

Preparation and Characterization of Nano/Micro-Calcium Carbonate Particles/Polypropylene Composites

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ABSTRACT: A new kind of polypropylene (PP)/CaCO₃ composites was prepared on a twin screw extruder with the nanoparticle content of 5 wt % and the 2500 mesh microparticle content of 15 wt %. The mechanical property of four different samples [pure PP (1), PP filled with 15 wt % microCaCO₃ particle composites (2), PP filled with 5 wt % nanoCaCO₃ particle composites (3) and PP filled with micro/nano-CaCO₃ complex size particle composites (4)] was investigated through tensile tests, notched Izod impact tests and SEM. The results indicated that the sample 4 had the best mechanical property. The proofs of SEM showed that the high impact energy could lead to debonding and creating microcavitation between the nano-

particle and polymer interface if the polymer was filled with the nanoparticles. This process could absorb a lot of mechanical failure energy, but too much mechanical failure energy would lead to the enlargement of microcavitation and the destruction of the composites in sample 3. In sample 4, the microparticle could be used to prevent the enlargement of microcavitation in the matrix polymer under the higher impact failure energy. In this article, the model of the impacting failure process of micro/nano-CaCO₃/PP composites was established. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3560–3565, 2011

Key words: PP; CaCO₃; toughening; complex sizes

INTRODUCTION

Polypropylene (PP) is a typical commercial polymer in many application areas due to its favorable price, versatility, and a broad range of modifications.^{1–5}

The properties of PP can be improved further by modification. For example, the combination of PP with other polymers, mineral particles or reinforcements can improve its advantageous properties and extend its application areas.^{6–10}

The purpose of adding mineral particles to polymers is primarily to reduce the product cost. In recent years, the particles have been often used to fulfil a functional role, such as increasing the stiffness or improving the dimension stability of the

polymer.^{7–16} The mineral particles used in semicrystalline polymers are usually talc or calcium carbonate (CaCO₃).^{17–21} Generally, the addition of mineral particles will have an effect on embrittling polymers and decrease the impact energy.²² In recent years, some studies show that filler particles can be used as a toughening agent in polymer composites. Their basic idea is that the rigid particles must create cavitation at a submicro or nanometer size level under the mechanical failure.^{23–31} The process of creating microcavitation around the submicro or nanometer size level particles can absorb a lot of impact energy and prevent matrix polymer from mechanical failure. But the submicro or nanosize level cavitation might be enlarged if absorbing higher mechanical failure energy, thus resulting in the production of craze.

Some researchers have studied microsize and nanosize particles and polymers filled with these particles. They included interfacial modification,^{32–34} crystal structure,³⁵ thermal ageing,^{36,37} thermal conductivity,³⁸ and mechanical properties. But most researches on mechanical properties were focused on the correlation between the size of particles and mechanical strength of composites.^{34,39–41} However,

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few articles have reported that both microsize particles and nanosize particles were together filled into the same polymer composites.

In our research, the results of tensile and impact tests show the mechanical property of PP is obviously improved once 5% nanoCaCO₃ and 15% 2500 mesh microCaCO₃ are filled into PP. The views of SEM indicate that the nanoparticles could create cavitation at a microsize level and the microparticles can prevent microcavitation from continuously developing and producing destructive crazes.

We used the most commonly polymers and filler materials to process by the most commonly method in practice. This can significantly improve the mechanical property of polymer composites without increasing production costs and without changing processing technology and equipment, thus having wide application prospect.

EXPERIMENTAL

Materials

The unfilled PP used as matrix was provided by Yangtze Chemical Ind. (Nanjing, China). MicroCaCO₃ was provided by Nanjing OMYA Fine Chemical Ind. (Nanjing, China). This kind of microCaCO₃ was modified with stearic acid.

NanoCaCO₃, which was synthesized according to our previous article,⁴² was treated with sodium stearate.

Measurement of size gradation of microCaCO₃

The size gradation of different CaCO₃ samples was measured by LS-CWM(2) laser particle sizer (OMEC, Zhuhai, China). The characteristic and size of CaCO₃ were: D25: 0.56 μm; D50: 1.32 μm; D75: 2.57 μm; D90: 4.20 μm. The content of CaCO₃ was more than 98.0 wt % in the samples. The integral coefficient of the sample was showed in Figure 1.

Measurement of size of nanoCaCO₃

The size of nanoCaCO₃ was observed by Hitachi-H-7650 transmission electron microscopy (Hitachi, Tokyo, Japan).

Samples preparation

A total of 50 g nanoCaCO₃, 150 g microCaCO₃, and 800 g PP were blended on the Haake torque rheometer (Polylab 600), which was provided by Thermo Fisher Scientific (Waltham, MA). In the extrusion step, barrel temperatures were set at 150, 180, 220, 230°C and a screw speed of 120 rpm was used. The length-to-diameter (L/D) ratio of the screws was 25.

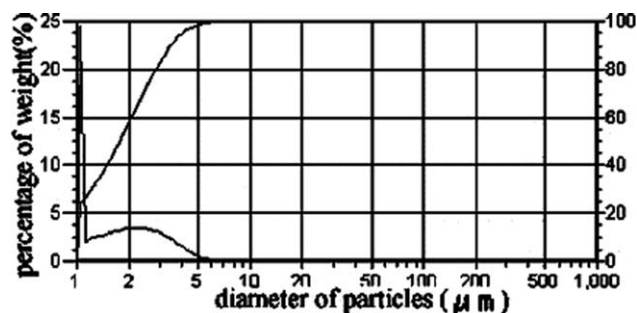


Figure 1 Integral and differential curves of size distribution of 2500 mesh CaCO₃ (10 × 3 times).

The PP filled with 15 wt % microCaCO₃ particle composites and the PP filled with 5 wt % nanoCaCO₃ particle composites were prepared in the same method.

After compounding, the blends were injection moulded into the rectangular bars (75 × 10 × 4 mm³, dumbbell shaped specimen) for the tensile experiments.

A single-edge V-shaped notch of 2 mm depth and tip radius 0.25 mm was milled in the moulded specimens for the notched Izod impact experiments.

Izod impact test

Izod impact tests were carried out by using a Zwick pendulum at the room temperature (Zwick, Ulm, Germany). All measurements were carried out ten times.

Tensile test

The tensile tests were done at the room temperature using an Instron 4200 tensile test machine (Instron, High Wycombe, U.K.). The test speed was 50 mm/min. All measurements were carried out ten times.

SEM test

The break surface of Izod impact and quenching (−110°C) samples was observed on X650 SEM (Hitachi, Tokyo, Japan). The operation voltage was 20 kV.

RESULTS AND DISCUSSION

TEM analysis

Figure 2 shows morphology of nanoCaCO₃ used in this study. From it, we can see that the size distribution of nanoCaCO₃ is narrow (from 25 to 43 nm) and its L/D ratio is nearly 1/1. The statistic result shows the average size of particles is 36 nm. The nanoparticle is well filled in the plastic matrix.

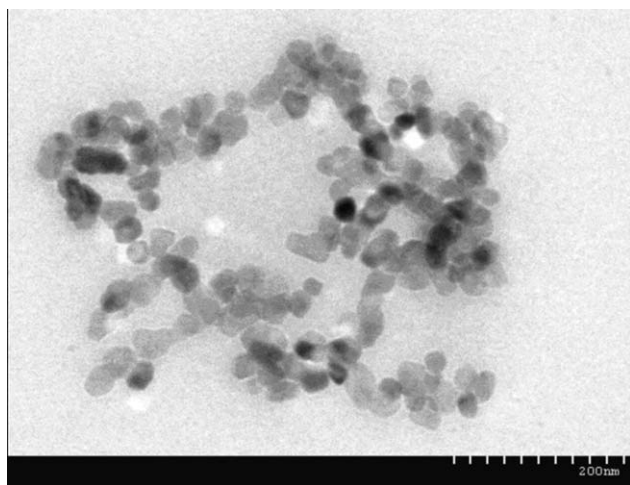


Figure 2 TEM view of nanoCaCO₃.

Mechanical strength

The tensile and impact strength data of Samples 1–4 were summarized in Table I. The results show that the Sample 2 has the worst mechanical property, in which the rigid particles result in the decrease of impact toughness, the Sample 3 has the better mechanical property than that of pure PP, and the Sample 4 has the best mechanical property.

SEM analysis

Figure 3(A) is the view of quenching surface of Sample 3 and Figure 3(B) is the view of impact surface of Sample 3 composites. It indicates that the quenching sample doesn't create the microcavitation around the nanoparticles, but the impact sample creates obvious microcavitation around the nanoparticles. So, the microcavitation is created by impact action and the system absorbs a lot of impact energy in this process. Therefore, the Sample 3 has the higher impact strength than pure PP. But the microcavitation would result in microcraze, thus resulting in composites fracture when nanoCaCO₃/PP composites suffer higher impact energy.

Figure 4 is the view of impact surface of Sample 4. It suggests that the microcraze is enlarged while it is prevented by microparticle (as the left of microparticle). When the size of the enlarged craze is larger

than that of microparticle (as the below of microparticle) the microcraze would walk around the microparticle and continue growth under the higher impact energy. This process would absorb higher impact energy and increase the toughness of the composites. So, the Sample 4 has the higher impact strength than that of Sample 3.

Figure 5 shows the impact surface of PP/nanoCaCO₃/microCaCO₃ composites whose interface between the nanoparticle and the matrix is modified with titanate coupling agent. This shows that the microcavitation around the particles can't create. This can be attributed to too strong interfacial consistency property between the nanoparticles and the polymer matrix.

Model of fracture process

The fracture process of nano/micro particles/resin matrix composites consists of five stages (as Fig. 6 shown):

1. Stress concentration: The modifier nanoparticles act as stress concentrators, because they have different elastic properties compared with the matrix polymer and larger surface area and curvature compared with the microparticles [Fig. 6 (a,A)].
2. Microcavitation creating: Stress concentration gives rise to free volume of triaxial stress around the particles and this leads to debonding at the particle–polymer interface when the interaction between particles and polymer is not too strong [Fig. 6(b, B)]. This is the important process of absorbing energy in impact.
3. Microcraze creating and growing: Under higher impact energy the microcavitation forms microcrazes and the microcrazes grow along the direction of impact stress [Fig. 6(c)]. If the growth of the microcrazes is not blocked by the microparticles, then it would destroy the composites [Fig. 6(d)].
4. Microcraze blocking: It is well-known that the strength of particles is much higher than that of resin, so microcrazes can not fracture the particles; and the size of microparticles is much

TABLE I
Mechanical Properties of PP, PP/microCaCO₃, PP/nanoCaCO₃, and PP/microCaCO₃/nanoCaCO₃ Composites Samples

Sample	Pure PP	PP filled with 15 wt % microCaCO ₃	PP filled with 5 wt % nanoCaCO ₃	PP filled with 5 wt % nanoCaCO ₃ and 15 wt % microCaCO ₃
Impact strength (kJ/M ²)	13.5	7.2	34.4	67.0
Tensile strength (MPa)	27.4	25.6	29.5	31.5

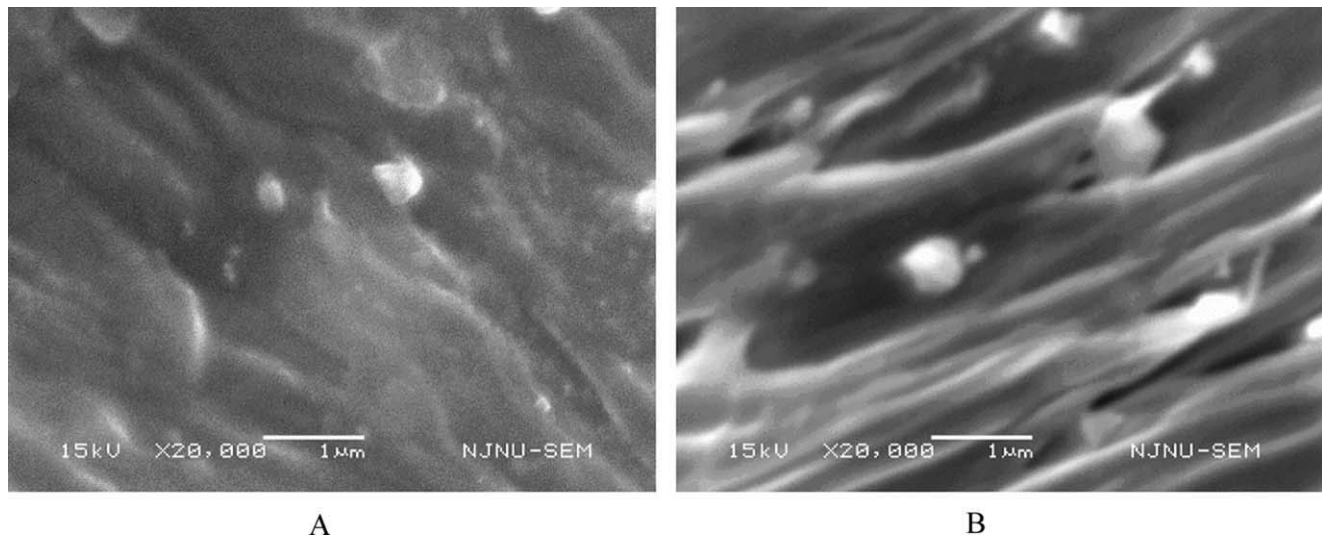


Figure 3 (A) View of quenching surface of PP/nanoCaCO₃ composites. (B) View of impact surface of PP/nanoCaCO₃ composites.

bigger than that of microcraze, so the microcrazes, which were created by nanoparticles, can not easily walk around the microparticles. When the microcrazes encounter the microparticles, the growth of microcrazes will be blocked by the microparticles. At this time, the microcrazes would be enlarged [Fig. 6(C)]. This is a most important process, in which it absorbs the most impact energy.

5. Composites fracture: When the microcraze size becomes larger than that of the microparticles, microcrazes would walk around the microparticles and continue to grow along the same direction [Fig. 6(D)]. This process would result in composites fracture.

The toughen process could be disturbed by two factors:

1. Interfacial consistency property between nanoparticles and the polymer matrix: The process of microcavitations creating would absorb low impact energy when the interactions between particles and polymers are weak. When interactions between particles and polymer are too strong the microcavitation creating can not be created.
2. The size ratio of microparticles and nanoparticles: The microcrazes easily walk around the microparticles when the ratio is too small.

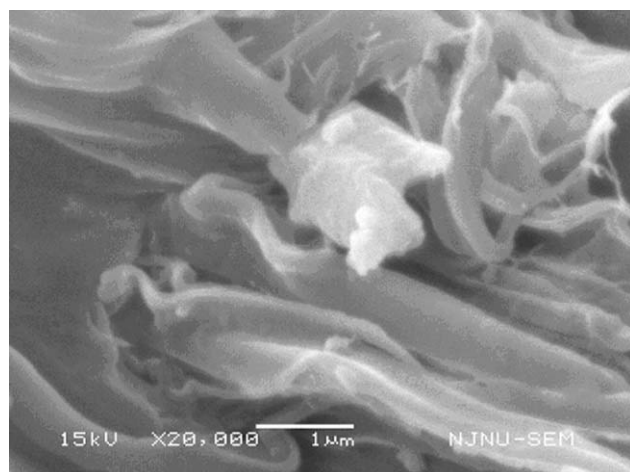


Figure 4 View of impact surface of PP/nanoCaCO₃/microCaCO₃ composites.

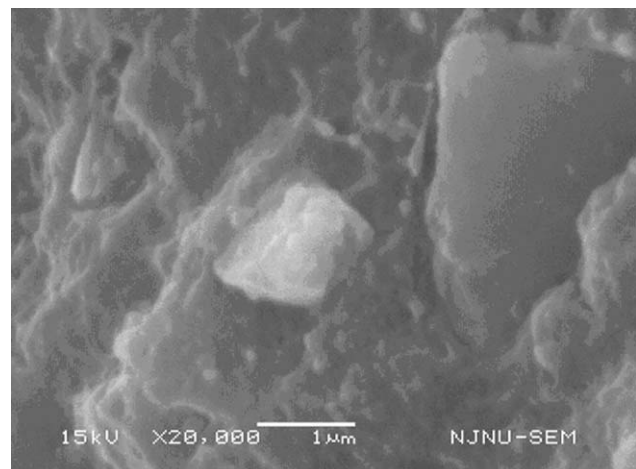


Figure 5 View of impact surface of PP/nanoCaCO₃/microCaCO₃ composites whose interface between nanofiller and matrix is modified by titanate coupling agent.

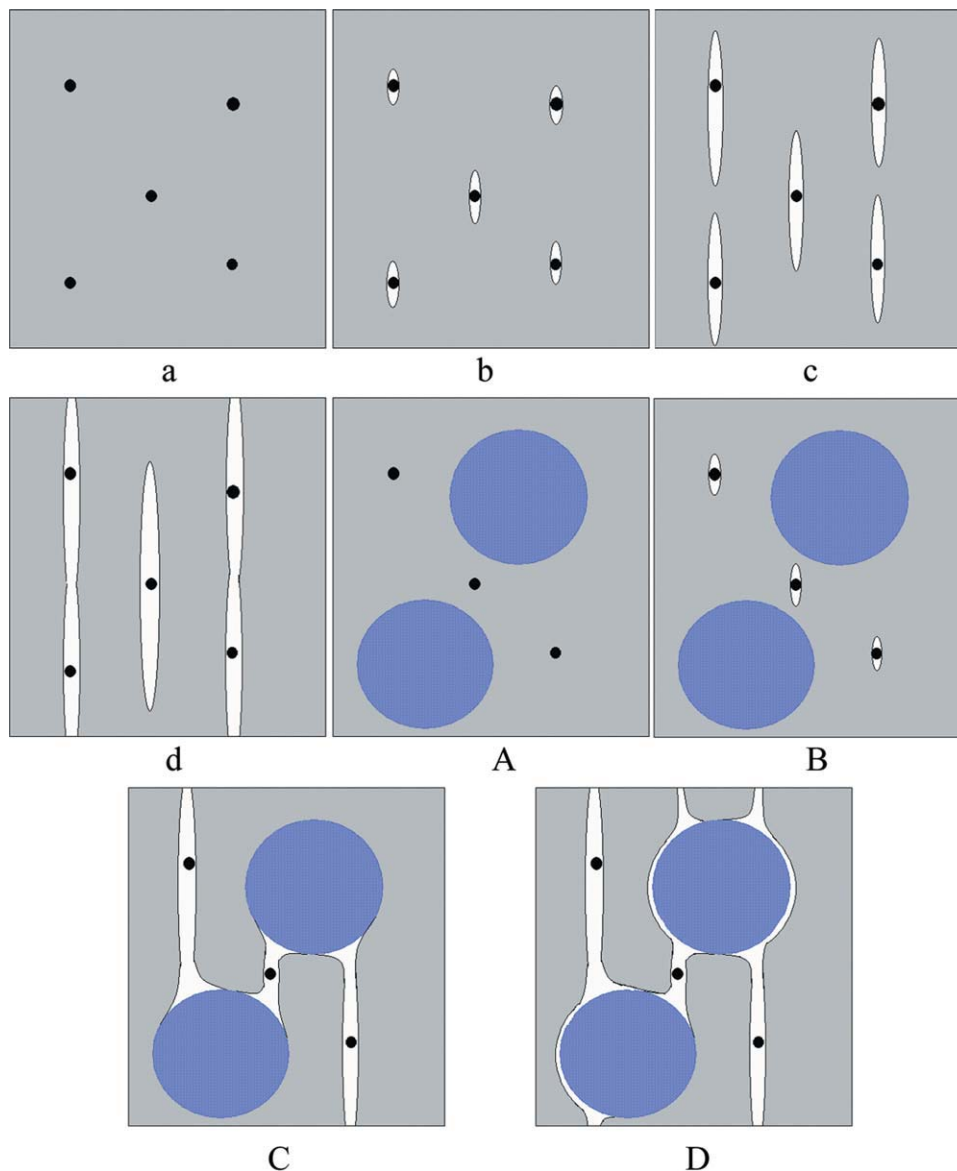


Figure 6 Fracture process of nanoparticle/resin composite and nano/microparticles/resin composite (a), (b), (c), (d) Nano particle/resin composite (A), (B), (C), (D) Nano/micro particles/resin composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

The mechanical property of PP is obviously improved once 5% nanoCaCO₃ and 15% 2500 mesh microCaCO₃ are filled into PP.

In the process of impact, the nanoparticles could create microcavitation and this is an important process of absorbing energy in impact while PP was filled with nanoCaCO₃. When the microcrazes encounter the microparticles, the growth of microcrazes will be blocked by the microparticles in the nano/microCaCO₃/PP composites. At this time, the microcrazes would be enlarged. This is a most important process, in which it absorbs the most impact energy.

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