

Effect of Oleic Acid-modified Nano-CaCO₃ on the Crystallization Behavior and Mechanical Properties of Polypropylene*

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Abstract Oleic acid (OA)-modified CaCO₃ nanoparticles were prepared using surface modification method. Infrared spectroscopy (IR) was used to investigate the structure of the modified CaCO₃ nanoparticles, and the result showed that OA attached to the surface of CaCO₃ nanoparticles with the ionic bond. Effect of OA concentration on the dispersion stability of CaCO₃ in heptane was also studied, and the result indicated that modified CaCO₃ nanoparticles dispersed in heptane more stably than unmodified ones. The optimal proportion of OA to CaCO₃ was established. The effect of modified CaCO₃ nanoparticles on crystallization behavior of polypropylene (PP) was studied by means of DSC. It was found that CaCO₃ significantly increased the crystallization temperature, crystallization degree and crystallization rate of PP, and the addition of modified CaCO₃ nanoparticles can lead to the formation of β -crystal PP. Effect of the modified CaCO₃ content on mechanical properties of PP/CaCO₃ nanocomposites was also studied. The results showed that the modified CaCO₃ can effectively improve the mechanical properties of PP. In comparison with PP, the impact strength of PP/CaCO₃ nanocomposites increased by about 65% and the flexural strength increased by about 20%.

Keywords polypropylene, nano-CaCO₃, oleic acid, crystallization, mechanical properties

1 INTRODUCTION

Isotactic polypropylene (PP) is a large tonnage polymer and has been widely used in various engineering areas owing to its attractive properties, such as low cost, low weight, anti-corrosion, good mechanical properties and processability. Its production and consumption rates are increasing more rapidly in comparison with other polymers. However, PP shows poor impact toughness at room and lower temperatures so as to restrict its application in structural materials. Among the various modification methods, the addition of rubber could improve the toughness of PP. However, it leads to decrease in stiffness. Conversely, rigid fillers are commonly used to reinforce the matrix, but usually with the decrease in impact toughness. The question of improving the impact toughness of PP without decreasing the stiffness has attracted considerable interest. At present the intensive research efforts have been devoted to develop PP/inorganic particle nanocomposites^[1-4]. However, inorganic nanoparticles are very easy to agglomerate because of their large specific surface area and high surface energy and show poor dispersion capacity in nonpolar polymers like PP, resulting in poor mechanical properties of PP-matrix nanocomposites. The major challenge is to find novel methods to improve the dispersion of nanoparticles in polymer matrix.

Fortunately, this problem can be resolved by using some special preparation techniques, such as, adding surface active agents and stearic acid, surface-grafting, and *in situ* polymerization^[3]. Oleic acid

(OA) is a surface modifying agent with carboxyl group, long alkyl chain and unsaturated bond. The carboxyl group in OA could react with active groups on the surface of nanoparticles. On the other hand, the presence of the long alkyl chain and unsaturated bond in OA provides significant hydrophobicity to the nanoparticles and is beneficial for a good interfacial bonding between the nanoparticles and the matrix^[5,6]. As a result, the nanoparticles modified by OA can prevent their aggregation, and enhance the mechanical properties of polymer/inorganic particle nanocomposites. Therefore, OA was commonly used to modify the nanoparticles such as SiO₂^[7], TiO₂^[8], Ag^[9], PbO^[10]. However, few papers studied the surface modification of CaCO₃ nanoparticles by OA and the effect of modified-CaCO₃ nanoparticles on the crystallization behavior and mechanical properties of PP. In the present work, OA-modified CaCO₃ nanoparticles (denoted by OA-m-CaCO₃) was prepared using the surface modification method. The structure of the modified nanoparticles was investigated using infrared spectroscopy (IR). The effects of OA-m-CaCO₃ on the crystallization behavior and mechanical properties of PP were also studied.

2 EXPERIMENTAL

2.1 Materials

PP (grade F401, supplied by Yangzi Petrochemical Corporation) was used in this study. The CaCO₃ nanoparticle with diameter of 80nm was obtained from Inner Mongolia Mengxi High-tech Materials

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Corporation. The reagents in the experiments, such as OA, heptane, *etc.*, were analytically pure, and commercially available. No further treatment was needed before use.

2.2 Preparation of OA-modified CaCO₃ nanoparticles

Heptane and OA were mixed under stirring, then an appropriate amount of CaCO₃ nanoparticle was added. The mixture was heated to 70°C under vigorous stirring for 4h. The solution was then filtered and the precipitate was rinsed thoroughly with a mixture of alcohol and deionized water. The precipitate was kept in a vacuum oven for 24h at 100°C. A white powder of OA-modified CaCO₃ nanoparticles was obtained. By changing the ratio of OA to CaCO₃ a series of samples were prepared.

2.3 Preparation of PP/CaCO₃ nanocomposites and test specimens

PP and OA-m-CaCO₃ nanoparticles ([OA]=7.5%, by mass) were fed into a TE35 twin-screw extruder (Jiangsu Keya Plastic Mechanical Factory, China) at a barrel temperature of 195–210°C with a screw speed of 40r·min⁻¹. The resulting pellets were injection moulded into test specimens by an Arburg Allrounder 221-55-250 injection moulding machine. The barrel had a flat temperature profile of 220°C, the mould temperature was kept at 40°C with an injection pressure of 5.5MPa, holding pressure was kept at 4.5MPa. Two types of specimens were made for flexural test with dimension of 80mm×10mm×4mm, and impact test with dimension of 80mm×8mm×4mm. Each Izod impact specimen was notched using a cutter of Taiwan Master International Co., Ltd to produce notches with radius of 0.254mm and depth of 2.54mm according to ASTM D256.

2.4 Apparatus and measurement

IR analysis of OA-modified CaCO₃ nanoparticles was carried out on a PE-200 FT-IR spectrometer.

The sedimentation time of OA-modified CaCO₃ nanoparticles in heptane was used to reveal the dispersion stability of the CaCO₃ nanoparticles in non-polar solvents. Certain amount of OA-m-CaCO₃ in heptane (CaCO₃ content was 0.2%, by mass) was added into a 25ml test tube and kept the tube at rest, and then the sedimentation time of CaCO₃ was recorded^[11].

A H-800 transmission electron microscopy (TEM) and a Philips 505 scanning electron microscopy (SEM) were used to examine the dispersion of CaCO₃ nanoparticles in PP matrix and the failure mechanism of PP/CaCO₃ nanocomposite, respectively.

Crystallization behavior and melting characterization of PP, PP/CaCO₃ and PP/OA-m-CaCO₃ nanocomposite samples were studied by differential scan-

ning calorimetry (DSC) (Perkin-Elmer DSC-7) under nitrogen atmosphere. The samples were heated to 210°C and kept for 5min to eliminate the thermal history of the samples, followed by the non-isothermal crystallization recorded from 210 to 50°C at a cooling rate of 10°C·min⁻¹. Then the samples were heated to 210°C at the heating rate of 10°C·min⁻¹, and melting parameters were obtained from the heating scan. The temperature scale of the DSC was calibrated using an indium (melting point, 156.63°C).

The Izod impact test was run using Tinius 892 impact test machines with pendulum speed at impact of 3.46m·s⁻¹. The flexural strength test was carried on a LWK-5 tester at a crosshead speed of 2mm·min⁻¹. The mechanical properties reported hereinafter are the average of five successful tests.

3 RESULTS AND DISCUSSION

3.1 Surface modification of CaCO₃ nanoparticles and their dispersion in PP matrix

Figure 1 showed the IR spectrum of OA-modified CaCO₃ nanoparticles. It was found that the peak at 1610.0cm⁻¹ corresponding to appearance of carboxylic salt, indicating that OA had been attached to the surface of CaCO₃ as the ionic bond^[12]. The peaks at 2925.9cm⁻¹, 2853.9cm⁻¹ and 712.7cm⁻¹ ascribed to long alkyl chain of OA further proved the presence of OA at the surface of CaCO₃.

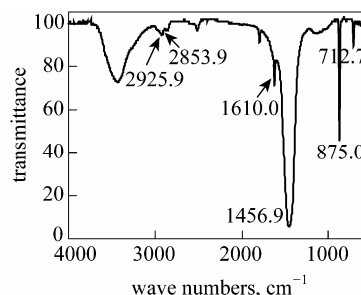


Figure 1 IR spectrum of OA-modified CaCO₃ nanoparticles ([OA]=7.5%, by mass)

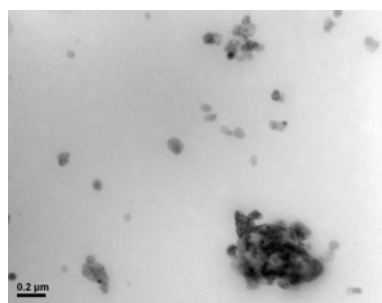
The sedimentation time of CaCO₃ in organic solvents can characterize the dispersibility of CaCO₃ in solvents. Unmodified CaCO₃ is a polar substance and aggregates easily in organic solvents, resulting in the short sedimentation time. Table 1 shows the effect of OA concentration on the sedimentation time of OA-m-CaCO₃ in heptane. It was found that the unmodified CaCO₃ nanoparticles cannot be stably dispersed in non-polar organic solvents, and the sedimentation time in heptane was short (21min), indicating the poor hydrophobic property. With the increase of OA concentration, the sedimentation time of OA-m-CaCO₃ in heptane was significantly prolonged, which showed that a modified hydrophobic layer existed on the surface of OA-m-CaCO₃ and the suspension was more stable. When OA concentration in the reactants was about 7.5%, the sedimentation time of

OA-m-CaCO₃ in heptane almost remained constant indicating that the optimal OA concentration was 7.5% (by mass).

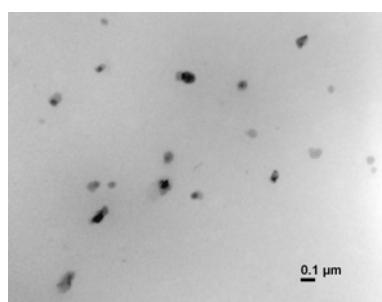
Table 1 Effect of OA concentration on the sedimentation time of OA-m-CaCO₃ in heptane

OA concentration, % (by mass)	Sedimentation time, min
0	21
2.5	298
5.0	355
7.5	432
10.0	446
15.0	452

The dispersion of CaCO₃ nanoparticles was carried out by using TEM. Fig.2 showed the TEM images of unmodified CaCO₃ nanoparticles and OA-m-CaCO₃ nanoparticles in PP matrix. It was seen from Fig.2(a) that some of the unmodified CaCO₃ nanoparticles were seriously aggregated and lapped over. It was found from Fig.2(b) that OA-m-CaCO₃ nanoparticles were dispersed well in PP matrix and individual nanoparticles could be distinguished. These results confirmed that the phenomena of nanoparticles agglomeration decreased effectively because the nanoparticles were kept apart by the surface-modification layer of OA.



(a) Unmodified CaCO₃



(b) OA-m-CaCO₃

Figure 2 TEM image of nanoparticles in PP matrix (PP/CaCO₃=97/3)

3.2 Effect of OA-m-CaCO₃ on the crystallization and melting behavior of PP

PP is a kind of typical semi-crystalline polymers, and the crystallization behavior of PP significantly influences its mechanical properties. Thus, investiga-

tion of the crystallization behavior is significant both from the theoretical and practical points of view.

The effect of OA-m-CaCO₃ on the melting behavior of PP was studied at a heating rate of 10°C·min⁻¹, and the result was shown in Fig.3. It was found that there were two peaks at 151.3°C and 165.4°C corresponding to the melting peaks of α -crystal and β -crystal after the introduction of both CaCO₃ and OA-m-CaCO₃ into PP, respectively^[13], while there was only one melting peak at 166.4°C corresponding to the presence of α -crystal for pure PP, indicating that both CaCO₃ and OA-m-CaCO₃ could induce the formation of β -crystal. In comparison with PP/CaCO₃ nanocomposite, there was a large melting peak at 151.3°C corresponding to the high content of β -crystal for PP/OA-m-CaCO₃ nanocomposite indicating that OA-m-CaCO₃ significantly induced the formation of β -crystal owing to the much finer dispersion of OA-m-CaCO₃ in PP and was an effective β -nucleating agent for PP.

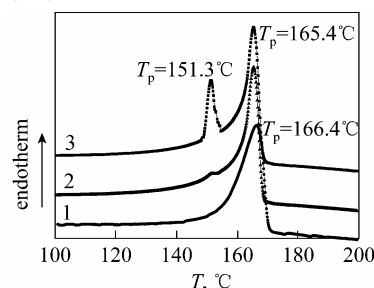


Figure 3 Melting curves of PP and PP/CaCO₃ nanocomposite (99/1)
1—PP; 2—PP/CaCO₃; 3—PP/OA-m-CaCO₃

The degree of crystallinity (x) can be determined from the calorimetric data with the knowledge of the melting enthalpy of the completely crystallized α - and β -crystal PP (ΔH_0). Although the literature values of the melting enthalpy vary, a comparison between $\Delta H_0(\alpha)$ and $\Delta H_0(\beta)$ determined *via* identical methods always reveals a higher value for α -crystal PP. The values for degree of crystallinity (x_α and x_β) were calculated using $\Delta H_0(\alpha)=209\text{J}\cdot\text{g}^{-1}$ and $\Delta H_0(\beta)=151.2\text{J}\cdot\text{g}^{-1}$ ^[14-16]. The effect of CaCO₃ and OA-m-CaCO₃ on x ($x=x_\alpha+x_\beta$) and x_β of PP are shown in Table 2. It was found that x_β for PP/OA-m-CaCO₃ nanocomposite was 21.4%, and both x_β and x were larger than those for PP and PP/CaCO₃ nanocomposites. It was also obvious that OA-m-CaCO₃ not only significantly induced the formation of β -crystal PP, but also caused the crystallization of the non-crystallizing PP chain owing to the heterogeneous nucleation, resulting in the increase of the total degree of crystallization of PP (x).

The effect of OA-m-CaCO₃ on the non-isothermal crystallization behavior of PP was also studied by means of DSC, and the results are shown in Fig.4.

The initial crystallization temperature (T_0), peak temperature of crystallization (T_p), initial slope of crystallization (S_i), half height width of crystallization

peak (ΔW), temperature difference between T_0 and T_p ($\Delta T = T_0 - T_p$) were obtained and listed in Table 2.

It was found from Table 2 and Fig.4 that in comparison to PP and PP/CaCO₃ nanocomposite, both T_0 and T_p moved toward high temperatures after introducing of OA-m-CaCO₃ into PP, indicating that PP containing OA-m-CaCO₃ crystallized at a high temperature because of the improved dispersion of OA-m-CaCO₃ nanoparticles as nucleating points. ΔT and ΔW at the same cooling rate also decreased upon the addition of OA-m-CaCO₃, which demonstrated that OA-m-CaCO₃ increased the crystallization rate of PP. The initial slope of the crystallization curve (S_i) increased upon the addition of OA-m-CaCO₃ at the same cooling rate, indicating that the initial nucleation rate increased owing to the heterogeneous nucleation.

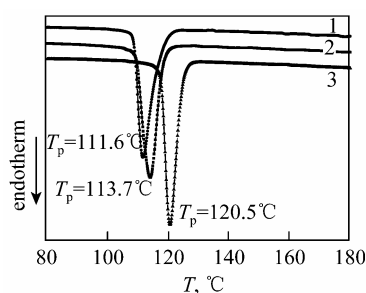


Figure 4 Crystallization curves of PP and PP/CaCO₃ nanocomposite (99/1)

1—PP; 2—PP/CaCO₃; 3—PP/OA-m-CaCO₃

Table 2 Crystallization and melting parameters of PP and PP/CaCO₃ nanocomposite (99/1)

Sample	T_0 , °C	T_p , °C	ΔT , °C	S_i	ΔW , °C	x_s , %	x_β , %
PP	117.2	111.6	5.6	2.8	3.0	46.3	0.0
PP/CaCO ₃	118.9	113.7	5.2	3.3	2.9	48.7	1.6
PP/OA-m-CaCO ₃	124.6	120.5	4.1	4.9	2.4	55.6	21.4

3.3 Effect of OA-m-CaCO₃ on the mechanical properties of PP

The impact strengths of PP/OA-m-CaCO₃ nanocomposites were plotted against CaCO₃ mass fraction in Fig.5. It was found that with the increase of OA-m-CaCO₃ content, the impact strength of the nanocomposites increased significantly first, and then decreased. When OA-m-CaCO₃ content was 1% (by mass), the maximum of the impact strengths of PP/OA-m-CaCO₃ nanocomposites was obtained (12.5kJ·m⁻²), and at that point the impact strength increased by about 65% in comparison to PP.

Figure 6 shows the impact-fractured surface of PP/OA-m-CaCO₃ (97/3) nanocomposite. Although the composite had fine dispersion of CaCO₃ particles, there were few signs that plastic deformation or debonding contributed to the improvement of the impact strength of PP. Therefore, the increase of the impact strength of the PP/OA-m-CaCO₃ nanocomposites probably con-

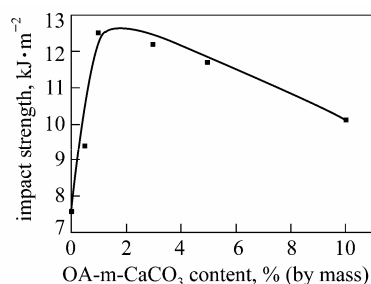


Figure 5 Impact strength of PP/CaCO₃ nanocomposites as a function of OA-m-CaCO₃ content

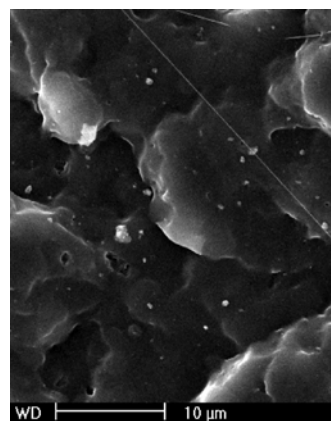


Figure 6 SEM image of impact-fractured surface of PP/OA-m-CaCO₃ (97/3) nanocomposite

tributed to the formation of β -crystal PP. Dou and Wang^[17] also reported that in comparison to α -crystal PP, PP with β -crystal showed good impact strength at room temperature. As discussed above, OA-m-CaCO₃ induced the formation of β -crystal PP, which resulted in the improvement of the impact strength of PP/OA-m-CaCO₃ nanocomposites. The decrease in the impact strength of PP/OA-m-CaCO₃ nanocomposites when OA-m-CaCO₃ content was more than 1% (by mass) was probably caused by the stress concentration owing to the inevitable aggregation of CaCO₃.

The effect of OA-m-CaCO₃ nanoparticles on the flexural strength of PP was also studied and the result was shown in Fig.7. It was found that the flexural strength of PP/OA-m-CaCO₃ nanocomposites increased with the increase of OA-m-CaCO₃ content first, and then decreased slightly with the further increase of OA-m-CaCO₃ content. When OA-m-CaCO₃ content was 1% (by mass), the maximum of the flexural strengths of PP/OA-m-CaCO₃ nanocomposites was obtained (43.9MPa) and at that point the flexural strength increased by about 20% in comparison to PP.

The increase of the flexural strengths of the PP/OA-m-CaCO₃ nanocomposites was probably ascribed to the increase of the total degree of crystallinity of PP after the introduction of OA-m-CaCO₃ into PP as shown in Table 2 and the enhancement effect of the inorganic nanoparticles. The slight decrease of the flexural strengths of PP/CaCO₃ nanocomposites when the OA-m-CaCO₃ content was more than 1% (by mass)

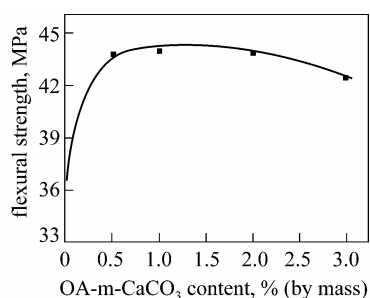


Figure 7 Flexural strength of PP/CaCO₃ nanocomposites as a function of OA-m-CaCO₃ content

was owing to the defects that existed in the nanocomposites which was caused by the aggregation of CaCO₃.

4 CONCLUSIONS

The OA-modified CaCO₃ nanoparticles (OA-m-CaCO₃) was prepared by a chemical surface modification method, and OA had attached to CaCO₃ surface with the ionic bond. The optimal concentration of OA was 7.5% (by mass). OA-m-CaCO₃ caused significant changes in crystallization and melting characteristics of PP. OA-m-CaCO₃ induced the formation of β -crystal and resulted in the increase of the total degree of crystallinity of PP due to the heterogeneous nucleation. OA-m-CaCO₃ also increased the crystallization rate and the crystallization temperature of PP. OA-m-CaCO₃ can effectively improve the mechanical properties of PP. In comparison to PP, the impact strength of PP/OA-m-CaCO₃ nanocomposites increased by about 65% and the flexural strength increased about by 20%.

NOMENCLATURE

S_i	initial slope of crystallization
T_o	initial crystallization temperature, °C
T_p	peak temperature of crystallization, °C
ΔW	half height width of crystallization peak, °C
x	total degree of crystallinity
x_α	degree of crystallinity for α -crystal
x_β	degree of crystallinity for β -crystal

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