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# Reinforcing polypropylene with calcium carbonate of different morphologies and polymorphs

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**Abstract:** The influence of calcium carbonate ( $\text{CaCO}_3$ ) with different polymorphs (calcite and aragonite) and morphologies (granular and rod-like) on mechanical and crystallization properties of polypropylene (PP) was investigated. Meanwhile, these  $\text{CaCO}_3$  fillers coated with oleic acid were added in different contents to PP. The results indicate that the tensile strength, flexural strength, modulus, and crystallization property of the filler-treated samples are improved, but the impact strength decreased. The crystallinity of the composites is higher than that of neat PP. Moreover, in the rod shape filler-treated sample, in both whisker species, the mechanical properties of composites are superior to the particles filled. Differential scanning calorimetry, X-ray diffraction, and mechanical tests display that calcite whisker-reinforced composite has higher crystallization enthalpy, melting enthalpy, degree of crystallinity, and mechanical properties than aragonite whiskers and calcite particles filled composites.

**Keywords:** calcium carbonate; mechanical properties; polypropylene.

## 1 Introduction

Polypropylene (PP) is an important commercial polymer, extensively applied in areas such as home appliances, construction, automobile, and other industrial appliances, owing to its attractive properties, easy processing, and low cost [1–4]. Therefore, it shows a raise in demand market in comparison with other polymers. However, they are seldom used as neat polymers and usually compounded with

mineral fillers [5–7]. The incorporation of fillers into thermoplastics has been widely used in the industry to extend them and to enhance certain properties [7, 8]. In general, modulus of elasticity, hardness, tensile stress at break, and melt viscosity are ameliorated significantly by filling with rigid inorganic particles. Some of the most popular fillers widely used in the industry are calcium carbonate, mica, and tale powder [9–13]. Among them, calcium carbonate is one of the most common used for PP, mainly due to its availability in readily usable form and low cost.

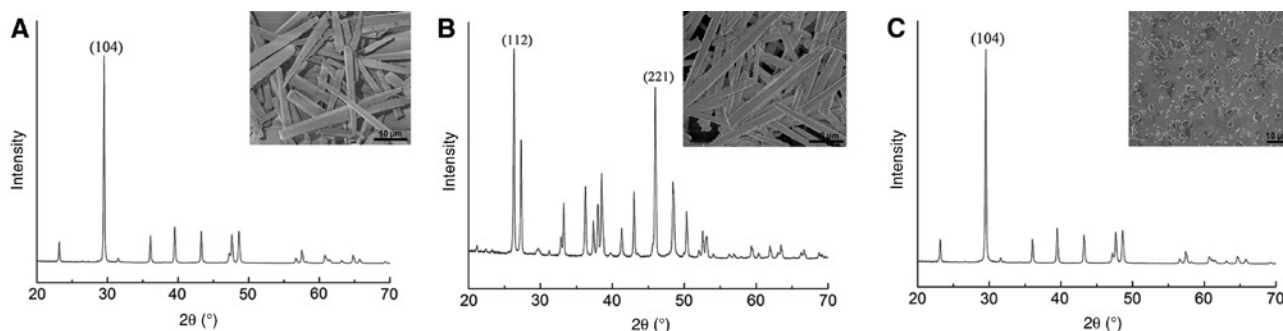
The common morphologies of the polymorphs of calcium carbonate are rhombohedral calcite, needle- or rod-like aragonite, and spherical vaterite. Calcite is the stable form under ambient conditions, while aragonite is metastable [14]. The rod-like morphology belongs to whisker, which is a type of inorganic single crystal with a diameter of 0.5–2  $\mu\text{m}$  and length of 20–60  $\mu\text{m}$ . It is a monocrystalline material with excellent physical, chemical, and mechanical properties of high strength, modulus, and good thermal performance [15, 16]. The use of either spherical or elongated particles that have different aspect ratio is expected to differently influence many properties of the final material, such as thermal and mechanical behavior [17]. Therefore, the effect of composite properties also depends strongly on the shape and crystallinity of the reinforcement, as well as on the modifier used [18, 19]. In general, a few comprehensive studies explicitly address the effect of different crystals and shapes of  $\text{CaCO}_3$  on PP properties [17, 18], especially the effect of calcite whisker (CW) in the context of PP property elucidation.

Therefore, this work was a comparative study to evaluate the effects of morphologies (calcite and aragonite), polymorphs (granular and rods-like), and different contents of fillers on mechanical and crystallization properties of PP/ $\text{CaCO}_3$  composites. Three composites containing 5, 10, 15, 20, and 25 wt% CWs, aragonite whiskers (AWs), and calcite particles (CPs), respectively, were prepared through melt-blending. In order to obtain tightly bonded composites, the fillers were modified with oleic acid. The mechanical properties of composites were investigated by instrument testing. The morphologies of composites were observed by field emission scanning electron microscopy (FESEM). Furthermore, the crystallization properties were determined by differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

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**Figure 1:** XRD pattern and FESEM micro-morphology: (A) calcite whiskers, (B) aragonite whiskers, (C) calcite particles.

## 2 Materials and methods

### 2.1 Materials

Isotactic PP (6331-11) was a commercial product (Taiwan Polymers Co., Ltd., Tao Yuan, Taiwan), with a melt flow index of 14 g/10 min. AWs, CWs, and CPs treated by oleic acid were used in this study. The AWs and CWs were home-built, in which the length, diameter, and aspect of whiskers were 10–60  $\mu\text{m}$ , 0.5–2  $\mu\text{m}$ , and 20–30, respectively. And CPs were purchased from Beijing Chemical Works (Beijing, China), where length, diameter, and aspect ratio were 1–4  $\mu\text{m}$ , 1–2  $\mu\text{m}$ , and 1–2. Antioxidant and other reagents belonged to chemically pure grade that were available.

The morphologies and XRD patterns of three types of calcium carbonate fillers were shown in Figure 1. Abbreviation and composition of the three composites were given in Table 1.

### 2.2 Specimen preparation

The composites were prepared by mixing PP with 5, 10, 15, 20, and 25 wt% of the treated individual filler and anti-oxidant (0.02 wt%) in the chamber of a mixer (RM-200C, Harbin Hapro Electric Technology Co., Ltd., Harbin, China) with a speed of 50 rpm at 200°C for 10 min. The material removed from the chamber was immediately compression-molded into a 4-mm-thick plate at 200°C for 15 min under a pressure of 10 MPa. The shape of molded samples was in accordance with ASTM D638, ASTM D790, and ASTM D256 standards.

### 2.3 Mechanical measurement

All mechanical tests were performed according to the standard testing methods. Tensile and flexural properties

**Table 1:** Abbreviation and composition of the studied composites.

Abbreviations	Compounds
PP/CWs	PP and rod-like calcite whiskers
PP/AWs	PP and rod-like aragonite whiskers
PP/CPs	PP and granular-calcite particles

were measured using a universal testing machine (SANS) in accordance with ASTM D638 and ASTM D790 procedures, at a crosshead speed of 50 mm/min and 2 mm/min, respectively. Notched Izod impact strength was measured using an impact tester (XJJD-50) according to ASTM D256. All the measurements were carried out at room temperature. The average value reported was derived from at least five specimens.

The impact-fractures surfaces of the samples were examined by FESEM (SU8010).

A DSC equipment (Axios, PANalytical, Eindhoven, the Netherlands) was used to study the crystallization and melting behaviors of the samples. Isothermal analyses were conducted by heating the samples from 30°C to 200°C and cooling from 200°C to the 30°C of each sample.

XRD (X'Pert PRO) was used to determine the crystal structure and the degree of crystallinity for neat and CaCO<sub>3</sub>-filled PP samples. The X-ray source (Al K $\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ ) was operated at a voltage of 40 kV and a filament current of 40 mA.

## 3 Results and discussion

### 3.1 Mechanical properties analysis

#### 3.1.1 Tensile properties

Figure 2A shows that tensile strength rose up to a maximum value and then gradually declined in the

blends with an increasing fraction of fillers. It reveals that the tensile strength of composites with 5 wt% CWs, AWs, and CPs increased by 18.9%, 15.9%, and 11.3% compared with the PP matrix. Figure 2B displays a moderately enhanced tensile modulus with increasing filler contents. The addition of 25 wt% CWs, AWs, and CPs caused a rise in tensile modulus by 20.8%, 17.2%, and 3.1%, respectively, in contrast to the pure PP. The increase in the composites stiffness is obviously a result of the high modulus of the fillers. When the filling content is low, it can evenly disperse and transfer stress in the matrix in order to enhance the strength of composites. Furthermore, according to load-transfer theory [20, 21], it shows that stress could transfer from polymer matrix to whiskers through the interfacial layer and afford parts of stress to disperse load in the matrix, because of the large interfacial area between them. And hence, whisker composites have superior tensile properties compared to the particles, permitting more stress transfer between the matrix and whiskers. However, the decrease of the strength for the composite

with higher CaCO<sub>3</sub> composition may be mainly influenced by the dispersibility of the fillers. The excessive amounts of fillers also damage the continuity of matrix.

### 3.1.2 Flexural properties

It is seen that flexural properties exhibit a similar trend as that of tensile properties (Figure 3); the addition of 5 wt% CWs, AWs, and CPs results in flexural strength of composites being increased by 12.5%, 8.2%, and 3.8%, respectively, over pure PP. Additionally, a maximum improvement of 1627 MPa, 1437 MPa, and 1355 MPa in flexural modulus is achieved with 25 wt% CWs, AWs, and CPs, respectively. The flexural properties for samples with three different species have almost the same behavior, where the explanation is similar to that of the tensile properties. The above results indicate that the composites reinforced whiskers show higher flexural strength and flexural modulus compared to the particle composites.

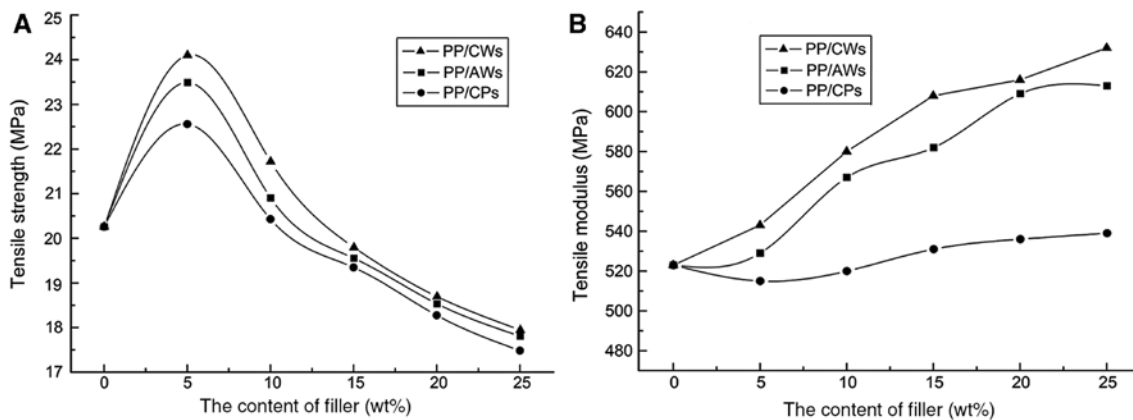


Figure 2: The results of tensile properties for PP/CWs, PP/AWs, and PP/CPs composites: (A) tensile strength, (B) tensile modulus.

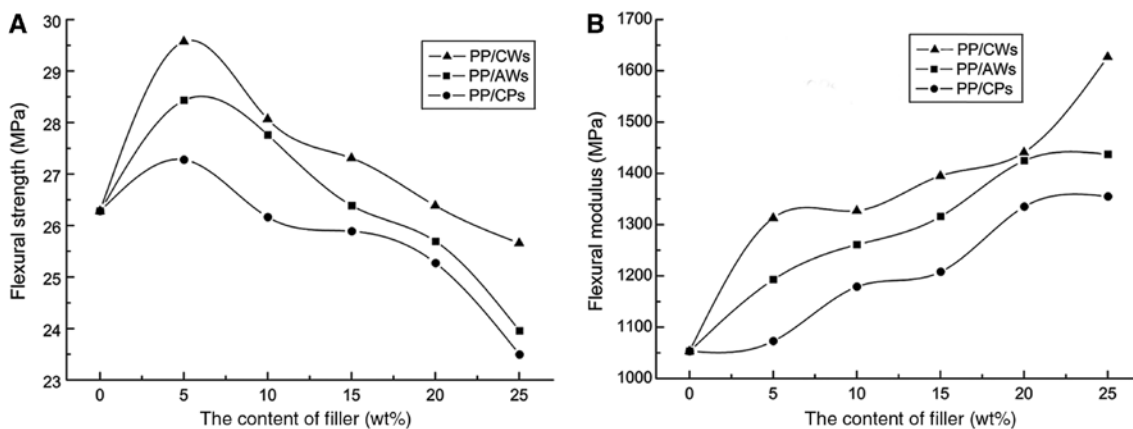
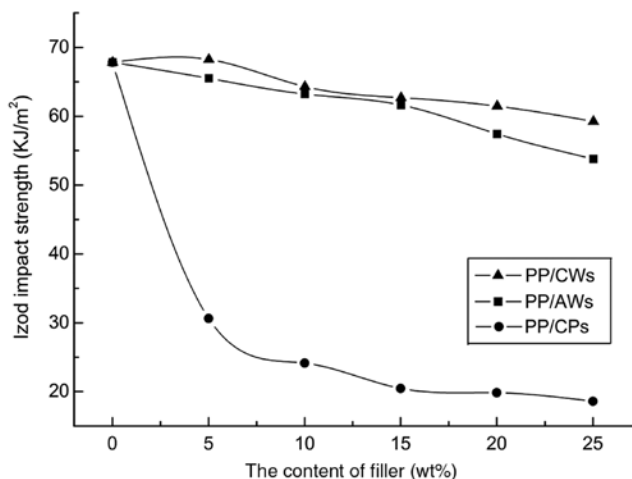


Figure 3: The results of flexural properties for PP/CWs, PP/AWs, and PP/CPs composites: (A) flexural strength, (B) flexural modulus.



**Figure 4:** The results of notched impact strength for PP/CWs, PP/AWs, and PP/CPs composites.

### 3.1.3 Izod impact strength

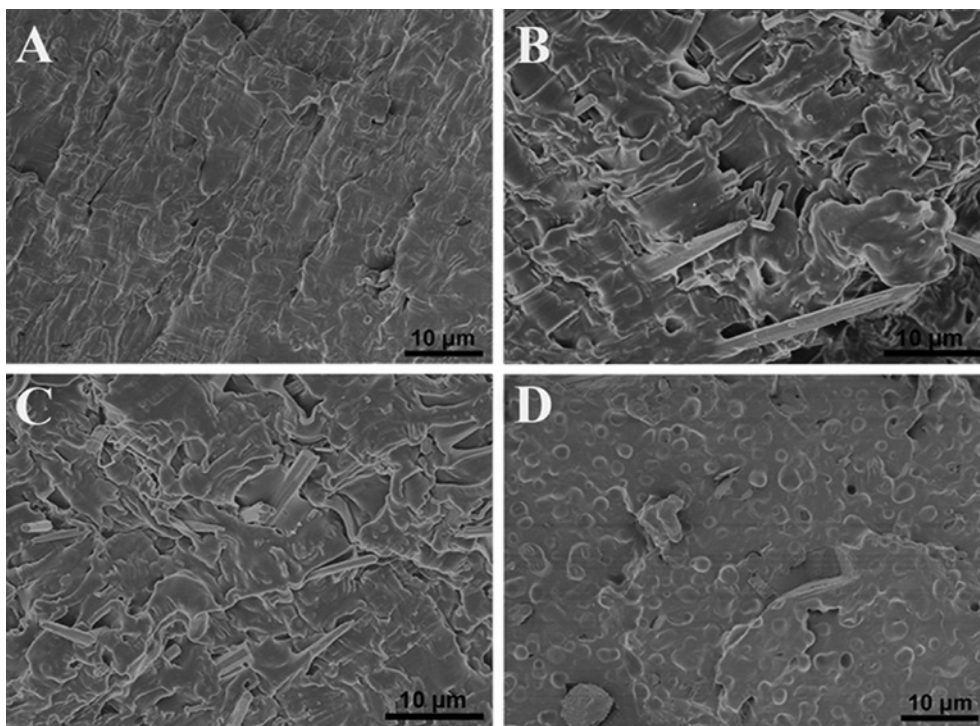
From Figure 4, it reveals that Izod impact strength decreased with the increase of filler content for the three kinds of composites. The addition of CPs to PP caused the impact strength to sharply drop from 67.83 kJ/m<sup>2</sup> to 18.60 kJ/m<sup>2</sup>, whereas there is no marked decreased in the PP blended with CWs and AWs. It implies that the PP/CWs and PP/AWs composites have higher strength compared to

PP/CPs. Based on the toughening mechanisms [15, 16], the main toughening models of whiskers are crack bridging, crack deflection, and whisker pullout. It shows the toughening effects related to energy-dissipating processes at the crack tip, which are dependent on the aspect ratio of the reinforcing fillers. The strengthening effects are enhanced with the increasing of aspect ratio of fillers. Therefore, the higher aspect ratio of whisker might be more effective in crack bridging and whiskers pullout than that of the CPs. Meanwhile, the whiskers should be more resistant to crack propagation in the matrix. Therefore, the whisker fillers have stronger toughening effect compared to the particles.

The above results suggest that the mechanical properties of the composites filled with whiskers are higher than that of the particles composites. Furthermore, PP/CWs have the best enhancing effect, accompanied by the highest tensile strength, flexural strength, impact strength, and modulus. The result indicates that the improvement of mechanical properties connects with morphologies and crystal forms.

## 3.2 Fractography

Figure 5 shows the micrographs of the fracture surfaces at notch roots of PP and composites with 5 wt% CWs, AWs,



**Figure 5:** FESEM micrographs of fracture surface of a broken Izod sample: (A) PP, (B) PP/CWs, (C) PP/AWs, (D) PP/CPs.

and CPs. The cross-section of neat PP is quite smooth, and no sign of shearing could be observed, as evidenced in Figure 5A. This reveals that PP basically undergoes a brittle fracture. In contrast to neat PP, Figure 5B and C display a part of whiskers that is pulled out from the matrix. During the pullout, energy normally causing crack propagation is partially expended by deponding and friction of the whiskers. In addition, the cracks are bridged by whiskers in fracture surface and produce closure stress, where the continuous propagates of cracks are inhibited. However, Figure 5D exhibits that the tips of the particles are embedded below the plane of fracture and the interface is relatively flat, indicating signs of brittle fracture behavior. There is no obvious bridging and pullout effect at fracture surface, which leads to a reduction in the impact strength for the PP with CPs. Obviously, toughening effect of whiskers is stronger than that of particles, attributed to the pullout and bridging mechanism of whiskers. Therefore, PP/CWs and PP/AWs have higher impact strength than that of PP/CPs.

### 3.3 Crystal structure and degree of crystallinity

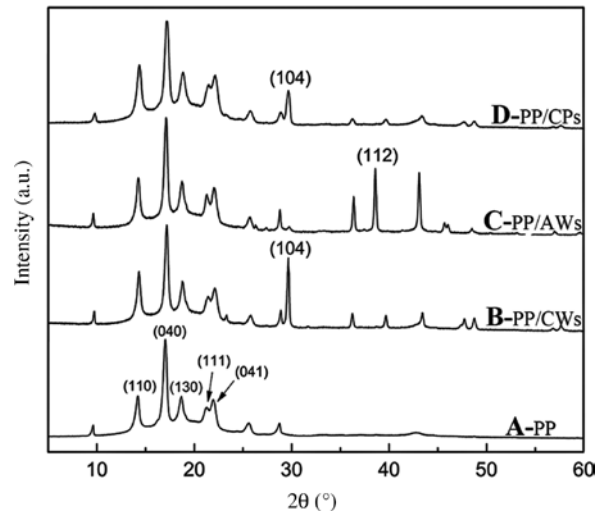
In Figure 6A, five diffraction peaks portraying the  $\alpha$ -phase of PP, given by the crystal planes of (110), (040), (130), (111), and (041), are expected at the scattering angles of 13.9°, 16.7°, 18.4°, 20.9°, and 21.7°, respectively [5, 22]. In addition, the XRD patterns of PP filled with 5 wt% CWs, AWs, and CPs show not only the five characteristic peaks of the  $\alpha$ -phase of PP but also the major diffraction peaks of fillers, which are found in Figure 6B and D. Additional diffraction peak appears at 29.7° and 37.9° responding to the crystalline structure of calcite and aragonite [23]. Result means that the three fillers have no influence on the crystalline structure of PP.

In order to evaluate the effect of different types of CaCO<sub>3</sub> on the crystalline properties of PP matrix, the degree of crystallinity ( $X_c$ ) is calculated and summarized in Table 2. The equation is followed by:

$$X_c = \frac{A_c}{A_c + A_a} \times 100, \quad (1)$$

where  $X_c$  is the degree of crystallinity,  $A_c$  is the integrated areas under the crystalline peaks, and  $A_a$  is the integrated areas of non-crystalline peaks.

Table 2 reveals that the crystallinity of PP/CWs, PP/AWs, and PP/CPs is 71.1, 69.4, and 68.2, respectively, which are higher than pure PP (54.0). It suggests that the filler



**Figure 6:** X-ray diffractions of neat PP and composites reinforced with 5% CWs, AWs, CPs.

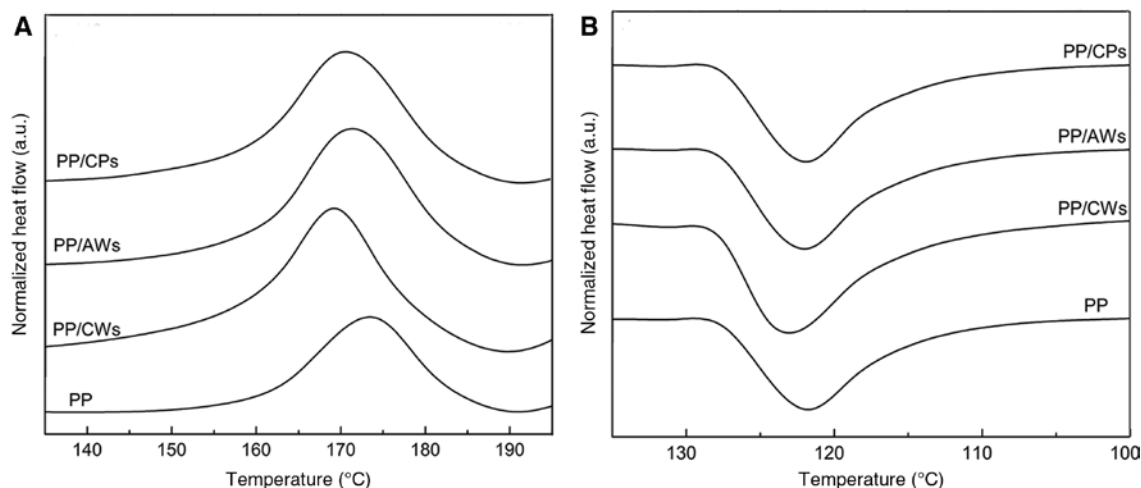
**Table 2:** Crystallinity data obtained by XRD measurements for neat PP and composites filled with 5 wt% CWs, AWs, CPs.

Sample	PP	PP/CWs	PP/AWs	PP/CPs
$X_c$ (%)	54.0	71.1	69.4	68.2

promotes nucleation of PP crystals and increases the crystallinity of composites. It can be attributed to the heterogeneous nucleation effect of CaCO<sub>3</sub> [24, 25]. The used filler is treated by oleic acid resulting in the long chain alkyl covered on the surface, which reduces the surface polarity of CaCO<sub>3</sub> and enhances the compatibility of the CaCO<sub>3</sub> filler and PP matrix. The long chain molecules of PP easily adsorb on the surface of modified CaCO<sub>3</sub>, and thus a closer interaction between the treated CaCO<sub>3</sub> and the PP has been established. Therefore, the modified CaCO<sub>3</sub> promotes the nucleating activity of PP. Furthermore, combined with the results of mechanical performance, it draws a conclusion that the tensile and flexural properties of composites reinforce as the crystallinity increases. On the contrary, the higher crystallinity in the PP matrix has an opposite effect on toughness, so that the impact strength of composites is lower than the primary PP. Furthermore, the decreased impact property is attributed to the whisker toughening and the increase of crystallinity.

### 3.4 Crystallization and melting properties

The crystallization and melting parameters are determined from Figure 7 and tabulated in Table 3. It exhibits that the



**Figure 7:** DSC thermograms portraying neat PP and composites reinforced with 5 wt% CWs, AWs, CPs (A) melting process, (B) crystallization process.

**Table 3:** Thermal data obtained by DSC measurements for neat PP and composites reinforced with 5 wt% CWs, AWs, CPs.

Sample	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
PP	172.8	50.7	121.6	70.9
PP/CWs	170.5	66.6	122.9	77.1
PP/AWs	171.7	63.9	122.2	71.5
PP/CPs	172.3	61.8	122.4	73.3

$\Delta H_c$ , crystallization enthalpy;  $\Delta H_m$ , melting enthalpy;  $T_c$ , crystallization temperature;  $T_m$ , melting temperature.

melting enthalpy of composites is higher than pristine PP (50.7 J/g). In Figure 7A and B, it is found that in the three composites, the addition of the fillers has a little effect on the melting and crystallization temperature. Moreover, as reported in Table 3, the incorporation of 5 wt% CWs, AWs, and CPs into PP exhibits that crystallization enthalpy is higher than that of pure PP (70.9 J/g). It illustrates that the fillers have a positive effect on the crystallization of PP, which is consistent with the crystallinity data of XRD. Finally, on the basis of DSC and XRD results, it is concluded that the PP/CWs composites have the best nucleating ability for PP in the three samples, which leads to the highest crystallinity, melting, and crystallization enthalpy.

## 4 Conclusions

In summary, the fracture morphologies, crystalline property, and mechanical behavior of PP/CWs, PP/AWs, and PP/CPs blends have been investigated. The highest tensile strength and flexural strength values are found in the composite with 5 wt% of fillers, while further increase of

the content reduces strength to a value below that of pure PP. The addition of fillers improves the modulus of composites in high content. Fractography of the broken specimens and impact test suggest that the whisker-reinforced ones obtained a relatively high impact strength compared to particles. In addition, the melting enthalpy, crystallization enthalpy, and crystallinity of composites are higher than those of pure PP, indicating that the fillers act as nucleating agents for the PP matrix. As a consequence, the composites with whiskers show a better property than particles. CWs have the highest reinforced effect on improving mechanical and crystalline properties in the three composites. The above results demonstrate that mechanical properties are dependent of the amounts of filler, morphologies, and polymorphs of calcium carbonate.

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