

# Enhancing thermal and mechanical properties of polypropylene using masterbatches of nanoclay and nano-CaCO<sub>3</sub>: A review

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## Abstract

Polymer nanocomposites (PNCs) can be considered as promising relatively new types of composite materials. PNCs give opportunity to develop new composites materials with different structure-property relationships compared to their conventional micro/macro scale composites. Polyolefin based nanocomposites nowadays become more important, because this type of composites has been largely used in various industries. For example, polypropylene based nanocomposites have been widely used in automobile – related industries to replace their conventional composites. This review paper will focus on the polypropylene based nanocomposites prepared using masterbatches of nanoclay and nano-CaCO<sub>3</sub> via melt compounding method. The thermal and mechanical properties of such nanocomposites were also discussed.

*Keywords:* Nanocomposites; polypropylene; nanoclay; nano-CaCO<sub>3</sub>; thermal properties; mechanical properties

## 1. Introduction

High performance plastics have usually been produced by reinforcing the polymers using fillers. The production of polymer filled fillers/particles (i.e. polymer composites) has been done in many years. The only purpose is to enhance the properties of the polymer material e.g. mechanical strength, barrier properties, heat resistance, thermal properties, impact resistance, or to decrease other properties e.g. gas permeability, flammability. Conventional polymer composites, in which the polymer matrix filled with fillers/particles (in micro/macro size) are vastly used. However, the incorporation of these fillers/particles sometimes can cause drawback to the resulted polymer composites (e.g. brittleness), which also affect other properties [1-3].

An alternative to these traditional/conventional polymer composites is called polymer nanocomposites (PNCs). It can be considered as a new type of composite materials. PNCs are made of polymeric matrix and reinforcing nanomaterial/nanoparticles. Since the nanoparticles are so small, hence a few amounts of these nanofillers are sufficient to improve the properties of the polymer properties. Therefore, the utilization of nanoparticles has little effect on density as well as processability of the polymer compared to the traditional composites. These excellence feature counterbalance the drawback of nanofillers, i.e. high costs [1, 3, 4].

The superior properties of PNCs are due to nano-scale

dimensions of the filler which alter the morphology of the PNCs material. The homogeneous dispersion and distribution of the nanomaterials can result in significantly large interfacial area, which leads to a strong interfacial interaction between the nanofiller and the polymer matrix [4]. PNCs give opportunity to develop new composites materials with unique structure-property relationships compared to their conventional micro/macro scale composites. Compared to the conventional/traditional composites, PNCs showed enhanced modulus and tensile strength [5-7], thermal stability [8], enhanced gas barrier [9, 10], less flammability [11], and increased electrical conductivity [10, 12].

Polyolefin based nanocomposites nowadays become more important, because this type of composites has been largely used in various industries. For example, polypropylene based nanocomposites have been widely used in automobile – related industries to replace their conventional composites [4]. Recently, commercial masterbatches were manufactured in large scale. Masterbatch is a polymeric material filled by nanoparticles/nanofillers at high weight percentage. Using commercial masterbatch can be considered as an alternative in the fabrication of PNCs compared with the use of bulk nanoparticles. It is because masterbatch is a dust-free filler since the nanoparticles are bounded inside the polymer matrix, thus it has less health and safety risks and also easy to handle. Fig. 1 shows the reasons why using masterbatch to prepare nanocomposites. Additionally, by using masterbatch, good dispersion and distribution of the nanoparticles are highly expected. Therefore, using masterbatch can be considered as the simplest and economist method to produce PNCs. Nevertheless, based on the literatures survey, there were only

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few research studies that reported the production of polyolefin nanocomposites by using masterbatch, as compared to direct addition of bulk nanoparticles into polyolefin matrix. Therefore, it makes masterbatch become an interesting topic of research [5, 13, 14].

### WHY MASTERBATCH ....?!?!

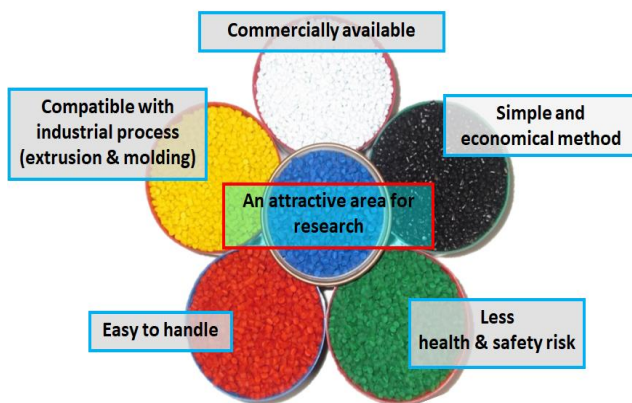


Fig. 1. The reasons of using masterbatch as a processing route to prepare nanocomposites

Polyolefins are belong to thermoplastic polymers, which made of olefinic monomers. They are considered to have the greatest production and consumption every year. This success is due to their low price, wide range of properties, as well as applications. They are also easy to recycle and their properties could be significantly enhanced via melt compounding or composite technologies. Polyolefins can also be extruded films (cast and blown), pipes, and as filaments (fibers). They can be easily molded into any shapes. Additionally, polyolefins can be coated onto other materials. Examples of polyolefins are: polyethylene (PE), polypropylene (PP), ethylene propylene rubber (EPR), etc.

Enhancing polyolefins properties using fillers (i.e. composites technologies) has been widely done to produce high performance polyolefins. Polyolefins can be incorporated either natural or synthetic compounds to enhance their properties. The one that attracted both academy and industry and perhaps the most important one is incorporation of nanoparticles (nanofillers) to produce polyolefins-based nanocomposites. Nowadays, this trend has gained more acceptances and become more attractive area for research. There are many research studies about polyolefin nanocomposites such as polypropylene (PP) [15-17], polyethylene (PE) [18-20].

## 2. Materials

### 2.1. Polypropylene

Among polyolefin, PP based nanocomposites have gained great interest [5]. Polypropylene is considered as one of the most frequently used polyolefins. This success is due to their relatively low price, the lightest among major thermoplastic (i.e. density about  $0.90 \text{ g/cm}^3$ ), easy to process and recycle, good chemical resistance, and good mechanical properties.

Polypropylene has many applications, from automotive (e.g. bumpers, interior parts) to packaging [21]. Its properties could also be improved significantly via blending and composite technologies.

### 2.2. Nanomaterials

There are many types of commercialized nanoparticles/nanofillers that can be used to produce polypropylene based nanocomposites. Depends on how many dimensions of the used nanoparticles are in the nanoscale, these nanoparticles can be categorized into three types. These three types are: 1) isotropic and spherical (i.e. 3D in nanoscale) such as  $\text{SiO}_2$  or  $\text{CaCO}_3$  nanomaterials, 2) highly anisotropic and needle-like (i.e. 2D in nanoscale) such as carbon nanotubes (CNTs), 3) sheet-like layers, i.e. layered silicate/nanoclay (i.e. 1D in nanoscale) [1, 22]. Figure 2 shows the photographs of polyolefin (HDPE and PP) based nanocomposites with three types of nanofillers/nanoparticles. In this paper, only two types of nanomaterials that were studied, layered silicate/nanoclay and nano-calcium carbonate ( $\text{CaCO}_3$ ). Each of these materials are explained in the next sections.

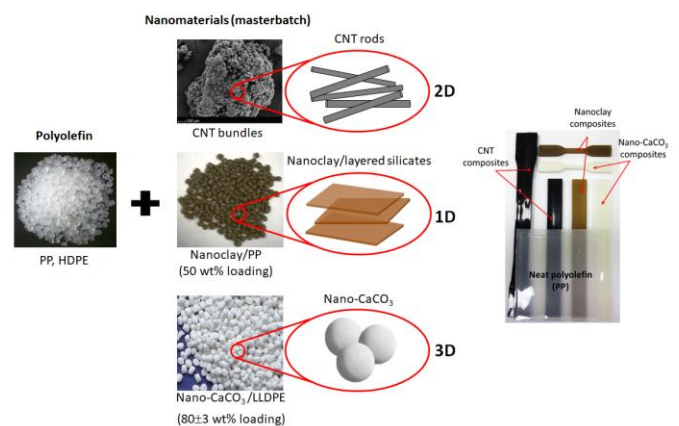


Fig. 2. Polyolefin based nanocomposites with three different types of nanofillers

### 2.3. Layered Silicate/Nanoclay Reinforced Polymer Nanocomposites

#### 2.3.1. Structure and Properties of Nanoclay

Among the entire potential nanoparticles, nanoclay has gained great attention among researchers. It is because clays are abundant, environmentally friendly, and their intercalation properties have been studied for a long period, which makes these nanoparticles as one of the most effective and widely accepted nanofillers [1, 4]. Nanoclay is belong to the family of 2:1 layered or phyllosilicates [23], and thus the other name nanoclay is layered silicate. The structure of its crystal consists of two dimensional layers, which obtained by combining two tetrahedral silica laminate with the central octahedral sheet of alumina or magnesium. Figure 3a shows a single layer of 2:1 phyllosilicates. Layered silicate/nanoclay consists of several layers that stacked together, with each layer thickness of approx.  $0.96 \text{ nm}$  and lateral dimension of approx.  $100 - 200 \text{ nm}$ . It also has a considerably high surface

area of approx. 750 m<sup>2</sup>/g. As illustrated in Figure 3b, these layers stack together by Van der Waals forces in between them (called gallery or interlayer). The total of a single layer thickness, (i.e.  $d_0 = 0.96$  nm) and the gallery/interlayer is what called basal spacing or d-spacing ( $d_{001}$ ), which represents the repeating unit of layered silicate [1, 24].

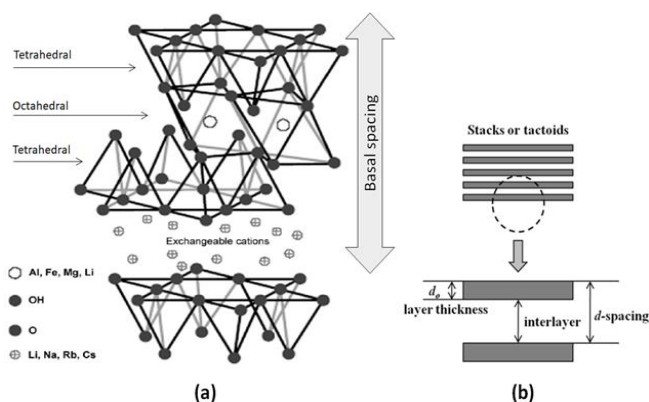


Fig. 3. a) A single layer of a 2:1 phyllosilicates, and b) Schematic structure of a repeating unit of layered silicate. Adopted from [23]

Electrically charged molecules (i.e. cations) may presence in the space between the layers of layered silicate (i.e. gallery/interlayer). This condition leads to the possibility of the layered silicate e.g. montmorillonite (MMT) to be partially modified through what is called as ion exchange modification. In case of MMT, the excess negative ions located on the surface of layered silicate obtained from isomorphous substitutions. For example,  $\text{Al}^{3+}$  is changed by  $\text{Mg}^{2+}$ , or  $\text{Mg}^{2+}$  is changed by  $\text{Li}^+$  [23].

### 2.3.2. Organic Modification of Layered Silicate (Organoclay)

The layered silicate/nanoclay are not easily dispersed into almost all of polymeric materials, since they intend to stack together in aggregated tactoids. The dispersion of these tactoids into discrete mono-layers is also hindered by incompatibility between nanoclay, which is naturally hydrophilic, and PP, which is one of the most hydrophobic polymeric materials. The blending of these two materials without pre-treatment usually results in a low dispersion level of the layered silicate in polypropylene matrix and also poor interfacial bonding force between surfaces of layered silicate and polypropylene matrix [4, 6]. In such immiscible composites system, the poor interfacial bonding force between the inorganic and organic components can lead to low thermal and mechanical properties. Conversely, a high interfacial bonding force between them will result in organic and inorganic components to be dispersed in nanoscale level. Consequently, the resulting nanocomposites system exhibits unique properties that differ from their traditional/conventional microcomposites [23, 25].

Therefore, there are two important characteristics needed to be considered during fabrication of polymer layered silicate (PLS) nanocomposites, which are: 1) The ability of the silicate layers to be dispersed into mono-layers within the polymer matrix. 2) The ability of the layered silicate to alter their surface chemistry via ion exchange reaction (i.e. organic

and inorganic cations). Both of these characteristics are related, since the dispersion ability of the silicates layers within a polymer matrix is affected by the interlayer/gallery cation. The interlayer of pristine layered silicate/nanoclay usually has hydrated  $\text{K}^+$  or  $\text{Na}^+$  ions. To make the nanoclay become miscible with polyolefin matrix such as polypropylene, the naturally hydrophilic nanoclay surface has to be changed to organophilic surface, which makes polymer intercalation to occur. Generally, this method can be done through ion exchange reaction using cationic surfactants, e.g. alkylammonium. It can decrease the surface energy of the inorganic component and increase the wetting ability of the polymer matrix, which leads to a bigger interlayer distance. In addition, alkylammonium cation can become functional group that may react with the matrix, which then enhance the interfacial bonding force between the polymer matrix and layered silicate [26].

### 2.4. Nano- $\text{CaCO}_3$ Material and Important Aspects

Among many types of nanomaterials/nanofillers, two of the most widely studied are layered silicate (or nanoclay) and carbon nanotubes (CNTs), which are 2D and 1D in nanoscale geometry, thus they have large aspect ratio. Apart from those two, growing interest also given to nanofiller with 3D nanoscale geometry with low aspect ratio, like cubical or ball nanofillers, such as nano- $\text{SiO}_2$  and nano- $\text{CaCO}_3$ . This material can be used at high loading level, since it is abundant and inexpensive. Calcium carbonate has important role as filler in industries such as textiles, plastics, rubbers, and paper. Such industrial applications need good nano- $\text{CaCO}_3$  particles with narrow size distribution, uniformly shape, and definite structure of crystal.

Most of conventional  $\text{CaCO}_3$  particles available in the market has size range from 1 to 50  $\mu\text{m}$  (i.e. micro- $\text{CaCO}_3$ ). Numerous research studies reported that enhancement in mechanical properties of the micro- $\text{CaCO}_3$  filled composites was minimum [3]. It is most likely caused by the poor interfacial bonding force between micro- $\text{CaCO}_3$  and the polymer matrix. Therefore, the use of nano- $\text{CaCO}_3$  as filler to produce nanocomposites and study the polymer – filler interaction is interesting topics of research. According to the literatures, three major reasons for selecting nano- $\text{CaCO}_3$  as fillers in polymer matrix are as follow [26]:

- To enhance mechanical properties of the materials, e.g. modulus elasticity, and toughness. It is because the interfacial area between filler and the polymer can be dramatically increased.
- Modification of the material's behaviors
- Cost reduction of final products (due to its low price)

Additionally, when smoothness and high gloss surface are needed, micron- $\text{CaCO}_3$  cannot be utilized; but nano- $\text{CaCO}_3$  particles can be a good filler candidate [26]. The synthesis of nano- $\text{CaCO}_3$  is getting more and more attention due to its good properties and high market demand. Recently,  $\text{CaCO}_3$  nanomaterials were commercially available in the market for toughening polymers. It has been one of the most commonly used inorganic filler for thermoplastics [27]

Generally, two types of interactions could occur in the

nanoparticles-filled polymer composites. Firstly, a polymer matrix adheres to the particle surface and creates an interphase with properties that differ from those of the polymer matrix. Secondly, the particles may also interact with each other and generate aggregates. The occurrence and magnitude of the aggregates are affected by the extent of adhesion and separating forces. The adhesion is determined by the surface tension of the filler and its particle size, while the separating force is determined by the level of shear forces.

In general, a good dispersion of nanofillers in the polymer matrix is not easy to achieve due to the strong tendency of the nanoparticles to agglomerate and the high melt viscosity of the matrix. Therefore, basically there are two important factors that control the properties of polymer/CaCO<sub>3</sub> nanocomposites, which are: (1) the dispersion state of nano-CaCO<sub>3</sub> in the polymer matrix, and (2) the interaction between polymer and nanofiller (i.e. polymer-filler interface). A good dispersion and adequate interfacial interaction are important if good nanocomposites properties are to be achieved [26, 28-30].

### 3. Polymer Nanocomposites Preparation

In general, there are four main processes to prepare polymer nanocomposites, which are template synthesis (sol – gel technology), in situ polymerization, intercalation from solution, and melt compounding (or melt intercalation) [23, 27]. The method that has gained a great interest from the researchers and also in particular become this work interest is melt intercalation or melt compounding.

The melt intercalation method has been extensively used to prepare polymer nanocomposites. This technique has gained a great interest from the researchers due to number of reasons [26]:

- No solvents are used, which will reduce the costs of the solvents and with their discharge and environmental effect;
- Its versatility and the compatibility with the industrial processes (e.g. extrusion and injection molding), thus can be easily commercialized.
- The high-shear stress during process in the may allow the dispersion of considerable higher loadings of nanofillers, as compared with the nanofillers loadings achieved by an in-situ polymerization process.
- This method shifts production downstream of nanocomposites, thus providing end-use manufacturers many possibility regarding with the final product specifications such as polymer types/grades, types of nanofillers, loadings level, etc.
- Finally, this method also can be applied to polymers which are not applicable with in-situ polymerization and other process/methods.

In the production of polymer nanoclay nanocomposites by using melt compounding/intercalation method, the layered silicate are blended with the molten polymer matrix. If the surfaces of layered silicate are adequately compatible with the polymer matrix, the molten polymer chains may diffuse/penetrate into the galleries of layered silicate to form either exfoliated or intercalated structure based on the level of

penetration.

Research studies in polymer nanoclay composites manufactured by melt compounding/intercalation method showed that the melt processing conditions play an important role to achieve high level of exfoliation. A good balance between the shear and residence time in the extruder is needed to help the exfoliation and dispersion of layered silicate. Fornes, et al. [31] proposed an exfoliation mechanism of layered silicate during the melt compounding of polymer nanocomposites, which based on various roles that the shear stress may play (see Fig. 4). As seen in Fig. 4a, initially, the shear stress in the extruder breakup large layered silicate into dispersed stacks of layered silicate. Then, in Fig. 4b, the extruders transfer the stress from the polymer melts to the dispersed layered silicate, and shear them into smaller stacks of silicate layers. Ultimately, as seen in Fig. 4c, individual platelets could peel apart by a combination of shear and penetration of polymer chains in the galleries of the layered silicate. Exfoliation state, therefore, involves peeling the platelets of the stacks one by one. This requires time and needs the polymer matrix to have adequate affinity for the organoclay surface to cause a spontaneous wetting. Since the individual aluminosilicate platelets are so flexible, they can slip away from others in the stack and interact with the polymer chains. The level of exfoliation seems to be considerably affected by the melt processing conditions.

For a constant residence time, the higher a stress is applied, the smaller stacks are resulted, and the less time needed for peeling the layers. Therefore, the level of exfoliation is affected by the average shear rate, the viscosity of polymer matrix, and the mean residence time during the melt compounding/intercalation process. It should be noted that according to this model, processing conditions alone are not sufficient to guarantee an adequate silicate exfoliation. It is obtained only by a good combination of the processing conditions and polymer-organoclay affinity. In fact if there is no good affinity between layered silicate and polymer matrix, a microcomposite structure is likely obtained.

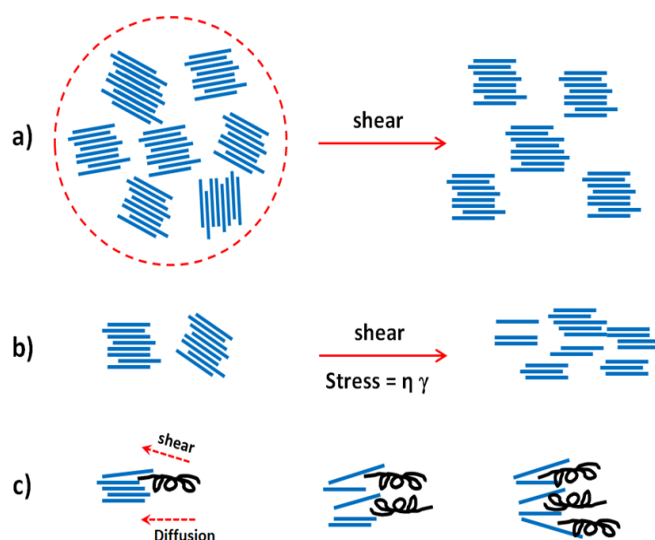


Fig. 4. Mechanism of layered silicate exfoliation during melt compounding of the clay nanocomposites: a) Layered silicate particles breakup; b) layered silicate breakup; c) layered silicate exfoliation. Adopted from [31]

In other hand, in term of polymer nano-CaCO<sub>3</sub> composites; the success achieved by direct melt-compounding limited because of the strong tendency of the nanoparticles to agglomerate, which results in clusters formation due to their high adsorption surface energies during melt compounding though when the nanoparticles content in the composites is small. In addition, the different polarity with polymer matrices, is likely to diminish the advantages of their ultra-small dimensions. Therefore, the key is to decrease the surface energy of the nanoparticles, however, the uniform surface coverage of nanoparticles is hard to realize by simply physical and mechanical means [32, 33]. Additionally, polymer decomposition during the melt compounding process is sometimes severe, which not easy to overcome. These drawbacks need to be considered when using melt compounding method to fabricate polymer nanocomposites. In addition to surface pre-treatment, size and loading percentage of nanoparticles, melt compounding conditions, such as temperature, time, shear force and configuration of the extruder, can also be considered in order to obtain homogeneous dispersion of nanoparticles in the polymer matrix [32].

Generally, to achieve homogeneous dispersion of nanofillers and avoid properties deterioration due to degradation during the melt compounding process, a masterbatch method can be used, i.e. melt-blending certain nanoparticles with a polymer matrix at a high concentration first (called masterbatch). Then melt compounding the resulted masterbatch with the raw polymer resin again to a low nanofiller content. This method is often used in fabrication of nanocomposites. Currently, many commercial masterbatches have been available in the market. Wang, et al. [34] reported that by using masterbatch method, a random dispersion of CaCO<sub>3</sub> particles in masterbatch and remarkable rheology enhancement of Polycarbonate (PC) matrix melt has been achieved due to the introduction of CaCO<sub>3</sub> particles.

#### 4. Polymer Nanocomposites Structures (Layered Silicate)

Generally, depending on the nature of the materials used (layered silicate/nanoclay, organic cation modification, and polymer matrix) and the fabrication method, three main nanocomposites structures can be achieved. If the polymer matrix is difficult to intercalate between the silicates layers (i.e. low dispersion level), a phase separated composite is achieved. This structure's properties is similar to the traditional micro-composites. Above this traditional family of composites, there are other two possible types of nanocomposites structures that can be achieved with good dispersion: a) intercalated structure, in which a single or maybe more than one extended polymer matrix chain is intercalated between the silicate sheets. The result is a well organized multilayer nanocomposites structure of alternating silicate layers and polymer matrix, with repeated few nanometers gap between them, and b) exfoliated or delaminated structure, in which the silicate sheets/layers are individually separated and homogeneously dispersed in a continuous phase of the polymer matrix.

The intercalated nanocomposites structure results in a well organized multilayer morphology made of alternating polymer

matrix and inorganic silicate layers, in which the gap between the silicate layers is increased (few nanometers) due to the presence of polymer matrix chains. Whereas, in the exfoliated nanocomposites structure, the organized structure collapsed and the homogeneous dispersion of anisotropic nanoparticles (silicate layers) can result in very large interfacial area between the silicate layers and polymer matrix. Additionally, the distance between the nano-elements (i.e. silicate layers) starts to approach molecular dimensions at considerably low loading level of the nanoparticles (layered silicate). This very large interfacial area and nano-scopic dimensions between the components may exclusively differentiate the resulted PNCs from the traditional/classical composites. As with the polymer matrix, when the dimensions of the nanoparticles approach the fundamental size of physical properties, improved mechanical, electrical, thermal, and optical properties emerge, which do not arise in the macroscopic composites structure.

### 5. Characterization of Polymer Nanocomposites

#### 5.1. Morphological Analysis

Morphological analysis of polymer nanocomposites (PNCs) is important. Uniform dispersion of nano-materials in the polymer matrix is an important aspect to be considered because it will strongly influence the properties of the nanocomposites, e.g. rheology, mechanical, thermal, etc.

#### 5.2. Thermal Analysis

A differential scanning calorimetry (DSC) is usually used to investigate the isothermal and non-isothermal crystallization process. Fig. 5 shows the typical DSC thermogram of PP/clay nanocomposites sample with temperature dependence. The 1<sup>st</sup> heating scan is carried out to remove the thermal and processing history of the sample. The 2<sup>nd</sup> heating scan and cooling scan data are the one which will be used to study the thermal properties [8]. To know the thermal properties of nanocomposites material is very important especially in the material processing. By knowing the melting temperature of PNCs material, we will know the optimum operating conditions for the material processing. It is possible that thermal properties of polymeric material is altered by the addition of nano-materials. In addition, a thermogravimetric analysis (TGA) can also be used to study the thermal stability of the nanocomposites.

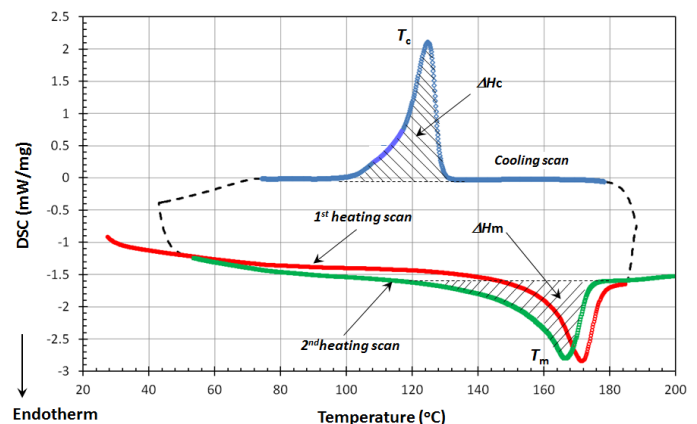


Fig. 5. Typical DSC thermograms of the nanocomposites

### 5.3. Mechanical Properties

Mechanical properties characterization usually carried out on dog-bone shape tensile bars (which fabricated by injection molding) by employing a tensile test machine. The ASTM D-638 is usually used as the test guidelines. All the test usually done at a room temperature. The tensile test results are usually in form of stress-strain curve. From this curve, tensile properties, such as modulus elasticity (E), tensile strength, toughness, and strain at break (%elongation) can be determined.

## 6. Thermal and Mechanical Properties of Polypropylene/Nanocomposites

This section will discuss about the thermal and mechanical properties of polypropylene based nanocomposites using masterbatches of nanoclay and nano-CaCO<sub>3</sub>.

### 6.1. Thermal Properties

In our previous work [5], it was found that the DSC thermograms of PP/nanoclay nanocomposites for all the nanoclay loadings have two crystallization temperatures (i.e. T<sub>c1</sub> and T<sub>c2</sub>), whereas the neat PP has one crystallization temperature (T<sub>c</sub>). It was suggested that the T<sub>c1</sub> (at lower temperature) could be attributed to the homogeneous crystallization of the PP matrix. The T<sub>c2</sub> (at higher temperature) could be attributed to the heterogeneous crystallization/nucleation done by the nanoclay particles. This explanation was further confirmed by comparing the T<sub>c2</sub> that was very close to the T<sub>c</sub> of the masterbatch (nanoclay), and the T<sub>c1</sub> that was very close to T<sub>c</sub> of the neat PP.

Overall, the crystallization temperature of the nanocomposites considerably increased from 113°C to approx. 126°C. This result indicated that the incorporation of nanoclay particles has changed the crystallization process of the PP matrix by acting as a nucleating agent. Other literatures have also reported the nucleating effect of the nanoclay [4, 35, 36]. Lei et al. [4] found that the addition of the nanoclay particles has increased the crystallization temperature from 107°C (neat PP) to 115°C. Additionally, the crystallinity index, X<sub>c</sub> of the nanocomposites slightly increased. The increase of X<sub>c</sub> was also attributed to the enhanced nucleation effect of nanoclay. However, X<sub>c</sub> only achieved maximum at 5 wt% nanoclay loading (i.e. 51.2%). Afterward, the X<sub>c</sub> decreased at higher loading (i.e. 15 wt%).

Whereas, for PP/CaCO<sub>3</sub> nanocomposites, Chafidz, et al. [37] reported that the T<sub>c</sub> of the nanocomposites has also increased from 112°C to 117°C, which indicated that nano-CaCO<sub>3</sub> also acting as nucleating agent, which enhanced the crystallization process, in which the crystallization process started earlier. The X<sub>c</sub> value of the nanocomposites also slightly increased, which achieved maximum at 10 wt% of nano-CaCO<sub>3</sub> loading (i.e. 40.8%). This increase was likely caused by the nucleating effect of the nano-CaCO<sub>3</sub> fillers, which influenced the crystallization process of the PP matrix [28]. However, the X<sub>c</sub> value decreased at higher nano-CaCO<sub>3</sub> loadings (i.e. 15 wt%). This decrease could be attributed by the large amount of nano-CaCO<sub>3</sub> fillers that could hinder the mobility of PP matrix chain, hence retarded its crystal growth

[38]. The excessive number of nucleation sites promoted by the presence of nano-CaCO<sub>3</sub> fillers dispersed in polymer matrix and the hindered crystal growth have led to produce small and imperfect spherulites [28].

### 6.2. Mechanical Properties

In our previous work [5], the mechanical properties of PP/nanoclay composites were characterized via tensile test. It was reported that there was an increase in the modulus elasticity and tensile strength. The modulus elasticity was improved by 38, 49, and 79% with the addition of 5, 10, and 15 wt% of nanoclay, respectively. Modulus elasticity improvements were also reported in other literatures (with other types of polymer matrix) [39-41]. Additionally, the yield stress of the nanocomposites also increased. In other hand, the toughness of the nanocomposites decreased with increasing nanoclay. This decrease was attributed to the presence of the nanoclay that acted as a stress concentrator, which will decrease the toughness of the nanocomposites. It was known that toughness was more sensitive to the strain compared to the modulus elasticity. Additionally, the modulus elasticity, E for the PP/nano-CaCO<sub>3</sub> composites also increased with the increase of nano-CaCO<sub>3</sub> particles [37]. The enhancement of E was approximately 6.9, 12.7, and 16.6% with the addition of 5, 10, and 15 wt% of nano-CaCO<sub>3</sub>, respectively. Despite the presence of few CaCO<sub>3</sub> aggregates, the nanocomposites at highest nano-CaCO<sub>3</sub> loading (i.e. 15 wt%) still gave the highest increase in the modulus elasticity/stiffness. It was also reported in other literature [42] that the modulus elasticity was not significantly affected by a few agglomerates of nano-CaCO<sub>3</sub>. In contrast to the modulus elasticity, the tensile strength was measured at high strain, and thus gave different mechanical properties dependency on the nano-filler concentration and the interfacial interaction between the nano-filler and the polymer matrix [43]. In our previous work [37], the tensile strength decreased monotonically with the increase of nano-CaCO<sub>3</sub> loading. This decrease was likely due to the debonding of CaCO<sub>3</sub> nanofillers.

## 7. Conclusion

From the reviewed literatures, it was found that there was an increase in the crystallization temperature T<sub>c</sub> for both of polypropylene/nanoclay and nano-CaCO<sub>3</sub> composites. These increases were likely attributed to the presence of the nano-fillers (i.e. nanoclay, nano-CaCO<sub>3</sub>) which acted as nucleating agent. Additionally, the crystallinity index, X<sub>c</sub> for both of the nanocomposites also increased. However, the X<sub>c</sub> of both nanocomposites decreased at higher nano-fillers loadings.

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