Effect of nanoclay loadings and reprocessing on dynamic mechanical thermal properties of polypropylene/nanoclay composites

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Abstract. In the present work, polypropylene (PP)/nanoclay composites were fabricated by melt compounding nanoclay based masterbatch and PP pellets using a twin screw extruder (TSE). The compounding process was carried out at four different nanoclay loadings (i.e. 0, 5, 10, and 15 wt%) and two times processing i.e. 1st cycle and 2nd cycle. The fabricated nanocomposites were then characterized by using Scanning Electron Microscopy (SEM) and oscillatory rheometer. The SEM images showed that the nanoclay materials were well distributed in the PP matrix, which were indicated by the white needle-like appearance. Additionally, the dynamic mechanical thermal analysis (DMTA) results showed that the storage modulus of all the nanocomposites both 1st and 2nd cycles were higher than that of the neat PP, and increased with increasing nanoclay loadings. The improvement of storage modulus of the nanocomposites as compared to the neat PP (at temperature of 60°C) were approximately 56%, 84.3%, and 138% for NC-5-I, NC-10-I, and NC-15-I, respectively; and 62%, 89.6%, and 128% for NC-5-II, NC-10-II, and NC-15-II, respectively. While, storage modulus of all samples decreased with increasing temperature, which indicates than the nanocomposites simply behaved as polymeric material. Additionally, the relationship between the storage modulus, nanoclay loading (wt%), and temperature (°C) was successfully modeled by using Equation (1): \( G' = A e^{B(T)} \) and Equation (2): \( A = 4.91E7 \times (\text{wt%}) + 7.47E8 \), while B constant value was -0.0221.

1. Introduction

In recent years, many researchers have been interested in studying polymer nanocomposites (PNCs) due to the enhanced properties of the nanocomposites, e.g. strength or modulus, thermal stability, electrical conductivity, fire retardancy, gas barrier, etc [1]. In the last two decades, the applications of PNCs have also been significantly developed [2]. Nano-sized materials or nanomaterials can be classified (based on the dimensions) into 3D-nanoparticles, 2D-nanotubes, and 1D-nanolayers. The 3d-nanoparticles mean that the nanomaterials have three dimensions in nano-scale range, such as nano-SiO\(_2\), Nano-CaCO\(_3\), nanosilver, etc. On the other hand, 2D-nanotubes have two dimensions in nano-scale range, such as carbon nanotubes.
(CNTs) and whiskers. The different between CNTs and whiskers is that CNTs are hollowed materials, while whiskers are filled materials. Whereas, the 1D-nanolayers are having only one dimension in nano-scale range and thus have high aspect ratio, such as nanoclay or layered silicates [3, 4]. Currently, nanoclay or layered silicates are the most widely used commercial nanomaterials and about 70% of the total market. The type of nanoclay that is mostly used to prepare polymer nanocomposites is montmorillonite (MMT) [4, 5].

In general, there are three major methods used to fabricate polymer nanocomposites, namely solution casting, in situ polymerization, and melt compounding/blending. The latter one is the one that most frequently used to fabricate polymer nanocomposites, due to its simplicity, low operational cost, and environmentally friendly. Moreover, this method is very suitable to be applied in industrial processes (e.g. extrusion and injection molding), and thus very suitable to be applied for large scale production of polymer nanocomposites [1]. In recent years, nanomaterials masterbatches have been widely commercialized. Materbatch is a polymer filled with nanomaterials at high concentration (50-80 wt%). Utilizing commercial masterbatch becomes an interesting alternative to fabricate polymer nanocomposites due to its simplicity (easy to handle), dust free (less health/safety risks), and economical method. The studies about polypropylene/nanoclay composites have been reported in numerous literatures [6-8]. Nevertheless, the studies of PP/nanoclay composites prepared by masterbatch are still limited, and thus becomes an interesting topic of research. Therefore, the objectives of this work are to prepare polypropylene/nanoclay composites using masterbatch via melt compounding method and study the effects of nanoclay loading and reprocessing on the surface morphology and dynamic mechanical thermal properties of the nanocomposites.

2. Experimental

2.1. Materials and preparation of PP/nanoclay composites

In this work, polypropylene (PP)/nanoclay composites have been prepared by melt blending the nanoclay masterbatch with PP pellets by using a co-rotating twin screw extruder (TSE). The nanoclay masterbatch (50 wt% of nanoclay loading) with product name: NanoMax was purchased from Nanocor (USA). Based on the supplier’s datasheet, the nanoclay material is an organophillic montmorillonite (MMT) type of clay or also known as organoclay. Additionally, according to supplier’s datasheet, the nanoclay has been modified by dimethyl-dihydrogenated tallow ammonium and the polymer carrier is PP. Whereas, the PP pellets with product name: PP570 were purchased from SABIC, Saudi Arabia. It is believed that the PP has been modified or compatibilized using maleic anhydride (MA). Figures 1a and 1b show the photographs of the nanoclay masterbatch and PP pellets, respectively.

Figure 1. Photographs of a) nanoclay masterbatch, and b) polypropylene (PP) pellets
2.2. Sample characterization

The prepared PP/nanoclay composites samples were characterized to study the effects of nanoclay loading (i.e. 0, 5, 10, 15 wt%) and reprocessing (1st and 2nd cycles) on surface morphology and dynamic mechanical thermal properties of the nanocomposites. The surface morphology of the nanocomposites was characterized by using a Scanning Electron Microscopy (SEM) JSM-6360A (JEOL, Japan). Prior to SEM characterization, the nanocomposites sample was cryo-fractured to maintain their structure originality by immersing the samples in a liquid nitrogen. The cryo-fractured samples were then finely coated by a thin layer of gold. The samples used for SEM characterization were nanocomposites with nanoclay loading of 15 wt% for both 1st cycle and 2nd cycle. The SEM analysis was carried out at 15kV voltage and magnification of 2,000X and 10,000X. Whereas, the dynamic mechanical thermal analysis (DMTA) was carried out by employing an oscillatory rheometer, AR-G2 (TA Instruments, USA). DMTA was performed to study viscoelastic properties of the nanocomposites at given range of temperatures. The DMTA was carried out using a rectangular fixture/geometry. The nanocomposites samples used for this DMTA were standard bar samples obtained from the injection molding machine with the dimensions of approximately 63.5 mm x 3.25 mm x 12.7 mm. The DMTA was performed under temperature sweep procedure with setting parameters, as follow: Range of temperature 30 - 160°C (increment of 3°C); constant angular frequency (ω) of 1 rad/s; and strain of 1%. This strain value was in the range of linear viscoelasticity region of the neat PP and its nanocomposites. The data generated from DMTA was a plot of storage modulus ($G'$) versus temperature. Figure 2 shows the photograph of the AR-G2 rheometer.

![Figure 2. Photo of an oscillatory rheometer with a rectangular fixture.](image)

3. Results and discussion

To investigate the surface morphology of the PP/nanoclay composites, a Scanning Electron Microscopy (SEM) analysis was conducted on nanocomposites samples of NC-15-I (1st cycle) and NC-15-II (2nd cycle) at magnifications of 2,000X and 10,000X. The SEM analysis results of these nanocomposites samples are depicted in Figures 3a-3d. As shown in Figures 3a and 3c (SEM magnification of 2,000X), the nanoclay materials (indicated by white needle-like) were well distributed in the PP matrix (indicated by dark area). This distribution was more clear in Figures 3b and 3c (SEM magnification of 10,000X). In Figure 3b and
3c, the nanoclay materials are indicated by the arrows. The good distribution of nanoclay materials in the PP matrix was the result of good processing from the twin screw extruder (TSE). Shear stress induced by the TSE was able to distribute nanoclay materials and blending them with molten PP matrix. The use of masterbatch was also helping in the good distribution of the nanoclay materials. Nevertheless, the dispersion states of the nanoclay materials, either exfoliated or intercalated were not observable in the SEM images due to the limitation of the SEM apparatus. A higher microscopy technique such as Transmission Electron Microscopy (TEM) should be used to study the dispersion levels of the nanoclay materials. This will be a good suggestion for the future study. Additionally, the effect of reprocessing (2nd cycle) on the surface morphology of the nanocomposites sample was not clear, since both 1st cycle and 2nd cycle gave similar SEM images. This indicates that at the 1st cycle the distribution of nanoclay materials was already good, and the reprocessing or re-compounding of the nanocomposites did not significantly affect the distribution level of the nanoclay materials. Additionally, the SEM images of other nanocomposites samples (i.e. NC-5-I and NC-5-II) also exhibited the similar trend, but they were not presented in this paper.

Figure 3. SEM micrographs of a) NC-15-I (2,000X); b) NC-15-I (10,000X); c) NC-15-II (2,000X); and d) NC-15-II (10,000X)

Additionally, dynamic mechanical thermal analysis (DMTA) was also carried out in this work to investigate the effects of nanoclay loadings (i.e. 0, 5, 10, 15 wt%) and reprocessing (1st cycle and 2nd cycle) on the viscoelastic properties or behaviour of the nanocomposites samples at given range of temperatures (i.e. 30-160°C). Figure 4 shows the plot of storage modulus ($G'$) as function of temperatures for PP/nanoclay
composites at different nanoclay loadings for 1st cycle and 2nd cycle. As shown in Figure 4, the storage modulus of all the nanocomposites samples were higher than the storage modulus of neat PP, and also increased with increasing nanoclay loadings. This increase of storage modulus was likely due to the restricted molecular mobility of the PP chains by the presence of the nanoclay materials and interfacial interaction between the PP chains and the nanoclay materials. The compatibilization of PP by maleic anhydride and modification of nanoclay by dimethyl-dihydrogenated tallow ammonium have strongly affected the interaction between both of them. Furthermore, the higher the nanoclay loadings the more interaction area between PP and nanoclay, and thus resulted in the increase of storage modulus of the nanocomposites [8, 9]. This similar trends were also reported by other researchers [7, 8]. Additionally, as observed in Figure 4, all the nanocomposites samples exhibited the similar trend, which was storage modulus of all the samples decreased with increasing temperature. This phenomena indicates that the PP/nanoclay composites simply behaved as polymeric materials which display decrease in stiffness with increasing temperature. This phenomena was likely attributed to the less hindered molecular mobility of the PP chains at higher temperature. It is because at high temperature polymer chains are easier to flow or move. Nevertheless, there was no significant difference in storage modulus between the nanocomposites samples of 1st cycle and 2nd cycle. The storage modulus values of both cycles were overlapping one to another. The storage modulus of 1st cycle was indicated by symbols, while the 2nd cycle was indicated by solid lines. This result was in accordance with surface morphological analysis result, in which the distribution level of the nanoclay was similar between the 1st cycle and 2nd cycle. It is known that the distribution and dispersion levels of the nanocomposites are playing important role on the properties of nanocomposites.

![Figure 4](image.png)

**Figure 4.** The plot of storage modulus ($G'$) as function of temperatures for PP/nanoclay composites at different nanoclay loadings for 1st cycle (symbols) and 2nd cycle (lines)

Additionally, to further observe the significant effect of nanoclay loading and reprocessing on the dynamic mechanical properties of the nanocomposites, several representative storage modulus of the
nanocomposites (for both 1st and 2nd cycle) are listed in Table 1 and also plotted in Figure 5. The significant enhancement of the storage modulus or stiffness of the nanocomposites can be noticed from Table 1. As seen in the table, for example at 60°C, the enhancements in storage modulus values of the nanocomposites compared to the neat PP were approximately 56%, 84.3%, and 138% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle, the enhancements of storage modulus (as compared to the neat PP) were about 62%, 89.6%, and 128% for NC-5-II, NC-10-II, and NC-15-II, respectively. As noticed, there were significant enhancements of the storage modulus of the nanocomposites for both 1st and 2nd cycles compared to the neat PP. Moreover, this significant improvement will look interesting in industrial point of view. For example, the design criteria for a particular industrial product is set at minimum modulus of 160 MPa. If that product was made from neat PP material, this limit value is reached at temperature 60°C. Whereas, if using nanocomposites as the raw material (i.e. NC-10-I), then this limit value is reached at much higher temperature of 90°C. This 30°C gap exhibits that the addition of nanoclay loadings in the PP matrix significantly improved the “thermal stability” of the PP.

### Table 1. Representative storage modulus of PP/nanoclay composites (1st cycle and 2nd cycle)

| Temperature (°C) | PP/nanoclay composites - 1st cycle | PP/nanoclay composites – 2nd 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                          |
| 30               | 3.93E+08                          | 5.73E+08                          | 6.80E+08                          | 7.62E+08                          |
| 60               | 1.60E+08                          | 2.49E+08                          | 2.94E+08                          | 3.80E+08                          | 3.81E+08                          | 5.56E+08                          | 7.04E+08                          | 8.42E+08                          |
| 90               | 9.02E+07                          | 1.39E+08                          | 1.64E+08                          | 2.00E+08                          | 8.81E+07                          | 1.40E+08                          | 1.64E+08                          | 1.97E+08                          |
| 120              | 4.91E+07                          | 7.70E+07                          | 8.92E+07                          | 1.05E+08                          | 4.72E+07                          | 7.78E+07                          | 8.95E+07                          | 1.05E+08                          |
| 150              | 8.52E+06                          | 1.97E+07                          | 2.25E+07                          | 2.63E+07                          | 7.79E+06                          | 1.92E+07                          | 2.29E+07                          | 2.73E+07                          |

Additionally, the trends of storage modulus in Figure 5 have been already explained in the previous paragraph. The storage modulus of the nanocomposites were all higher than that of the neat PP, and increased with increasing nanoclay loadings. Additionally, all the samples also exhibited decreases of storage modulus with increasing temperature. Nevertheless, the important thing to note is that at lower temperature (about 30°C) the storage modulus of NC-10-II and NC-15-II were little higher than that of NC-10-I and NC-10-I. At higher temperature, the trends were same as explained in the previous paragraph. Additionally, the relationship between the storage modulus (MPa), nanoclay loading (wt%), and temperature (°C) was also modeled using Equation (1) as follows:

\[
G' = Ae^{B(T)}
\]  

where, \( G' \) is the storage modulus as function of nanoclay loading (wt%) and temperature (T). Constants A and B were determined by fitting the experimental data from Table 1 for the 1st cycle nanocomposites. The fitting results showed that the constant A was a function of nanoclay loading, which expressed by Equation (2).

\[
A = 4.91E7 \times (\text{wt}) + 7.47E8
\]

Whereas, constant B was not affected by the nanoclay loading. For the prepared nanocomposites, it has a value of -0.0221. In general, Equation (1) and (2) have modeled the storage modulus of the nanocomposites as function of nanoclay loading (wt%) and temperature (°C) satisfactory.
4. Conclusion
In this work, polypropylene (PP)/nanoclay composites were successfully prepared by melt compounding nanoclay based masterbatch pellets and PP pellets using a co-rotating twin screw extruder (TSE). The compounding process was carried out twice namely 1st cycle and 2nd cycle. The prepared nanocomposites were then characterized to study the effects of nanoclay loadings (i.e. 0, 5, 10, and 15 wt%) and reprocessing (i.e. 1st cycle and 2nd cycle) on their surface morphology and dynamic mechanical thermal properties by using a Scanning Electron Microscopy (SEM) and an oscillatory rheometer. The SEM micrographs showed that the nanoclay materials were well distributed in the PP matrix, which were indicated by the white needle-like appearance. Nevertheless, the dispersion states, either exfoliation or intercalation of the nanoclay were not observable due to the limitation of the microscopy technique. Additionally, the dynamic mechanical thermal analysis (DMTA) results showed that the storage modulus of the nanocomposites both 1st and 2nd cycles were all higher than that of the neat PP and increased with increasing nanoclay loadings. The enhancement of the storage modulus of the nanocomposites (at temperature of 60°C) were approximately 56%, 84.3%, and 138% for NC-5-I, NC-10-I, and NC-15-I, respectively and 62%, 89.6%, and 128% for NC-5-II, NC-10-II, and NC-15-II, respectively (as compared to the neat PP). While, the storage modulus of all the samples decreased with increasing temperature, which indicates than the nanocomposites simply behaved as polymeric material. Additionally, the relationship between the storage modulus, nanoclay loading (wt%), and temperature (°C) was successfully modeled by using Equation (1): $G' = Ae^{BT}$ and Equation (2): $A = 4.91E7 \times \text{wt\%} + 7.47E8$, while B constant value was -0.0221.

References
[1] A. Chafidz, F.H. Latief, U.A. Samad, A. Ajbar, W. Al-Masry 2016 Polym.-Plast. Technol. Eng. 55 2373-1385.
[2] G. Zhang, T. Wu, W. Lin, Y. Tan, R. Chen, Z. Huang, X. Yin, J. Qu 2017 Compos. Sci. Technol. 145 157-164.
[3] A.P. Kumar, D. Depan, N. Singh Tomer, R.P. Singh 2009 Prog. Polym. Sci. 34 479-515.
[4] K. Majeed, M. Jawaid, A. Hassan, A.A. Bakar, H.A. Khalil, A. Salema, I. Inuwa 2013 Materials & Design 46 391-410.
[5] C. Silvestre, D. Duraccio, S. Cimmino 2011 Prog. Polym. Sci. 36 1766-1782.
[6] E. Manias, A. Touny, L. Wu, K. Strawhecker, B. Lu, T.C. Chung 2001 Chem. Mater. 13 3516-3523.
[7] N. Hasegawa, H. Okamoto, M. Kato, A. Usuki 2000 J. Appl. Polym. Sci. 78 1918-1922.
[8] C.M. Koo, M.J. Kim, M.H. Choi, S.O. Kim, I.J. Chung 2003 J. Appl. Polym. Sci. 88 1526-1535.
[9] A. Chafidz, W.D.P. Rengga, R. Khan, M. Kaavessina, A.M. Almutlaq, W.A. Almasry, A. Ajbar 2017 J. Appl. Polym. Sci., 134 45293-n/a.