

CRYSTALLIZATION, MECHANICAL AND THERMAL PROPERTIES OF SORBITOL DERIVATIVES NUCLEATED POLYPROPYLENE/CALCIUM CARBONATE COMPOSITES*

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Abstract The effect of α phase nucleating agent (NA) 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) on crystallization and physical properties of polypropylene/calcium carbonate (PP/CaCO₃) composites has been comparatively investigated. Compared with binary PP/CaCO₃ composites, in which CaCO₃ exhibits weak heterogeneous nucleation, inconspicuous reinforcement and toughening effects for PP, the introduction of a few amounts of DMDBS induces a great increase of the degree of crystallinity. Largely improved tensile properties, fracture toughness at relatively higher temperature and heat deformation temperature (HDT) are observed for DMDBS nucleated PP/CaCO₃ composites.

Keywords: Crystallization; Physical properties; Polypropylene; Calcium carbonate; Sorbitol derivatives.

INTRODUCTION

CaCO₃ has been proved to be an efficient filler in improving the physical properties of PP. Compared to the neat PP, higher tensile strength, modulus, flexural strength and heat deformation temperature (HDT) of PP have been reported when CaCO₃ is added into PP^[1–4]. Furthermore, CaCO₃ exhibits simultaneously the role of improving the fracture toughness of PP. For example, PP/CaCO₃ composites present largely improved impact strength compared to pure PP when high content of CaCO₃ is introduced into PP^[5–9]. The variation of physical properties of PP with introduction of CaCO₃ is ascribed to the change of crystallization structure. More homogeneous spherulites with smaller average diameter, increased degree of crystallinity and reduced crystallization half time of PP have been achieved^[10–12]. Especially, surface modified CaCO₃ with some coupling agents and/or surfactants induces the formation of β -phase PP, which is believed to be one of the main toughening mechanisms of CaCO₃ for PP^[7, 13–17].

Nucleating agent (NA) is one of the additives used in semi-crystalline polymer processing. A few amounts of NA (not more than 0.5 wt%) affect the crystallization behavior of polymers greatly because it increases the nucleation density, enhances the crystallization temperature of polymer and decreases the spherulites size apparently as well as reduces the defects of spherulites. Generally, NA exhibits more superior nucleation effect for PP crystallization compared to the common inorganic fillers on one hand. On the other hand, β -phase NA induces more β -PP formation than common inorganic fillers. For example, the content of β -PP is not more than 50% in surface modified CaCO₃ nucleated PP system, much lower than that of β -phase NA nucleated PP system

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(more than 80%)^[14, 18]. Thus, some work has been done to investigate the synergistic effect of β -phase NA and CaCO_3 in PP matrix^[19].

As a part of serial work about the combination effects of NA and minor component^[20–23], such as elastomer and/or inorganic filler, on crystallization behavior, morphology and physical properties of PP and its blends, in this study, we investigate the effect of α -phase NA, *i.e.* DMDBS on the crystallization and physical properties of PP/ CaCO_3 composites. Although CaCO_3 exhibits heterogeneous nucleation effect for PP crystallization and mainly induces the formation of α -PP, the nucleation effect at low CaCO_3 load is very weak compared to that of the sorbitol derivatives^[24]. Thus, the changes of the crystalline structures, including degree of crystallinity and spherulites average diameter, are very inconspicuous. It is well known that the decrease of polymer spherulites size and the increase of degree of crystallinity are in favor of the improvement of physical properties. Here, it is expected that through controlling the crystalline structure of PP matrix by addition of DMDBS, PP/ CaCO_3 /DMDBS samples will exhibit good mechanical and thermal properties at low CaCO_3 load.

EXPERIMENTAL

Materials

All the materials used in this study are commercially available. PP (F401) with a melt flow rate (MFR) of 2.5 g/10min (230°C/2.16 kg) was obtained from Lanzhou Petrochemical Co, Ltd., Lanzhou, China. NA 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS, Millad 3988) was produced by Milliken Chemical, Belgium. Nano-sized CaCO_3 with an average diameter of 90 nm was obtained from Keli New Materials Co, Ltd (Henan, China).

Sample Preparation

CaCO_3 was surface modified prior to melt blending with PP using 2 wt% sodium stearate. In order to achieve the good dispersion of DMDBS and CaCO_3 particles in the composites, a two-step process was used to prepare PP/ CaCO_3 /DMDBS composites. At first, master batches of PP/DMDBS (5 wt%) and PP/ CaCO_3 (10 wt%) (The data show the weight fraction of DMDBS and/or CaCO_3 in PP) were prepared. Then, the master batches of PP/DMDBS and/or PP/ CaCO_3 were blended with different contents of PP to obtain the corresponding compositions. In this work, the contents of CaCO_3 and DMDBS were maintained at 2 wt% and 0.2 wt%, respectively. The melt blending of such compositions was carried out on a twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder, China) with the setting temperatures of 150–200°C from hopper to die and the screw speed of 120 r/min. After making droplets, the pellets were dried at 80°C for 4 h. Then, the pellets were injection-molded, and the standard specimens for mechanical and thermal properties measurements were prepared using an injection-molding machine (K-TEC 40, Germany). The melt temperatures from hopper to nozzle were set as 190–200–200–215°C, and the mould temperature was 25°C.

Mechanical Measurements

Tensile properties were measured through an SANS (China) tensile testing machine in accordance with ISO 527-1-1993. A crosshead speed of 50 mm/min was used and the measurement was carried out at room temperature (23°C). Notched Izod impact strength was measured using an impact tester (XC-22Z, China) according to ISO180–2000, and the measurement was carried out at 0°C, 23°C and 50°C, respectively. For all the mechanical measurements, the average value reported was derived from at least five specimens.

Polarization Optical Microscopy (POM)

A Polarization Optical Microscope (POM) (XPN203, China) with a hot stage was used to characterize the crystallization morphologies of the composites. First, a sample of about 5 mg was placed between two glass slides and was heated to melt completely, then the sample was pressed to obtain a slice with a thickness of about 20 μm . Secondly, the sample was transferred to the hot-stage set at a temperature of 120°C and maintained at this temperature until the crystallization was finished. The images of crystallization morphologies of the samples were recorded *via* a digital camera.

Differential Scanning Calorimetry (DSC)

A DSC equipment Netzsch STA449C Jupiter (Germany) was used to study the crystallization and melting behaviors of the samples. The weight of each sample was about 8 mg. DSC scanning program was set as follows: first, the sample was heated from 30°C to 200°C at the heating rate of 10 K/min and maintained at 200°C for 5 min to erase the thermal history; secondly, the sample was cooled down to 30°C at the cooling rate of 5 K/min. All the measurements were carried out in nitrogen atmosphere.

Scanning Electronic Microscopy (SEM)

A Fei Quanta 200 environmental scanning electronic microscope (ESEM, USA) was used to characterize the distribution of CaCO₃ particles. The accelerating voltage was 20 kV. The sample was cryogenically fractured perpendicular to flow direction after being immersed in liquid nitrogen for 0.5 h, and the fractured surface was then coated with a thin layer of gold prior to SEM characterization. The impact-fractured and tensile-fractured surfaces of samples were also characterized by using SEM.

Heat Deformation Temperature

Heat deformation temperature (HDT) was measured on a Heat distortion/Vicat softening point instrument (RV-300, Chengde, China) in accordance with ISO75. The standard pressure was calculated as 1.4 MPa and the heating rate was 120 K/h.

RESULTS AND DISCUSSION

Distribution of CaCO₃

It has been widely accepted that the distribution of CaCO₃ is one of the most important factors which determines its reinforcement and toughening effects in PP, especially for the use of nano-CaCO₃^[25] due to its large specific surface area and high surface energy. The more homogeneous the distribution of CaCO₃ is, the better the mechanical properties of composites are. Figure 1 shows the distribution of CaCO₃ in PP/CaCO₃ and PP/CaCO₃/DMDBS composites. In the former composite, CaCO₃ tends to form some small aggregates with the size of about 200–450 nm, about the aggregation of 2–5 CaCO₃ particles (Shown by the white circles). However, in the latter composite, CaCO₃ tends to disperse singly in the matrix (Shown by the arrows). In other words, more homogeneous distribution of CaCO₃ has been achieved in PP/CaCO₃/DMDBS composites compared to PP/CaCO₃ composites. This can be partly ascribed to the increase of melt viscosity due to the formation of DMDBS gel network structure when DMDBS has been introduced into the PP melt^[26], leading to the increase of local shear stress during the processing, which is in favor of the homogeneous distribution of CaCO₃^[27]. Furthermore, DMDBS accelerates the crystallization process of PP through increasing the nucleation density greatly, leading to the solidification of PP in a very short time and avoiding the possible aggregation of CaCO₃ from a single dispersed particle during the PP crystallization process.

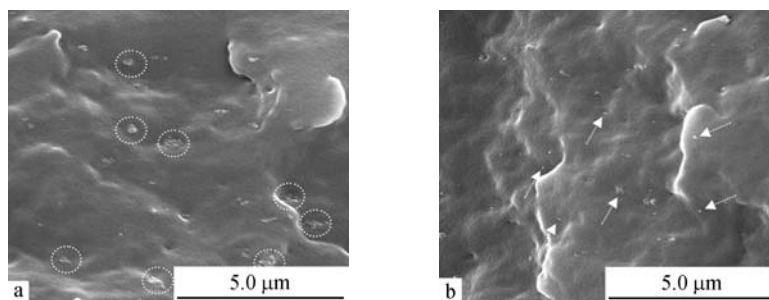


Fig. 1 SEM images show the distribution of CaCO₃ in (a) PP/CaCO₃ and (b) PP/CaCO₃/DMDBS composites

Melting and Crystallization Behaviors

The crystallization and melting behaviors of PP/CaCO₃ and PP/CaCO₃/DMDBS composites are shown in Fig. 2.

One can see from Fig. 2(a) that the crystallization peak temperature (T_c) is enhanced from 114.7°C of pure PP to 116.7°C of PP/CaCO₃ composite. Furthermore, one should notice that the crystallization start temperature (T_{onset}) of PP is nearly not affected although 2 wt% CaCO₃ is in the melt. This indicates that CaCO₃ exhibits very weak nucleation effect for PP crystallization possibly due to the weak interfacial interaction. For PP/DMDBS sample, the T_c is increased up to 125.1°C, indicating the great nucleation effect of DMDBS for PP crystallization. It is interesting to observe that the T_c of PP/CaCO₃/DMDBS is increased up to 130.7°C, much higher than that of PP/CaCO₃ composite, and even higher than that of PP/DMDBS. This means that there is a synergistic effect of DMDBS and CaCO₃ in PP crystallization process possibly due to that, CaCO₃ increases the viscosity of PP melt, leading to the increase of local shear stress and making more homogeneous gel network structure formation of DMDBS in PP/CaCO₃/DMDBS compared to that in PP/DMDBS. Furthermore, the melt temperature (T_m) of PP matrix has not been influenced by the addition of CaCO₃ and/or DMDBS apparently. Figure 2(c) shows the variation of degree of crystallinity (X_c (%)) of the samples. Obviously, CaCO₃ has inconspicuous effect on X_c (%) whereas DMDBS induces the great enhancement of X_c (%) in both PP/DMDBS and PP/CaCO₃/DMDBS sample. Considering the nucleation effect of DMDBS in pure PP^[28], one can believe that the crystallization of PP in PP/CaCO₃/DMDBS is mainly determined by DMDBS rather than by CaCO₃. This will be further proved by the variation of crystalline morphologies in the follows.

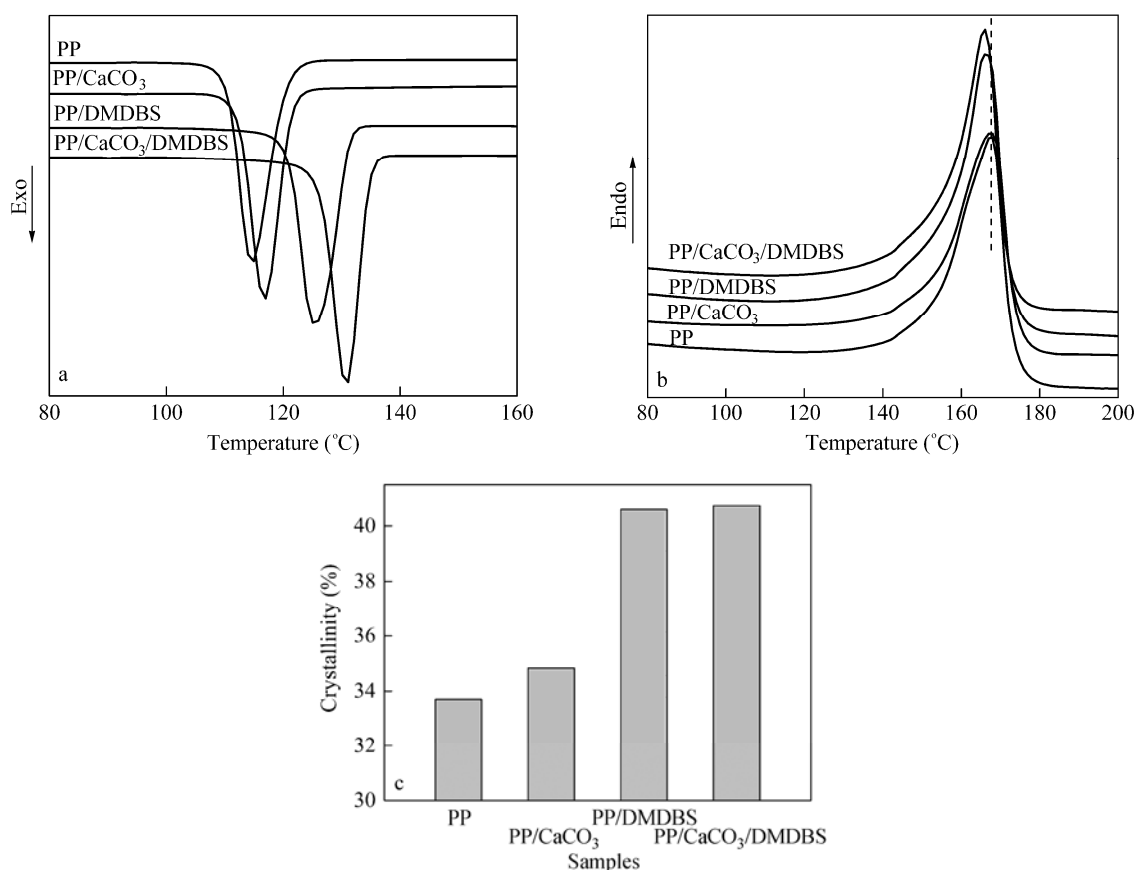


Fig. 2 DSC cooling curves (a), heating curves (b) and crystallinity (c) of PP, PP/CaCO₃, PP/DMDBS and PP/CaCO₃/DMDBS composites

The isothermal crystallization morphologies of samples were characterized by POM and the results are shown in Fig. 3. For pure PP, the perfect and big spherulites are observed and the average diameter is larger than 200 μ m. The present of 2 wt% CaCO₃ in the matrix increases the nucleation density and decreases the spherulite

diameters of PP. As shown in Fig. 3(b), the average spherulite diameter is about 100 μm , much smaller than that obtained in pure PP. For PP/DMDBS and PP/CaCO₃/DMDBS samples, the spherulite diameter decreases greatly, and the average spherulite diameter is calculated as 1–5 μm . Much smaller, more homogeneous and better dispersion of PP spherulites are observed due to the excellent nucleation efficiency of DMDBS for PP crystallization. The POM results further suggest that the crystallization behavior and crystalline structure of PP in PP/CaCO₃/DMDBS specimen is exclusively determined by 0.2 wt% DMDBS rather than by 2 wt% CaCO₃.

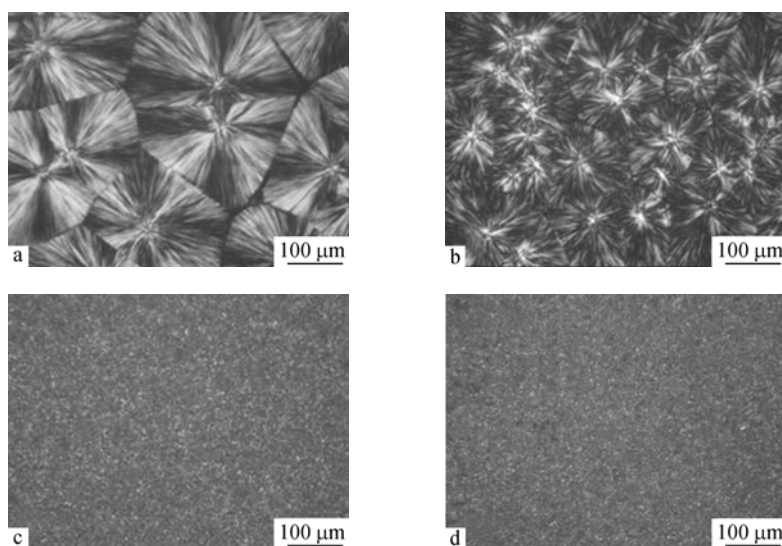


Fig. 3 POM images of pure PP and its composites obtained at 120°C: (a) PP, (b) PP/CaCO₃, (c) PP/DMDBS and (d) PP/CaCO₃/DMDBS

Mechanical Properties

The mechanical properties of all samples were comparatively investigated through the measurements of tensile and impact testing. The typical engineering stress-strain curves and the optical images of tensile fractured samples are shown in Fig. 4, and the corresponding tensile modulus, tensile strength and elongation at break (%) are shown in Fig. 5. Pure PP exhibits the typical stress-strain curve of semi-crystalline polymers, and the stress-strain curve can be delineated as follows: (a) the elastic region (linear increase in engineering stress with engineering strain), (b) yield point (maximum yield stress on the stress-strain curve), (c) stress drop region (dramatic decrease in engineering stress with little engineering strain change), (d) cold-drawing region (almost invariant engineering stress with engineering strain), and (e) fracture point. Addition of 2 wt% CaCO₃ induces a slight change of stress-strain curve. PP/CaCO₃ sample exhibits a second-yielding behavior at the later stage of the tensile process, *i.e.* second stress-drop and cold-drawing regions are observed. The similar double-yielding behavior of semi-crystalline polymer has been reported in other researches, and the reason for the dramatic decrease of stress in the engineering stress-strain curve is ascribed to the fact that the stress is calculated using the initial width and thickness of the sample and the strain hardening of the necked material is not sufficient to counteract the reduction in the cross-sectional area of the necked region^[29]. PP/DMDBS sample shows the similar stress-strain curve but with enhanced yield stress and decreased cold-drawn region compared to pure PP. However, PP/CaCO₃/DMDBS sample exhibits the typical brittle-fracture mode with largely reduced elongation at break (%). From the shape of the fractured specimen, one also can see that pure PP, PP/DMDBS and PP/CaCO₃ specimens show the apparent necking and stress whitening phenomena. However, PP/CaCO₃/DMDBS sample exhibits inconspicuous necking and only a local stress whitening at the fracture point, indicating that the plastic flow involving nucleation of voids is suppressed and the severity of deformed features is reduced possibly due to the increased modulus and X_c (%) of specimens. Misra has developed a

methodology to investigate the reinforcement effect of inorganic filler based on the analysis of stress whitening and he believes that, if both modulus and yield stress are significantly enhanced through reinforcement and the elastic recovery zone is greater than the pure polymer, then it is an idea material from the viewpoint of resistance to stress whitening^[30]. The effect of DMDBS on tensile properties of PP/CaCO₃ can be further proved from Fig. 5. Largely improved modulus, tensile strength and great reduced elongation at break (%) have been achieved for nucleated PP/CaCO₃ sample most likely due to the improved distribution of CaCO₃ particles and largely increased X_c (%) of PP matrix. In other words, CaCO₃ and DMDBS exhibit a certain degree of synergistic effect in the reinforcement of PP.

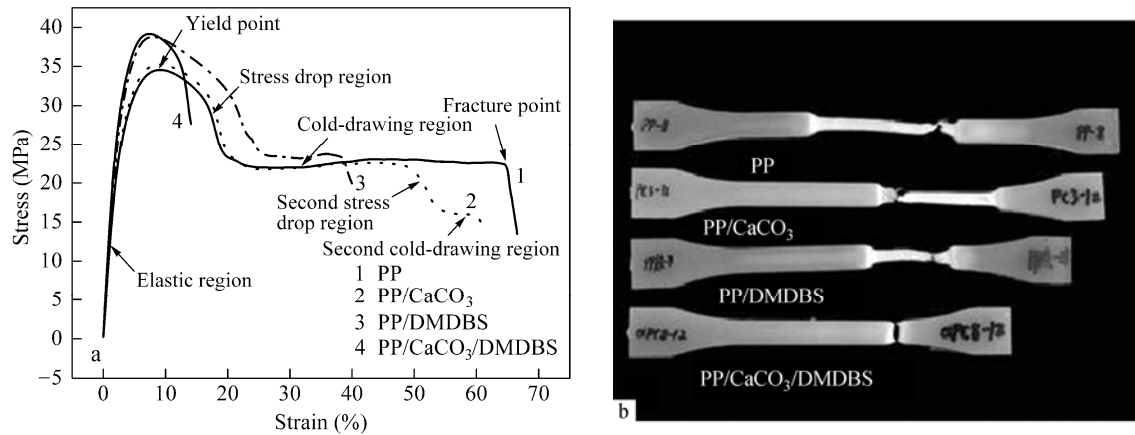


Fig. 4 Typical stress-strain curves (a) and optical images (b) of tensile fractured samples of pure PP and its composites

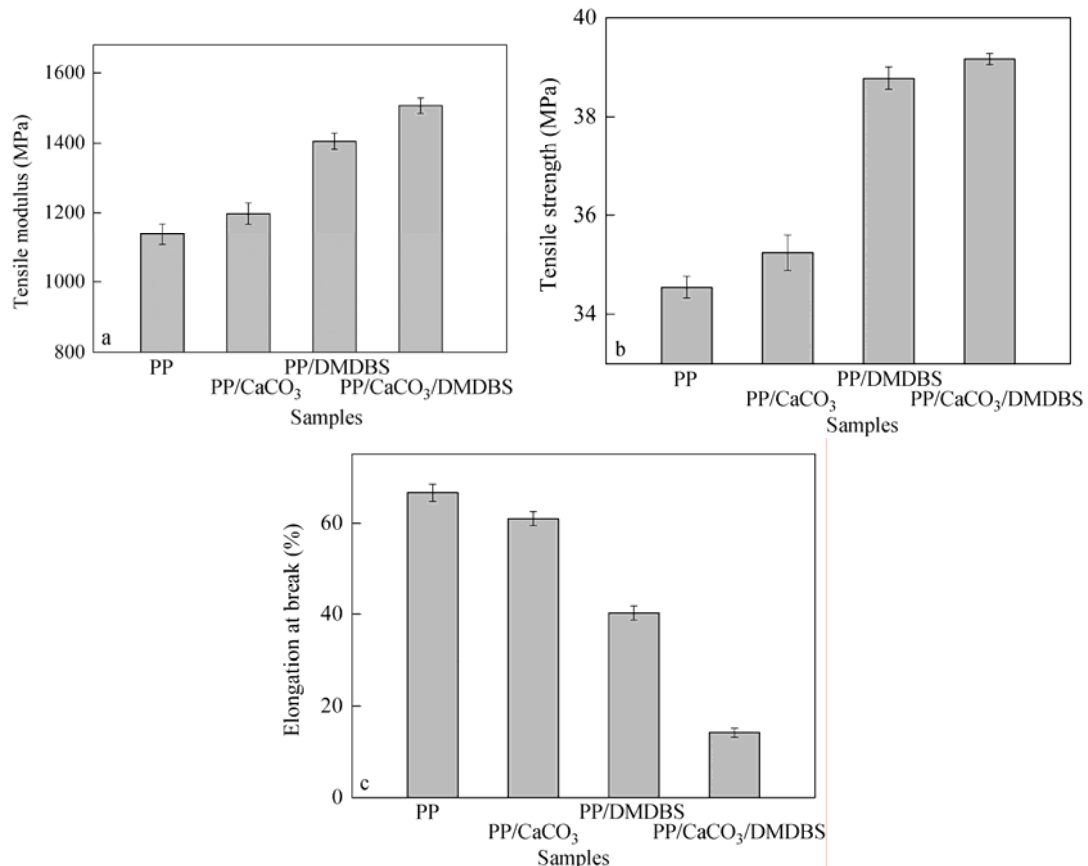


Fig. 5 (a) Tensile modulus, (b) tensile strength and (c) elongation at break of pure PP and its composites

Figure 6 shows the SEM images of the tensile-fractured surfaces of specimens. Pure PP, PP/CaCO₃ and PP/DMDBS samples exhibit the typical plastic deformation behavior involving the formation and separation of wedges from matrix, which are the result of surface and bulk deformation, and the fracture is characterized by severely deformed fibrils^[30]. However, very smooth and flat surface morphologies are observed for PP/CaCO₃/DMDBS samples, indicating the typical feature of brittle fracture mode.

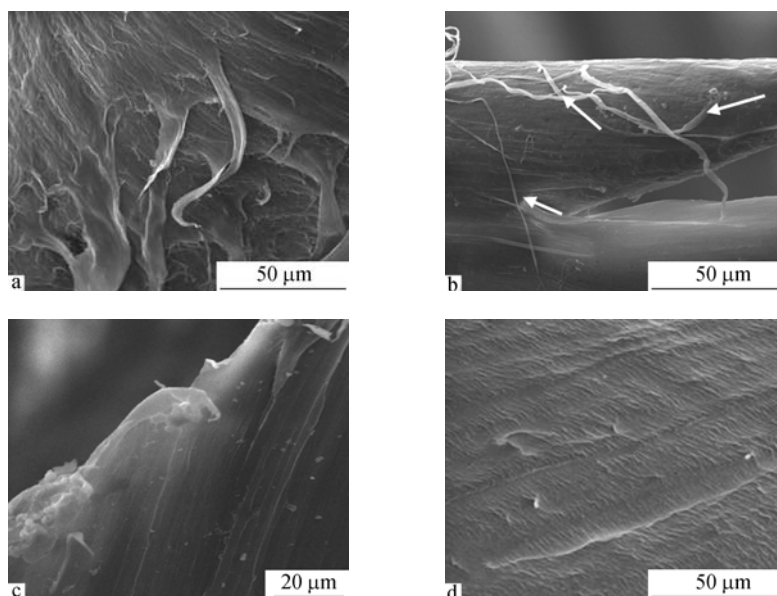


Fig. 6 SEM images of the tensile-fractured surfaces of (a) pure PP, (b) PP/CaCO₃, (c) PP/DMDBS and (d) PP/CaCO₃/DMDBS samples

The impact fracture behavior and impact strength were also characterized and the results are shown in Fig. 7 and Fig. 8. Importantly, the impact strength was measured at different atmosphere temperatures, such as 0°C, 23°C (room temperature) and 50°C, to provide more information about the fracture behavior of such samples. From Fig. 7 one can see that at relatively low temperature, all the samples exhibit the typical brittle fracture mode, and the effect of CaCO₃ and/or DMDBS is inconspicuous. This can be ascribed to the fact that the atmosphere temperature is lower than the glass transition temperature of PP and the motion of the chain segments is totally frozen. As a consequence, all the samples exhibit the brittle fracture feature. At room temperature, CaCO₃ exhibits weak toughening effect for PP whereas the effect of DMDBS is more conspicuous. However, the impact strength of PP/CaCO₃/DMDBS is more inferior to that of PP/DMDBS. This trend is more apparent at 50°C. PP/DMDBS exhibits the maximum impact strength compared to other three samples. This can be further explained as follows: DMDBS increases the spherulites number and simultaneously improves the interface among spherulites due to the enhancement of tied-molecule structure among the intra- and inter-spherulites^[31]. During the impact process, the increase of the interface among spherulites prevents the development of the crack in the matrix, which results in the improvement of the toughness of the blends. However, although CaCO₃ exhibits more homogeneous distribution in PP/CaCO₃/DMDBS sample compared to in PP/CaCO₃ sample, which avoids the strong stress concentration resulted by the aggregation of CaCO₃ particles, some CaCO₃ particles disperse in the interface among spherulites and possibly decrease the tied-molecule structure, leading to the decline of the impact strength. But one should notice that, PP/CaCO₃/DMDBS exhibits higher impact strength compared to PP/CaCO₃.

The SEM images of impact-fractured surfaces obtained at different conditions show similar fracture features possibly due to the fact that the impact measurements were carried out at a relatively high rate, 3.5 m/s, and the whole fracture energy is relatively low for all samples. Thus, the shear yielding or the crazing of matrix

is inconspicuous. Further work will be done to study the tensile fracture behavior of such samples at different testing temperatures.

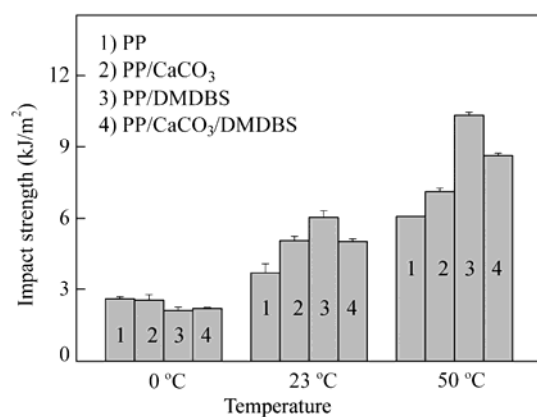
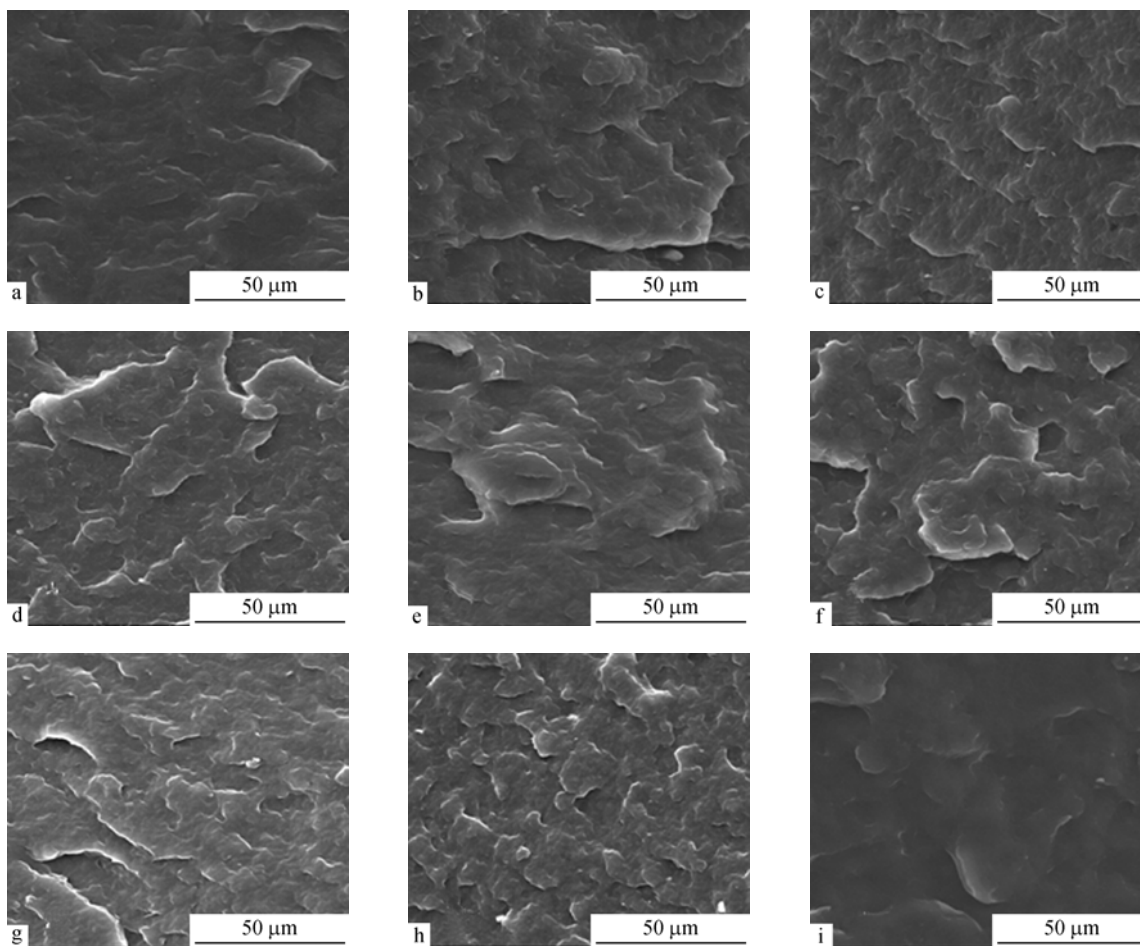


Fig. 7 Impact strength of pure PP and its composites obtained at different temperatures



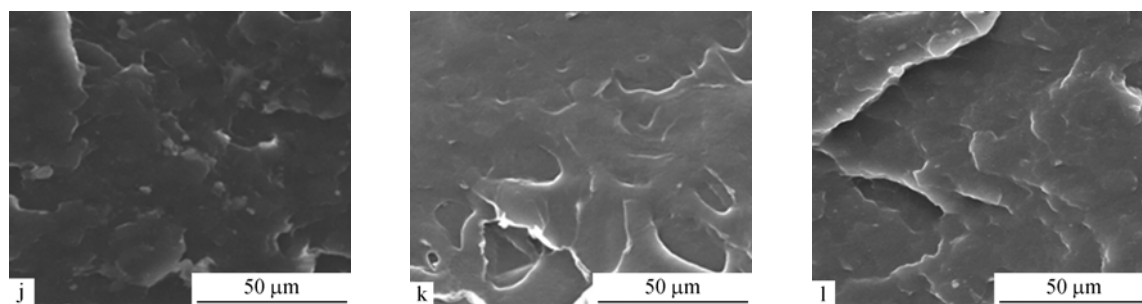


Fig. 8 SEM images of the impact-fractured surfaces of pure PP (a, e, i), PP/CaCO₃ (b, f, j), PP/DMDBS (c, g, k) and PP/CaCO₃/DMDBS (d, h, l) samples obtained at different temperatures such as 0°C (a–d), 23°C (e–h) and 50°C (i–l)

Heat Deformation Temperature

Figure 9 shows the HDT of all samples. It is clear that pure PP sample exhibits the lowest HDT, only about 67°C. Addition of CaCO₃ induces a slight enhancement of HDT to 72.5°C possibly due to the introduction of rigid filler and the formation of a few amounts of β -PP^[32, 33]. PP/DMDBS exhibits higher HDT due to the largely increased X_c (%). For PP/CaCO₃/DMDBS sample, the HDT is further increased up to 90°C. It is known to all that the HDT of samples is dependent on the crystalline structure of matrix, the content and the distribution of fillers. The improvement of HDT of PP/CaCO₃/DMDBS samples is mainly ascribed to the more homogeneous distribution of CaCO₃ and the largely increased X_c (%) of matrix induced by DMDBS. In other words, there is also a synergistic effect of DMDBS and CaCO₃ in improving the thermal properties of PP.

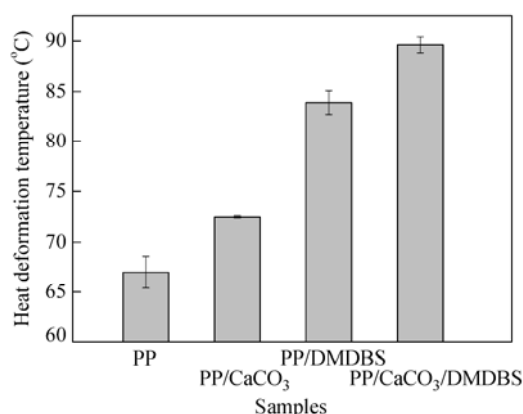


Fig. 9 HDT of pure PP and its composites

CONCLUSIONS

In summary, the crystallization behaviors and physical properties of PP, PP/CaCO₃, PP/DMDBS and PP/CaCO₃/DMDBS have been comparatively investigated. The addition of a few amounts of DMDBS into PP/CaCO₃ induces the great change of crystallization behavior of PP matrix. Improved distribution of CaCO₃, enhanced crystallization temperature, reduced spherulites diameters, and improved spherulites distribution as well as the largely increased X_c (%) are achieved for PP/CaCO₃/DMDBS samples. As a consequence, the tensile modulus and tensile strength are greatly improved as well as the enhancement of HDT. Although the fracture toughness is not improved as expected, DMDBS nucleated PP/CaCO₃ sample still exhibits improved impact strength compared to PP/CaCO₃. This investigation provides a fresh insight into the understanding of reinforcement and toughening mechanism of CaCO₃ in PP composites and facilitates to the design of excellent PP composites with very low CaCO₃ load.

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