# Mechanical Properties and Morphologies of Polypropylene With Different Sizes of Calcium Carbonate Particles

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**Three polypropylene (PP) matrixes with different intrinsic toughness were used to study the morphologies and mechanical properties of PP filled with four sizes of calcium carbonate particles. PP1 was a homopolymer, PP2 was a propylene-ethylene copolymer, and PP3 was a mixture of PP1 and PP2 (PP1:PP2 = 1:1, weight ratio). Calcium carbonate (CC25, CC4, CC1.8, and CC0.07) with an average particle size of 25, 4, 1.8, and 0.07 $\mu$m, respectively, was used. It was clear that the PP matrix and filler size had key effects on improvement of mechanical properties of PP matrix. For all three PP matrixes, the yield strength, the flexural strength and modulus of the composites filled with CC25, CC4, and CC1.8 could be regarded as the same. But the yield strength, the flexural strength and modulus of composites filled with CC0.07 were obviously lower than those of composites filled with other sizes of particles. Among four sizes of calcium carbonate particles, CC0.07 had the best toughening effect to improve the impact strength of PP matrix, and the toughening effect of CC0.07 was influenced by PP matrix. For all PP matrixes, only in the case of moderate matrix toughness (PP3 matrix), the composite could receive the highest extent of toughness increase (4.3 times that of matrix). With regard to all PP composites, the best combination of properties was PP2 nanocomposite filled with 20 wt% CC0.07. POLYM. COMPOS., 27:443–450, 2006. © 2006 Society of Plastics Engineers**

## INTRODUCTION

   Polypropylene (PP), regarded as one of the most important commodity polymers, is widely used in technical applications. Because of its good processability, relatively high mechanical properties, great recyclability, and low cost, PP has found a wide range of applications in the household goods, packaging, and automobiles. However, owing to its low modulus, high notch sensitivity, and poor impact resistance, especially under extreme conditions such as low temperatures or high strain rates, the usefulness of PP as an engineering thermoplastic is still limited. So, the challenge of increasing the impact toughness and modulus of PP has provoked considerable interest [1–5].

   The toughening of PP with elastomers is a well-known approach. Rubber particle cavitation, crazing, and shear yielding are among the major toughening mechanisms in rubber-modified PP [1, 2]. However, the addition of elastomers often results in damage to some properties of PP, such as stiffness and hardness. Addition of inorganic filler into PP enhances many of its mechanical and thermal characteristics, including stiffness, creep resistance, heat deflection temperature and shrinkage. On the other hand, the presence of inorganic filler usually deteriorates strength and toughness [3–8]. The effects of inorganic filler on the mechanical properties of the composites depend strongly on its shape, particle size, aggregate size, surface characteristics, and the properties of the matrix. The required condition for using an inorganic filler to toughen PP is that the PP matrix should have sufficient intrinsic toughness. In addition to the sufficient intrinsic toughness, two other requirements stated as important are (1) filler dispersion must be uniform to avoid creation of crack-initiating large agglomerates and (2) matrix–particle debonding must occur to allow unhindered plastic deformation around the particles [9].

   Calcium carbonate ($CaCO_3$) is one of the most commonly used inorganic fillers in PP. Many researchers have studied the toughening of PP with $CaCO_3$ [9–17]. Thio et al. [9] studied the toughening of PP with $CaCO_3$, and found that filler size had a key effect on improvement of impact strength of PP. Only 0.7-$\mu$m diameter fillers improved Izod impact energy of PP, whereas 0.07 and 3.5 $\mu$m diameter fillers had either an adverse or no effect on the impact toughness. Zuiderduin and Westzaan [10] also observed that, among four different sizes of calcium carbonate particles (0.07, 0.3, 0.7, and 1.9 $\mu$m), the 0.7-$\mu$m diameter $CaCO_3$ fillers treated with stearic acid gave the best combination of properties. Chan and Wu [11] used 44 nm diameter $CaCO_3$ fillers to noticeably increase the impact

toughness of PP, because $CaCO_3$ nanoparticles could act as stress concentration sites, which promoted cavitation at the filler–PP interface during loading.

In our previous study [18], the morphologies and mechanical properties of PP filled with nanosized calcium carbonate particles CC0.07 (0.07 $\mu$m) were studied. It was found that when the CC0.07 content was appropriate, the impact strength of PP nanocomposite could be improved. In this study, the morphologies and mechanical properties of PP composites filled with different sizes of calcium carbonate particles were studied, and three PP matrixes with different intrinsic toughness were used, in order to find the influence of PP matrix on the mechanical properties of composites.

## EXPERIMENTAL

### Materials

PP1, a commercial grade of isotactic polypropylene (F401, homopolymer) with a MFI of 2.2 g/10 min, was supplied as pellets by Langang Petrochemical Company, China. A propylene–ethylene copolymer (K8003) with an MFI of 2 g/10 min was supplied as pellets by Yangzi Petrochemical Company, China, which was named as PP2. PP3, which is a polypropylene mixture (F401:K8003 = 1:1, weight ratio) of isotactic polypropylene and propylene–ethylene copolymer with an MFI of 2.1 g/10 min was also used. Calcium carbonate (CC25) with an average particle size of 25 $\mu$m, and calcium carbonate (CC4) with an average particle size of 4 $\mu$m were provided by Baoxin Company, China. The precipitated calcium carbonate (CC1.8) with an average particle size of 1.8 $\mu$m was purchased from Dujiangyan Company, China. The precipitated calcium carbonate (CC0.07) with an average particle size of 0.07 $\mu$m (Winnofil'S) was purchased from Solvay.

### Pretreatment of the Calcium Carbonate Particles

All calcium carbonate particles were treated with 1 wt% liquid silane coupling agent (KH550, $\gamma$-aminopropyl triethoxy silane, Hengda, China). The desired content of liquid silane coupling agent KH550 was first dissolved into acetone (the volume ratio of KH550:acetone was 1:5), then the $CaCO_3$ particles and acetone solution were mixed in the high speed mixer for 10 min, at a speed of 2000 rpm.

### Specimen Preparation

The PP composites were prepared in a corotating twin-screw extruder with a length/diameter ratio of 32, and a screw diameter of 25 mm (TSSJ-25/32, China). The composites were extruded at 230°C and at 140 rpm, and the parameters were optimal for dispersing the calcium carbonate particles, in particular the CC0.07 particles. The extrudates were pelletized and molded in a Nissei PS40E5ASE machine into dumbbell-shaped tensile bars (GB1040 typeII specimens, $150 \times 10 \times 4$ mm$^3$) and rectangular bars ($150 \times 10 \times 4$ mm$^3$). Flexural test bars (GB9341, $80 \times 10 \times 4$ mm$^3$) and impact test bars (GB1843, $63.5 \times 10 \times 4$ mm$^3$) were cut from the rectangular bars. A single-edge 45° V-shaped notch (tip radius = 0.25 mm and depth = 2 mm) was milled in the Impact test bar.

### Mechanical Properties

The tensile and flexural properties were studied with a Shimadzu AG-10TA Universal Testing Machine at room temperature. The tensile tests (GB1040) were performed at a crosshead speed of 50mm/min. For flexural tests (GB9341), a three-point loading system was used, and the support span length was adjusted to 60 mm, the crosshead speed was 2 mm/min. According to GB1843, the notched Izod Impact strength was performed at a rate of 3.5 m/s. The values reported were the average values of five individual measurements.

### Microscopy

SEM (JSM-5900LV, JEOL) was used to study the morphologies of fracture surfaces of Izod specimens. The fracture surfaces were coated with gold and then examined by SEM.

Polarized optical microscopic (POM) photographs were obtained by using an Olympus BX51 microscope equipped with a Linkam LTS350 hot stage. The samples were heated from 50 to 200°C at a rate of 100°C/min, held at 200°C for 10 min in order to remove prior thermal histories, and then cooled to 50°C at a rate of 10°C/min.

## RESULTS AND DISCUSSION

Zuiderduin and Westzaan [10] studied the influence of particle sizes (0.07, 0.3, 0.7, and 1.9 $\mu$m) on the tensile properties of PP composites filled with calcium carbonate particles. It was clearly demonstrated that the yield stress decreased upon addition of calcium carbonate particles, and the yield stress was unaffected by particle size for these composites. Thio and Argon [9] toughened PP with three different sizes (0.07, 0.7, and 3.5 $\mu$m) of calcium carbonate particles, and found for all three particles, the yield stress decreased with increasing particle volume fraction. Supaphol and Harnsiri [7] also observed that, the tensile strength of PP composites filled with different sizes (1.9, 2.8, and 10.5 $\mu$m) of calcium carbonate particles was not affected by variation in the particle size. The tensile strength decreased with increasing particle content and was controlled primarily by the filler content, while in our experiment, there were some differences.

Figure 1 shows the yield strength of composites filled with different sizes of calcium carbonate particles. As a whole, in view of the scatter in the data, it was clear from Fig. 1 that, the yield strength of composites decreased with
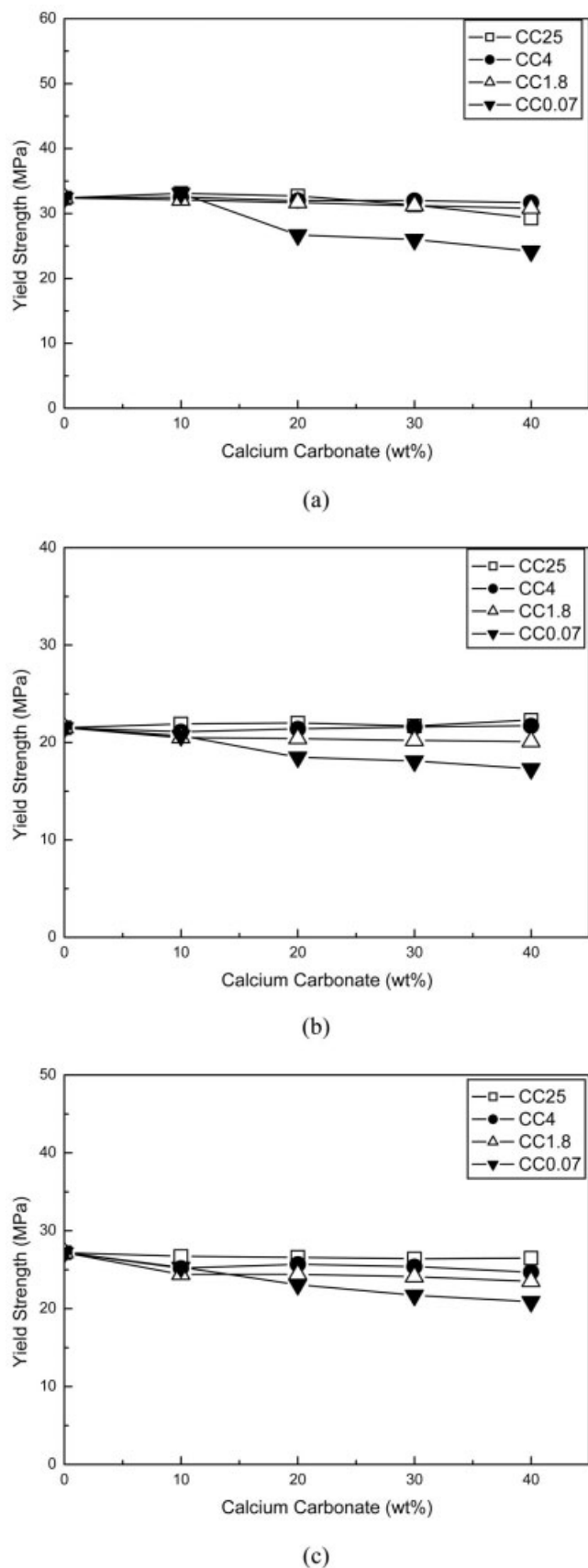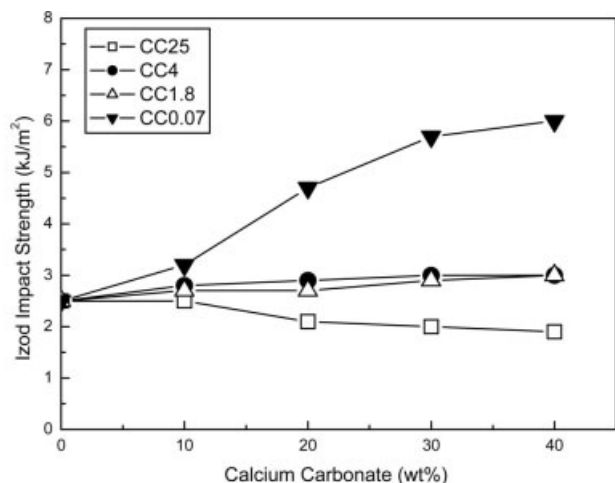
FIG. 1. Yield strength of composites filled with different sizes of calcium carbonate particles. (a) PP1 matrix (b) PP2 matrix (c) PP3 matrix.

increasing particle content, which was similar to the results obtained by Thio and Argon [9, 10], and the yield strength was influenced by filler size. When the filler content was the same, the yield strength of composites filled with CC25, CC4, and CC1.8 could be regarded as the same, which was consistent with the results obtained by Supaphol and Harnsiri [7]. Whereas the yield strength of composites filled with CC0.07 was obviously lower than that of composites filled with other sizes of particles, which was different from that observed by Zuiderduin and Westzaan [10]. The reason would be discussed in later SEM photographs.

It had been widely accepted that, for particulate-filled nanocomposites, the nanoparticle would increase the composite strength. This seemed contradictory to the results observed by Zuiderduin and Westzaan, Thio and Argon, and by us [9, 10]. Our results showed that the yield strength of composites filled with 0.07 $\mu$m calcium carbonate particles decreased with increasing particle content. Actually, it was not contradictory. The reason was that, the nanoparticles could increase the composite strength when the nanoparticle content was low (often lower than 10 wt%). If the nanoparticle content was high, the yield strength would decrease. This could be proved in our previous paper [18]. When the CC0.07 content was low (from 2 to 10 wt%), the yield strength of composites increased, while the yield strength of composites filled with high content (higher than 10 wt%) of CC0.07 decreased.

The notched impact strength of composites filled with different sizes of calcium carbonate particles is displayed in Fig. 2. It was obvious that filler size had a key effect on improvement of impact strength of PP matrix. For all PP matrixes, CC0.07 had the best toughening effect to improve the impact strength of PP matrix. This was different from the result obtained by Thio and Argon [9, 10]. In their experiment, the impact strength of composites filled with 0.07 $\mu$m calcium carbonate particles was decreased or unchanged with increasing particle content. It was because that the dispersion of nanoparticles was very difficult, nanoparticles with high surface energy were easy to aggregate. In their experiment, the dispersion of nanoparticles was bad, many aggregates larger than 25 $\mu$m were present in these compounds [9, 10]. While in our experiment, the CC0.07 was first pretreated with 1 wt% liquid silane coupling agent in the high speed mixer for 10 min, at the speed of 2000 rpm. This step was very important, and could help to the relatively good dispersion of CC0.07, which could be seen in later SEM photographs.

It could also be concluded that, as the filler content was appropriate, the impact strength of composites filled with CC1.8 improved. Whereas for CC4 or CC25, the impact strength of composites decreased with increasing filler content, except for PP1 composites filled with CC4. For PP2 and PP3 matrixes, when the same content of CC4 or CC25 was incorporated, the impact strength of composites was almost the same, which would be discussed later. But for PP1 matrix, the impact strength of composites filled with CC4 was always higher than that of composites filled with
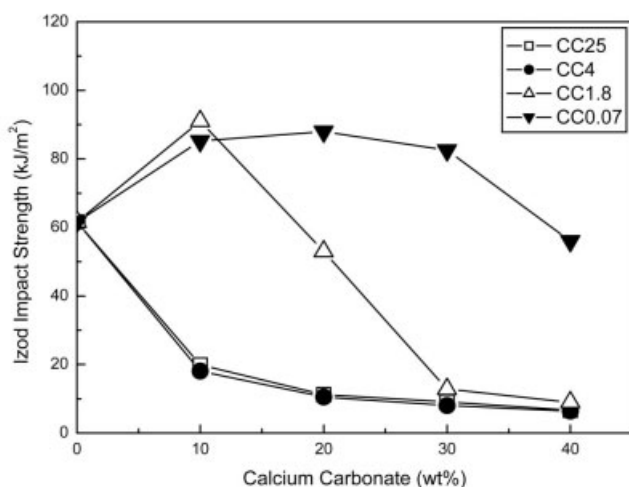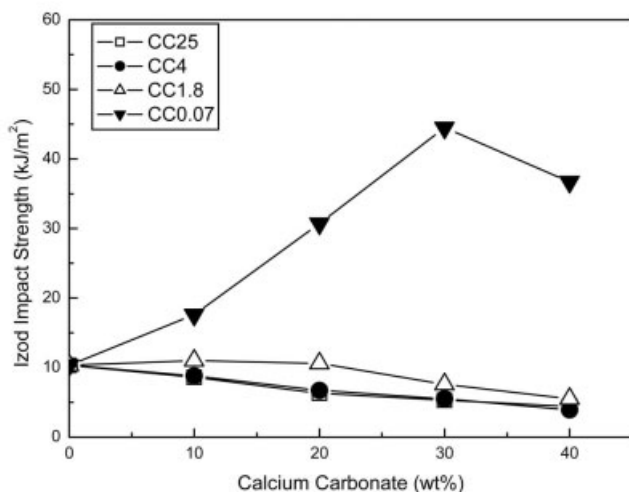
FIG. 2. Izod impact strength of composites filled with different sizes of calcium carbonate particles. (a) PP1 matrix (b) PP2 matrix (c) PP3 matrix.

CC25. This meant that the PP matrix would influence the toughening effect of calcium carbonate particles, which could be testified with a view to the toughening effect of CC0.07.

Some researchers [19–22] had found that the intrinsic toughness of PP matrix would influence the toughening effect of inorganic fillers. Chen and Mai [19] used the copolymer GWM101 and the hompolymer GXM43, and observed that the effect of adding the calcium carbonate fillers was more appreciable for the homopolymer that had a lower matrix toughness. Tjong and Li [21] thought that, the tougher the matrix was, the better the toughening effect of inorganic fillers was. In our experiment, for all PP matrixes, only in the case of moderate matrix toughness (PP3 matrix), the composite filled with CC0.07 could receive the highest extent of toughness increase (4.3 times that of matrix). This result was the same as that obtained by Wu et al. [20].
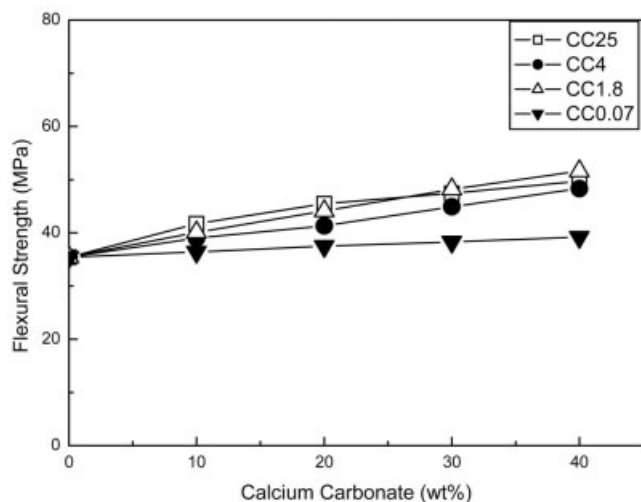
Figure 3 was the flexural strength of composites filled with different sizes of calcium carbonate particles. For all particles, the flexural strength of composites increased with increasing filler content. The flexural modulus of composites filled with different sizes of calcium carbonate particles was displayed in Fig. 4. The result obtained from Fig. 4 is similar to that observed in Fig. 3. For all particles, the flexural modulus of composites also increased with increasing filler content. The influence of particle size on the tensile properties and impact strength was studied widely [9, 10, 19, 23, 24], but the influence of particle size on the flexural properties was not investigated much. It could be concluded from Figs. 3 and 4 that, although the data obtained were scattered, when the filler content was the same, the flexural strength and modulus of composites filled with CC0.07 were obviously lower than those of composites filled with other sizes of particles. Considering the scatter in the data, the flexural strength and modulus of composites filled with CC25, CC4, and CC1.8 could be regarded as the same.

The toughening effect was most clearly present for CC0.07. For this material, the interest would be to plot the Izod impact strength as a function of the modulus for the three PP matrix materials, which is displayed in Fig. 5. From this graph, it was clear that the best combination of properties was PP2 nanocomposite filled with 20 wt% CC0.07.

For all calcium carbonate particles, CC0.07 had the best toughening effect to improve the impact strength of PP matrix, so the morphologies of fracture surface of Izod specimen of composites filled with CC0.07 were first examined by SEM. When 30 wt% CC0.07 was incorporated, the impact strength of these nanocomposites was much higher than that of the respective PP matrix, and this composition was chosen to be observed by SEM.

Figure 6 shows the micrographs of the fracture surface of Izod sample of PP composites filled with 30 wt% CC0.07. It was obvious that, although the content of CC0.07 was very high, the dispersion of nanoparticles was relatively good, only a few aggregates existed. And the interfacial
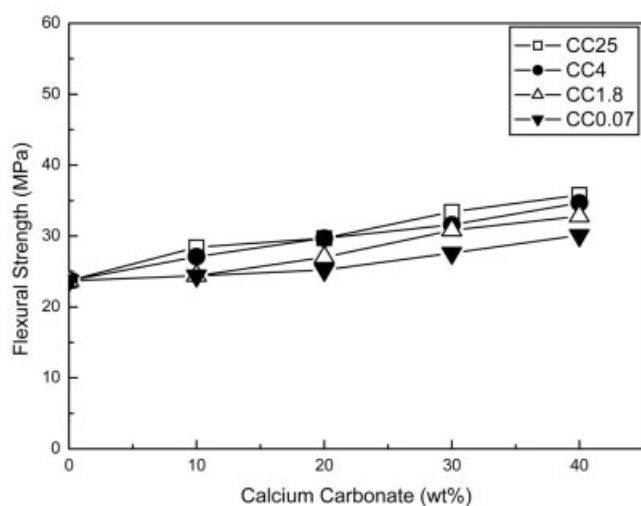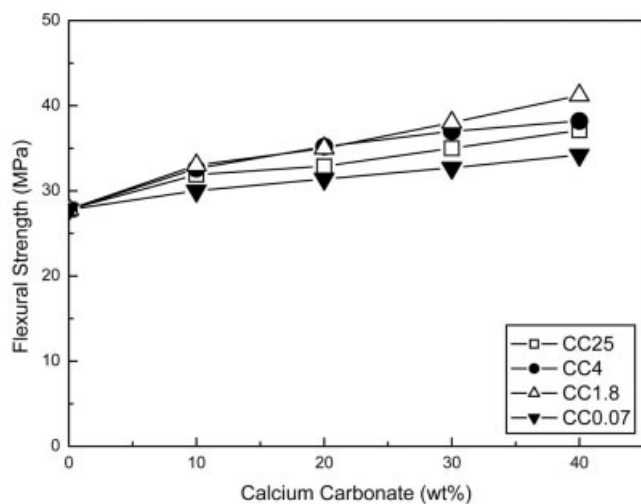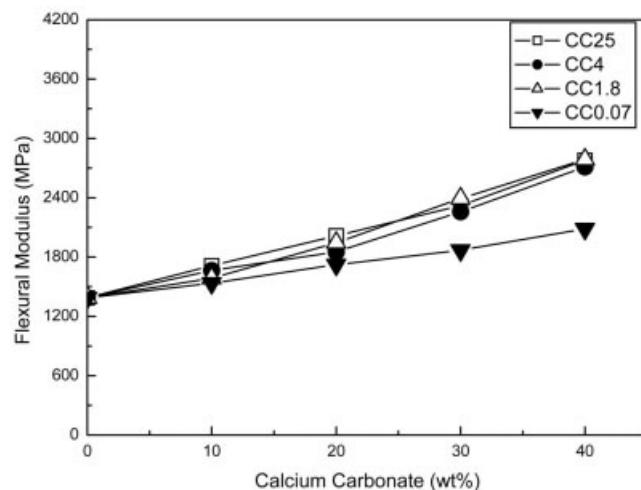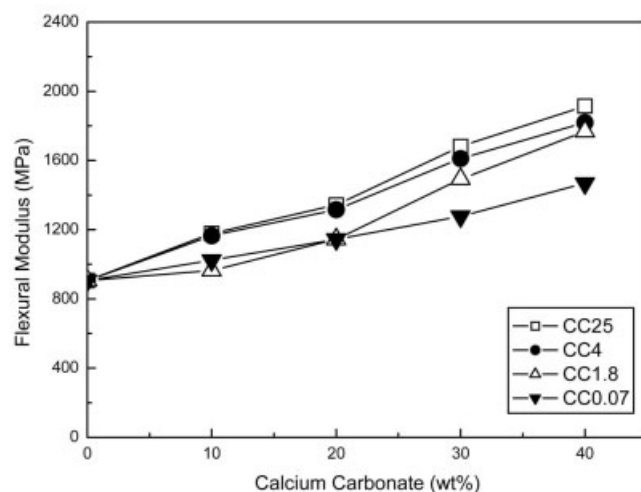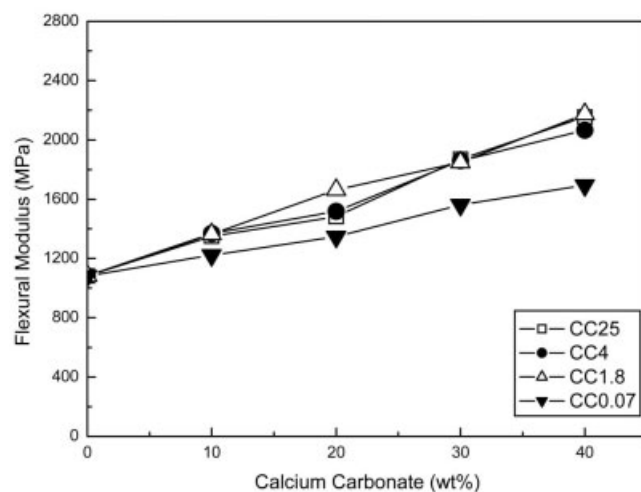
FIG. 3. Flexural strength of composites filled with different sizes of calcium carbonate particles. (a) PP1 matrix (b) PP2 matrix (c) PP3 matrix.

FIG. 4. Flexural modulus of composites filled with different sizes of calcium carbonate particles. (a) PP1 matrix (b) PP2 matrix (c) PP3 matrix.
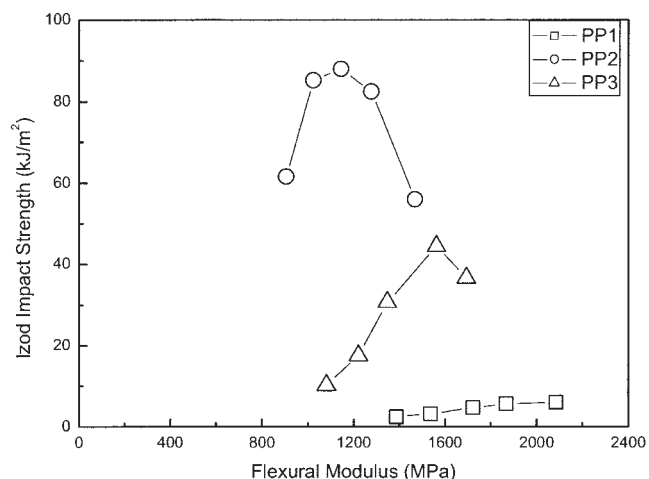
FIG. 5. Izod impact strength as function of flexural modulus for the three PP nanocomposites filled with CC0.07.

interaction between nanoparticles and matrix was strong, the fracture path was mainly through the matrix. This meant that the pretreatment of nanoparticles in the high speed mixer for 10 min was effective. These highly dispersed nanoparticles and the strong interfacial interaction between nanoparticles and matrix were believed to favor the pinning effect in the case of crack propagation [25–27]. Hence, the impact strength improved. However, because a few aggregates still existed, although these few aggregates influenced the impact strength of composites little, the yield strength of composites was largely influenced by these few aggregates. The mode of failure initiation depended on particle size, debonding was the dominating deformation mechanism in composites containing large particles, while cracks were initiated inside large aggregates forming at small particle size [24]. It could be concluded, that the yield strength of composites filled with CC0.07 was obviously lower than that of composites filled with other sizes (CC25, CC4, CC1.8) of particles. It was because that, although the aggregates of the CC0.07 particles were few and smaller than 1.8 $\mu$m, when the tensile test was performed, the cracks were more easily initiated inside these aggregates than the particles debonded from the matrix, so the yield strength was lower. Another reason was that debonding was the dominating deformation mechanism in composites containing large particles. And the filler particles (CC25, CC4, and CC1.8) were pretreated in the high speed mixer for 10 min, so the bonding between filler particles and PP matrix was good, which can be seen in Fig. 7, and more stress could be transferred from the matrix to the fillers during external loading, the particles could bear some fraction of the external load [5, 8]. As a result, the yield strength of composites filled with CC25, CC4, or CC1.8 was higher than that of composites filled with CC0.07.
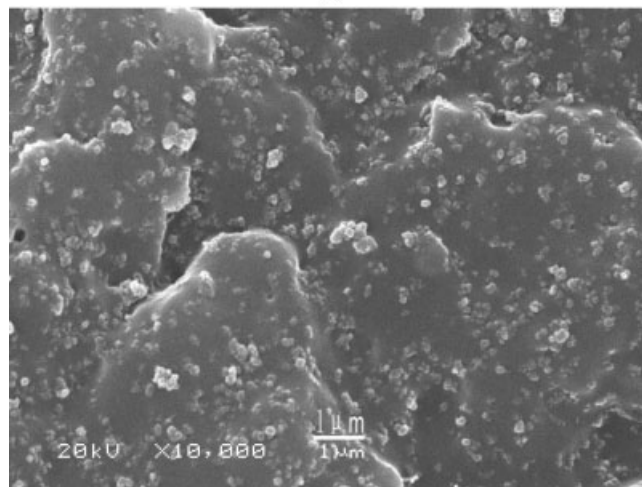
Because the intrinsic toughness of these three PP matrixes was different, the morphologies of fracture surface were dissimilar. Figure 6a shows that PP1 nanocomposite exhibited brittle fracture, and the surface was rather smooth.
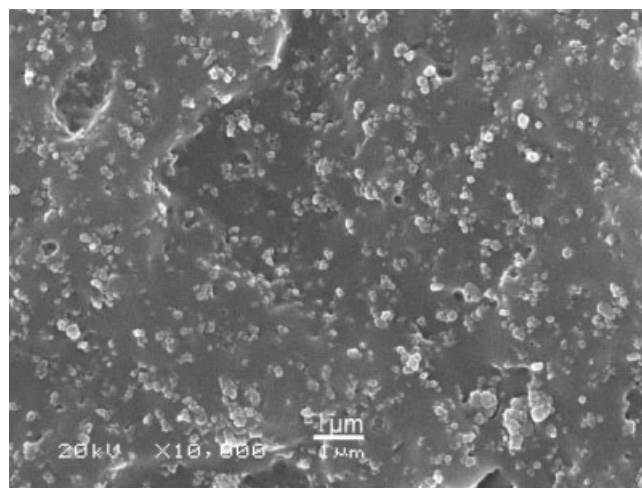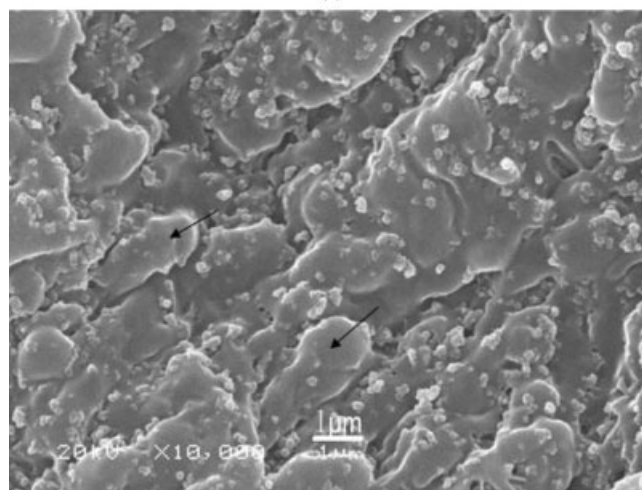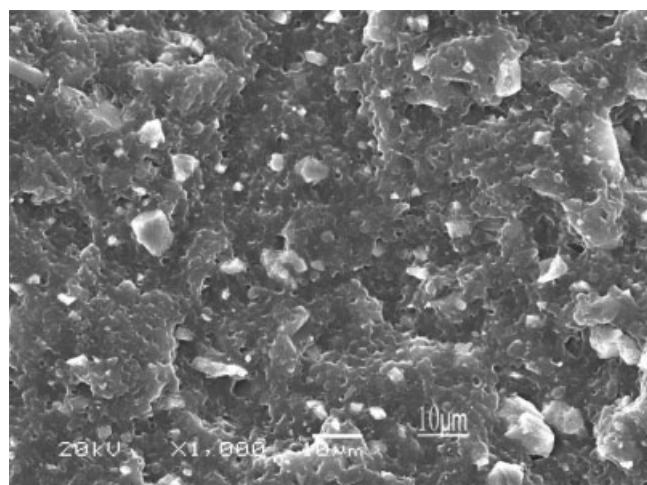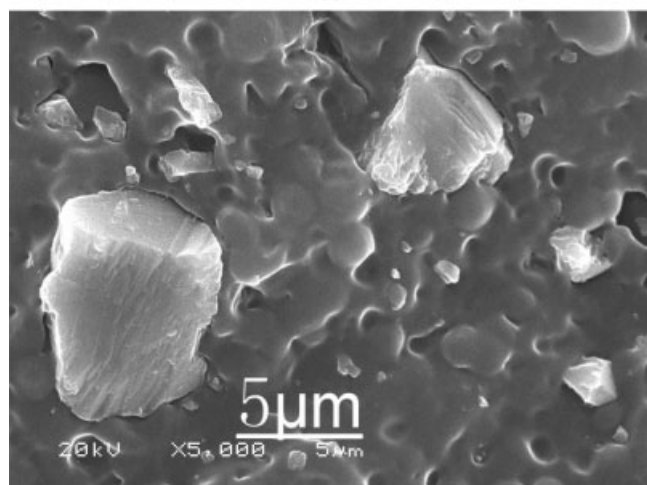


FIG. 6. The micrographs of the fracture surface of Izod sample of PP nanocomposites filled with 30 wt% CC0.07 near the notch. (a) PP1 nanocomposite (b) PP2 nanocomposite (c) PP3 nanocomposite.

Two rough surfaces are shown in Fig. 6b and 6c, meaning that these two nanocomposites exhibited ductile fracture. Especially in Fig. 6b, the large plastic deformation is dis-

(a)



(b)

FIG. 7. The micrographs of the fracture surface of Izod sample of PP2 composite filled with 30 wt% CC25 away from the notch (a) magnification at 1000× (b) magnification at ×5000.

played, which is depicted using an arrow. The morphologies showed in Fig. 6 were consonant with the impact strength described above.

It was interesting for PP2 and PP3 matrixes, when the same content of CC4 or CC25 was incorporated, the impact strength of composites was almost the same, so the micrographs of the fracture surface of Izod specimen of PP2 composite filled with 30 wt% CC25 were examined by SEM, which are displayed in Fig. 7. Figure 7a showed that a few particles had been pulled out of the fracture surface after the Izod impact test, and the particles breaked-up, which were much smaller than the original ones (25 $\mu$m), the average particle size was similar to CC4, so the impact strength of composites was almost the same. The break-up of the original particles was due to the large shear stress in the corotating twin-screw extruder. But when the original particles were small enough, such as CC4 or CC1.8, the shear stress in the corotating twin-screw extruder could not break up these small particles. For PP2 composites

filled with CC25, the original particles became small, but they were still large enough, act as super-critical sized flaws, and the propagating crack became brittle soon after initiation [9]. This was the reason for the decrease in impact strength of the composite filled with 30 wt% CC25. To examine the fracture surface clearly, the micrograph of the fracture surface at higher magnification of 5000× is displayed in Fig. 7b. It was obvious that, even though some holes existed in the fracture surface, because of the pull-out of particles, the adhesion of particles seemed good and the particles debonded little from the PP2 matrix. Hence, the plastic deformation around the particles could not occur [9], the impact strength decreased.

The specimens for tensile test, flexural test, and impact test were obtained by injection molding. This was a nonisothermal crystallization process, so the nonisothermal crys-
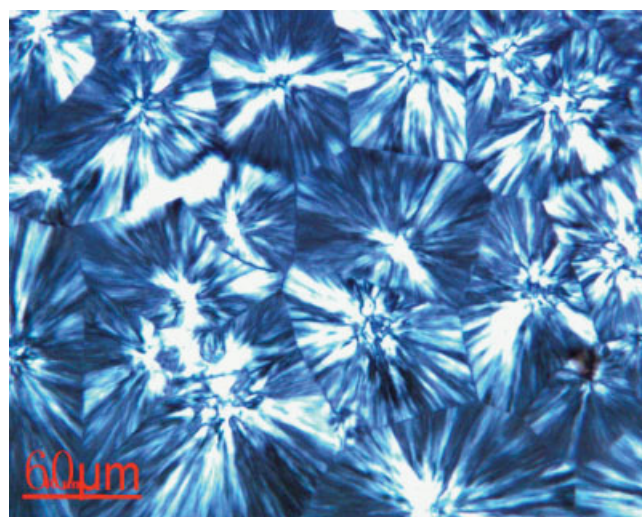


(a)
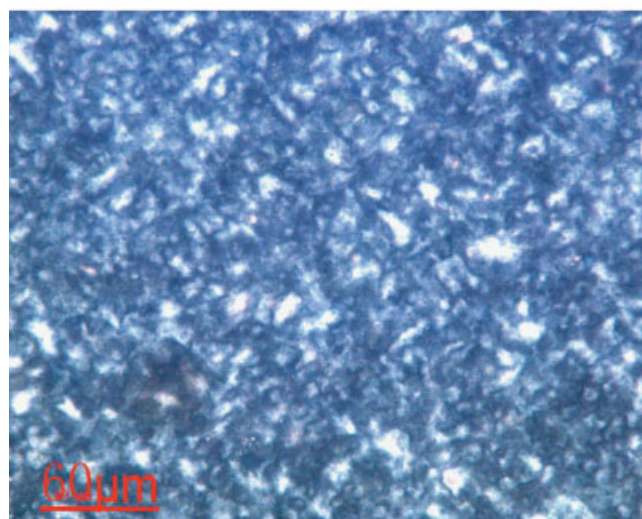


(b)

FIG. 8. Morphologies of (a) pure PP1 (b) PP1 nanocomposite filled with 30 wt% CC0.07 under a polarizing microscope. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tallization of pure PP and PP nanocomposites were observed by POM. Figure 8 showed the POM photographs of the PP1 nanocomposite filled with 30 wt% CC0.07 as well as that of the pure PP1. The pure PP1 (Fig. 8a) revealed common spherulitic structure with a diameter of the spherulite of 100 $\mu$m or more. With the introduction of 30 wt% CC0.07 (Fig. 8b), the clear spherulitic structure could not be observed, the shape of the spherulites distorted, and the crystalline size decreased, much smaller than that of pure PP1. This was another reason that the impact strength of PP1 nanocomposite filled with 30 wt% CC0.07 improved 2.3 times that of PP1 matrix. It was clear that the introduction of the CC0.07 greatly affected the crystallization of PP1 and the size of the PP1 spherulites. The nucleation of CC0.07 resulted in a large number of nucleus, causing a large number of spherulites in the limited space. Therefore, the perfect spherulites could not form when the CC0.07 content was high. In addition, the large number of the nuclei centers would also cause more crystalline defects [28]. The crystalline size of PP2 or PP3 nanocomposite filled with 30 wt% CC0.07 was also smaller than that of the respective PP matrix (PP2 or PP3 matrix), which is not showed in this study.

## CONCLUSIONS

The mechanical properties and morphologies of PP composites filled with four different sizes of calcium carbonate particles were studied. It was clear that the PP matrix and filler size had key effects on improvement of mechanical properties of PP matrix. For all three PP matrixes, the yield strength, the flexural strength, and modulus of composites filled with CC25, CC4, and CC1.8 could be regarded as the same. And the yield strength, the flexural strength, and modulus of composites filled with CC0.07 were obviously lower than those of composites filled with other sizes of particles. For all particles, the flexural strength, and modulus of the composites increased with increasing filler content, while the yield strength decreased with increasing filler content. Among four sizes of calcium carbonate particles, CC0.07 had the best toughening effect to improve the impact strength of PP matrix. The impact strength of composites filled with appropriate CC1.8 would improve, while for CC4 or CC25, the impact strength of composites decreased with increasing CC4 or CC25 content, except for PP1 composites filled with CC4. The toughening effect of CC0.07 was influenced by PP matrix. And for all PP matrixes, only in the case of moderate matrix toughness (PP3 matrix), the composite could receive the highest extent of toughness increase (4.3 times that of matrix). With regard to all PP composites, the best combination of properties was PP2 nanocomposite filled with 20 wt% CC0.07.

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