Influence of β Nucleation Agent on the Dispersion of Nano-CaCO$_3$ in Isotactic Polypropylene Matrix

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ABSTRACT: To study the interaction between β-nucleation agent and nano-CaCO$_3$ in iPP matrix, the dynamic rheology properties, crystallization and melting behaviors, impact fracture surface of β-nucleation agent (β-NA) nucleated and nano-CaCO$_3$ filled iPP were investigated in details in this study. Under suitable conditions, the β-NA has a "promoting dispersion effect" on the dispersion of nano-CaCO$_3$ in PP matrix. However, 0.2 wt % β-NA nucleated sample has a worse "promoting dispersion effect" than 0.05 wt % β-NA nucleated sample at relatively high nano-CaCO$_3$ content (7.5 wt %). The reason is that 0.2 wt % β-NA aggregates on the surface of nano-CaCO$_3$ agglomerations. The α crystals induced from β-crystals grow more regular and perfect than conventional α crystals. For the relative fraction of β crystals (K_β), the nano-CaCO$_3$ content has little influence on 0.05 wt % β-NA nucleated samples, but obvious effect on 0.2 wt % β-NA nucleated samples. Based on the investigated results, a mechanism model about the interaction between β-nucleation agent and nano-CaCO$_3$ in iPP matrix is proposed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most important thermoplastic polymers due to its low cost and excellent properties.[1] It has four modifications: α, β, γ, and smectic,[2–5] among them the β-form is the most attractive one for its better impact resistance as well as higher heat distortion temperature than other forms.[6,7] The β-form is metastable thermodynamically and can be obtained under some special conditions, such as in the presence of specific heterogeneous nucleation agents,[8–10] by crystallization in a temperature gradient during processing,[11,12] or by shear-induced crystallization.[13–15] Adding β-nucleation agent is the most effective and accessible method to get a high level of β-PP.[16] However, the yield strength and stiffness of iPP parts is lowered by the presence of β crystals.[17,18] It has been speculated that adding some inorganic fillers, such as calcium carbonate, to β-crystals-rich matrix is a potential way to achieve a stiffness-impact balance of PP.[19]

Labour et al.[20,21] investigated the influence of the β crystalline phase caused by specific temperature gradient on the mechanical properties of unfilled and CaCO$_3$-filled polypropylene and found that 0.1–1 μm CaCO$_3$ particle size is the most optimum for stopping cracks. Kotek et al.[22] explored the tensile properties of isotactic polypropylene modified by specific nucleation and active fillers (CaCO$_3$), and discovered that the combination of specific β-nucleation and inorganic fillers can lead to materials with higher ductility and higher modulus than neat isotactic polypropylene. Mai et al.[7,23] proposed a way for producing a novel highly efficient β-NA for polypropylene using nano-CaCO$_3$ as a support, and found that the crystallization and melting temperatures as well as the content of β phase in iPP nucleated using the supported β-nucleator are higher than those of iPP nucleated using traditional β-nucleator.

Nevertheless, to the best of our knowledge, there are few studies concerning the interaction between β nucleation agent and nano-CaCO$_3$ in the matrix. In the present work, the interaction between β nucleation agent (TMB-5) and nano-CaCO$_3$ particles in isotactic polypropylene matrix was investigated in details using dynamic rheology test, DSC investigation, SEM observation. Based on the investigated results, a mechanism model about the interaction between β-nucleation agent and nano-CaCO$_3$ in iPP matrix is proposed.

EXPERIMENT

Materials

A commercial grade of iPP (T30S) was supplied by Lanzhou Petrochemical Company, China, with a melt flow index (MFI)

Table I. Formula of PP/Nano-CaCO$_3$/β-NA Composites Prepared via Melt Compounding

Sample abbreviation	Nano-CaCO$_3$ content (wt %)	β-NA content (wt %)
PP/0/0	0	0
PP/0/0.05	0	0.05
PP/0/0.2	0	0.2
PP/2.5/0	2.5	0
PP/2.5/0.05	2.5	0.05
PP/2.5/0.2	2.5	0.2
PP/5/0	5	0
PP/5/0.05	5	0.05
PP/5/0.2	5	0.2
PP/7.5/0	7.5	0
PP/7.5/0.05	7.5	0.05
PP/7.5/0.2	7.5	0.2

of 2.6 g/10 min (230°C/2.16 kg) and a density of 0.91 g cm^{-3}, respectively. The β-nucleation agent (β-NA, TMB-5) is aryl amide-based system and was provided by Fine Chemicals Department of Shanxi Provincial Institute of Chemical Industry, with a melting temperature of 348.9°C. The nano-calcium carbonate, with an average particle size of 15–30 nm, was purchased from Shanxi Haize Nano-materials and it was pretreated with stearic acid.

The designed composites formula is depicted in Table I.

Sample Preparation
A two-step process was employed to prepare the composites. TMB-5 was first melt mixed with pure iPP to form master-batch containing 5 wt % β-NA. Then, the master-batch was compounded with pure iPP and nano-CaCO$_3$ using a SHJ-25 twin-screw extruder. The screw speed was fixed at 120 rpm, and the processing temperature profile was limited within 135–200°C from hopper to die.

The mixed pellets were then injection molded into a rectangular parallelopiped shape by a PS40E5ASE injection molding machine with a barrel temperature of 205°C, mold temperature of 60°C and injection pressure of 35 MPa.

For preparing dynamic rheology tests, the mixed pellets were compression molded into specific disks (1.2-mm thick with a diameter of 25 mm) at 200°C for 5 min. The applied pressure was 10 kN. The force was released to zero twice to allow any potential gas to escape.

Characterization
Dynamic Rheology Tests. Dynamic rheology properties were investigated using a rotational rheometer (Malvern Instruments, Bohlin Gemini 200). Steady shear measurement was performed at the shear rate of 0.01–100 s^{-1} at 200°C.

DSC Tests. The crystallization and melting behaviors of the samples were carried out on a TA Q200 differential scanning calorimeter in a nitrogen atmosphere. A sample about 8 mg was first heated up to 200°C and held on for 5 min to release ther-

mal history. Then, it was cooled down to 40°C at a cooling rate of 10°C min^{-1} to investigate the crystallization behavior of the sample. After maintaining at 40°C for 1 min, it was heated up again to 200°C at 10°C min^{-1} to explore the melting behavior of the sample.

The fusion enthalpy (ΔH_i) of α crystal and β crystals was obtained by the methods proposed by Li,[24] and the crystallinities of the α- and β-phase were calculated separately according to equation:

$$X_i = \Delta H_i / (\Delta H_i^0 \times \Phi c) \times 100\% \qquad (1)$$

where ΔH_i is the calibrated specific fusion heat of either the α-phase or the β-phase, ΔH_i^0 is the standard fusion heat of either α-phase or the β-phase crystals, 178 J g^{-1} for the former and 170 J g^{-1} for the latter, and Φ_c is the weight percentage of iPP in composites. The relative fraction of β-phase (K_β) in the matrix can be calculated from the following equation:

$$K_\beta = \frac{X_{c\beta}(\%)}{X_{c\alpha}(\%) + X_{c\beta}(\%)} \times 100\% \qquad (2)$$

where $X_{c\alpha}$ (%) and $X_{c\beta}$ (%) are the degrees of crystallinity for α-phase and β-phase, respectively.

SEM Observation. Impact fracture surface of the composites was observed using a Hitachi scanning electron microscope (S4800). The surface was coated with gold prior to the observation and the SEM was operated at 5.0 kV.

RESULTS AND DISCUSSION
Dynamic Rheology Analysis
Dynamic rheology test is a good way to investigate the dispersion of fillers in the composites melt. Figure 1 shows the effect of nano-CaCO$_3$ content on the complex viscosity of non-nucleated sample, 0.05 wt % β-NA nucleated sample and 0.2 wt % β-NA nucleated sample, respectively. It can be seen that the composites exhibit non-Newtonian (shear thinning) behavior at all shear rate ranges. In Figure 1(a), complex viscosity increases with nano-CaCO$_3$ content at first (PP/2.5/0 and PP/5/0), but decreases when the content reaches 7.5 wt % in non-nucleated sample. It indicates that 2.5 and 5 wt % nano-CaCO$_3$ can disperse well in non-nucleated matrix, while there exists many agglomerations in PP/7.5/0 sample. However, as shown in Figure 1(b), 7.5 wt % nano-CaCO$_3$ filled PP (PP/7.5/0.05) has a higher complex viscosity than 2.5 and 5 wt % nano-CaCO$_3$ filled PP, which reflects that better dispersion of nano-CaCO$_3$ particles can be achieved by the incorporation of β-NA. One possible reason for this phenomenon is that the β-NA particles have some effective interaction with nano-CaCO$_3$ particles, which has lowered its surface energy, thus leading to a relative good dispersion of nano-CaCO$_3$ particles. Nevertheless, the PP/7.5/0.2 sample exhibits similar viscosity to PP/5/0.2 and PP/2.5/0.2 sample, as shown in Figure 1(c). It indicates that 0.2 wt % β-NA nucleated sample has a worse "promoting dispersion effect" than 0.05 wt % β-NA nucleated sample at relatively high nano-CaCO$_3$ content (7.5 wt %).
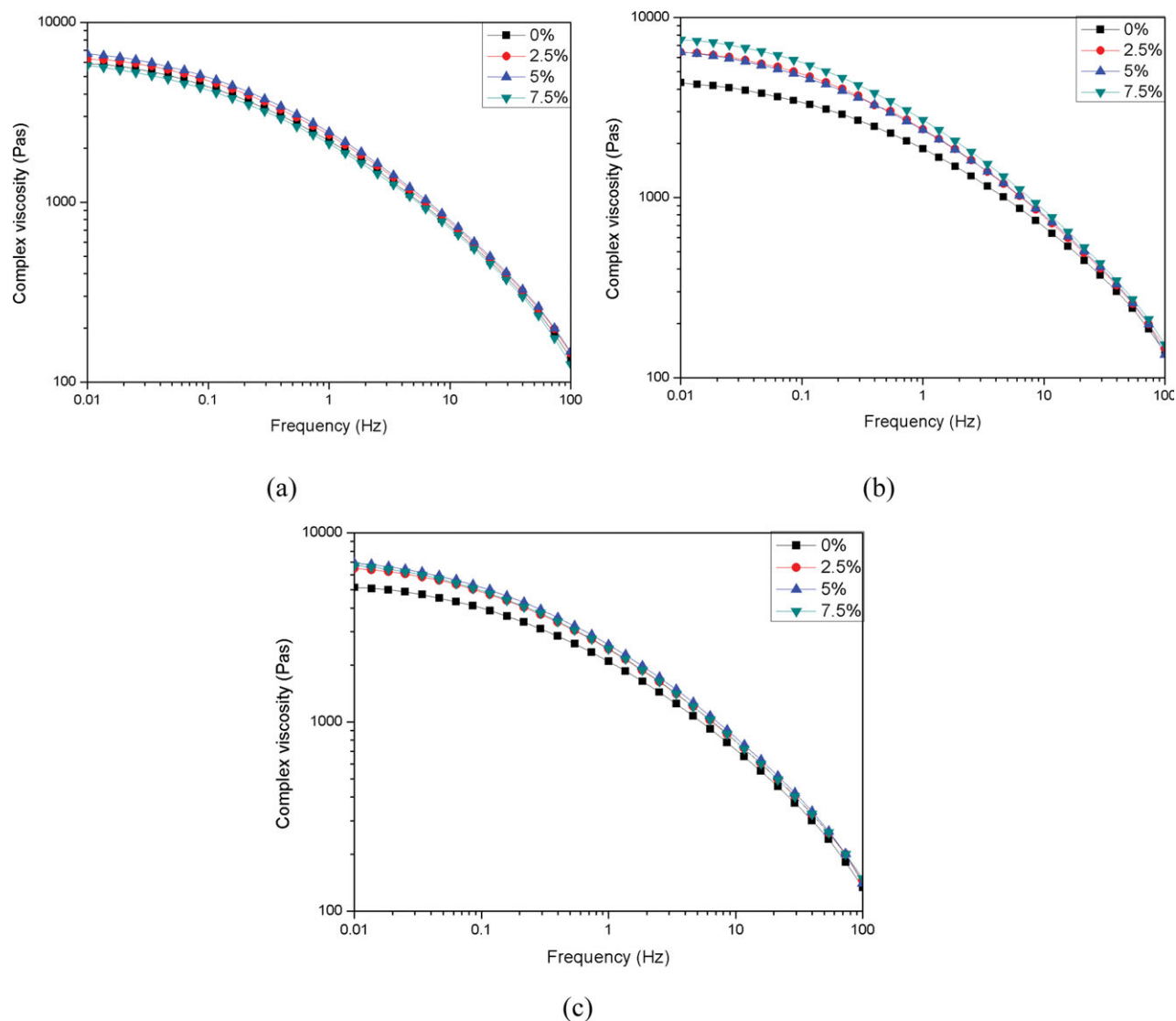
Figure 1. Effect of nano-CaCO$_3$ content on the complex viscosity of (a) non-nucleated sample, (b) 0.05 wt % β-NA nucleated sample and (c) 0.2 wt % β-NA nucleated sample, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2(a) shows the effect of β-NA on the rheology behavior of nonfilled sample. The addition of β-NA has lowered the viscosity of composites, and it's more obvious for PP/0/0.05 than PP/0/0.2. It suggests that β-NA, as small molecules, can diminish the viscosity of melt, acting like a lubricant. However, 0.2 wt % β-NA tends to aggregate, which is detrimental to the lubricant effect. As exhibited in Figure 2(b) no obvious difference can be seen for 2.5 wt % nano-CaCO$_3$ filled sample with various β-NA content, for the reason that 2.5 wt % nano-CaCO$_3$ tends to disperse well in the matrix, the "promoting dispersion effect" of β-NA has little influence on it. Figure 2(c) presents the effect of β-NA on the complex viscosity of 7.5 wt % nano-CaCO$_3$ filled sample. The β-NA tends to accumulate at a concentration of 0.2 wt %, which limits its "promoting dispersion effect" in the matrix. As a result, 0.2 wt % nucleated sample has a lower viscosity than 0.05 wt % β-NA nucleated sample and a higher viscosity than non-β-NA-nucleated sample when the nano-CaCO$_3$ content is 7.5 wt %.

DSC Results Analysis
Crystallization Behavior. Figure 3 depicts the crystallization temperature of composites of various β-NA contents and nano-CaCO$_3$ contents. It can be seen that nano-CaCO$_3$ has less effect on crystallization temperature than β-NA, indicating that β-NA content is the key factor for determining crystallization temperature. For non-β-NA-nucleated and 0.05 wt % β-NA nucleated sample, the crystallization temperature increases a little with the addition of nano-CaCO$_3$, while the crystallization temperature of 0.2 wt % β-NA nucleated sample keeps almost constant. There are two reasons to explain this phenomenon: first, 0.05 wt % β-NA is not saturated for nucleation, while 0.2 wt % β-NA tends to reach the saturated state; second, there may exist a specific intrinsic construction weakening the nucleation ability of nano-CaCO$_3$ in 0.2 wt % β-NA nucleated sample.

Melting Behavior. Figure 4(a) shows the effect of nano-CaCO$_3$ content on the melting behavior of non-β-NA-nucleated sample.
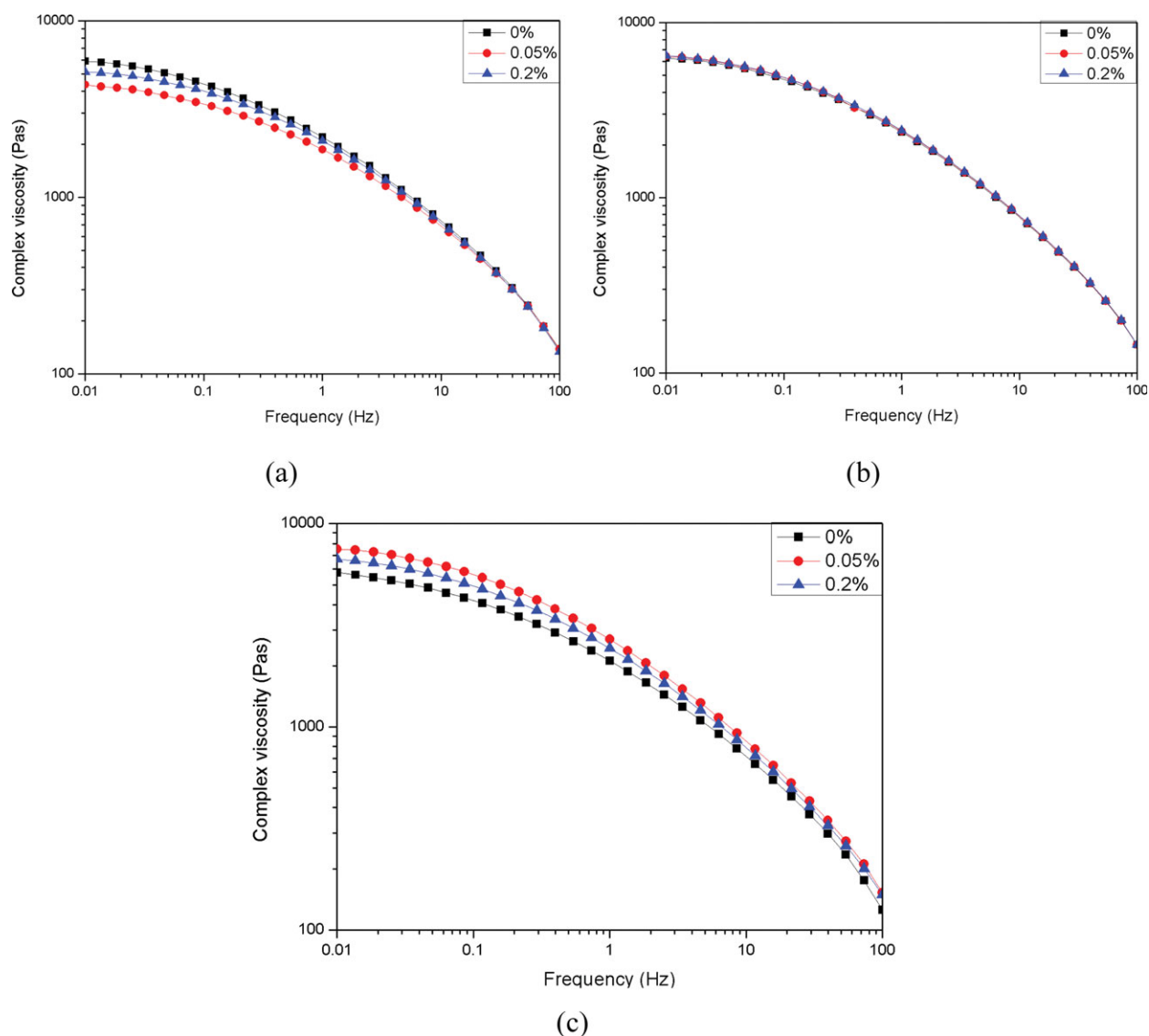
(a)

(b)

(c)

Figure 2. Effect of β-NA content on the complex viscosities of (a) non-filled sample, (b) 2.5 wt % nano-CaCO$_3$ filled sample and (c) 7.5 wt % nano-CaCO$_3$ filled sample, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

With increasing the nano-CaCO$_3$ content, the crystallinity increases from 53.56% (PP/0/0) to 55.41% (PP/7.5/0). Besides, there exists a tiny β crystals melting peak in PP/7.5/0 sample, while not in other three samples. It has been reported that nano-CaCO$_3$ is a kind of β nucleation agents by some researchers.[25,26]

Figure 4(b) depicts the effect of nano-CaCO$_3$ content on the melting behavior of 0.05 wt % β-NA nucleated sample. One can observe that there are two α melting peaks in some samples, one lies in 161–163°C region (low α melting peak), the other one lies in 167–168°C region (high α melting peak). In Figure 4(a)the α melting peak lies in 161–163°C region. With the addition of 0.05 wt % β-NA, the high α melting peak appears. It can be attributed to that some α nuclei grows on β crystals in a specific temperature gradient that has been reported by some researchers.[21] The α crystals initiated by

these nuclei grow more regular and perfect than conventional α crystals. There is only the high α melting peak in PP/0/0.05, for the reason that the majority of α crystals are induced by β crystals, indicating a fine dispersion of 0.05 wt % β-NA. With the addition of nano-CaCO$_3$, the low α melting peak emerges. It can be explained that the dispersion of β-NA in nano-CaCO$_3$ filled samples is somewhat different, some "conventional" α crystals come into being in some "without-β-NA" region.

Figure 4(c) presents the effect of nano-CaCO$_3$ content on the melting behavior of 0.2 wt % β-NA nucleated sample. There are two α melting peaks in samples PP/0/0.2. It indicates that 0.2 wt % β-NA can not disperse well in the composites. But as the nano-CaCO$_3$ content increases to 7.5 wt %, only the low α melting peak exists. The possible reason is that the dispersion of 0.2 wt % β-NA in PP/7.5/0.2 is relatively bad, there is more
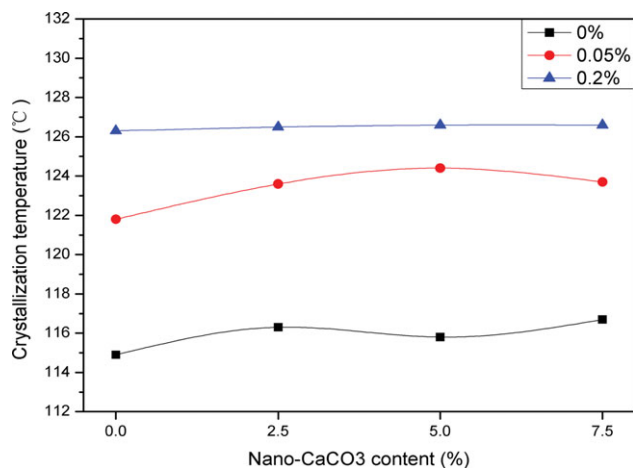
Figure 3. The crystallization temperature of composites of various β-NA contents and nano-CaCO$_3$ contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
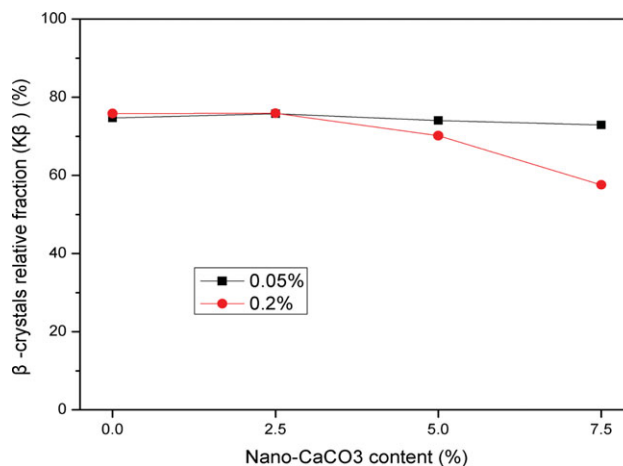

Figure 5. The relative fraction of β crystals (K_β) of 0.05 and 0.2 wt % β-NA nucleated with the addition of nano-CaCO$_3$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
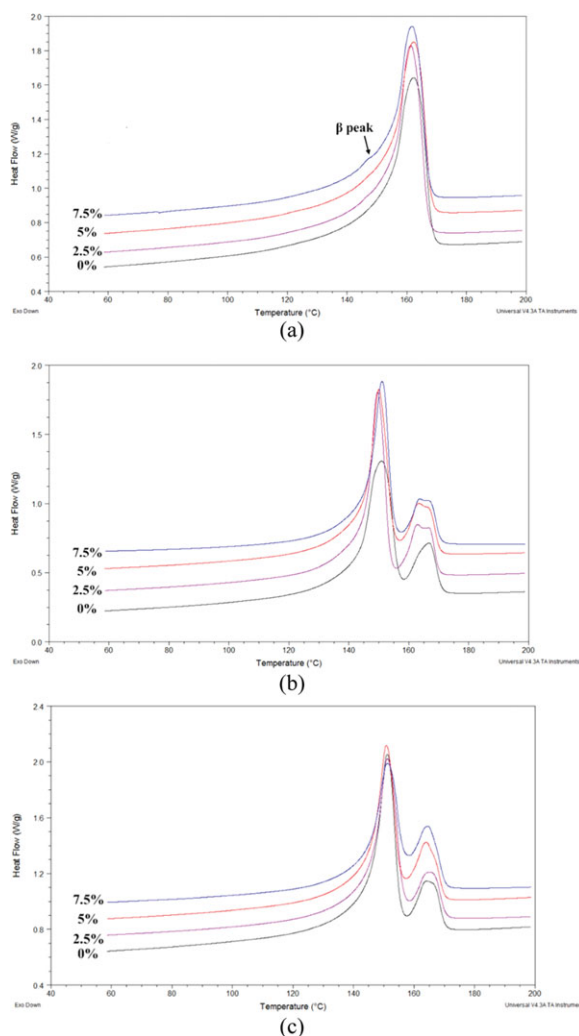

Figure 4. Effect of nano-CaCO$_3$ content on the melting behavior of (a) non-nucleated sample, (b) 0.05 wt % β-NA nucleated sample and (c) 0.2 wt % β-NA nucleated sample, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

"blank" region in composites to promote the growth of "conventional" α crystals.

The relative fraction of β crystals (K_β) of 0.05 and 0.2 wt % β-NA nucleated with the addition of nano-CaCO$_3$ is shown in Figure 5. No obvious difference can be found between non-filled and 2.5 wt % nano-CaCO$_3$ filled samples for the reason that 0.05 wt % β-NA can disperse well in the matrix, so the nano-CaCO$_3$ has little influence on it. As the nano-CaCO$_3$ concentration increases to 5 or 7.5 wt %, the K_β of 0.2 wt % β-NA decreases gradually, while that of 0.05 wt % β-NA keeps nearly unchanged. It indicates that the nucleation ability of 0.2 wt % β-NA is weakened by the incorporation of nano-CaCO$_3$.

SEM Observation

Figure 6 shows the impact fracture surface of various samples. It can be seen from Figure 6(a) that the fracture surface of sample PP/0/0 is relatively smooth, indicative of a brittle behavior. Comparatively, the fracture surface of PP/0/0.05 and PP/0/0.2 is relatively rough, as shown in Figure 6(b, c)which suggests that the incorporation of β-NA can lead to ductile behavior. It can also be observed that some small dots exist in Figure 6(b, c)which may be due to the agglomerations of β-NA. As exhibited in Figure 6(d)there are many nano-CaCO$_3$ agglomerations in the fracture surface, hinting bad dispersion of nano-CaCO$_3$ in the composites when the concentration reaches 7.5 wt %. However, the addition of β-NA has promoted the dispersing of nano-CaCO$_3$, as displayed in Figure 6(e, f).

MECHANISM MODEL

Based on the aforementioned investigated results, a mechanism model about the interaction between β-nucleation agent and nano-CaCO$_3$ in PP matrix is proposed, which is exhibited in Figure 7. With the increment of nano-CaCO$_3$ in non-β-NA-nucleated samples, the nano-CaCO$_3$ particles tend to aggregate (described in Section 3.1), and its average agglomeration size
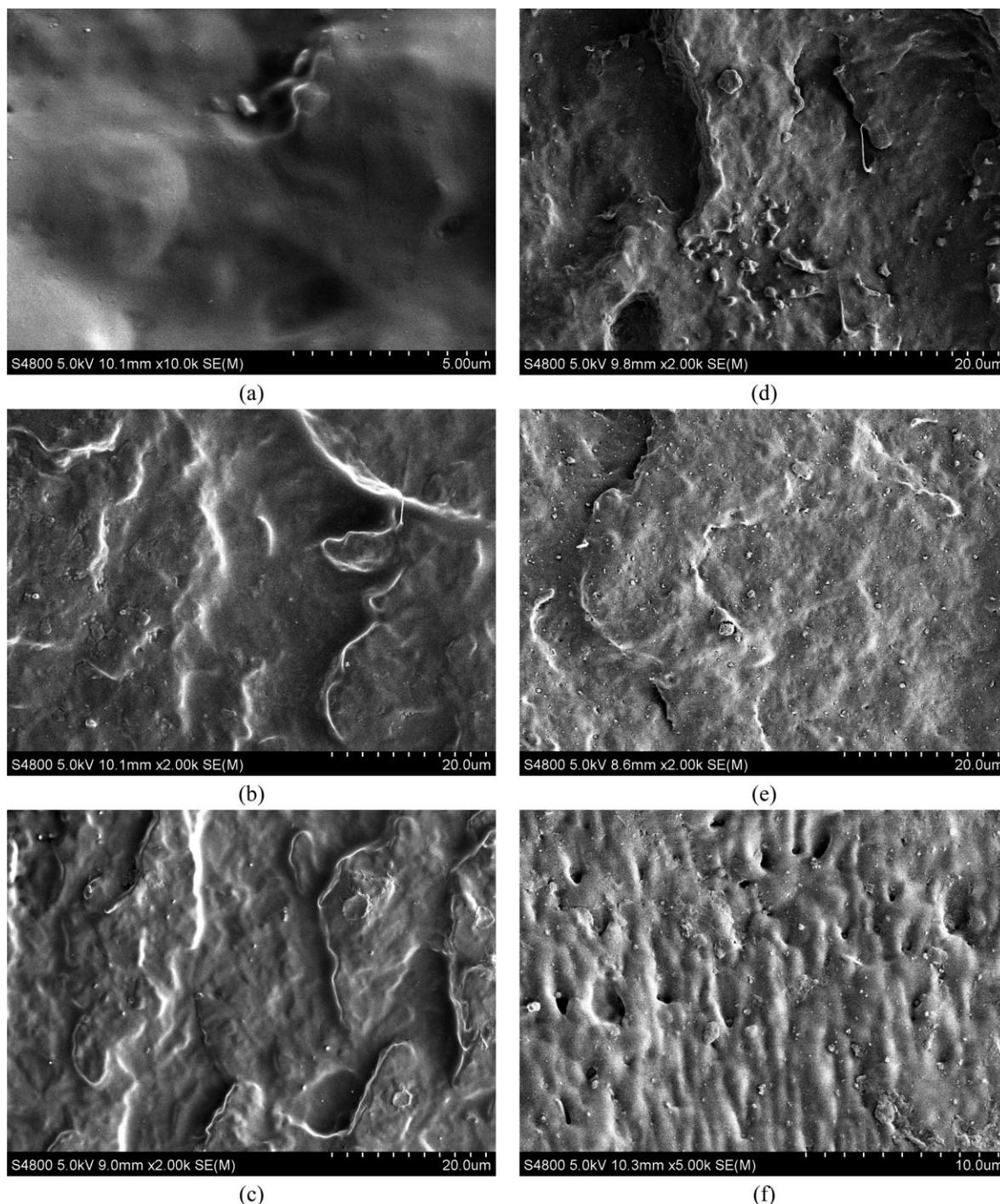
Figure 6. Impact fracture surface of (a) PP/0/0, (b) PP/0/0.05, (c) PP/0/0.2, (d) PP/7.5/0, (e) PP/7.5/0.05, and (f) PP/7.5/0.2, respectively.

become larger, as shown in Figure 7(b, c). For the non-filled sample, 0.05 wt % β-NA can disperse well, leading to a homogeneous structure. However, 0.2 wt % β-NA particles can't keep a fine dispersion in the matrix, as proposed by Varga,[27] and the particles have a tendency to form agglomerations, which is exhibited in Figure 7(g). When the nano-CaCO$_3$ concentration is 2.5 wt %, no clear distinction can be observed among PP/2.5/0, PP/2.5/0.05 and PP/2.5/0.2 for the reason

that 2.5 wt % nano-CaCO$_3$ can disperse well in the matrix by itself, which has been deducted from dynamic rheology analysis. Under such circumstance, even the β-NA particles are attached to the surface of nano-CaCO$_3$, the β-NA has little influence on its dispersion. Thus, the rheology behavior vary little among PP/2.5/0, PP/2.5/0.05, and PP/2.5/0.2. For PP/7.5/0.05, the nano-CaCO$_3$ particles have a intensive tendency to aggregate, but the role of attached β-NA is to lower the surface
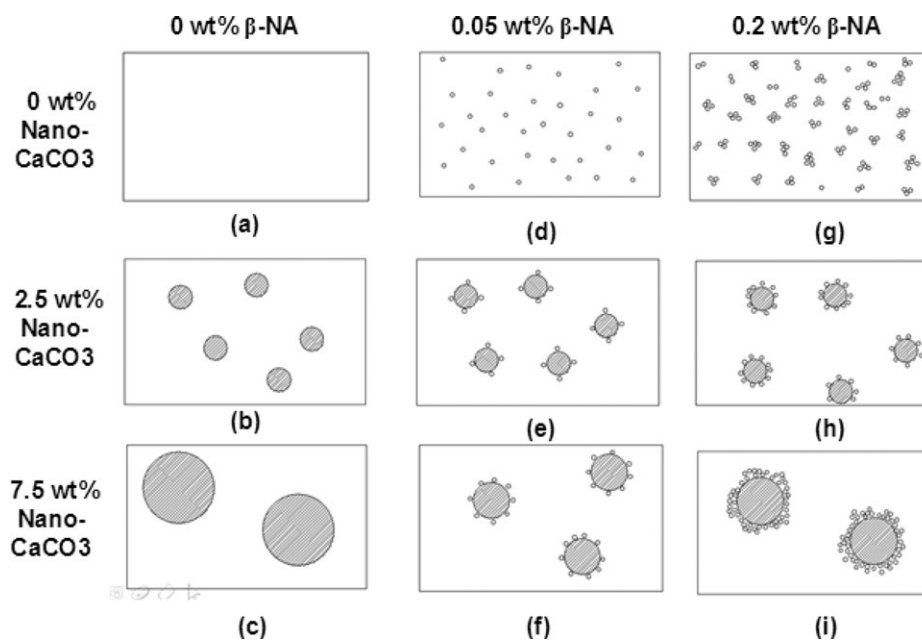
Figure 7. The schematic diagram of the mechanism model about the interaction between β-nucleation agent and nano-CaCO$_3$ in PP matrix. (Circles without hatching lines stand for β-nucleation agent, while the circles with hatching lines mean nano-CaCO$_3$ particles or agglomerations.)

energy of nano-CaCO$_3$ particles, so they can disperse better than PP/7.5/0, which has been deducted from Figure 1(a). However, 0.2 wt % β-NA particles are easy to gather together, too, so its "promoting dispersion effect" is weakened. Accordingly, the dispersion of nano-CaCO$_3$ of PP/7.5/0.2 is not so well as that of PP/7.5/0.05. Although the nano-CaCO3 content increases from 2.5 wt % (PP/2.5/0.2) to 7.5 wt % (PP/7.5/0.2), the total aggregates surface area of PP/7.5/0.05 is larger than that of PP/7.5/0.2 due to the particles agglomeration of the latter. As a result, the β-NA aggregate on the surface of nano-CaCO$_3$ agglomeration, thus some β-NA is covered so that its β-nucleation effect is influenced, which is presented in Figure 5.

CONCLUSIONS

The dynamic rheology properties, crystallization and melting behaviors, impact fracture surface of β-nucleation agent nucleated and nano-CaCO$_3$ filled PP were investigated, to study the interaction between β-nucleation agent and nano-CaCO$_3$ in iPP matrix. Some interesting results can be obtained:

Under suitable conditions, the β-NA has a "promoting dispersion effect" on the dispersion of nano-CaCO$_3$ in PP matrix. However, 0.2 wt % β-NA nucleated sample has a worse "promoting dispersion effect" than 0.05 wt % β-NA nucleated sample at relatively high nano-CaCO$_3$ content (7.5 wt %). The reason is that 0.2 wt % β-NA aggregates on the surface of nano-CaCO$_3$ particles. The α crystals induced from β-crystals grow more regular and perfect than conventional α crystals. For the relative fraction of β crystals (K_β), the nano-CaCO$_3$ content has little influence on 0.05 wt % β-NA nucleated samples, but obvious effect on 0.2 wt % β-NA nucleated samples.

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