Investigation on Preparation and Property of Nano-$CaCO_3$/PP Masterbatch Modified by Reactive Monomers

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ABSTRACT: Nano-$CaCO_3$/polypropylene (PP) masterbatch containing above 80 wt % nano-$CaCO_3$ was prepared by nano-$CaCO_3$ coated PP modified by reactive monomers. The chemical interaction, crystallization and melting behavior, thermal stability, morphology, and surface contact angle of masterbatch were investigated with IR, DSC, TEM, TGA, ESCA, and surface contact angle. The results indicated that nano-$CaCO_3$ was coated by PP graft copolymers in the masterbatch modified by reactive monomers. The graft ratio and crystallization and melting behavior of PP in the masterbatch depended on the type and content of reactive monomer. The crystallization temperatures of masterbatch modified by reactive monomer is methyl methacrylate $>$ butyl acrylate $>$ methyl acrylate $\approx$ mixture of acrylic acid and styrene $>$ unmodified $\approx$ maleic anhydride $\approx$ acrylic acid $>$ styrene. Modification by reactive monomer increased the thermal stability and surface contact angle of masterbatch. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3907–3914, 2006

Key words: nano-$CaCO_3$; polypropylene; masterbatch; property

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INTRODUCTION

With the development of nanometer technology, many kinds of filler used in polymer material were made into nanoparticles. Among all kinds of nanoparticles, nano-$CaCO_3$ has the characteristic of low cost, volume-production, and excellent filled effect. Therefore, there have been lots of investigation on the polymer composites filled with nano-$CaCO_3$, especially for the polypropylene (PP) filled with nano-$CaCO_3$.[1–20] To prepare nano-$CaCO_3$/PP composites with high performance, many work have been done to further improve the dispersion of nano-$CaCO_3$ in the PP and to further strengthen the interaction between nano-$CaCO_3$ and PP, and among the nano-$CaCO_3$ particles. Many reports on the filled polymer material have indicated that the dispersant used in the polymer composites could improve the dispersion of the filler, but slightly improves the interface adhesion between filler and polymer. Traditional coupling agent could enhance the interface adhesion, but could little improve the interface interaction between coupling agent and polymer because of the short organic part. Although macromolecular compatibilizer has been widely used in polymer composites, macromolecular compatibilizer with large molecular weight may not easily insert into the gap between the nano-$CaCO_3$ particles. If the surface of nano-$CaCO_3$ particles is coated by reactive monomers, the reactive monomers can easily enter into the gap between the nano-$CaCO_3$ particles and interface and between nano-$CaCO_3$ particle and PP. The reactive monomers coated on the surface of nano-$CaCO_3$ particles *in situ* copolymerize or react with PP to form the macromolecular compatibilizer. Reactive monomers can improve the dispersion of the nano-$CaCO_3$ in PP matrix. The formation of macromolecular compatibilizer can enhance the interface adhesion between the nano-$CaCO_3$ particles and between nano-$CaCO_3$ and PP. The above effect of reactive monomers has been demonstrated in the investigation of $Al(OH)_3$/PP[21,22] and $Mg(OH)_2$/PP[23–25] modified by acrylic acid (AA). Therefore, to improve the dispersion of nano-$CaCO_3$ in PP and increase the interface adhesion in PP composites, masterbatch coated with PP grafted by many kind of reactive monomers had been prepared in xylene solution. The surface properties and morphology of masterbatch, the crystallization and melting behavior of PP masterbatch, and the interaction of the prepared

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TABLE I
The Compositions of Nano-$CaCO_3$/PP Masterbatch

Masterbatch	Reactive monomer	Monomer:PP:$CaCO_3$ (w/w/w)
PP	none	
C masterbatch	none	0:5:20
A1 masterbatch	Acrylic acid	1:5:20
A3 masterbatch	Acrylic acid	3:5:20
A5 masterbatch	Acrylic acid	5:5:20
A7 masterbatch	Acrylic acid	7:5:20
AS masterbatch	Acrylic acid and styrene	AA/ST 2.5/2.5:5:20
BA masterbatch	Butyl acrylate	5:5:20
MA masterbatch	Methyl acrylate	5:5:20
MH masterbatch	Maleic anhydride	5:5:20
MM masterbatch	Methyl methacrylate	5:5:20
ST masterbatch	Styrene	5:5:20

masterbatch were investigated by IR, DSC, TEM, TGA, ESCA, and surface contact angle in this study.

EXPERIMENTAL

Materials

Polypropylene was provided in pellet by Guangzhou Yinzhu Polypropylene Limited (China) with the trade name of CTS-700 with MI of 10 g/10 min. Nano-$CaCO_3$ was provided by Guangzhou JBS Industries Limited with the size of 40–60 nm, without any surface treatment. Reactive monomers were acrylic acid (AA) (Foshan Chemical Plant, China), methyl acrylate (MA) (Tianjin Chemical Reagent Institute, China), styrene (ST) (Shanghai Chemical Reagent Chemical Plant, China), butyl acrylate (BA) (Guangzhou Xinjian Chemical Plant, China), methyl methacrylate (MM) (Tianjin Chemical Reagent Institute, China), and maleic anhydride (Tianjin Chemical Reagent Number One Plant, China) in CP grade. Benzoyl peroxide (BPO) in CP grade was purchased from Guangzhou Chemical Reagent Plant, China. Antioxidant was provided by Albemarle Limited (America). Xylene in CP grade was purchased from Guangzhou Chemical Reagent Plant, China.

Preparation of masterbatch

PP was dissolved in xylene at 120°C. The reactive monomer with 0.5 wt % BPO was dropped into the PP solution, and then nano-$CaCO_3$ was added. After the reaction time of 2 h, the solution was cooled down to room temperature. After filtration, the solution was washed with ethanol and vacuum-dried, and the nano-$CaCO_3$/PP masterbatch modified with different reactive monomer marked according to Table I were prepared.

Characterization method and apparatus

IR characterization of masterbatch was performed on a EQUINOX 55 FTIR spectrum of Germany Bruker Limited in KBr slice. Thermal stability of masterbatch was measured using a thermogravimetric analyzer (Germany NETZSCH TG-209) in air atmosphere with a heating rate of 20°C/min up to 800°C. The crystallization and melting behavior were characterized using a PerkinElmer differential scanning calorimeter DSC 7 and all samples were heated from 50 to 260°C at a heating rate of 10°C/min, and then held at 220°C for 5 min, and cooled down to 50°C at 10°C/min. The DSC heating and cooling curves were recorded. The surface chemical composition of the masterbatch was determined using an electron spectroscopy for chemical analysis (VG ESCALAB MK II) with Mg Kα rate and 1–3 × 10^{-8} Pa of vacuum tightness. The masterbatch morphology was observed by a JEM-2010 (HR) transmission electron microscope (TEM) operated at an accelerating voltage of 15 kV. The surface contact angle against water was determined using a surface energy tester (German Data Physics OCA20).

RESULTS AND DISCUSSION

IR characterization of grafted polymer in nano-$CaCO_3$/PP masterbatch

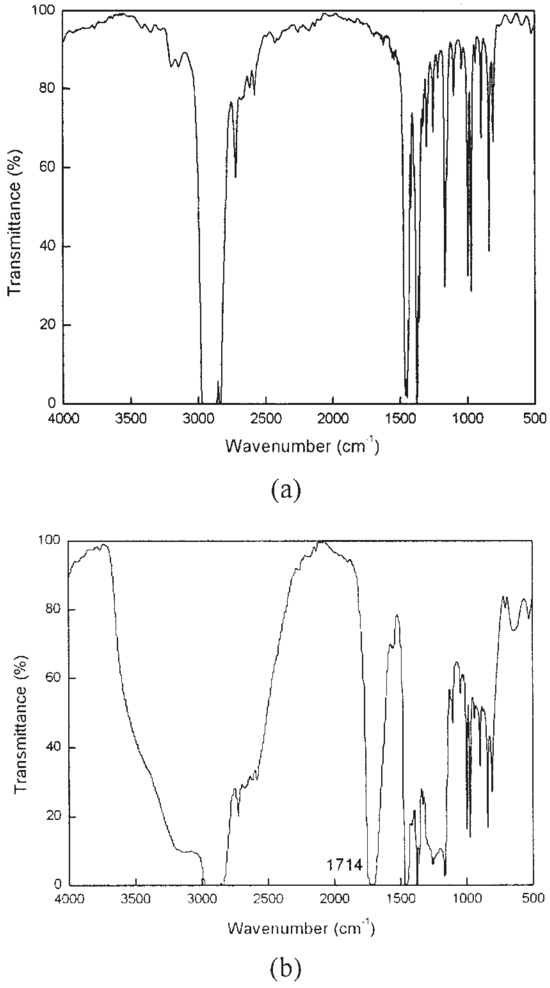
Figure 1 shows the IR spectra of nano-$CaCO_3$/PP masterbatches. Compared with the IR spectra of pure PP, IR spectra of nano-$CaCO_3$/PP masterbatch was basically the same. It is suggested that the chain structure of PP coated on the surface of nano-$CaCO_3$ didn't greatly change. In the IR spectra of PP modified with AA in nano-$CaCO_3$/PP masterbatch, carboxyl band at 1710 cm^{-1} was observed and the intensity of peak at 1710 cm^{-1} increased with increasing content of AA. This result indicated that AA was grafted onto the PP chain coated on the surface of nano-$CaCO_3$. For the PP modified with ST in nano-$CaCO_3$/PP masterbatch, the phenyl bank at 699 cm^{-1} was observed, indicating that ST took place a grafting reaction with PP. In the PP modified with the mixture of AA and ST in nano-$CaCO_3$/PP masterbatch, both phenyl bank and carboxyl band were observed on the IR spectra in Figure

2. This means that AA and ST can simultaneously be grafted onto the PP chain.

In Figure 3, the IR spectra of the masterbatch modified with BA, MA, and MM also showed the ester band at 1738 cm^{-1}. For the masterbatch modified with maleic anhydride, a carboxyl band at 1707 cm^{-1} was observed. These results of IR demonstrated that grafted PP copolymers had been formed in nano-$CaCO_3$/PP masterbatches modified by reactive monomers.

Thermal stability of nano-$CaCO_3$/PP masterbatch

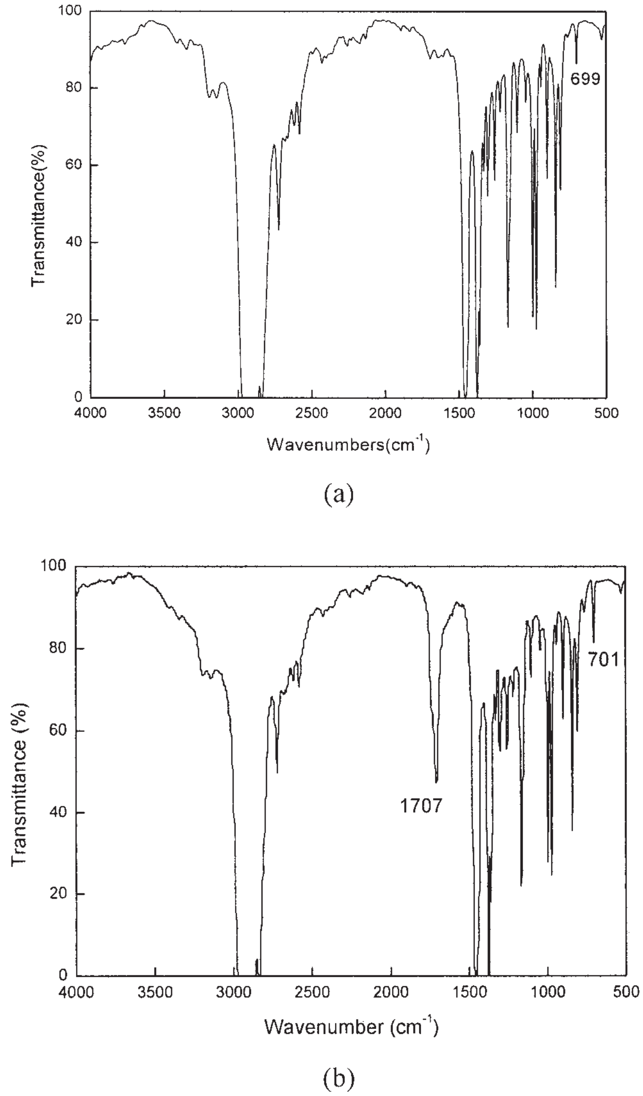
Figure 4 shows the TG curses of the nano-$CaCO_3$/PP masterbatches. It is obvious that there are two decomposition stages. Compared with the TG curve of pure nano-$CaCO_3$, the decomposition stage of low temperature related to the decomposition of the PP coating on the surface of nano-$CaCO_3$, and the decomposition stage of high temperature related to the decomposition of nano-$CaCO_3$. The modification of reactive monomers increase the decomposition temperature of PP, especially the masterbatch modified with AA. This means that the modification of reactive monomers can not only enhance the thermal stability of PP, but also improve the thermal stability of nano-$CaCO_3$.



(a)

(b)

Figure 1 IR spectra of PP extracted from nano-$CaCO_3$/PP masterbatch (a) unmodified and (b) modified with AA.

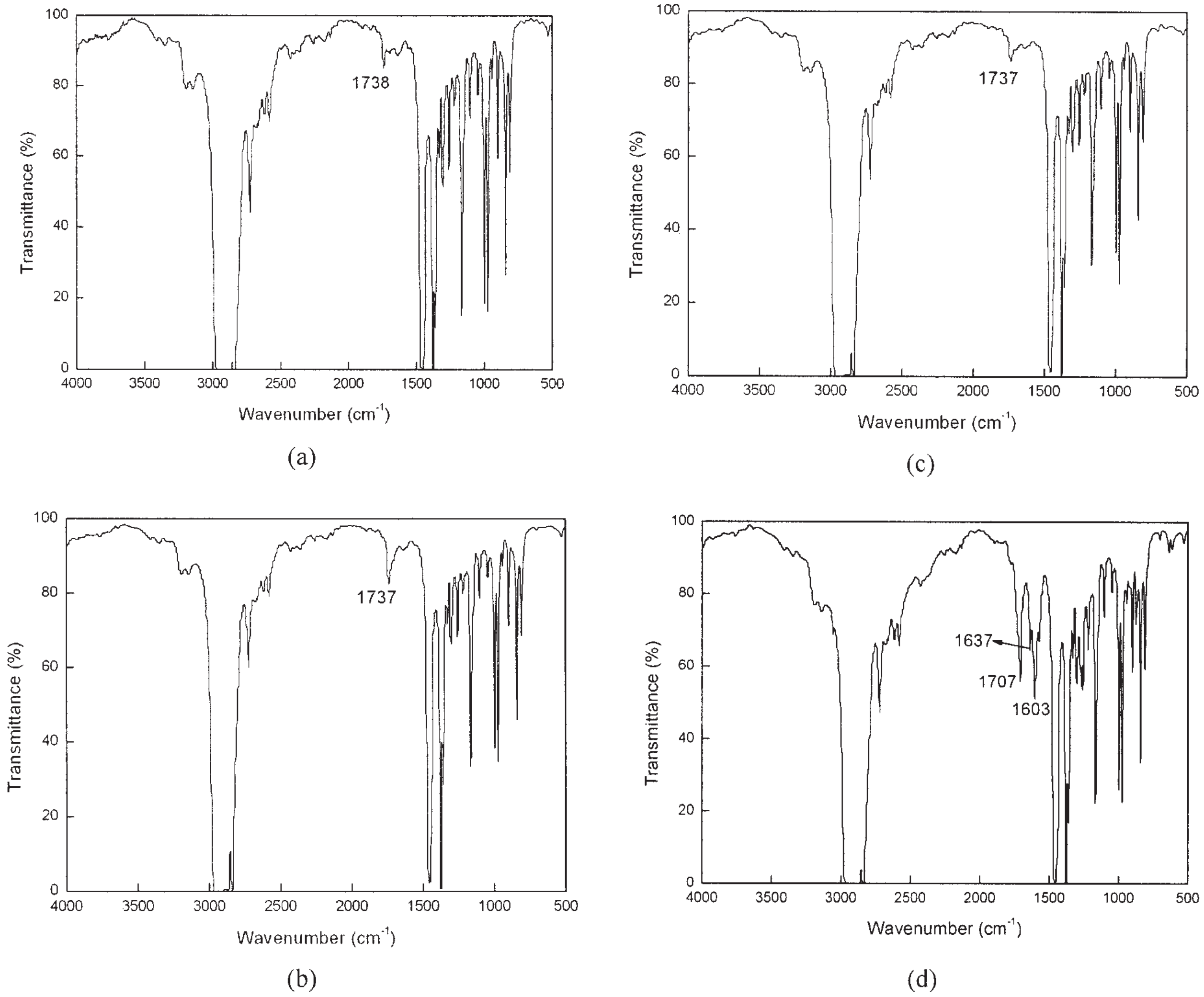


(a)

(b)

Figure 2 IR spectra of PP extracted from nano-$CaCO_3$/PP masterbatch modified with (a) ST and (b) AA and ST.

Since the decomposition stage at low temperature is related to the decomposition of PP coating on the surface of nano-$CaCO_3$, the weight of the PP coating and the grafted ratio of reactive monomers calculated according to the weight loss is shown in Table I. It can be seen from Table II that the weight of PP in the nano-$CaCO_3$/PP masterbatch was between 16 and 20 wt % and the masterbatch containing very high content of nano-$CaCO_3$ was obtained. The order of grafting ratio from high to low is AA > maleic anhydride > MM > BA > ST > mixture of AA and ST > MA. The grafted ratio increased with the increased content of monomer.



(a) (c)

(b) (d)

Figure 3 IR spectra of PP extracted from nano-CaCO$_3$/PP masterbatch modified with (a) BA, (b) MA, (c) MM, and (d) maleic anhydride.

XPS analysis of nano-CaCO$_3$/PP masterbatch

Figure 5 shows the XPS spectra and the carbon CIs spectrum of nano-CaCO$_3$. It can be seen from the XPS spectra of nano-CaCO$_3$ that there were three major elements of the surface of nano-CaCO$_3$ including carbon, oxygen, and calcium. The carbon CIs spectrum showed four binding energy peaks at 284.82, 286.50, 288.00, and 289.32 eV. The binding energy peak at 284.82 eV represent the carbon of C—C and C—H, the binding energy peaks at 286.50 and 288.00 eV represent the carbon of C—O and C═O, and the binding energy peak at 288.00 eV represent the carbon of CO$_3$ group. According to the peak area under the binding energy peaks, the amount of carbon, oxygen, and calcium were calculated as 1 : 2.97 : 0.98, which was close to composition of CaCO$_3$. Figure 6 shows the XPS spectra and the carbon CIs spectrum of unmodified nano-CaCO$_3$/PP masterbatch. The content of C—C and C—H at 284.82 eV was higher than that of nano-CaCO$_3$. However, the binding energy peaks at the carbon of C—O and C═O, and the carbon of CO$_3$ group did not change. It indicated that no chemical interaction between nano-CaCO$_3$ and PP took place. The amount of carbon, oxygen, and calcium were calculated as 1 : 3.22 : 0.97, which was close to the composition of CaCO$_3$. Figure 7 shows the carbon CIs spectrum of the nano-CaCO$_3$/PP masterbatch modified with AA and MH. All the binding energy peaks of C═O, O—C═O, and Ca shifted towards higher binding energy. It can be considered that the groups grafted on the PP chain had strong chemical combination with Ca on the surface of nano-CaCO$_3$.

Crystallization and melting behavior of nano-CaCO$_3$/PP masterbatch

Figure 8 shows the DSC cooling curves of nano-CaCO$_3$/PP masterbatch. Although the PP coating on

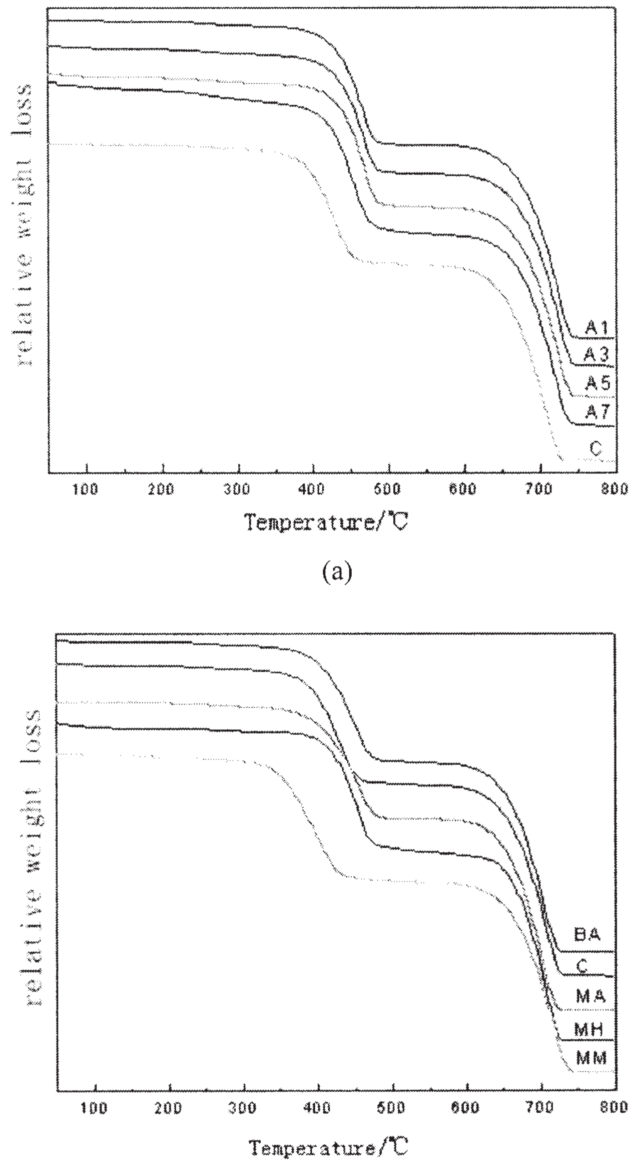


Figure 4 TG curves for nano-CaCO$_3$/PP masterbatch modified with reactive monomers.

TABLE II
Grafting Rate of Reactive Monomers in Masterbatchs

Masterbatch	Weight of PP (%)	Grafting ratio (%)
C	19.2	0
ST	16.7	28.8
AS	16.7	27.7
BA	16.7	28.8
MA	16.7	24.4
MH	16.7	37.6
MM	16.7	37
A1	19.2	13.3
A3	17.9	25.2
A5	16.7	40
A7	15.6	68.9

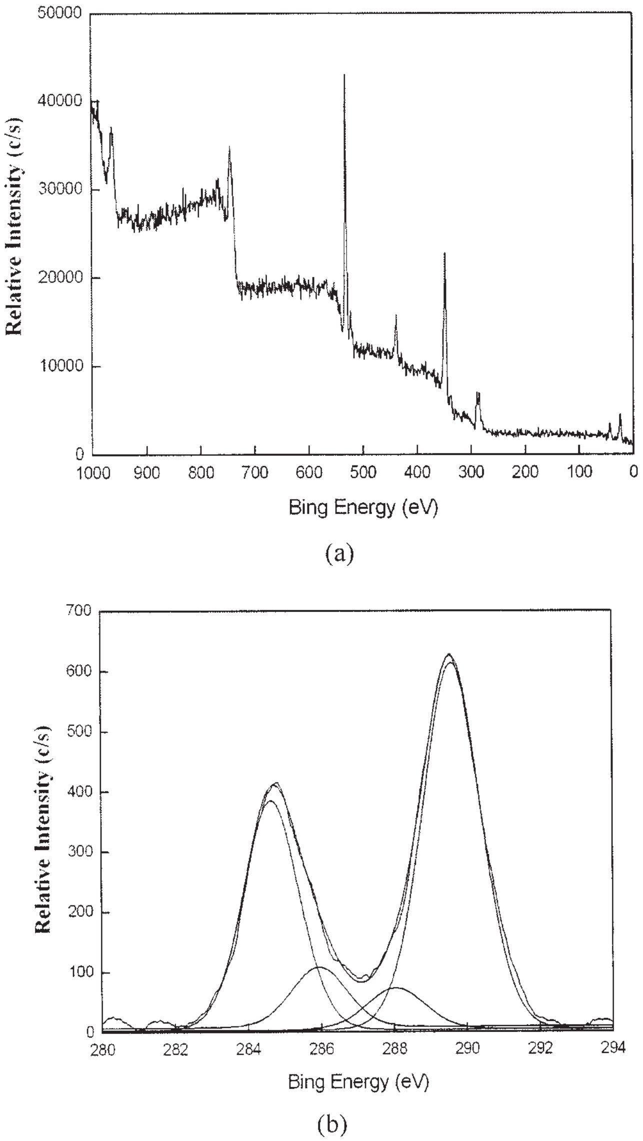
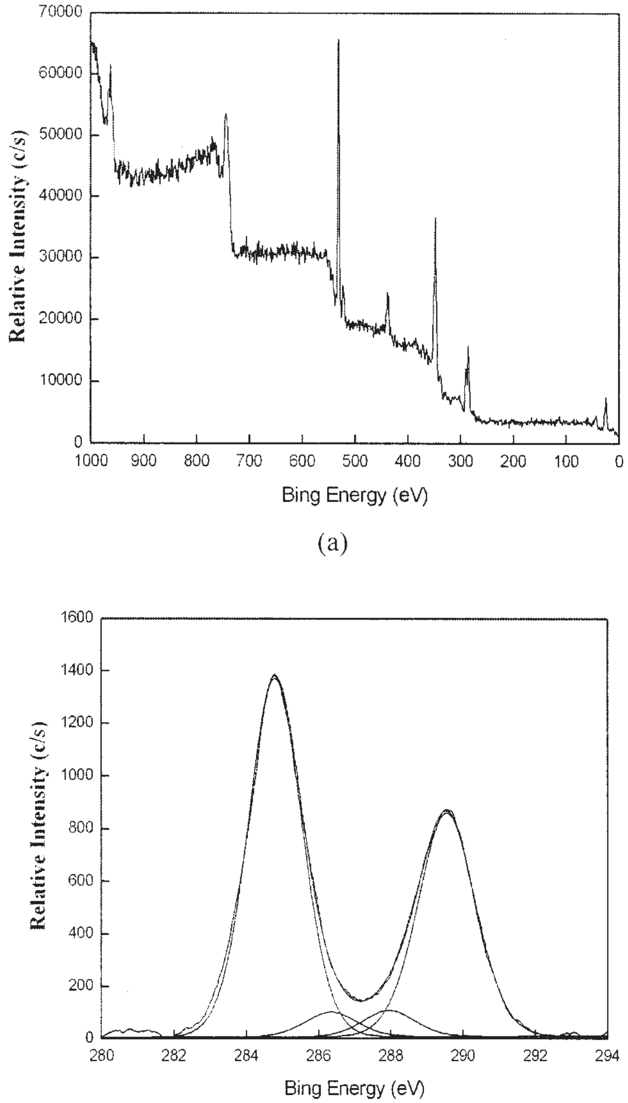


Figure 5 XPS spectra of nano-CaCO$_3$: (a) XPS spectra and (b) CIs fitted spectra.

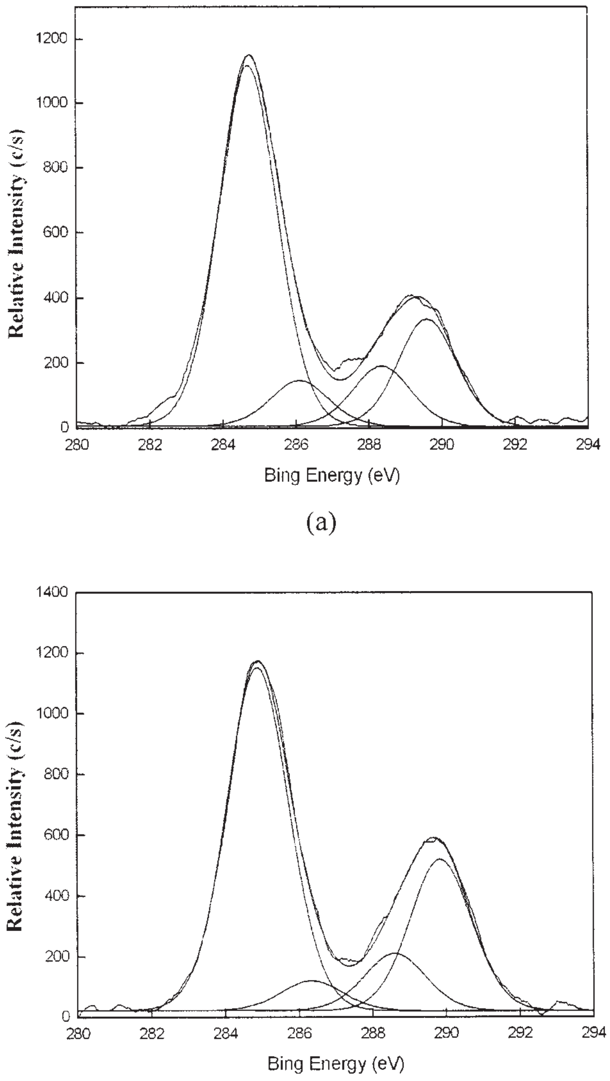
the surface of nano-CaCO$_3$ is lower than 20%, the crystallization peak of PP was still observed in all the nano-CaCO$_3$/PP masterbatches. The crystallization peak of PP decreased in the nano-CaCO$_3$/PP masterbatch modified with AA comparing with pure PP and with the increased content of AA in nano-CaCO$_3$/PP masterbatch. It is attributed to the fact that with the increased content of AA, the carboxyl group grafted onto the PP chain increased, which reduced the regularity of PP chain and increased the difficulty of crystallization. Different monomers have different effect on the crystallization peak of PP. The order of the crystallization peak temperature from high to low is MM (119.1°C) > BA (118.5°C) > MA (117.9°C) ≈ mixture of AA and ST (117.4°C) > unmodified (111.4°C) ≈ maleic anhydride (111.2°C) ≈ AA (111.1°C) > ST (103.6°C). Compared with the unmodified masterbatch, the crystallization peak temperatures of masterbatch modified by MM, BA, MA, mixture of AA, and ST are higher than that of unmodified masterbatch. The crystallization peak temperatures of masterbatch modified by maleic anhydride, AA, and ST are lower than that of unmodified masterbatch. For the masterbatch with lower crystallization peak temperatures, it is considered that the grafting reaction of PP with reactive monomer had more effect on the regularity of PP chain and hinders the crystallization of PP. For the masterbatch with higher crystallization peak temperatures, it is suggested that PP grafted with reactive monomer exhibited heterogeneous nucleation effect on the crystallization of PP and increased the crystallization temperature of PP.



(a)

(b)

Figure 6 XPS spectra of C masterbatch: (a) XPS spectra and (b) CIs fitted spectra.



(a)

(b)

Figure 7 CIs fitted spectra: (a) AA masterbatch and (b)MH masterbatch.

Figure 9 shows the DSC heating curves of nano-$CaCO_3$/PP masterbatches after the cooling process mentioned earlier. The modification of MM, BA, MA, mixture of AA, and ST have little effect on the melting temperatures of PP, while the modification of maleic anhydride, AA, and ST decreased the melting temperatures of PP. It is considered that the decrease of the melting temperature of PP in nano-$CaCO_3$/PP masterbatches was due to the decrease in regularity of PP chain and the crystallization temperature of PP.

Morphology of nano-$CaCO_3$/PP masterbatch

TEM morphology of nano-$CaCO_3$ and nano-$CaCO_3$/PP masterbatch are shown in Figure 10. It can

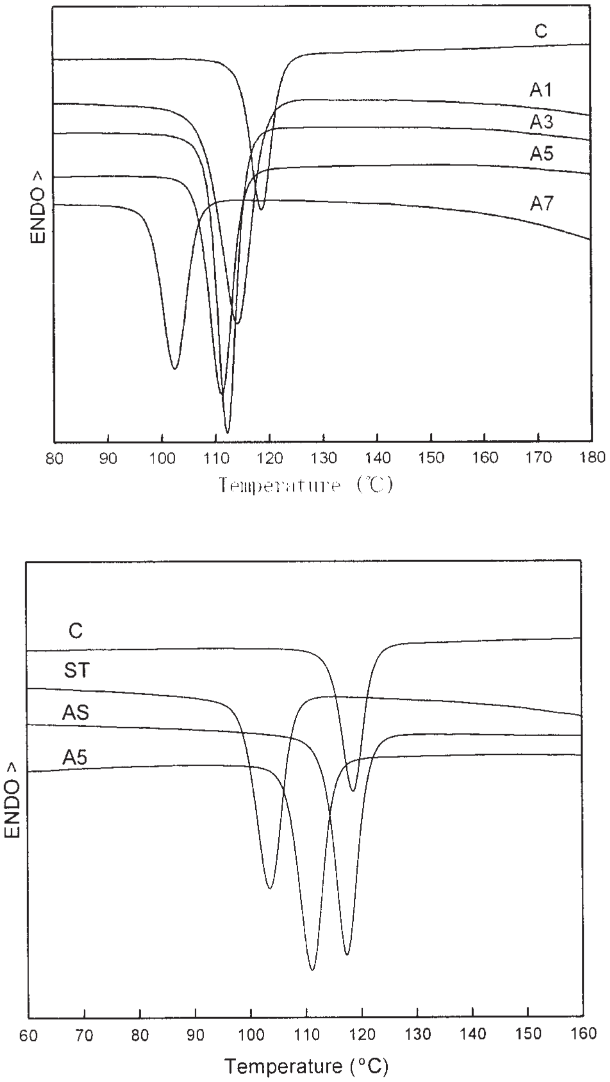


Figure 8 DSC crystallization curves of masterbatch.

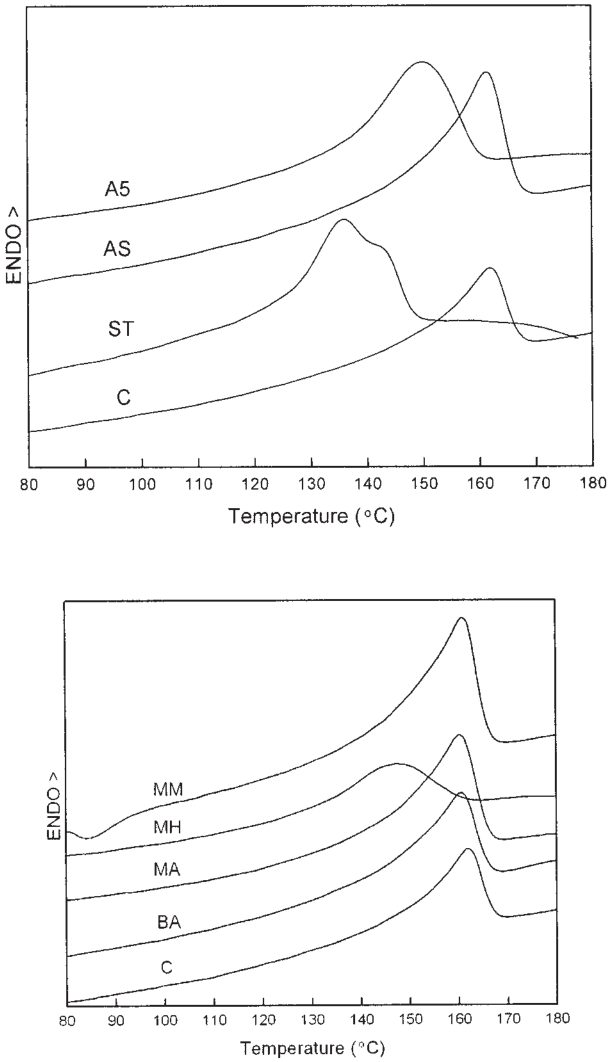


Figure 9 DSC melting curves of nano-CaCO$_3$/PP masterbatch.

be seen that nano-CaCO$_3$ particle has an approximative round shape with lubricous and clear boundary. While in the nano-CaCO$_3$/PP masterbatch modified reactive monomer, the nano-CaCO$_3$ particle aggregate into congeries with the size of 200–300 nm, the boundary is clear, and there is a layer of film between the nano-CaCO$_3$ particles. This indicated that after the modification of reactive monomer, reactive monomer could insert into the gap between nano-CaCO$_3$ particles and enhance the interaction in the nano-CaCO$_3$/PP interface.

Surface properties of nano-CaCO$_3$/PP masterbatch

Table III shows the contact angle of nano-CaCO$_3$/PP masterbatch modified with different reactive monomers against water. It is obvious that pure nano-CaCO$_3$ had the contact angle of 3.9°, which demonstrated that nano-CaCO$_3$ had a polar surface. When the nano-CaCO$_3$ was coated with pure PP in C masterbatch, the contact angle reached 47.0°, which indicated that large part of the polar surface of nano-CaCO$_3$ had occupied by PP and became nonpolar. When the nano-CaCO$_3$ coated with PP grafted by

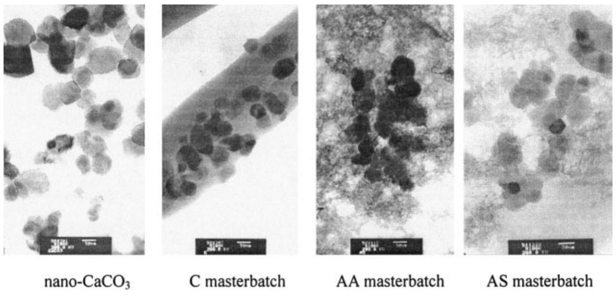

nano-CaCO$_3$ C masterbatch AA masterbatch AS masterbatch

Figure 10 TEM photograph of nano-CaCO$_3$/PP masterbatch.

TABLE III
Surface Contact Angle of Nano-CaCO$_3$/PP Masterbatch

Masterbatch	Contact angle (degrees)
CaCO$_3$	3.9
C	47
A1	54.6
A3	102.3
A5	81.9
A7	76.7
BA	114
MM	100.5
MH	92.3
MA	91.2
AS	68.5
ST	60.1

different reactive monomers in nano-CaCO$_3$/PP masterbatch was modified by reactive monomer, further increment in the contact angle were observed with the order of BA > A3 > MM > MA > A5 > A7 > AS > AI > C > nano-CaCO$_3$. The increase in the contact angle after modification with reactive monomer was attributed to the interaction among nano-CaCO$_3$, reactive monomer, and PP. On one hand, the polar interaction between nano-CaCO$_3$ and reactive monomer promoted the reactive monomer to cover onto the surface of nano-CaCO$_3$. On the other hand, the reactive monomer grafted onto the chain of PP and promoted more PP to cover on the surface of nano-CaCO$_3$. This is the reason why the modified masterbatch exhibited higher nonpolarity compared with the C masterbatch. The above results demonstrated that the modification of reactive monomer could not only promote the dispersion of nano-CaCO$_3$ in PP matrix, but also improve the interface adhesion.

It can also be seen from Table III that the contact angle of A series masterbatch firstly increased and then decreased with the increased content of AA monomer. This is attributed to the high polar of AA monomer. When the high content of AA monomer was used the polarity of nano-CaCO$_3$/PP masterbatch would elevate and the contact angle would reduce. For the AA, MH, MM, and BA masterbatch, the contact angle related with the grafted ratio of the monomer. The contact angle of nano-CaCO$_3$/PP masterbatch increase with increasing grafted ratio. It is considered that the higher grafted ratio led to a more polarity and a more complete coating of the surface of nano-CaCO$_3$. MA masterbatch has a lower grafted ratio but higher contact angle, indicating that MA grafted polymer has stronger coating ability. Styrene is nonpolar and have no interaction with nano-CaCO$_3$, so it is difficult for ST to cover the surface of nano-CaCO$_3$ completely, leading to a lower contact angle for ST masterbatch.

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