

# Investigating the Effect of Nanoclay Loadings and Re-Processing on the Melting and Crystallization Behavior of PP/Clay Nanocomposites

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**Abstract.** In this study, PP/clay nanocomposites have been fabricated at different nanoclay loadings, i.e. 0, 5, 10, and 5 wt% for the 1<sup>st</sup> cycle and 2<sup>nd</sup> cycle (re-processing). The prepared nanocomposites were then characterized by a Differential Scanning Calorimetry (DSC) to investigate the effects of nanoclay loadings and re-processing on the melting and crystallization of the nanocomposites. The DSC results showed that the melting temperature,  $T_m$  was not significantly affected by the nanoclay loadings and re-processing. In the other hand, the degree of crystallinity,  $X_c$  of the nanocomposites was higher than that of neat PP, but only reached a maximum at nanoclay loading of 5 wt% (i.e. 51.2% for NC-5-I and 48.3% for NC-5-II). Thereafter, the  $X_c$  decreased at higher nanoclay loadings. There was no significant difference in  $X_c$  between 1<sup>st</sup> cycle and 2<sup>nd</sup> cycle. Additionally, in all nanocomposites samples for both cycles, there were two crystallization temperatures, i.e.  $T_{c1}$  and  $T_{c2}$ . In the overall crystallization process, the  $T_c$  of nanocomposites increased by 11-12°C compared to that of neat PP. Whereas, the onset crystallization temperature,  $T_{oc}$  also increased by approx. 13°C. Apparently, there was no significant effect of nanoclay loadings and re-processing on the  $T_c$  and  $T_{oc}$  of the nanocomposites.

## Introduction

Polymer nanocomposites (PNCs) have become an interesting topic of research for many researchers and have been intensively developed in the last two decades for many uses [1]. PNCs consist of polymeric materials as the matrix and nano-sized materials as the filler. Example of nanomaterials that have been widely used in the production of PNCs are layered silicates or nanoclay [2]; carbon nanotubes (CNTs) [2, 3]; and nano-silica, which correspond to the 1D-nanolayers, 2D-nanotubes, and 3D-nanoparticles, respectively. The 1D-nanolayers are the type of nanomaterials that only have one dimension that in nano-scale range, and therefore have a high aspect ratio (L/D), such as layered silicates or nanoclay [4, 5]. In recent years, nanoclay has attracted great interest among researchers in both academic and industry [6]. Additionally, nanoclay or layered is one of the most frequently used nanofillers for preparation of PNCs and approx. 70% of the market [5, 7].

Recently, nanomaterials-based masterbatch has been available in the market. Masterbatch is a polymer matrix filled with a high concentration of nanomaterials (typically 50-80wt%). The use of masterbatch is a promising method to fabricate polymer nanocomposites. It is because this method is simple (easy to process), no-dust since the nanomaterials are embedded inside the polymer matrix (less risk of health and safety), and less expensive. Additionally, using this method could increase the dispersion level as compared with the use of bulk nanomaterials. Moreover, this method also very compatible with the melt compounding method and thus most industrial processes, such as extrusion and injection molding [8]. In particular, polypropylene (PP)/clay nanocomposites is attractive due to their potential applications in the automotive industry, construction, etc. [9]. Based on the literature

review, there have been numerous research studies about PP/clay nanocomposites [1, 6, 9-11]. In our knowledge, the investigation about the effect of nanoclay loadings and re-processing effect on the melting and crystallization of the PP/clay nanocomposites prepared via melt compounding using masterbatch was still limited and therefore was considered as an attractive research topic.

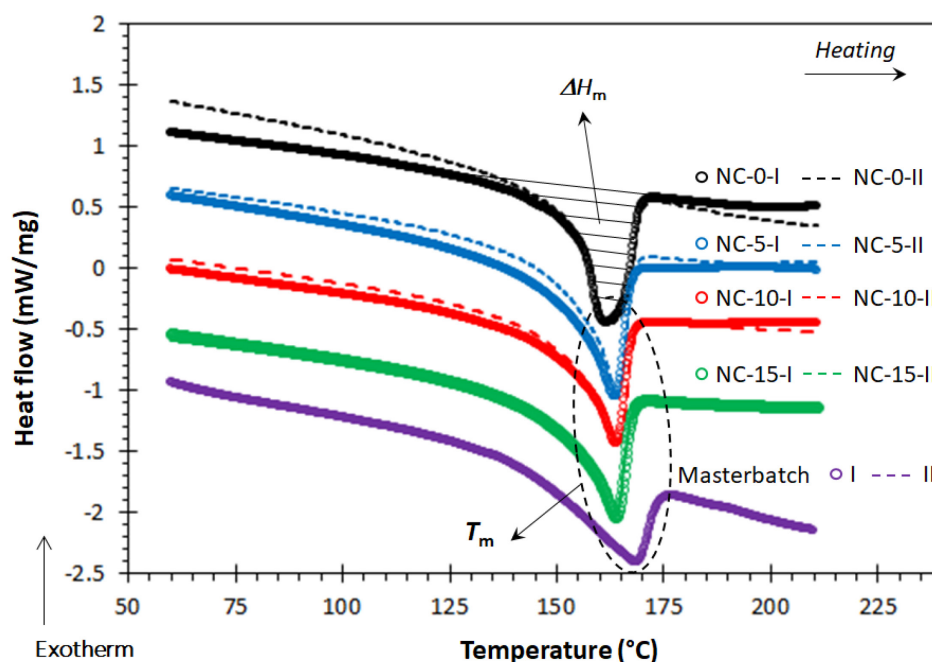
## Experimental

**Materials and Fabrication of Nanocomposites.** We have prepared PP/clay nanocomposites by melt compounding Polypropylene (PP) pellets and nanoclay-based masterbatch pellets in a twin-screw extruder. Injection molding grade PP pellets (PP570) were provided from SABIC, Saudi Arabia. Whereas, the nanoclay-based masterbatch with a weight ratio of nanoclay: PP matrix 50:50 (product name: NanoMax) was obtained from Nanocor, USA. The type of nanoclay material used was montmorillonite (MMT). The PP carrier is believed to be already compatibilized with maleic anhydride (MA). The method to prepare the nanocomposites was described in our previous work [8].

**Nanocomposites Characterization.** A Differential Scanning Calorimetry (DSC) was employed to investigate the effect of nanoclay loadings and re-processing on the thermal properties (i.e. melting and crystallization) of the PP/clay nanocomposites. The DSC analysis procedure for the PP/clay nanocomposites was already explained in our previous work [8].

## Results and Discussion

Figure 1 shows the thermograms from the DSC heating scan of PP/clay nanocomposites for both 1<sup>st</sup> and 2<sup>nd</sup> cycles. As seen in the figure, the 1<sup>st</sup> cycle samples were presented by different colored symbols (o) and the 2<sup>nd</sup> cycle samples were presented by different colored dashed-lines. From the Fig. 2, some parameters could be derived, e.g. melting temperature ( $T_m$ ), which was taken as the peak temperature of the DSC heating curve; degree of crystallinity ( $X_c$ ), which was determined from the experimental heat of fusion  $\Delta H_m$  and the literature value of 100% crystalline  $\Delta H_m^0$  (see our previous work [8]). These parameters are listed in Table 1. As seen in Fig. 1, all the nanocomposites samples for 2<sup>nd</sup> cycle were nicely overlapping with that of the 1<sup>st</sup> cycle, especially at higher nanoclay loadings (e.g. NC-10-I and NC-15-I). Moreover, the  $T_m$  of all nanocomposites samples were in the close range of temperature (i.e. 162-164°C) (see Table 1).



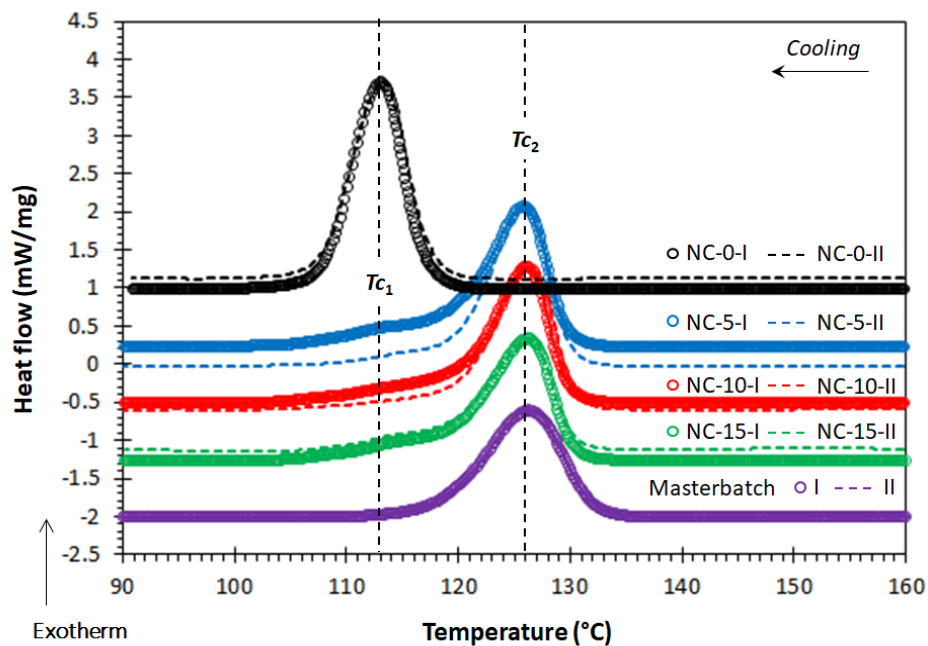
**Fig. 1.** DSC heating thermograms of PP/clay nanocomposites for 1<sup>st</sup> and 2<sup>nd</sup> cycles. The 1<sup>st</sup> cycle samples were presented by symbol (o) and the 2<sup>nd</sup> cycle samples were presented by dashed-lines

This indicates that the nanoclay loadings and re-processing did not significantly affect the melting properties of the nanocomposites. Additionally, the degree of crystallinity ( $X_c$ ) of the nanocomposites was slightly higher than the of neat PP, which reached a maximum at nanocomposites samples with 5 wt% nanoclay loading (i.e. 51.2% for NC-5-I and 48.3% for NC-5-II). The increase of  $X_c$  could be related to the existence of nanoclay, which acted as nucleating agent and thus enhanced “heterogeneous” nucleation and crystallization process of the nanocomposites. Afterward, the  $X_c$  decreased at higher nanoclay loadings. This phenomenon could be related to the excessive existence of nanoclay, which could hinder the crystal growth of the nanocomposites. Since there are two opposing effects of nanoclay on the crystallization of the nanocomposites, i.e. heterogeneous nucleation and crystal growth inhibition [8].

**Table 1.** Representative storage modulus values ( $G'$ ) of the composites at several temperatures

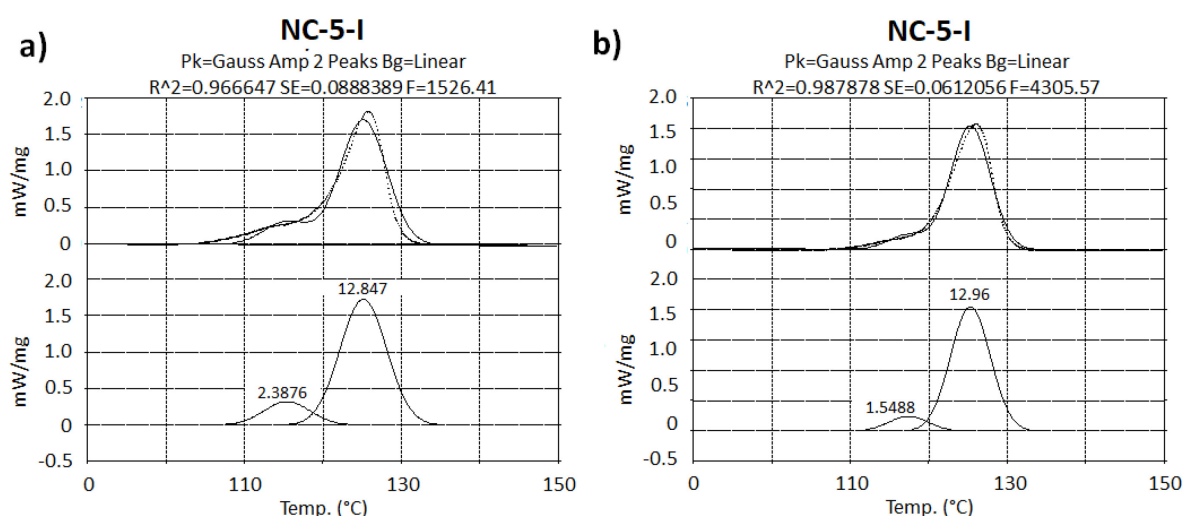
PP/clay Nanocomposites Sample		$T_m$ [°C] ± 0.2 %	$\Delta H_m$ [J/g] ± 2 %	$X_c$ [%] ± 2 %	$T_{c1}$ [°C] ± 0.2 %	$T_{c2}$ [°C] ± 0.2 %	$T_{oc}$ [°C] ± 0.2 %
1 <sup>st</sup> cycle	NC-0-I	162	98	47.3	113	-	117
	NC-5-I	164	106	51.2	114	126	130
	NC-10-I	164	102	49.3	114	126	130
	NC-15-I	164	91	44.0	114	126	130
	Masterbatch-I	168	68	32.9	-	126	132
2 <sup>nd</sup> cycle	NC-0-II	162	96	46.4	113	-	117
	NC-5-II	164	100	48.3	115	126	130
	NC-10-II	164	93	44.9	115	126	130
	NC-15-II	164	87	42.0	115	126	130
	Masterbatch-II	168	68	32.9	-	126	132

Additionally, the DSC cooling thermograms of PP/clay nanocomposites for both 1<sup>st</sup> and 2<sup>nd</sup> cycles are presented in Fig. 2. As seen in the figure, the 1<sup>st</sup> cycle samples were presented by different colored symbols (o) and the 2<sup>nd</sup> cycle samples were presented by different colored dashed-lines. From this figure, several parameters could be derived, which are: crystallization temperature ( $T_c$ ), which was taken as the peak temperature of the DSC cooling curve; and onset crystallization temperature ( $T_{oc}$ ). These parameters are also listed in Table 1.



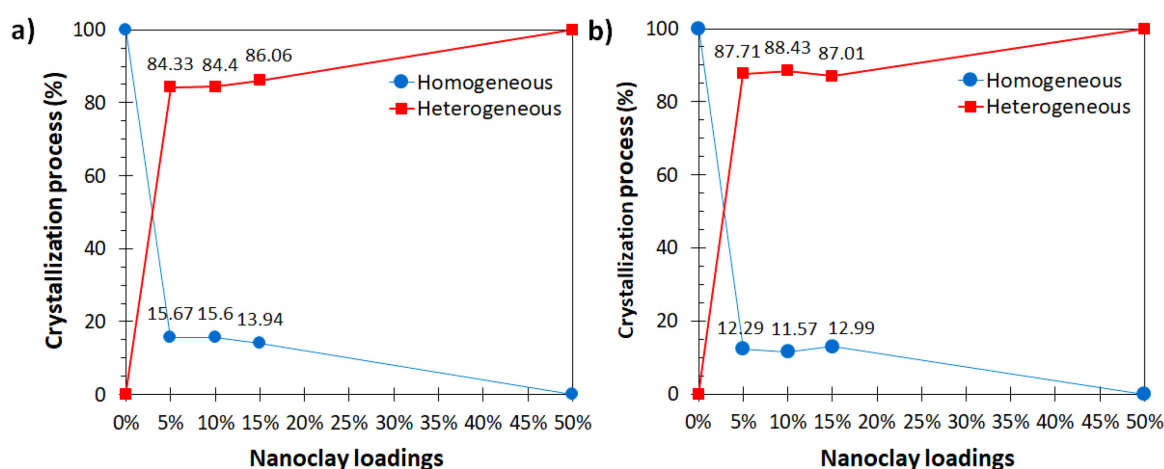
**Fig. 2.** DSC cooling thermograms of PP/clay nanocomposites for 1<sup>st</sup> and 2<sup>nd</sup> cycles. The 1<sup>st</sup> cycle samples were presented by symbol (o) and the 2<sup>nd</sup> cycle samples were presented by dashed-lines

As seen in Fig. 2, there were two crystallization peaks, i.e.  $T_{c1}$  and  $T_{c2}$ . The  $T_{c1}$  was associated with the “homogeneous” crystallization process of the neat PP. Whereas,  $T_{c2}$  was associated with the “heterogeneous” crystallization process, which promoted by the “heterogeneous” nucleation by the nanoclay materials. This was confirmed by comparing the  $T_c$  of the nanocomposites to that of PP and masterbatch. The  $T_{c1}$  was close to the  $T_c$  of neat PP, while,  $T_{c2}$  was close to the  $T_c$  of the masterbatch. This clearly indicates that the incorporation of nanoclay in the PP matrix has significantly increased the  $T_c$  as well as altered the crystallization mechanism/process of the nanocomposites by acting as a nucleating agent. Many literatures have reported the similar behavior of nanoclay [9-11]. Furthermore, the  $T_{oc}$  of the nanocomposites also shifted to a higher temperature (i.e. approx.. 13°C) compared to the neat PP. Additionally, the percentage of heterogeneous and homogeneous in overall crystallization mechanism of the nanocomposites were determined by deconvoluting the two crystallization peaks of the nanocomposites using the “Peak Fit” commercial software (Systat Software Inc. USA). Figures 3a and 3b show the deconvolution result of nanocomposites sample, NC-5-I and NC-5-II, respectively. It is worth noting that the rest of the samples were not shown here.



**Fig. 3.** Deconvolution result of crystallization peak of: **a)** NC-5-I and **b)** NC-5-II

Figure 4 shows the plot of these percentages. As seen in Fig. 4, the 2<sup>nd</sup> cycle of nanocomposites samples showed higher heterogeneous percentage compared to the 1<sup>st</sup> cycle. This can be explained that in the 2<sup>nd</sup> cycle, the nanoclay materials were better dispersed than in the 1<sup>st</sup> cycle, which was due re-processing effect. Therefore, the effect of heterogeneous nucleation also become better in 2<sup>nd</sup> cycle compared to the 1<sup>st</sup> cycle.



**Fig. 4.** The plot of the homogeneous and heterogeneous crystallization process of PP/clay nanocomposites samples, **a)** 1<sup>st</sup> cycle and **b)** 2<sup>nd</sup> cycle

## Conclusion

The effects of nanoclay loadings and re-processing (i.e. 1<sup>st</sup> cycle and 2<sup>nd</sup> cycle) on the melting and crystallization of the nanocomposites have been investigated by using a Differential Scanning Calorimetry (DSC). The DSC results showed that the melting temperature,  $T_m$  was not significantly affected by the nanoclay loadings and re-processing. In the other hand, the degree of crystallinity,  $X_c$  of the nanocomposites was higher than that of neat PP, but only reached a maximum at nanoclay loading of 5 wt% (i.e. 51.2% for NC-5-I and 48.3% for NC-5-II). Thereafter, the  $X_c$  decreased at higher nanoclay loadings. There was no significant difference in  $X_c$  between 1<sup>st</sup> cycle and 2<sup>nd</sup> cycle. Additionally, in all nanocomposites samples for both cycles, there were two crystallization temperatures, i.e.  $T_{c1}$  and  $T_{c2}$ . The  $T_{c1}$  was associated with the “homogeneous” crystallization process of the neat PP. Whereas,  $T_{c2}$  was associated with the “heterogeneous” crystallization process which promoted by the “heterogeneous” nucleation by the nanoclay materials. In the overall crystallization process, the  $T_c$  of nanocomposites increased by 11-12°C compared to that of neat PP. Whereas, the onset crystallization temperature,  $T_{oc}$  also increase by approx. 13°C. Apparently, there was no significant effect of nanoclay loadings and re-processing on the  $T_c$  and  $T_{oc}$  of the nanocomposites.

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