New Hyperdispersant Agent for Polypropylene/CaSO$_4$ Composites

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ABSTRACT: A new hyperdispersant agent with Si─OH as an anchoring group and poly(butyl acrylate) as a solvatable chain was synthesized, and its effect on the properties of polypropylene (PP)/CaSO$_4$ composites was investigated. Fourier transform infrared spectroscopy results showed that the hyperdispersant agent reacted on the CaSO$_4$ surface and the modified CaSO$_4$ particles. The tensile strength and impact strength of the PP/CaSO$_4$ composites increased about 14 and 34%, respectively, versus that of PP/CaSO$_4$ (filled with the same unmodified fraction). According to surface analysis by scanning electron micros- copy, the CaSO$_4$ particles were buried well in the PP matrix when CaSO$_4$ was coated with the hyperdispersant agent. CaSO$_4$ significantly increased the crystallization temperature and crystallization rate of PP by differential scanning calorimetry, but the addition of hyperdispersant-agent-modified CaSO$_4$ did not lead to the formation of crystalline PP through X-ray diffraction. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 532–538, 2009

Key words: composites; crystallization; poly(propylene) (PP)

INTRODUCTION

Polypropylene (PP) as a plastic is used extensively, but it has obvious shortcomings, including a low modulus, slight impact strength, and weak heat re- sistance.[1–7] In comparison with neat PP, superfine- particulate-filled PP composites exhibit markedly improved properties at low concentrations of the inorganic components (1–10 wt %).[8–12] Fillers can hardly be uniformly dispersed in polymers by con- ventional techniques because of the strong agglomer- ating tendency of superfine particles.[13–17] Surfactants, coupling agents, and hyperdispersant agents have been developed to modify the surface polarity of fill- ers to improve their dispersion in polymers.[18–22] Among these additives, hyperdispersant agents have gained much attention because of their special struc- tures, which have two different functional groups: an anchoring group attracted to the surface of the fillers and a solvatable chain attracted to the resin.[22–24] Sun and Sun[25] prepared a polyethylene polyamine/ poly(12-hydroxylauric acid) ester hyperdispersant agent with 12-hydroxylauric acid as the solvatable chain and with polyethylene polyamine as the anchoring group. The hyperdispersant agent pro- vided the best dispersing performance when the molar ratio of poly(12-hydroxylauric acid) ester to polyethylene polyamine was 4 : 6. Zhang et al.[26] syn- thesized a hyperdispersant agent with poly(ethylene glycol) and poly(acrylic acid) as the solvatable chain and studied its influence on the dispersion and stabi- lization of SiO$_2$, finding that the optimal dosage of the hyperdispersant agent was 1.6 mg/L. Yan et al.[27] used hyperdispersant agents to modify nano-CaCO$_3$ to improve the intensity and toughening of poly (vinyl chloride)/nano-CaCO$_3$ composites, finding that the tensile strength and impact strength of the composites were 37.7 MPa and 39.7 kJ/m^2, respec- tively. Feng et al.[28] investigated the effect of a poly- ester-type hyperdispersant agent on the mechanical properties of PP/inorganic particle composites, find- ing that the tensile strength and impact strength of the composites were enhanced 29% and 22.8%, respectively, in comparison with composites with no hyperdispersant agent.

A new hyperdispersant agent with Si─OH as the anchoring group and poly(butyl acrylate) as the sol- vatable chain was synthesized in this study. How- ever, the use of hyperdispersant-agent-coated CaSO$_4$ inorganic fillers in composites has rarely been reported in published articles so far. The hyperdis- persant agent was used to modify superfine CaSO$_4$, and then PP/CaSO$_4$ composites were prepared. The effect of the hyperdispersant agent on the PP/CaSO$_4$ composites was assessed on the basis of their me- chanical properties, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and X-ray diffraction (XRD).
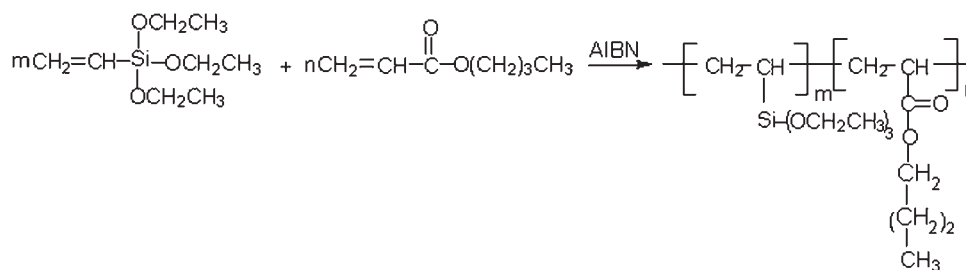
Scheme 1 Reaction scheme for the synthesis of the hyperdispersant agent.

EXPERIMENTAL

Materials

PP (weight-average molecular weight = 110,000) was supplied by Yanshan Chemical, Ltd. (Beijing, China). Superfine $CaSO_4$, with a purity of 99.5% and an average particle size of 8 μm, provided by Anhui Hengtai Co., Ltd. (Chaohu, China), was dried at 120°C for 10 h before use.

Synthesis of the hyperdispersant agent

Butanone, used as a solvent, was placed in a reactor flask equipped with a temperature-control electric heating device, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. When the temperature of the system reached 78°C, a mixture of silane, butyl acrylate, 2,2′-azobisisobutyronitrile, and 1-dodecanethiol was fed into the reactor by means of a dropping funnel. The temperature of the system was maintained at 78°C for 2 h. The butanone was removed by a rotary evaporator; when the reaction was finished, the hyperdispersant agent was obtained. The number-average molecular weight of the hyperdispersant agent was about 5000, as

determined with a viscosimeter. The reaction scheme for the synthesis of the hyperdispersant agent is presented in Scheme 1.

Preparation of the PP/CaSO₄ composites

Different fractions (1.2, 1.5, and 1.8 wt %) of the hyperdispersant agent were mixed with superfine $CaSO_4$ fillers in a laboratory kneader (SHR-10C, Beier Machinery, China) with a mixing head operating at 600 rpm and 120°C for 10 min. Then, different fractions (10, 20, and 30 wt %) of $CaSO_4$ were compounded with PP in the kneader with a mixing head operating at 600 rpm and 150°C for 8 min. The composites were prepared in a corotating twin-screw extruder mixer (SJSH-30, Nanjing Rubber and Plastics Machinery Plant, Nanjing, China) with a length/diameter ratio of 30. The speed was 150 rpm, and the barrel temperature was 220°C. The rod extruder was cooled in a water bath, and then pelletization was performed. Subsequent injection molding was carried out in a reciprocating screw-injection machine with a barrel temperature of 220°C, a mold temperature of 20°C, an injection speed of 10.2 cm³/s, and an injection pressure of 35 MPa.
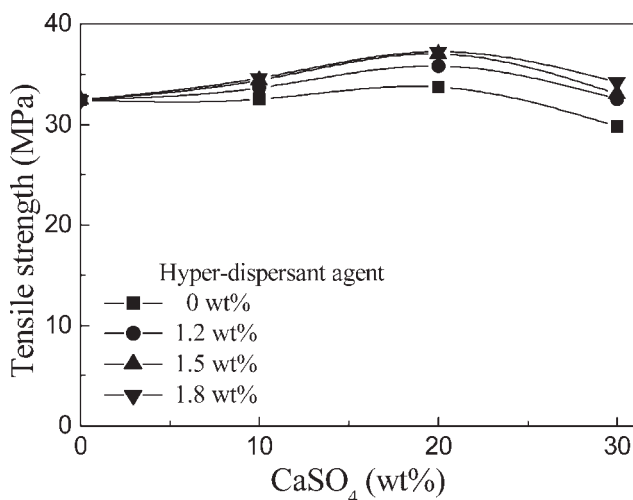

Figure 1 Effects of the amounts of $CaSO_4$ and the hyperdispersant agent on the tensile strength of the PP/CaSO₄ composites.
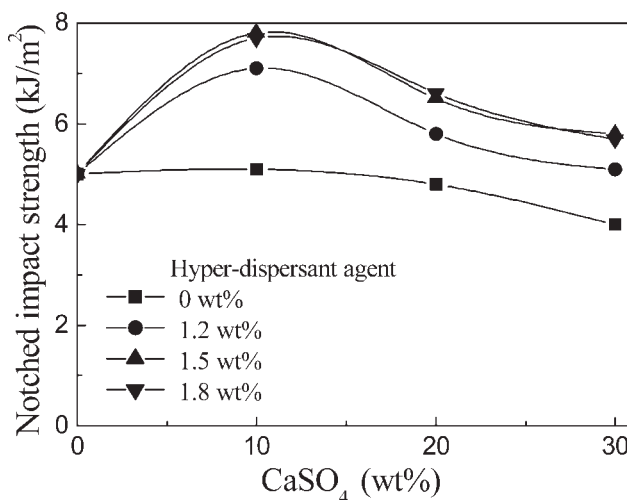

Figure 2 Effects of the amounts of $CaSO_4$ and the hyperdispersant agent on the notched impact strength of the PP/CaSO₄ composites.
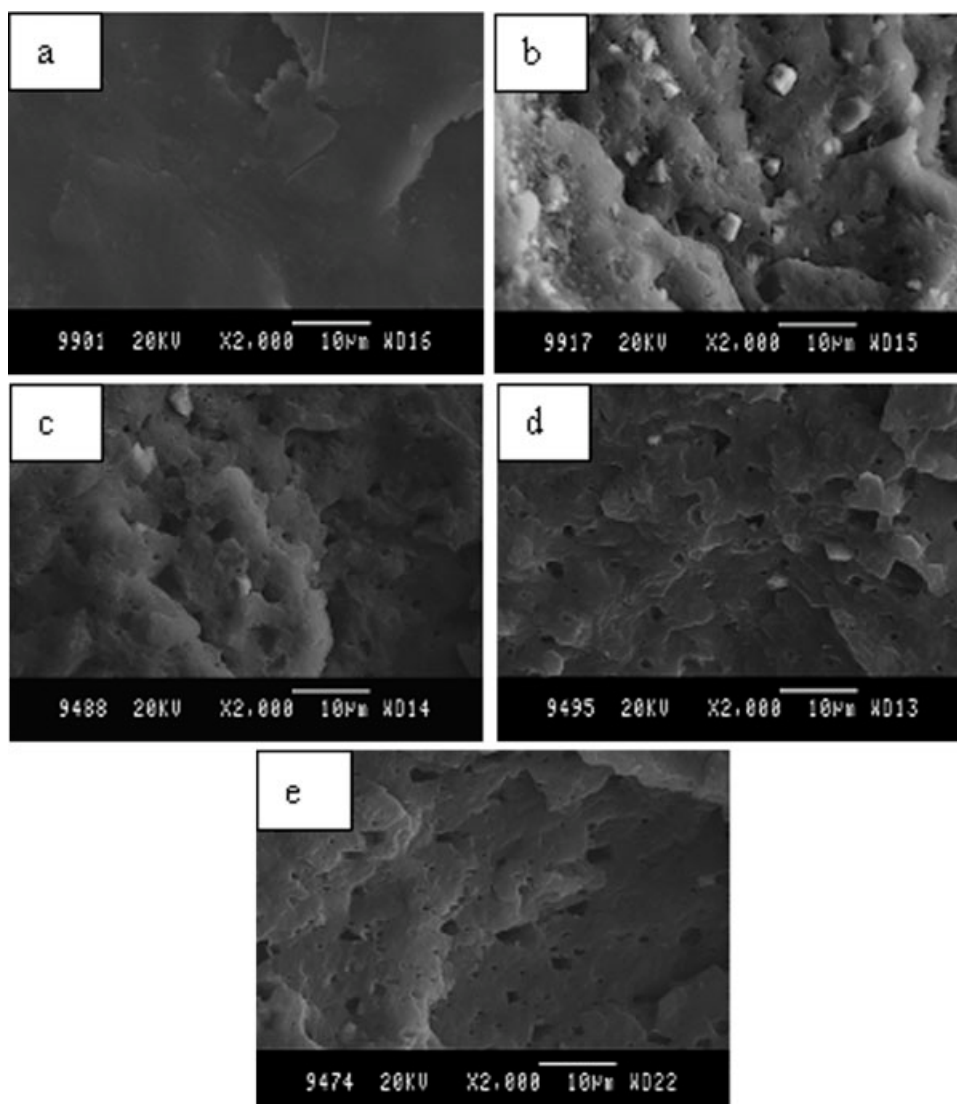
Figure 3 SEM images of fractured surfaces of the PP/CaSO$_4$ composites: (a) pure PP, (b) PP with 20 wt % unmodified CaSO$_4$, and (c–e) PP with 20 wt % CaSO$_4$ modified with 1.2, 1.5, and 1.8 wt % hyperdispersant agent, respectively.

Characterization

XRD

The crystal types of the PP/CaSO$_4$ composites were studied by XRD with a Rigaku (Tokyo, Japan) D/max-γB diffractometer at a voltage of 40 kV and a current of 100 mA with Cu Kα radiation (λ = 0.145 nm) at a scanning rate of 6°/min in the 2θ range of 5–60°.

Morphology

The fracture surfaces of the notched impact samples were observed by SEM with a Hitachi (Donggang, Japan) S-4300 microscope after gold coating.

Mechanical properties

The tensile samples were prepared according to the recommendation of ASTM D 638-96. The tensile strength of the PP/CaSO$_4$ composites was measured

with an Instron 1186 mechanical tester (Norwood, MA) with a 10 kN load cell at a crosshead speed of 50 mm/min. At least five specimens were tested.

The notched impact strength was measured with a Reger (Shenzhen, China) impact tester according to ASTM D 256. The impact samples were prepared with a size of 4 mm × 10 mm × 80 mm. The notched depth of each sample was 0.2 times its width. Impact testing at room temperature was performed after each sample was held at 23°C over 24 h.

Thermal properties

Calorimetric analysis of the pure PP and the PP/CaSO$_4$ composites was performed with a Mettler–Toledo (Zurich, Switzerland) DSC-821e/400 differential scanning calorimeter. The samples were first heated from 50 to 200°C at a heating rate of 20°C/min, held at 200°C for 5 min to eliminate any

previous thermal history, and then cooled to 50°C at a constant cooling rate of 5, 10, 20, or 40°C/min.

RESULTS AND DISCUSSION

Mechanical properties

The effects of the amounts of $CaSO_4$ and the newly synthesized hyperdispersant agent on the tensile strength of the $PP/CaSO_4$ composites are shown in Figure 1. The tensile strength of the $PP/CaSO_4$ composites initially increased with the amount of $CaSO_4$ increasing, but it decreased when the amount of $CaSO_4$ exceeded 20 wt % in all cases. The tensile strength of the $PP/CaSO_4$ composites in which $CaSO_4$ was modified by the hyperdispersant agent was considerably higher than that of the $PP/CaSO_4$ composites in which $CaSO_4$ was unmodified. The tensile strength of the $PP/CaSO_4$ composites increased with the amount of the hyperdispersant agent increasing when the amount of $CaSO_4$ in the $PP/CaSO_4$ composites was the same, but the tensile strength of the $PP/CaSO_4$ composites changed indistinctively when the amount of the hyperdispersant agent exceeded 1.5 wt %. The tensile strength of the $PP/CaSO_4$ composites reached 37 MPa when the amounts of the hyperdispersant agent and $CaSO_4$ were 1.5 and 20 wt %, respectively.

Figure 2 shows the effects of the amounts of $CaSO_4$ and the newly synthesized hyperdispersant agent on the notched impact strength of the $PP/CaSO_4$ composites. The impact strength of the $PP/CaSO_4$ composites initially increased rapidly with the amount of $CaSO_4$ increasing but decreased when the amount of $CaSO_4$ exceeded 10 wt % in all cases. The impact strength of the $PP/CaSO_4$ composites in which $CaSO_4$ was modified by the hyperdispersant agent
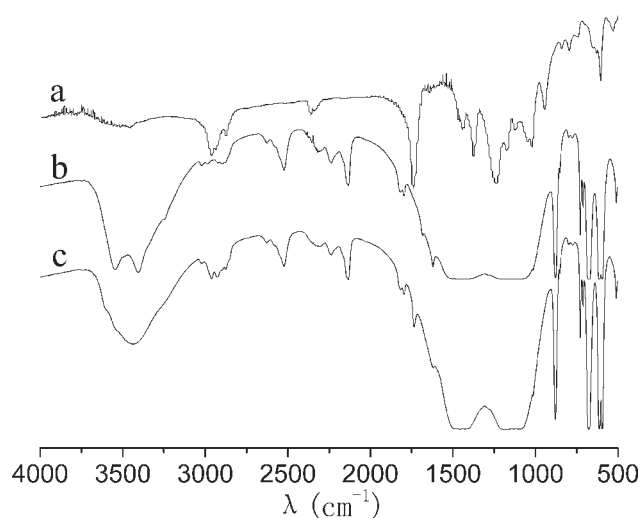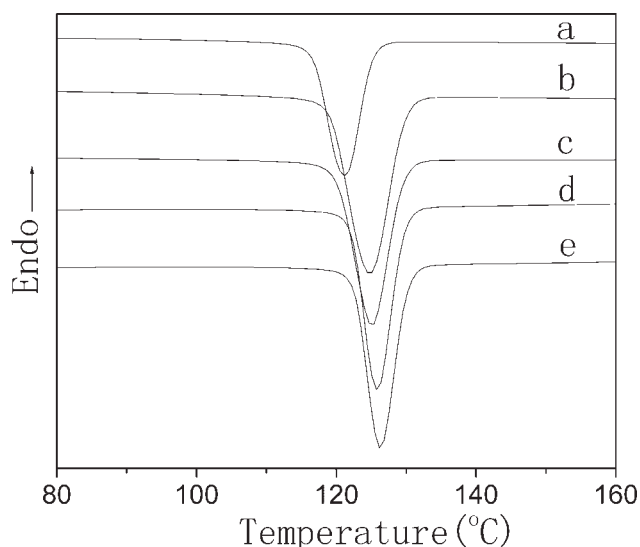

Figure 5 DSC thermoanalytical curves of PP and PP/$CaSO_4$ composites crystallized at a cooling rate of 10°C/min: (a) pure PP, (b) PP with 20 wt % unmodified $CaSO_4$, and (c–e) PP with 20 wt % $CaSO_4$ modified by 1.2, 1.5, and 1.8 wt % hyperdispersant agent, respectively.

was much higher than that of the $PP/CaSO_4$ composites in which $CaSO_4$ was unmodified. The impact strength of the $PP/CaSO_4$ composites was almost the same when the amount of the hyperdispersant agent exceeded 1.5 wt %. The impact strength of the $PP/CaSO_4$ composites reached 7.8 kJ/m^2 when the amounts of the hyperdispersant agent and $CaSO_4$ were 1.5 and 10.0 wt %, respectively.

As the interfacial interaction in a composite material governs the stress transfer efficiency and extent

Figure 4 FTIR spectra of (a) the hyperdispersant agent, (b) pure $CaSO_4$, and (c) $CaSO_4$ modified by the hyperdispersant agent.

TABLE I
Half-Time of Crystallization ($t_{1/2}$), Onset Temperature of Crystallization (T_c), and Peak Temperature of Crystallization (T_p) of the PP/$CaSO_4$ Composites

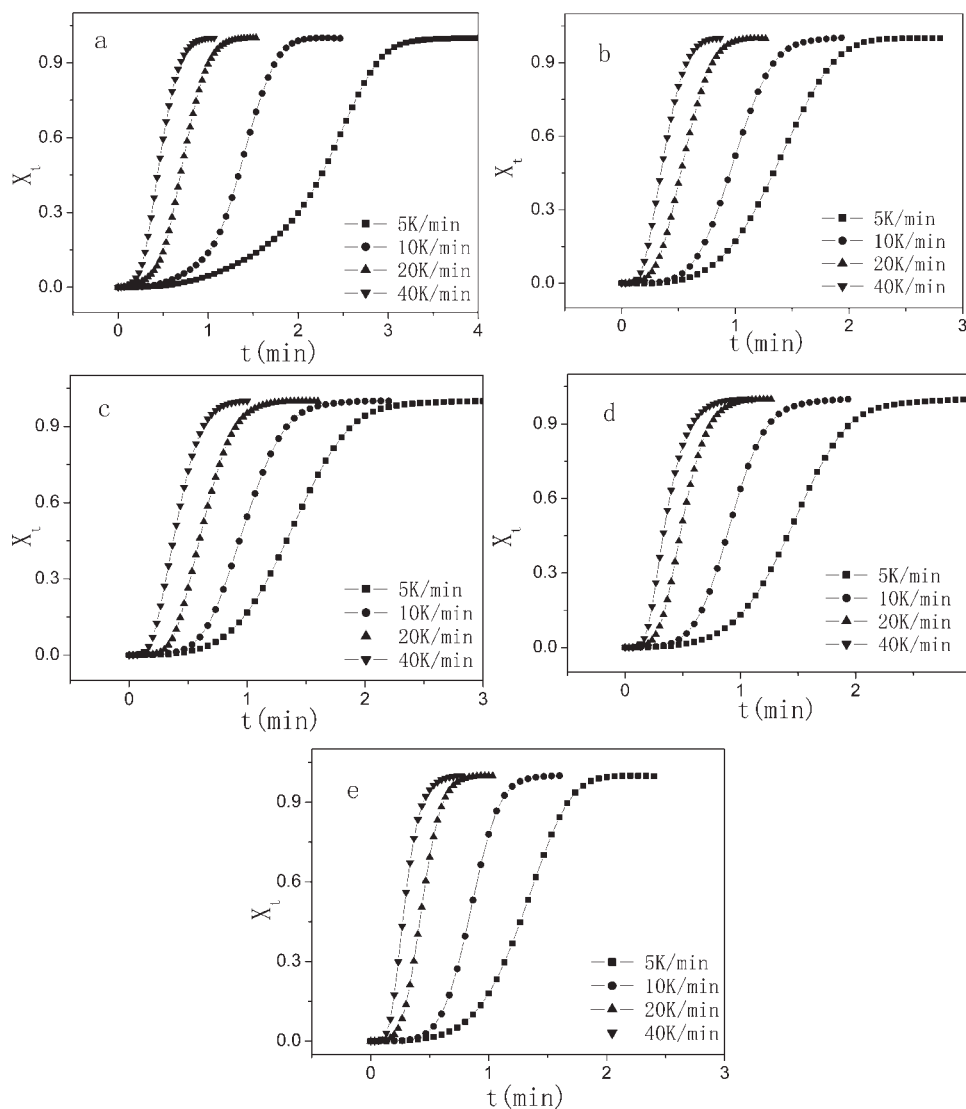| Sample	Cooling rate (K/min)	T_c (°C)	$t_{1/2}$ (min)	T_p (°C)
a	5	125.0	2.25	113.2
	10	121.0	1.37	109.0
	20	114.8	0.73	104.8
	40	104.0	0.45	97.5
b	5	129.0	1.37	122.0
	10	124.9	0.98	117.9
	20	119.2	0.59	112.2
	40	112.7	0.38	103.7
c	5	129.4	1.35	122.4
	10	125.2	0.93	118.2
	20	120.2	0.54	113.2
	40	112.8	0.36	104.8
d	5	131.8	1.32	123.8
	10	125.7	0.91	118.7
	20	121.0	0.50	114.0
	40	113.0	0.31	106.0
e	5	132.5	1.30	125.5
	10	126.2	0.84	119.3
	20	123.0	0.43	116.0
	40	115.0	0.28	108.0

Figure 6 Plots of the degree of crystallinity (X_t) versus the time (t) for PP and PP/CaSO$_4$ composites during the noniso-thermal crystallization process: (a) pure PP, (b) PP with 20 wt % unmodified CaSO$_4$, and (c–e) PP with 20 wt % CaSO$_4$ modified by 1.2, 1.5, and 1.8 wt % hyperdispersant agent, respectively.

of induced matrix deformation and eventually determines the mechanical performance of the composite, the filler loading dependence of the strength should be analyzed from this angle.[29] When the CaSO$_4$ content was not more than 10 wt %, the particles had a high degree of dispersion in the PP matrix. However, when the CaSO$_4$ content exceeded 20 wt %, because of the very high surface area of the particles in the PP/CaSO$_4$ composites, the CaSO$_4$ particles agglomerated easily, resulting in the mechanical properties of PP/CaSO$_4$ decreasing.

At the same time, the mechanical properties of the composites increased with the amount of the hyperdispersant agent increasing. This was accomplished because, during the preparation of the composites, the surface hydroxyl groups of the CaSO$_4$ particles reacted as nucleophiles with the Si—O groups of the

hyperdispersant agent. Thus, the CaSO$_4$ particles could chemically bind to the macromolecular PP chain, and this resulted in the prevention of their agglomeration and breakup of large aggregates into smaller ones. All this could improve the compatibility between the PP matrix and the particles, increasing the degree of dispersion of the CaSO$_4$ particles and improving the mechanical properties of the composites.

The fact that the tensile and notched impact strength of the PP/CaSO$_4$ composites in which CaSO$_4$ was modified by the hyperdispersant agent was higher than that of the PP/CaSO$_4$ composites in which CaSO$_4$ was unmodified may be explained by the following experimental results for the morphology, Fourier transform infrared (FTIR), and thermal analysis again.

Morphology and FTIR analysis

Figure 3 shows representative SEM images of the fractured surfaces of impact PP/CaSO$_4$ composite samples in which the amount of CaSO$_4$ was 20 wt %. Figure 3(b) shows that CaSO$_4$ particles were isolated from the PP matrix clearly, and the CaSO$_4$ used in this sample was unmodified. In Figure 3(c–e), CaSO$_4$ was modified by 1.2, 1.5, or 1.8 wt % hyperdispersant agent, respectively, and the CaSO$_4$ particles were buried well in the PP matrix. This may be due to the fact that the hyperdispersant agent coated the CaSO$_4$ particle surfaces and improved the interactions between the CaSO$_4$ particles and PP matrix.

The presence of the hyperdispersant agent on the surface of the CaSO$_4$ particles was characterized with FTIR, and the results are shown in Figure 4. The appearance of new absorbance at 1745 and 2969 cm^{-1} for the modified CaSO$_4$ indicated the introduction of C=O and C—H groups of the hyperdispersant agent onto the surface of CaSO$_4$. The absorbance of C=O at 1737 cm^{-1} and C—H at 2969 cm^{-1} for the hyperdispersant agent was shifted to 1745 and 2976 cm^{-1} for the modified CaSO$_4$; this indicated a strong interaction between the carboxylic group of the hyperdispersant agent and the surface of CaSO$_4$.

Crystallization

The nonisothermal crystallization of the PP/CaSO$_4$ composites was analyzed at various cooling rates from the melt with DSC. Figure 5 shows the DSC curves of PP/CaSO$_4$ composite samples at a cooling rate of 10°C/min; it reveals that PP crystallized at a higher temperature when CaSO$_4$ was added [Fig. 5(b)], and the crystallization temperature increased with an increasing amount of the hyperdispersant agent in the modified CaSO$_4$. Table I shows the onset and peak temperatures of the DSC curves of the PP/CaSO$_4$ composite samples at various cooling rates. The onset and peak temperatures of the PP/CaSO$_4$ composites were higher than those of pure PP and increased with an increasing amount of the hyperdispersant agent.

The half-time of nonisothermal crystallization was obtained from Figure 6 for PP and the PP/CaSO$_4$ composites, and the results are listed in Table I. With the cooling rate increasing, the half-time decreased for all the samples. Comparing the crystallization rates of PP in the presence of CaSO$_4$ particles coated with the hyperdispersant agent, we found that the addition of both CaSO$_4$ and the hyperdispersant could accelerate the overall crystallization process.
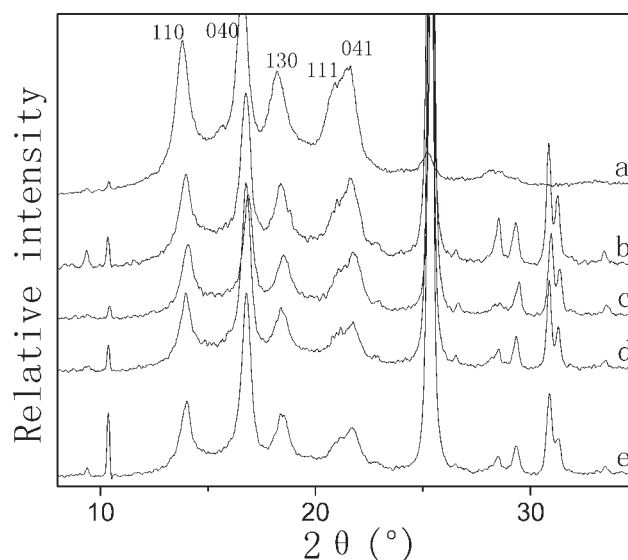

Figure 7 XRD patterns of PP and the PP/CaSO$_4$ composites: (a) pure PP, (b) PP with 20 wt % unmodified CaSO$_4$, and (c–e) PP with 20 wt % CaSO$_4$ modified by 1.2, 1.5, and 1.8 wt % hyperdispersant agent, respectively.

For this result, there are two reasons. The first is that the hyperdispersant agent on the backbone could act as a nucleating reagent to promote the heterogeneous nucleation of PP, which could increase the crystallization speed and make the crystallization happen at a higher temperature. The second is that the hyperdispersant-agent-modified PP/CaSO$_4$ composites could crystallize at a higher speed and temperature because of improved dispersion of CaSO$_4$ in the PP matrix, and this may have resulted in a further increase in the crystal rate and temperature of PP.

XRD analysis

The XRD spectra of the PP/CaSO$_4$ composites are shown in Figure 7. The peaks at 13.8, 16.6, 18.2, 20.8, and 21.5° were assigned to the PP(110), PP(040), PP(111), PP(130), and PP(041) crystalline plane diffraction peaks, respectively.[17–21] CaSO$_4$ showed a typical peak at 30.7°. Figure 7(b–e) shows that the intensities of the diffraction peaks of PP were significantly depressed by the presence of CaSO$_4$, but the position of the PP crystalline plane diffraction peaks was rarely changed. This reveals that CaSO$_4$ and the hyperdispersant agent did not change the crystal type of PP.

CONCLUSIONS

The use of small amounts of a hyperdispersant agent can produce remarkable increases in the mechanical properties of PP/CaSO$_4$ composites. The prerequisites for this result are the establishment of a

suitable phase structure and interfacial adhesion in the composites. In this case, hyperdispersant-agent-coated $CaSO_4$ and good dispersion in the composites proved to be the key factors. The SEM images of the fractured surfaces of the composites showed improved interfacial adhesion due to the presence of the hyperdispersant agent and proved that the hyperdispersant agent could change the polar surfaces of $CaSO_4$ particles and improve the compatibility with the PP matrix. The $CaSO_4$ fillers and the hyperdispersant agent had an active influence on the enhancement of the starting temperature of crystallization of the PP matrix. Moreover, they had the ability to quicken the crystallization time with various cooling times, but the addition could not change the type of crystallization of the PP matrix.

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