, the melt rheological analysis of the PP/clay nanocomposites for both 1st and 2nd cycle samples were also carried out using an oscillatory rheometer instrument. The melt rheological analysis results were presented as the plot of complex viscosity, $|\eta^*|$ vs angular frequency (ω), as shown in Figure 3. As seen in the figure, the nanocomposites 1st cycle and 2nd cycle have similar trends. As seen in the figure, the complex viscosity of the nanocomposites for both cycles increased with increasing nanoclay loadings at all angular frequencies. This indicates that the incorporation of nanoclay in the PP matrix has enhanced the complex viscosity of the nanocomposites [10]. This improvement of the $|\eta^*|$ was likely due to the interaction of nanoclay platelets with the PP matrix that restricted the mobility of the molten PP chains. The higher the nanoclay loadings, the more hindered mobility of the molecular PP chains, and the higher the $|\eta^*|$ values. Additionally, it was also in accordance with the literature's reports, which mentioned that the distribution and dispersion of nano-materials in the polymer matrix could affect the melt rheological behavior of the nanocomposites [5, 11]. The better the distribution and dispersion of the nano-materials, the better the interaction between the nano-materials and the polymer matrix. Therefore, the $|\eta^*|$ of the 2nd cycle (indicated by solid lines) was slightly higher than that of the 1st cycle (indicated by symbols). It was likely due to the better distribution of the nanoclay in the PP matrix compared to the 1st cycle.

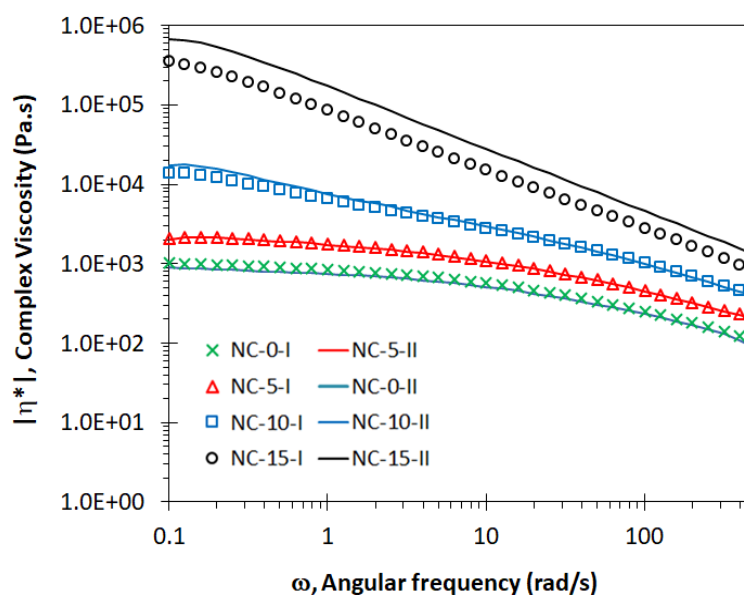


Figure 3. The plot of complex viscosity $|\eta^*|$ vs angular frequency (ω) for PP/clay nanocomposites at different nanoclay loadings for 1st cycle (symbols) and 2nd cycle (lines)

Furthermore, to observe effect of nanoclay loadings and reprocessing on the melt rheological characteristics of the nanocomposites, several representative complex viscosities of PP/clay nanocomposites (1st cycle and 2nd cycle) are listed in Table 1 and also plotted in Figure 4. As seen in the table and figure, the $|\eta^*|$ of both nanocomposites (1st and 2nd cycle) were all higher than the neat PP, and increased with the increasing nanoclay loadings. Additionally, as mentioned in the previous paragraph, the nanocomposites 2nd cycle showed a slightly higher improvement of $|\eta^*|$ compared to the 1st cycle. Additionally, as seen in Table 1 and Figure 4, the improvement of $|\eta^*|$ was more prominent at lower angular frequencies (e.g. 0.1, 1, 10 rad/s) than at higher ones (e.g. 100, 500 rad/s). For example, at angular frequency of 0.1 rad/s, for the PP/clay nanocomposites 1st cycle, the increases of complex viscosity compared to the neat PP (i.e. NC-0-I) were about 101.38%; 1255.77%; and 34,423.23% for NC-5-I; NC-10-I; and NC-15-I, respectively. Whereas, at angular frequency of 500 rad/s, for the PP/clay nanocomposites 1st cycle, the increases of complex viscosity compared to the neat PP (i.e. NC-0-I) were about 97.34%; 292.49%; and 626.59% for NC-5-I; NC-10-I; and NC-15-I, respectively.

Table 1. Representative complex viscosity of PP/clay nanocomposites (1st cycle and 2nd cycle)

Ang. Freq. (rad/s)	PP/clay nanocomposites - 1 st cycle				PP/clay nanocomposites - 2 nd cycle			
	NC-0-I	NC-5-I	NC-10-I	NC-15-I	NC-0-II	NC-5-II	NC-10-II	NC-15-II
0.1	1022.5	2059.1	13862.7	353000.0	895.5	2007.8	17045.0	666000.0
1	846.7	1778.0	6499.7	85060.5	746.2	1739.1	7547.2	172000.0
10	567.4	1101.4	2811.3	15000.8	512.3	1071.2	2936.4	27733.3
100	250.5	458.3	1027.5	2787.0	232.5	448.1	1001.4	4585.4
500	105.3	207.8	413.3	765.1	87.5	202.5	408.8	1270.7

The similar results also found for the PP/clay nanocomposites 2nd cycle. For example, at angular frequency of 0.1 rad/s, the increases of complex viscosity compared to the neat PP (i.e. NC-0-II) were about 124.21%; 1803.41%; and 74,271.86% for NC-5-II; NC-10-II; and NC-15-II, respectively. Whereas, at angular frequency of 500 rad/s, for the PP/clay nanocomposites 2nd cycle, the increases of complex viscosity compared to the neat PP (i.e. NC-0-II) were about 131.43%; 367.2%; and 1352.23% for NC-5-II; NC-10-II; and NC-15-II, respectively. As seen from the results, at low angular frequencies,

the presence of nanoclay platelets on the melt rheological properties of the nanocomposites was more prominent. The interaction between the matrix and the nanoclay resulted in considerable improvement of complex viscosity of the nanocomposites. Whereas, at higher angular frequencies, the nanoclay layers have oriented due to the shear induced by the rheometer apparatus, thus the effect of interaction between the matrix and the nanoclay on the complex viscosity of the nanocomposites was much lower.

Additionally, as seen in Figure 4, the $|\eta^*|$ of the 2nd cycle (indicated by dashed lines) was higher than that of the 1st cycle (indicated by solid lines). The differences of $|\eta^*|$ were more prominent at higher nanoclay loading (e.g. 15 wt%) than at neat PP (i.e. 0 wt%) and at lower nanoclay loadings (e.g. 5, 10 wt%). Whereas, the effect of angular frequencies on the differences of $|\eta^*|$ between 1st and 2nd cycles for all nanoclay loadings was not significant. As seen in Table 1 and Figure 4, the differences of $|\eta^*|$ between 1st and 2nd cycles at 15 wt% of nanoclay loading (i.e. NC-15-I vs NC-15-II) were about 313,000; 86,939; 12,732; 1798; and 505 Pa.s for angular frequencies of 0.1; 1; 10; 100; and 500 rad/s, respectively.

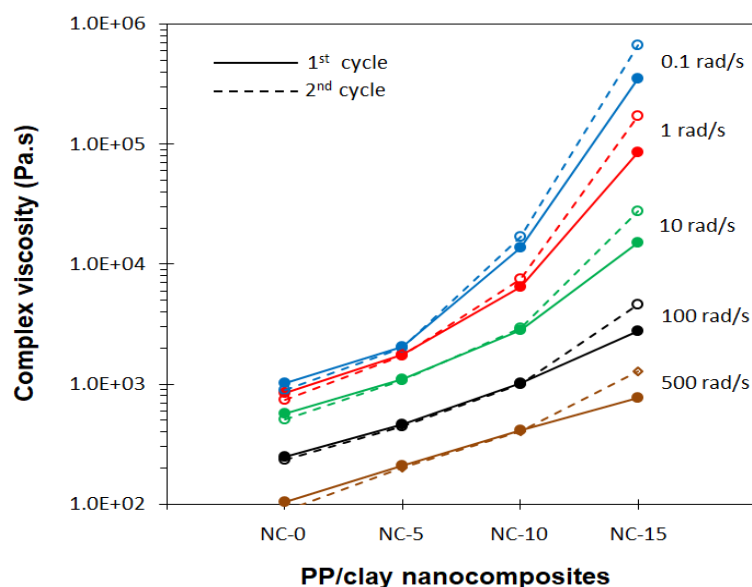


Figure 4. The plot of representative complex viscosity $|\eta^*|$ at several angular frequencies (ω) for PP/clay nanocomposites at different nanoclay loadings for 1st cycle (solid lines) and 2nd cycle (dashed lines)

4. Conclusion

The effects of nanoclay loadings and reprocessing on the morphology and melt rheological properties of the PP/clay nanocomposites have been investigated. In order to study the reprocessing effect on the properties of PP-nanoclay composites, melt compounding was carried out twice/recycle (i.e. 1st cycle and 2nd cycle). Morphological study on the nanocomposites revealed that all the nanocomposites samples (both 1st cycle and 2nd cycle) showed good distribution of nanoclay platelets in PP matrix at all nanoclay loadings. In melt rheological behavior, all the nanocomposites samples for both 1st cycle and 2nd cycle exhibited higher complex viscosity than the neat PP. The complex viscosity of the nanocomposites increased with increasing nanoclay loadings at all angular frequencies. However, the improvement of $|\eta^*|$ was more prominent at lower angular frequencies (e.g. 0.1, 1, 10 rad/s) than at higher ones (e.g. 100, 500 rad/s). For example, at angular frequency of 0.1 rad/s, for the PP/clay nanocomposites 1st cycle, the increases of complex viscosity compared to the neat PP (i.e. NC-0-I) were about 101.38%; 1255.77%; and 34,423.23% for NC-5-I; NC-10-I; and NC-15-I, respectively. Whereas, at angular frequency of 500 rad/s, for the PP/clay nanocomposites 1st cycle, the increases of complex viscosity compared to the neat PP (i.e. NC-0-I) were about 97.34%; 292.49%; and 626.59% for NC-5-

I; NC-10-I; and NC-15-I, respectively. Additionally, the 2nd cycle showed a slightly higher improvement of $|\eta^*|$ compared to the 1st cycle. The differences of $|\eta^*|$ were more prominent at higher nanoclay loading (e.g. 15 wt%) than at neat PP (i.e. 0 wt%) and at lower nanoclay loadings (e.g. 5, 10 wt%). Whereas, the effect of angular frequencies on the differences of $|\eta^*|$ between 1st and 2nd cycles for all nanoclay loadings was not significant.

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