

Polypropylene Filled Nano-CaCO₃ Composites: Effect of Nano-CaCO₃ Loadings and Reprocessing on the Crystallization Behavior of the Nanocomposites

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This paper discusses about the production and characterization (i.e. morphology and crystallization behavior) of polypropylene filled nano-CaCO₃ composites (i.e. PNCCs). The PNCCs were successfully prepared via melt mixing/compounding process using nano-CaCO₃ masterbatch in a twin-screw extruder (TSE) machine. Different nano-CaCO₃ concentrations (i.e. 5, 10 and 15 wt%) and two times process (i.e. 1st cycle and 2nd cycle) were used to analyze the influence of nano-CaCO₃ concentrations and reprocessing on the morphology and crystallization properties of the PNCCs. The morphology and crystallization properties of the PNCCs were studied using SEM and DSC, respectively. The SEM images exhibited that at low nano-CaCO₃ concentration (i.e. 5 wt%), the nano-CaCO₃ fillers were well distributed and dispersed in the PP matrix for both NCC-5-I and NCC-5-II samples. Nevertheless, the size of the nanofillers in NCC-5-II sample were smaller than that of the NCC-5-I sample. Additionally, the DSC crystallization thermograms showed that crystallization temperature (T_c) and onset crystallization temperature (T_{oc}) of the PNCCs were higher than the pristine PP. The increases of T_c and T_{oc} for both PNCCs (i.e. 1st cycle and 2nd cycle) were not much different, which were about 4-5 °C and 3-4 °C, respectively.

1. Introduction

Since few decades ago until now, numerous research studies in the field of polymer nanocomposites (PNCs) have been conducted by researchers both in industry and academic (Nayak et al., 2019). It is because the PNCs have been widely used in many applications due to their enhanced properties (i.e. mechanical strength, gas barrier, flame retardancy, thermal and electrical properties, rheological, etc.) compared to the pristine polymer matrix (Bilisik and Akter, 2022; Idumah and Obele, 2021; Chafidz et al., 2016a; Chafidz et al., 2017; Sepet et al., 2016). The PNCs are made by combining polymer matrix and nano-size filler (i.e. nanomaterials). Among the commercial polymer matrices, polypropylene has been commonly used in the production of PNCs due to its mechanical properties, stability and rigidity, easy to process, and wide range of utilization (Chafidz et al., 2016b; Zhao et al., 2019; Nisar et al., 2018). Whereas, for the nano-filler, it is known that type of nano-filler materials that have been rigorously investigated in the last few decades are carbon nanotubes (CNTs) and layered silicate/nanoclay. Both of them were considered as one- and two- dimensional materials in geometry, thus they have large aspect ratio. Nevertheless, there has also been a trend to utilize nano-filler with three-dimensional geometry and thus have low aspect ratio (e.g. spheres or shaped cubic nano-materials) such as calcium carbonate (i.e. nano-CaCO₃). Nano-CaCO₃ has been selected as nano-filler for production of polymer nanocomposites because this material is not expensive and abundant, and thus it can be used at relatively high level of loadings and can decrease the cost of PNCs products (Sepet et al., 2016; Eskizeybek et al., 2018; Chafidz et al., 2017).

Thermal properties is one of important aspect that must be considered, especially during the production of PNCs. Two main parameters of thermal properties are including melting and crystallization properties. Knowing melting properties of the nanocomposites will enable us to set the processing conditions of the twin screw extruder for conducting melt compounding process. Whereas, understanding the crystallization properties or behavior of the nanocomposites will help us in setting up the processing condition

of the injection molding process. One type of methods that can be used for fabrication of PNCs is called melt compounding process. Melt compounding process can be considered as simple, economical, and mostly match with current plastic industrial technologies, like extrusion and injection molding, and thus more feasible for large-scale production of PNCs (Leung et al., 2018; Rane et al., 2018; Chafidz et al., 2016a). Additionally, masterbatch is polymer matrix loaded with high nano-fillers at high concentration, and this masterbatch is considered to be very suitable with the melt compounding process. There have been several literatures that studied about thermal properties of the PP filled nano-CaCO₃ composites (Eiras and Pessan 2009; Fuad et al. 2010; Wang et al. 2014). Nevertheless, to the best of our knowledge, there were still limited investigation reports about polypropylene filled nano-CaCO₃ nanocomposites (PNCCs) prepared using masterbatch by employing melt compounding and reprocessing. Hence, it is worth of investigation. In this work, PP/CaCO₃ nanocomposite has been made by using commercial nano-CaCO₃ masterbatch via melt compounding process. The aim of this research is to study the effects of nano-CaCO₃ loadings and reprocessing on the crystallization behavior of the PNCCs.

2. Experimental

2.1 Materials

To prepare polypropylene filled nano-CaCO₃ nanocomposites (i.e. PNCCs), polypropylene (PP) was used as the matrix. The PP was procured from SABIC, Saudi Arabia. As for the nano-filler, masterbatch filled with about 80% of nano-CaCO₃ were procured from Wuxi Changhong Masterbatches, China. Figure 1 shows the appearances of polypropylene (PP) and masterbatch pellets.



Figure 1: Photographs of polypropylene (PP) pellets (left) and nano-CaCO₃ masterbatch (right)

2.2 Production of PP/CaCO₃ nanocomposites

The PNCCs were produced by melt mixing/compounding the PP and masterbatch of nano-CaCO₃. The process was conducted using a twin-screw extruder (TSE). Details of production of the PNCCs were already described in our previous published work (Chafidz et al., 2016b). Effect of nano-CaCO₃ weight concentrations (i.e., 5, 10, and 15 wt%) and reprocessing (1st and 2nd cycles) on the crystallization behavior of the PNCCs samples was investigated. The nomenclature of the PNCCs samples prepared is shown in Table 1. Whereas, Figure 2 shows the schematic diagram of fabrication of the PNCCs.

Table 1. Nomenclature of the PNCCs samples

Run	Nano-CaCO ₃ loadings (wt%)	Sample	Run	Nano-CaCO ₃ loadings (wt%)	Sample
1 st cycle	0	NCC-0-I	2 nd cycle	0	NCC-0-II
	5	NCC-5-I		5	NCC-5-II
	10	NCC-10-I		10	NCC-10-II
	15	NCC-15-I		15	NCC-15-II

2.3 Samples characterization

The PNCCs pellets from extruder machine was further processed into injection molding machine to make ASTM standard molded samples. The molded PNCCs samples were then cryo-fractured before analyzed for surface morphology using a Scanning Electron Microscopy (SEM) JEOL JSM-6360A machine (made in Japan) operating at 15 kV and magnification of 10,000X. Additionally, the PNCCs samples were also analyzed for the crystallization behavior using a Differential Scanning Calorimetry (DSC) Shimadzu DSC-60 (made in Japan). Details of the characterization procedures for SEM and DSC are already described in our previous published works (Chafidz et al., 2016b; Chafidz et al., 2017).

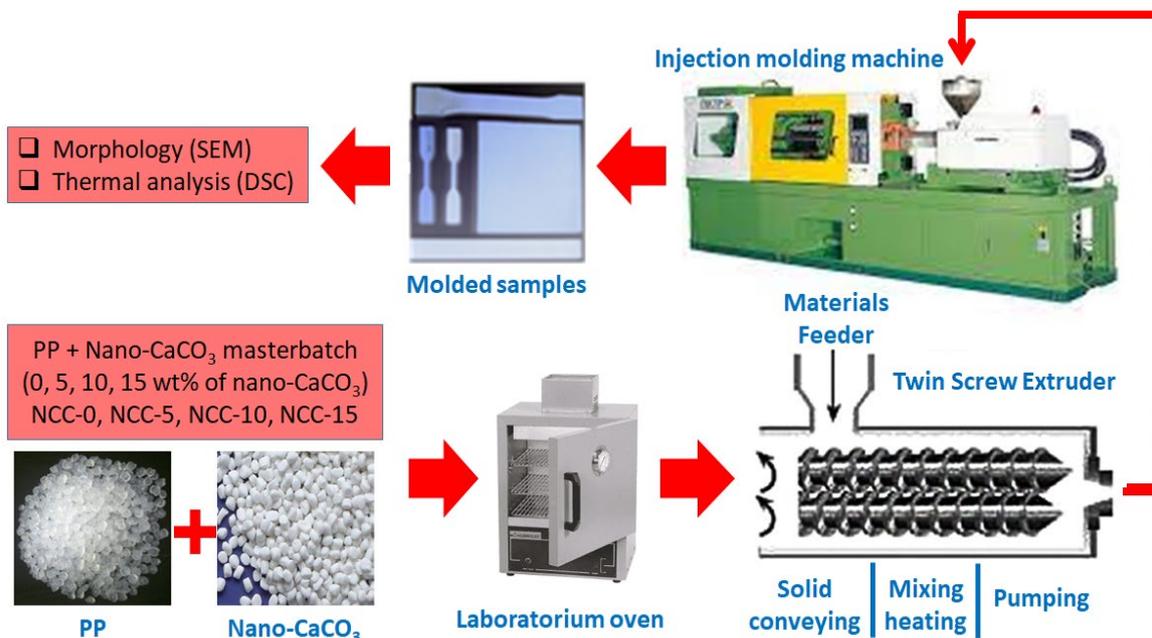


Figure 2: Schematic diagram of PNCCs production

3. Results and discussion

3.1 Scanning Electron Microscopy (SEM)

Figures 3a and 3b exhibits the SEM micrographs of the polypropylene filled nano-CaCO₃ nanocomposites (i.e. PNCCs) samples with nano-CaCO₃ concentration of 5 wt% for 1st and 2nd cycles, respectively. The SEM micrographs were taken from the cryo-fractured surface of the nanocomposites samples. As noticed from the SEM images with 10,000X of magnification, the nano-CaCO₃ materials had quite well distribution and dispersion in the PP matrix for both NCC-5-I and NCC-5-II samples, as indicated by the dashed-circle. Additionally, as observed in Figure 3b (i.e. NCC-5-II), the size of the nano-CaCO₃ particles were smaller than that of the NCC-5-I sample. This was possibly due to two times of melt compounding process that gave the polymer melt more shear-stress hence breaking down the nano-CaCO₃ particles aggregates. A good dispersion/distribution could be obtained by appropriate conditions of melt compounding process (Chan et al., 2002).

3.2 Differential Scanning Calorimetry (DSC)

The DSC crystallization thermograms of the PNCCs for 1st and 2nd cycles are shown in Figure 4. The thermograms were generated using non-isothermal crystallization scheme. It is worth to note that the DSC crystallization thermograms of the PNCCs for 1st cycle were looked similar to that of the 2nd cycle. From the figure, crystallization (T_c) and onset crystallization (T_{oc}) temperatures could be determined. The T_c is the temperature of exothermic curve peak from the DSC crystallization thermograms (see Figure 4). Whereas, T_{oc} is the temperature at which the exothermic heat value started to rise during the crystallization process (see Figure 4) or in the other word, the temperature at which the molten PNCCs started to solidify or crystallize. The values of T_c and T_{oc} for all the PNCCs samples were summarized in Table 2.

As noticed from Figure 4 and Table 2, increasing nano-CaCO₃ concentration also shifting the T_c of the PNCCs to higher values as compared to that of the neat PP. The increases of T_c for both PNCCs prepared via 1st and 2nd cycles were similar, which were about 4-5 °C (see Table 2 and Figure 4). It can be suggested that nano-CaCO₃ nanoparticles could act as nucleating agent. The similar results have been found in other literatures. Fuad et al. (2010) studied the crystallization behavior of PNCCs at nano-CaCO₃ loadings of 0, 5, 10, 15 wt%. They reported that the incorporation of nano-CaCO₃ in the PP matrix had shifted the DSC exothermic peak, hence increased the crystallization temperature of the neat PP about 1 to 3 °C from 109 °C to 110-112 °C. While, Eiras and Pessan (2009) studied the crystallization behavior of PNCCs at nano-CaCO₃ loadings of 0, 3, 5, 7, 10 wt%. They also reported an increase of crystallization temperature, T_c of the PNCCs. The increase of T_c was about 7 to 9 °C from 117 °C to 124-126 °C.

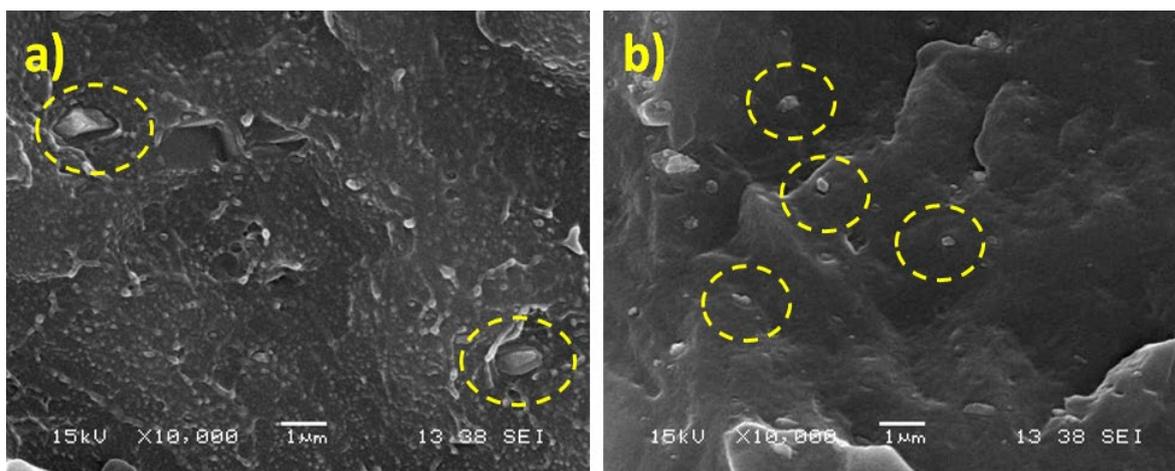


Figure 3: SEM images of a) NCC-5-I and b) NCC-5-II at magnification of 10,000X

Many other nanoparticles were also reported to have nucleation effect for the crystallization of PP (Chan et al., 2002; Wang et al., 2010). They found that incorporating CaCO₃ nanoparticles into PP matrix has increased the T_c of the PNCCs relatively to that of PP matrix. However, the increase of T_c with the increase of nano-CaCO₃ loading was not significant. It is suggested that there would be a saturated loading of nano-CaCO₃ for nucleation effect in crystallization of PP nano-CaCO₃ composites, just as reported by Fuad et al. (2010). Hence, the addition of nano-CaCO₃ particles modified the crystallization process by shifting the crystallization temperature. It is also believed that the nano-CaCO₃ particles only acted as nucleating agent by becoming nucleating sites and did not take a part on the whole crystallization process e.g. crystals/spherulites growth. Thus the nucleation effect of nano-CaCO₃ particles on the mechanical properties will likely be different compared to other nano-filler.

Additionally, similar results were also found for the onset crystallization temperature (T_{oc}). As noticed from Figure 4 and Table 2, increasing nano-CaCO₃ loading also shifting the T_{oc} of the PNCCs to higher values than the neat PP. The increases of T_{oc} for both PNCCs prepared via 1st and 2nd cycles were similar, which were about 3-4 °C (see Table 2 and Figure 4). The increase of T_{oc} could give an economic advantage in term of large scale production of the PNCCs especially during injection molding process. It is because the molten polymer nanocomposites could start to solidify (crystallize) at higher temperature than the neat PP or shorter molding cycle time, which means more production. Additionally, it also means less cooling load to solidify the molten polymer nanocomposites. Furthermore, in a crystallization (or cooling) scan of DSC analysis, the crystallization temperature represents the overall rate of crystallization, taking into account the combined effect of nucleation and growth. Therefore, the degree of supercooling, which is $\Delta T = T_m - T_c$ could be considered as a mean to measure the polymer's crystallizability. The smaller ΔT value, the higher the overall rate of crystallization. The ΔT values of PP nano-CaCO₃ composites are also summarized in Table 2, which shows a decrease of ΔT as nano-CaCO₃ loading increased. The decrease of ΔT values were about 3 – 4 °C for both PNCCs prepared via 1st and 2nd cycles. These results indicate that the overall rate of crystallization of the PP matrix also increased by the addition of nano-CaCO₃ in PP matrix. Khare et al. (1996) reported that with the addition of CaCO₃ nanoparticles, the crystallization rate of PP matrix increased, while the size of spherulite decreased with increasing CaCO₃ loading.

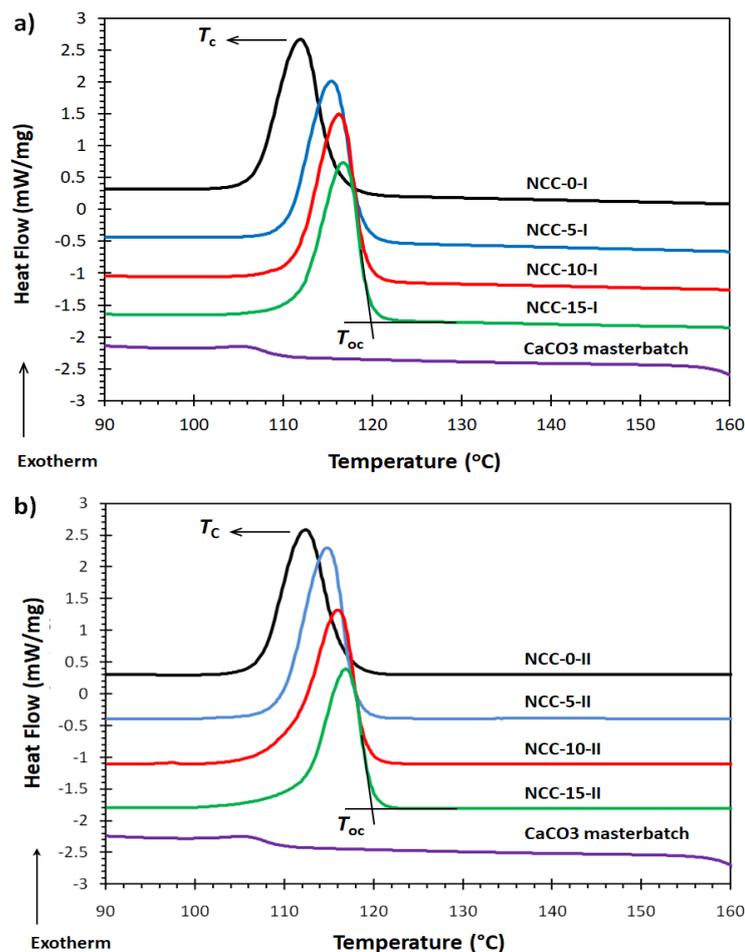


Figure 4: DSC crystallization thermograms of the PNCCs for a) 1st cycle and b) 2nd cycle

Table 2: DSC results of the PNCCs (1st cycle versus 2nd cycle)

Sample	1 st cycle			2 nd cycle		
	T_c (°C) ± 0.2 %	T_{oc} (°C) ± 0.2 %	ΔT (°C) ± 0.2 %	T_c (°C) ± 0.2 %	T_{oc} (°C) ± 0.2 %	ΔT (°C) ± 0.2 %
NCC-0	112	116	45	112	116	45
NCC-5	116	119	42	116	119	42
NCC-10	116	119	42	116	119	42
NCC-15	117	120	41	117	120	41
CaCO ₃ masterbatch	106	110	-	105	109	-

4. Conclusions

In this work, polypropylene filled nano-CaCO₃ nanocomposites (i.e. PNCCs) were produced by melt mixing/compounding the masterbatch with neat PP in a co-rotating Twin Screw Extruder (TSE). The effects of reprocessing (recycle) and nano-CaCO₃ at different concentrations (i.e. 0, 5, 10, 15 wt%) on the morphology and crystallization of the PNCCs were studied by utilizing Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC), respectively. The SEM images exhibited that at low nano-CaCO₃ concentration level, the nano-CaCO₃ fillers were well distributed and dispersed in the PP matrix for both 1st and 2nd cycles. Nevertheless, there were still a few of small aggregates of nano-CaCO₃ particles due to the Van der Waals forces among the particles. Additionally, the DSC analysis results showed that the addition of nano-CaCO₃ particles into PP matrix had increased the T_c of the PNCCs relatively to that of PP matrix. The

increases of T_c for both PNCCs prepared via 1st and 2nd cycles were similar, which were about 4-5 °C. It can be suggested that nano-CaCO₃ nanoparticles could act as nucleating agent in the crystallization process of the PNCCs. Moreover, the degree of supercooling (ΔT) values of the PNCCs also decreased as nano-CaCO₃ loading increased, which indicated that the overall rate of crystallization of the PP matrix also increased by the addition of nano-CaCO₃ in PP matrix. Hence, the addition of nano-CaCO₃ particles modified the crystallization process by shifting the crystallization temperature and decreasing the degree of supercooling.

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