

# STUDY ON STRUCTURE AND CRYSTALLIZATION OF POLYPROPYLENE GRAFTED MALEIC ANHYDRIDE/NANOCLAY COMPOSITE

Bui Chuong\* and Dang Viet Hung

Polyme Centre, Hanoi University of Technology,  
01 Dai Co Viet Rd., Hanoi, Vietnam

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## ABSTRACT

Nanocomposite from polypropylene grafted maleic anhydride (PP-g-MA) and nanoclay were prepared by melt processing in Brabender extruder. XRD analysis shows the formation of nanostructure (intercalated and exfoliated) of nanocomposite with interlayer space (d-space) increasing from 26.3Å to 30.9Å. These structures, however, do not affect the microcrystalline structure of polymer part of nanocomposite in whole. The study on nonisothermal crystallization shows the development in 3-dimensional direction of crystallites, that means spherulite form of crystalline structure.

## 1. INTRODUCTION

Polymer nanoclay composites (PNC) are a new class of materials that attracts great attention due to their excellent mechanical, thermal properties as well as reduced gas and liquid permeability [1, 2]. Among them the thermoplastic PNC (polyolefins, polyamides, polystyrene *et al.*) have been studied most intensively.

Polypropylene (PP) as a very popular thermoplastic resin is involved in PNC preparation due to its very good mechanical properties in combination with low price. However, pure PP hardly forms nanocomposite with nanoclay because of its nonpolarity. So, for nanocomposite preparation, PP is often modified by polar groups such as hydroxyl, maleic anhydride, *etc.* [3, 4]. From these modified PP, the most popular is PP grafted maleic anhydride (PP-g-MA).

It is well known that PP properties depend on its crystalline structure. Subsequently, the properties of PP/nanoclay composite should also depend on PP crystalline structure. However, using PP-g-MA instead of PP inevitably lead to some changes in crystallization behavior of nanocomposite. For that reason, there are the works devoted to crystallization behavior of nanocomposites based on PP-g-MA and nanoclay and their properties as well [5 - 9].

In this paper, the formation of nanostructure of PP-g-MA/nanoclay composite and its nonisothermal crystallization have been studied.

## 2. EXPERIMENTAL

### 2.1 Materials

In this study, PP-g-MA is prepared in our laboratory according to [10] by melt grafting. The

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\* Corresponding author e-mail: polymercentre@mail.hut.edu.vn

grafted MA content is 0.5% (by weight). Nanoclay is I28E derived from Nanocor Company (USA).

PP-g-MA/nanoclay composite was prepared by direct melt mixing in Brabender mixer (Germany) with the speed 120 rpm and temperature 165°C. Clay loading is 6% (by weight).

## 2.2 Experimental methods

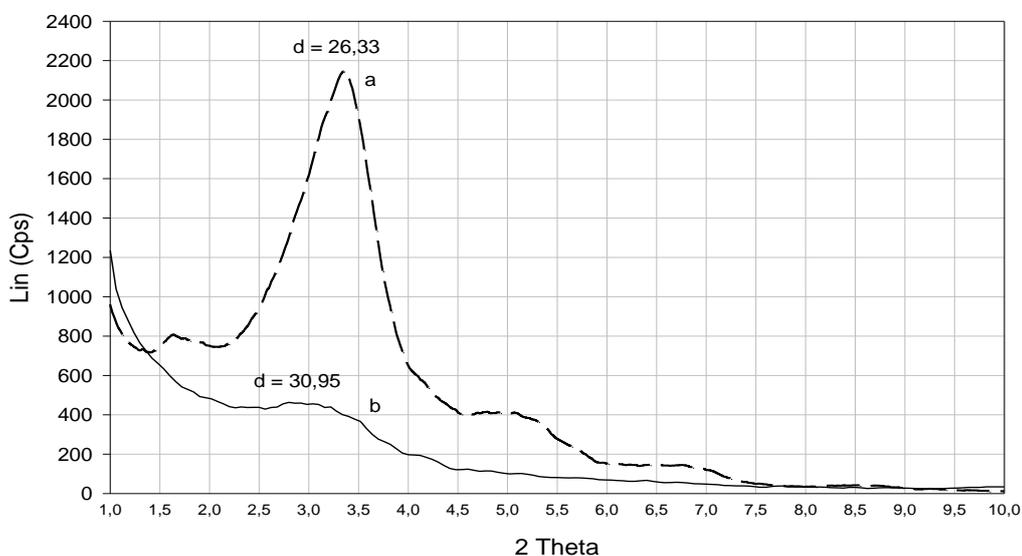
Structure of nanocomposite is characterised by XRD method. X-ray diffraction is performed by Bruker D5005 diffractometer operated at 40 kV and 30 mA. Scanning rate is 2°/min. from 0.6 to 40°.

Crystallisation is studied using differential scanning calorimetry (DSC) on Bahr DSC 310 calorimeter (Germany) according to ISO 11357-1: 1997 (E). The temperature is correlated with indium. For elimination of thermal history, the samples were melted at 200°C for 10 min. and then cooled at constant cooling rates of 2.5 and 10 K/min.

## 3. RESULTS AND DISCUSSION

### 3.1 Formation of nanostructure

When PP-g-MA was mixed with nanoclay at high temperature and appropriate shear rate, its molecules would intercalate into silicate layers and expand the interlayer space. The formation of these structures should be expressed on XRD pattern of PP-g-MA/nanoclay composite (Fig. 1).



**Fig. 1:** XRD pattern for (a) nanoclay I28E, (b) PP-g-MA/ nanoclay composite.

From X-ray diffraction data, one can see that the interlayer space  $d$  extend remarkably: from 26.3Å for I28E to 30.95Å for nanocomposite. That means polymer molecules were able to move into silicate layers and form intercalated structure.

Based on XRD data, some parameters of nanocomposite may be calculated, using Scherer

formula [11]

$$t = \frac{0.95\lambda}{B \cdot \cos \theta}$$

where  $t$  - the crystallite thickness

$\lambda$  - X-ray wave length

$\theta$  - Bragg angle

$B$  - nominated peak width, defined as  $B^2 = B_s^2 - B_{st}^2$ ;  $B_s$ ,  $B_{st}$  are peak width of sample and standard material respectively.

The average number of silicate layer ( $n$ ) may be calculated roughly as:

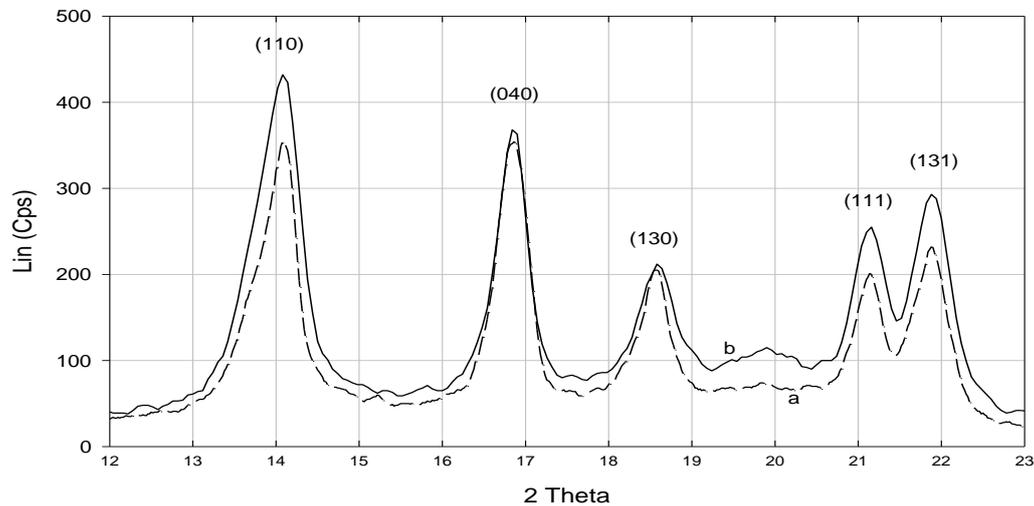
$$n = \frac{t}{d}$$

where  $d$  - interlayer space of nanoclay.

Calculated parameters are presented in Table 1.

**Table 1:** Characteristic parameter of nanoclay and nanocomposite (PPNC).

Item	I28E	PPNC
Interlayer space, Å	26.33	30.95
Crystallite thickness, Å	313	80
Number of silicate layer	12	2.5



**Fig. 2:** XRD pattern at wide angle for (a) PP-g-MA, (b) PP-g-MA/nanoclay composite.

Calculated values of crystallite thickness and average number of silicate layers, as shown in Table 1, indicate that beside intercalated structure, in nanocomposite exist even exfoliated

structures. The crystallite thickness reduces from 313Å (for I28E) to 80Å (for nanocomposite), and average number of silicate layers decreases from 12 to 2.5 respectively, that means a part of nanoclay splits off from crystallite edges.

The existence of exfoliated structure may be seen also on XRD pattern (Fig. 1): characteristic peak for nanocomposite at small angle  $2\theta$  is obviously more obtuse than that of I28E.

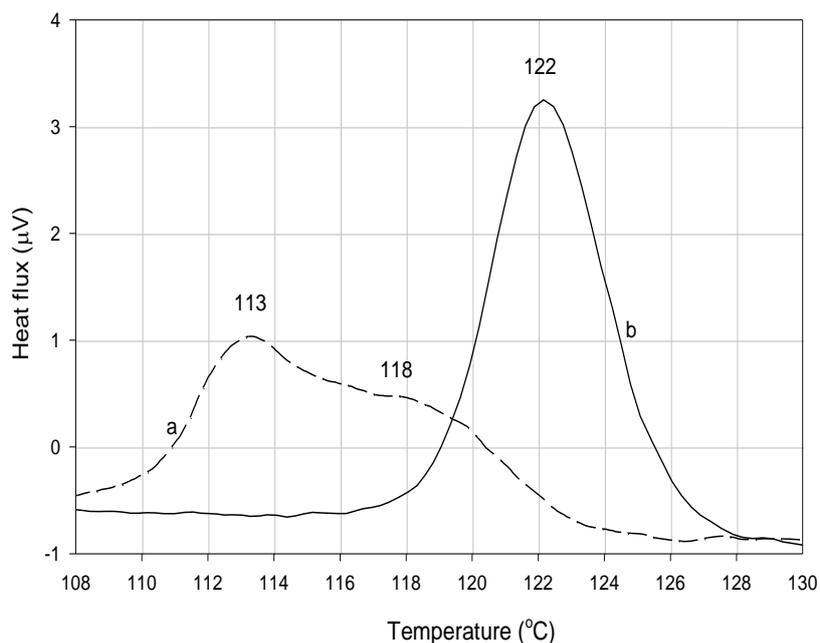
For more detail assess to microstructure of PPNC, the comparison of XRD patterns at wide angles for PP-g-MA and PP-g-MA/nanoclay composite was made (Fig. 2).

From Fig. 2 one can see these patterns almost coincide to each other at wide angle. That mean there is no change in microstructure (crystalline) of nanocomposite. The formation of intercalated and exfoliated structures of nanoclay does not affect to microcrystalline structure on the whole.

In general, the XRD analysis of PP-g-MA/nanoclay composite shows the formation of nanostructures (exfoliated and intercalated). Beside, it also indicates the structure of polymer part outside of nanocrystallites is similar to that of virgin polymer.

### 3.2 Crystallization behavior of PP-g-MA/nanoclay composite

The crystallization behavior of PP-g-MA/nanoclay composite was studied by using differential scanning calorimetry (DSC). The DSC curve of PP-g-MA/nanoclay composite at cooling rate 10 K/min was presented in Fig. 3. For comparison, the DSC curve of PP-g-MA was presented, too.



**Fig. 3:** DSC exotherms of (a) PP-g-MA, (b) PP-g-MA/nanoclay composite (cooling rate 10 K/min).

From exotherms on Fig. 3 obviously that PP-g-MA/nanoclay composite crystallised at temperature higher (122°C) than PP-g-MA (113°C). Besides, the exotherm of nanocomposite shows only one peak with smaller width, while PP-g-MA exotherm shows two obtuse peak. It

indicates that crystallization of PP-g-MA/nanoclay composite occurs in one stage at higher rate than PP-g-MA, where crystallization has two stages. The reason of this may be the nucleation effect of nanoclay, that points out in literature [5, 12, 13].

For more detail study on nonisothermal crystallization of PP-g-MA/nanoclay composite, the Avrami equation is used. Although this equation is well known for isothermal crystallization, it can be successfully applied for nonisothermal crystallization of nanocomposite [5, 13].

$$1 - X_t = \exp.(- Z.t^n) \tag{1}$$

where  $X_t$  - relative crystallization degree at moment  $t$  and defined as:

$$X_t = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_{T_0}^{T_e} (dH_c/dT)dT}$$

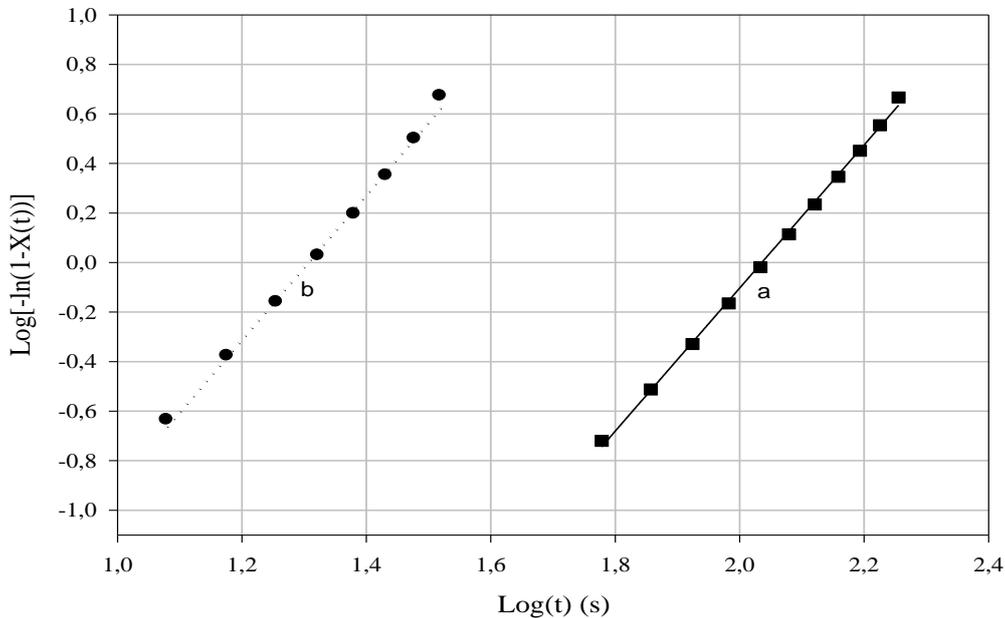
$T_0, T_e$  - the temperatures at beginning and end of crystallization process  
 $dH_c/dT$  - heat flow at temperature  $T$

Avrami equation (1) can be converted as:

$$\log[-\ln(1 - X_t)] = \log Z_t + n \log t \tag{2}$$

where  $n$  - isothermal Avrami exponent  
 $Z$  - crystallisation kinetic rate constant

Dependence of  $\text{Log}[-\ln(1 - X_t)]$  on  $\log t$  is presented on Fig. 4.



**Fig. 4:** Plot of  $\text{Log}[-\ln(1 - X_t)]$  versus  $\log t$  at cooling rate 2.5 K/min (a) and 10 K/min (b).

From data presented on Fig. 4 and equation (2) the crystallisation parameters were calculated (Table 2).

**Table 2:** Parameters  $Z_t$  and  $n$  for crystallisation of PP-g-MA/nanoclay composite.

Cooling rate	$Z_t$	$n$
2.5 K/min	$1.31 \cdot 10^{-6}$	2.889
10 K/min	$1.51 \cdot 10^{-4}$	2.927

As clearly shown in Table 2, in both case the value of Avrami parameter  $n$  is around 3. Due to nucleation effect of nanoclay, it may be considered that crystalline nuclei are formed immediately at the beginning of process, so crystalline structures of nanocomposite developed in 3-dimensional directions independently on cooling rate. It quite agreed with the authors [12 - 14] who point out the spherulite structures of polypropylene-clay nanocomposite. The difference in values of parameter  $Z$  shows only various crystallisation degrees.

#### 4. CONCLUSIONS

1. In formation of PP-g-MA/nanoclay composite, the intercalated and exfoliated structures were formed. However, in the polymer part outside of nanostructure, the crystalline character remains unchanged.
2. PP-g-MA/nanoclay composite crystallise at higher temperature with higher rate in comparison with neat PP-g-MA. Analysis of nonisothermal crystallisation show that crystalline structures of nanocomposite develop in 3-dimensional directions (in form of spherulites) independently on the crystallisation rate. It is due to nucleation effect of nanoclay in polymer matrix.

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