

# MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ISOTACTIC POLYPROPYLENE REINFORCED WITH TiO<sub>2</sub> NANOPARTICLES

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## 1 Introduction

As a semi-crystalline polymer, mechanical properties of polypropylene (PP) are strongly affected by its crystalline structure and degree of crystallinity. The main effect of nanoparticles on PP is the alteration of its crystalline structure [1]. Monoclinic crystalline structure ( $\alpha$ ) is the most stable crystal form of isotactic PP (iPP). Special thermal/mechanical conditions or addition of external agent could lead to the less common trigonal ( $\beta$ ) form crystals [2]. Presence of  $\beta$ -form crystals in PP could enhance its impact toughness [3]. Mina et al. [4] reported that adding titanium dioxide (TiO<sub>2</sub>) particles alters the crystalline structure of iPP from a mixture of  $\alpha$ ,  $\beta$  and  $\gamma$  forms to only  $\alpha$ -form and decreases PP crystallite size. On the contrary, a  $\beta$  nucleating agent effect was also reported for CaCO<sub>3</sub> nanoparticles used to toughen iPP [5, 6].

The aim of present work is to study the effect of adding TiO<sub>2</sub> nanoparticles on the crystalline structure and mechanical properties of polypropylene based nanocomposites.

## 2 Experimental

### 2.1 Materials

A homopolymer iPP resin with melt flow index (MFI) 2.8 dg/min and density 0.9 g/cm<sup>3</sup> was used as the polymer matrix. An anhydride-modified polypropylene (AM-PP) with MFI of 3.5 dg/min and density of 0.89 g/cm<sup>3</sup> was utilized as the compatibilizer. A commercial grade TiO<sub>2</sub>

nanoparticle with an average primary particle size of 21 nm was used as the additive.

### 2.2 Nanocomposite Preparation

The compatibilized and uncompatibilized PP/TiO<sub>2</sub> nanocomposites containing 1 to 15 vol% (4.6 to 45.5 wt%) of TiO<sub>2</sub> were prepared via a masterbatch method using a melt compounding process in a co-rotating twin-screw extruder. For further characterization, the samples were compression-molded into discs and dumbbell specimens.

### 2.3 Sample Characterization

Thermal properties and crystallization behavior of PP in the presence of TiO<sub>2</sub> nanoparticles were analyzed using differential scanning calorimetry (DSC). The samples were heated up 10°C/min and cooled down using different cooling rates. Crystalline structure of the nanocomposite samples was investigated through wide angle X-ray diffraction (WAXD). Tensile characterization was carried out according to ASTM D638 using an Instron 3365 Universal Testing System. Morphology of the samples was studied by a JEOL scanning electron microscope (SEM). In order to observe crystal structure of iPP, the samples were etched using a permanganic solution as described in [7].

## 3 Results and Discussion

Fig. 1a shows DSC thermograms of neat polymers and the nanocomposites during first melting run. As it can be seen, there is an extra melting peak around 147 °C in the samples containing 1 vol% of TiO<sub>2</sub>

which could be attributed to the formation of  $\beta$ -form crystalline structure in the presence of  $\text{TiO}_2$ . Fig. 1b compares XRD patterns of  $\text{TiO}_2$ , neat PP and PP/ $\text{TiO}_2$ -1 nanocomposite. Obviously, the nanocomposite sample has a characteristic diffraction peak around  $16^\circ$ , which corresponds to the (300) crystal plane of  $\beta$ -phase of polypropylene [8].

Fig. 3 representatively illustrates effect of  $\text{TiO}_2$  nanoparticles on crystallization behavior of PP. It shows DSC curves of the samples recorded during crystallization at different cooling rates. As it can be seen, crystallization peak temperature ( $T_c$ ) decreases with cooling rate in all the samples. On the other hand, adding nanoparticles increased  $T_c$ . It could be attributed to heterogeneous nucleation effect of the  $\text{TiO}_2$  nanoparticles.

In order to calculate a value for the overall effective activation energy of nonisothermal crystallization ( $\Delta E$ ), the Kissinger's method has been used [9]. It relates variation of  $T_c$  with cooling rate ( $\Phi$ ) to  $\Delta E$ :

$$\frac{d\left(\ln \frac{\Phi}{T_c^2}\right)}{d\left(\frac{1}{T_c}\right)} = -\frac{\Delta E}{R} \quad (1)$$

where  $R$  is the universal gas constant. Fig. 2 shows plots of  $\ln(\Phi/T_c^2)$  versus  $1/T_c$  for different samples. The lines represent the best linear fit on the data. Values of  $\Delta E$  obtained from the slope of the lines are reported in Table 1. It shows that adding up to 3 vol%  $\text{TiO}_2$  nanoparticles decreases activation energy of crystallization. However, adding 4 and 5 vol% nanoparticle increased the activation energy of crystallization to higher than  $\Delta E$  of neat PP.

Crystallization from polymer melts is influenced by nucleation and growth. Presence of nanoparticles leads to a heterogeneous nucleation in all the  $\text{TiO}_2$  contents causing higher crystallization rate and higher  $T_c$ . However,  $\Delta E$  represents the activation energy for the transport of the polymer molecular chain segments to the growing surface of crystal [10]. Accordingly, decrease of  $\Delta E$  values in the presence of low contents of  $\text{TiO}_2$  (1 and 3 vol%) reveals that the nanoparticles do not reduce (or may even facilitate) the molecular chain mobility of PP in

the melt state. Higher  $\text{TiO}_2$  contents (4 and 5 vol%) limit molecular mobility resulting in higher activation energy, but nucleation role of the nanoparticles is still controlling parameter leading to higher  $T_c$ .

Fig. 4 illustrates melting behavior of the nanocomposite samples during the second heating run at rate of  $20^\circ\text{C}/\text{min}$  following the nonisothermal crystallization at different cooling rates. It shows the effect of cooling rate on crystalline structure of the samples. DSC curves of neat PP samples (Fig. 4a) have single melting peaks around  $160^\circ\text{C}$  associated with  $\alpha$ -form crystals of isotactic PP. It is noticeable that the PP samples, crystallized at higher cooling rates, have lower melting peak temperature. All the PP/ $\text{TiO}_2$ -1 samples have double melting point behavior indicating that both  $\alpha$ - and  $\beta$ -form crystals are formed under crystallization at different cooling rates (Fig. 4b). It can be seen in Fig. 4b that the melting peak temperatures decrease by increasing the cooling rate. In addition, the relative intensity of melting peak of  $\beta$ -form to  $\alpha$ -form increases with cooling rate. Although there is only one major melting peak for PP/ $\text{TiO}_2$ -4 in Fig. 4c, increasing cooling rate leads to formation of a small peak at lower temperature. It could be attributed to presence of  $\beta$ -form iPP.

Fig. 5 representatively depicts tensile stress-strain curves of PP/ $\text{TiO}_2$  nanocomposites. The elastic modulus of the nanocomposites increased with increasing  $\text{TiO}_2$  concentration, except for the nanocomposites containing 1 vol% of  $\text{TiO}_2$ . In addition, presence of the  $\beta$ -form crystals in PP-T-1 led to the lower tensile stress at yield,  $\sigma_y$  compared to the other samples. It is noticeable that the presence of the nanoparticles eliminated strain hardening in the nanocomposite containing more than 1 vol%  $\text{TiO}_2$ .

SEM micrographs from etched samples of neat iPP and PP/ $\text{TiO}_2$ -1 are presented in Fig. 6. While a typical spherulitic morphology of crystals is observed in the neat sample (Fig. 6a), addition of  $\text{TiO}_2$  nanoparticles causes the formation of small and imperfect spherulites (Fig. 6b).

### 3 Conclusion

Adding TiO<sub>2</sub> nanoparticles caused to formation of  $\beta$ -form crystals of iPP. Nonisothermal crystallization analysis showed that, unlikely to concentrated nanocomposites, low content of the nanoparticles, up to 3 vol%, does not decrease molecular motion of PP during crystallization. It results in the lower values of effective activation energy of crystallization. Presence of  $\beta$ -form crystals causes lower elastic modulus and yield strength in the PP/TiO<sub>2</sub> nanocomposites.

### Acknowledgment

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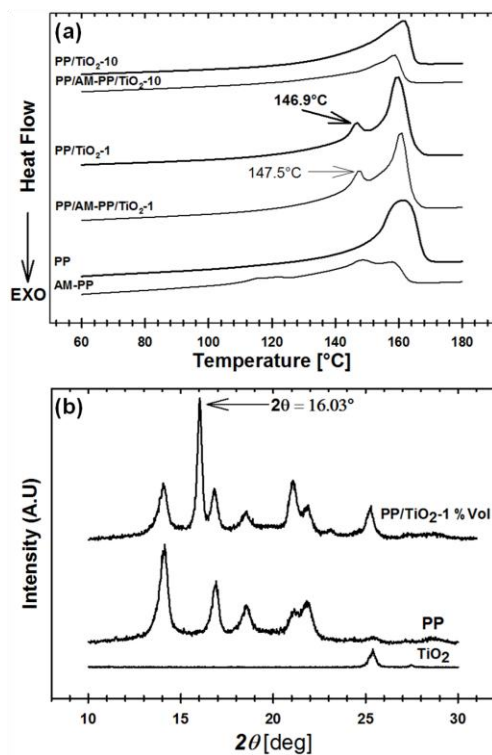
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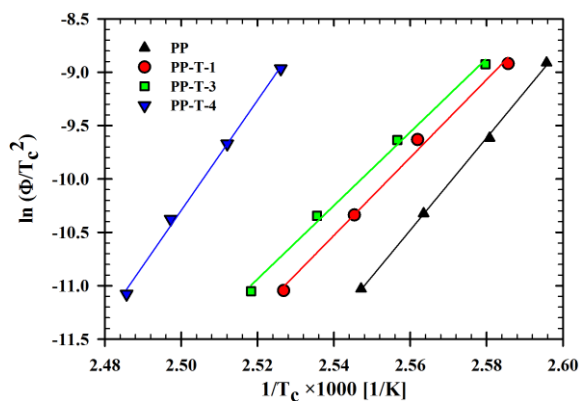
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**Table 1.** Activation energy of nonisothermal crystallization.

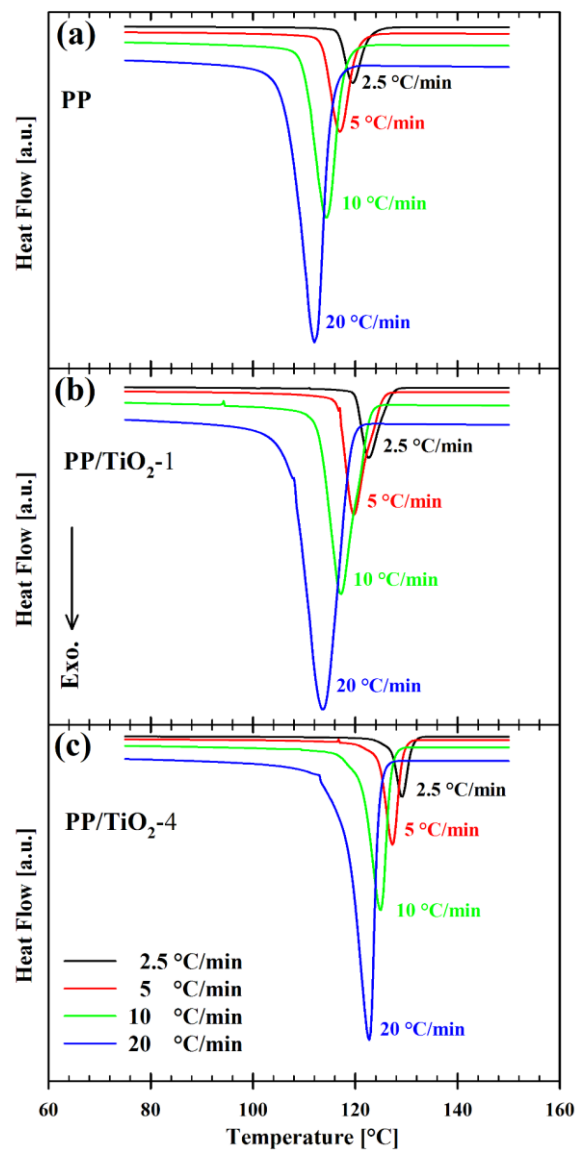
Sample	$\Delta E$ kJ/mol
PP	360
PP-T-1	303
PP-T-3	286
PP-T-4	430
PP-T-5	415



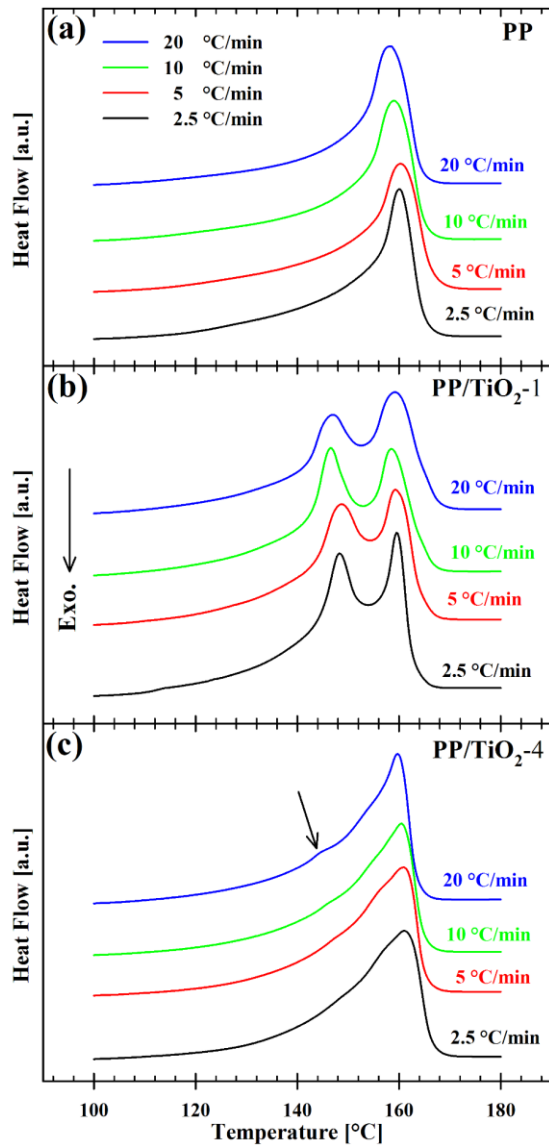
**Fig. 1.** (a) DSC thermograms and, (b) XRD pattern of PP/TiO<sub>2</sub> nanocomposites.



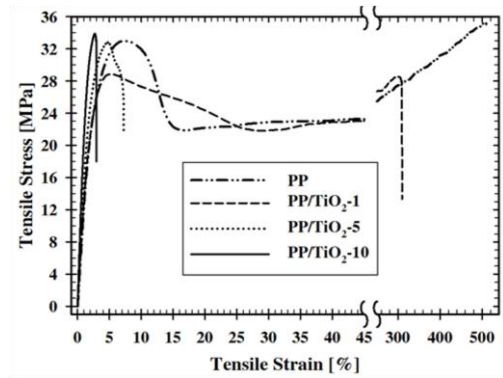
**Fig. 2.** Plots of  $\ln(\Phi/T_c^2)$  versus  $1/T_c$ .



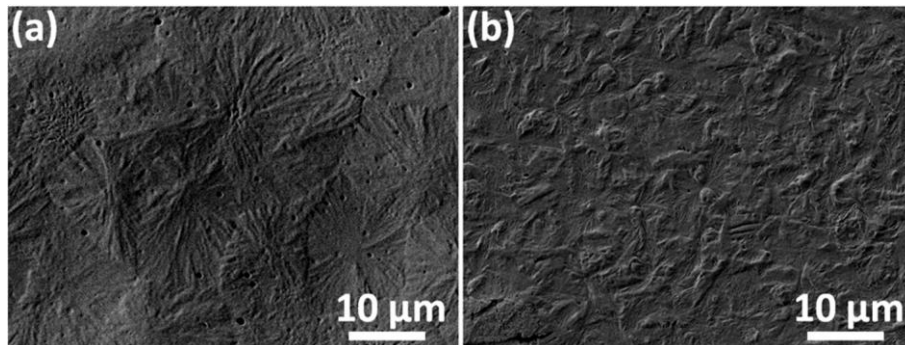
**Fig. 3.** DSC thermograms of non-isothermal crystallization at different cooling rates for (a) PP, (b) PP/TiO<sub>2</sub>-1 and, (c) PP-TiO<sub>2</sub>-4.



**Fig. 4.** DSC melting curves after non-isothermal crystallization at different cooling rates for (a) PP, (b) PP/TiO<sub>2</sub>-1 and, (c) PP-TiO<sub>2</sub>-4.



**Fig. 5.** Tensile stress versus strain of neat PP and PP/TiO<sub>2</sub> nanocomposites.



**Fig. 6.** SEM micrographs of etched samples; (a) neat PP, (b) and (c) PP/TiO<sub>2</sub>-1 vol%.