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Effects of zinc acetate and cucurbit[6]uril on PP composites: crystallization behavior, foaming performance and mechanical properties

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Abstract: In this study, polypropylene (PP) foams were prepared with 1.0 wt% of cucurbit[6]uril (Q[6]), zinc acetate ($\text{Zn}(\text{Ac})_2$), $\text{Zn}@Q[6]$ (a supramolecular compound synthesized from Q[6] and $\text{Zn}(\text{Ac})_2$), or a mixture of $\text{Zn}(\text{Ac})_2$ and Q[6] (weight ratio of 1:1) through injection molding in the presence of a chemical blowing agent, azodicarbonamide. The effect of the additions on the crystallization behavior and foaming performance of PP and the mechanical characterizations of the foaming samples were determined. The results showed that the additions can change the crystallization type from homogeneous to heterogeneous, increase the crystallization rate and shrink the size but increase the density of spherulites. Among the additions, Q[6] most significantly altered the crystallization properties. Scanning electron microscopy (SEM) images revealed that the PP foaming performance can be improved by $\text{Zn}(\text{Ac})_2$ addition at a lower temperature (175°C); however, further increasing the temperature had an undesirable effect. Q[6] exhibited the optimum foaming improvement effect on PP in a wide temperature range (175–195°C). Adding nanoparticles also enhanced the tensile properties, flexural strength and impact strength of foaming PP at low temperatures. However, with increasing temperature, the poor cell structure demonstrated undesirable effects in terms of tensile strength, flexural strength and impact strength.

Keywords: azodicarbonamide; crystallization; injection molding; mechanical properties; polypropylene.

1 Introduction

Polypropylene (PP) foams have developed rapidly in recent years. Because of their excellent properties, PP foams are widely used in many fields, such as in packaging materials, automobile parts and in thermal insulation. Therefore, the development of a simple method to prepare PP foams is challenging (1–3). Among all the foaming processes (either batch or continuous), microcellular injection molding employing chemical foaming agents is the most important commercial process due to its lower injection pressure, lower cost, shorter cycle times and less material used (4–6). However, microcellular injection molding performs poorly in technological applications, which mainly arise in the high processing temperatures for melting polymers and chemical blowing agents for decomposition (7).

During PP foaming with a chemical foaming agent, azodicarbonamide (AC) working in conjunction with in zinc salt is widely applied because of its high gas yield (8) and the catalysis of zinc salt (9). Zinc salt can significantly increase the decomposition rate and lower the decomposition temperature of AC (10, 11), which means zinc salt makes polymer foaming at relative low temperature a possibility. Meanwhile, the melting strength increased at low temperature to suppress cell ripening and cell coalescence. In the PP foaming process employing the AC blowing agent system, cell nucleation can be effected by dispersed zinc salt in the polymer matrix (12). However, few studies have explored the effect of zinc salt on the foaming performance of polypropylene so far.

Adding nanofillers has demonstrated its effectiveness for improving PP foam morphology. Nanofiller not only reduces the nucleation energy barrier through the evolved interaction between nanofiller and polymer macromolecules, but also induces the crystallization of the polymer. That is, nanofillers can affect the foaming performance of the PP system through cell nucleation and changing its crystallization behavior (13). To the best of our knowledge, however, most of recent studies have focused on inorganic particles, such as clay (14), nano-calcium carbonate (15) and so on, little attention has been given to functional

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organic nanoparticles, which can also be used as effective nucleating agent and functional reinforcement (16).

In our previous studies, cucurbit[6]uril (Q[6]) (17) with relative low content (1.0 wt%) was successfully used to improve PP microcellular foaming behavior in the presence of AC as a chemical blowing agent. After that, a novel inorganic-organic nucleating agent (18) supramolecular compound Zn@Q[6] was synthesized by Q[6] and zinc acetate $[Zn(Ac)_2]$ through a chemical method. The underlying mechanisms of improved cell morphology were discussed using thermal and rheological analyses, but not involving the properties of foamed materials. In this current paper, we utilized $Zn(Ac)_2$ as an activator for the chemical blowing agent AC. The microcellular PP structures composited with $Zn(Ac)_2$, Q[6], Q[6]@Zn and a mixture of $Zn(Ac)_2$ and Q[6] were prepared through an injection molding process. Considering the effect differences of organic and inorganic nucleation agents on the foaming performance of PP, we prepared the foaming samples at different temperatures. The crystallization behavior of the PP composites was then systematically studied. The cell morphology was compared, and finally, the mechanical properties of the foamed samples were comprehensively studied. We aimed to evaluate the comprehensive property of PP foams with the new nucleation agent for further applications in future.

2 Experimental

2.1 Materials

Chemicals, such as $Zn(Ac)_2$ and HCl (Chongqing Co., China) were of reagent grade and used without further purification. Q[6] was prepared according to the previously reported procedure in our laboratory (19, 20). PP was purchased from SINOPEC Co. (China). The blowing agent AC with gas production of about 220 ml/g was obtained from Hanhong Co. (China).

2.2 Preparation of Zn@Q[6] supramolecular compound

$Zn(Ac)_2$ and Q[6] (equivalence ratio was 5:1) was first dissolved in HCl (3M), respectively. Next, the Q[6] solution was slowly added into $Zn(Ac)_2$ solution accompanied by stirring at 250 rpm. Then, the reaction solution was placed at room temperature to ensure the slow evaporation of the volatiles. Colorless crystals were finally obtained from the reaction solution within 1 week.

2.3 Preparation of PP composites

PP composites were prepared with 1.0 wt% of Zn@Q[6], Q[6], $Zn(Ac)_2$ or a mixture of $Zn(Ac)_2$ and Q[6] (weight ratio of 1:1) through a twin-screw extruder (Ruiya SE40A, Nangjing, China) with an increasing extrusion temperature profile (175–195°C). Thereafter they were coded as P(Zn@Q[6]), PQ, PZn and P(Q[6] + Zn), respectively.

2.4 Injection molding foaming

The foaming samples were fabricated through a microcellular injection foaming molding machine (Nangjing Ruiya, China) equipped with a volume-adjustable cavity. The temperature from hopper to nozzle was set from 175 to 195°C with a gradient of 5°C. The sample expansion ratio was controlled by a cavity thickness expanding from 3.5 mm to 4.0 mm. The gas (N_2) content was 1%, determined by the gas production of the AC percentage.

2.5 Characterization

A differential scanning calorimetry (DSC, Netzsch 499C, Germany) experiment was performed under a nitrogen atmosphere. Every sample was approximate 5 mg with an aluminum crucible. The samples were first heated to eliminate the thermal history at a rate of 10°C/min from 35 to 200°C. Then, the samples were cooled to 35°C and finally reheated to 200°C at the same temperature variation rate.

Wide-angle X-ray diffraction (WAXD, Bruker D8, Germany) and polarized optical microscopy (POM; PM6000, Nanjing, China) were conducted to show the crystallization properties of the composites. The samples were prepared by hot pressing polymer into a 50 μ m-thick film at 230°C, and then crystallized completely at 110°C.

Scanning electron microscope (SEM, KYKY-2800B) (Beijing Zhongke, China) was conducted to show the morphologies of the foamed samples. The samples were freeze fractured in liquid nitrogen and sputter-coated with gold, they were observed with an accelerating voltage of 25.0 kV. The cell sizes determined from the SEM micrographs were calculated via image analysis (Image-Pro Plus software). The cell density was calculated from the equation:

$$N_0 = \left[\frac{nM^2}{A} \right]^{3/2} \left[\frac{\rho}{\rho_f} \right] \quad [1]$$

where N_0 is the cell density (cells/cm³), n is the number of cells on the SEM micrograph, M is the magnification factor and A is the area of the micrograph (cm²). The densities of

unfoamed (ρ) and foamed (ρ_f) samples were measured in accordance with ASTM D792.

Mechanical property tests were performed according to ASTM D638-10 for tensile test, ASTM D790-10 for three-point flexural test and ASTM D256-10 for Izod notched impact strength test, respectively. Five measurements per sample were taken to check the repeatability of data.

3 Results and discussion

3.1 Crystallization behavior of PP composites

Figure 1 shows the non-isothermal crystallization behavior of PP and PP composites measured by DSC. The corresponding crystallization parameters are listed in Table 1, where T_p is the temperature of crystallization peak and T_c is the temperature at the onset of crystallization. The crystallization rate can be characterized by $(T_c - T_p)$, that is, high $(T_c - T_p)$ value results in low total crystallization rate under the same crystallization conditions. Non-isothermal crystallization kinetics were analyzed via the Jeziorny method (21), the half crystallization time ($t_{1/2}$), the Avrami exponent (n) and the corrected crystallization rate constant (Z_c) were calculated (Table 1). As shown, the

Figure 1: Curves of crystallization of PP and PP composites.

Table 1: Crystallization kinetic parameters of PP and PP composites.

Sample	T_c (°C)	T_p (°C)	$T_c - T_p$ (°C)	$t_{1/2}$ (min)	n	Z_c
PP	123.5	109.0	14.5	1.41	2.49	0.84
PZn	122.9	109.7	13.2	1.36	2.80	0.95
P(Zn + Q)	124.3	113.3	11.0	1.35	3.10	0.99
PQ	128.3	119.2	9.1	1.13	3.43	1.25
P(Zn@Q)	122.9	111.8	11.1	1.31	2.83	1.06

T_p and T_c were improved in the composites modified by the additions. The values for $(T_c - T_p)$ of the PP composites decreased because of the heterogeneous nucleation of the additions. For example, when Q[6] was added, the value of $(T_c - T_p)$ decreased from 14.5 of pure PP to 9.1 of PQ. This observation indicates that the crystallization rate of PP composites increased noticeably. For PP composites, $t_{1/2}$ was smaller than that of PP (Table 1). This result means that the half crystallization time of PP was shortened by adding Q[6], $Zn(Ac)_2$ and their compounds, with Q[6] being the most effective. Greater values of n and Z_c can be observed in PP composites compared with those of PP under the non-isothermal conditions, which implies that the nucleation and growth mode of the crystallization for PP composites were altered, and the completion of crystallization was accelerated.

3.2 Melting behavior of PP composites

The melting curves of PP and the PP composites are shown in Figure 2. Compared with pure PP, almost no change can be observed in the melting temperature of PP composites, which means the melting behavior did not change considerably with the addition of Q[6], $Zn(Ac)_2$ and their two compounds. The crystallinity of the system can be characterized by the melting peak area, namely, a large peak area results in a high crystallinity. Notably, the melting peak area of the PP composites shrank relative to that of the pure PP. This result suggests that the additions decreased the crystallinity.

3.3 Crystal structure of PP composites

For PP, three kinds of crystal forms exist, that is, α -form, β -form and γ -form, which can be distinguished by

Figure 2: Melting curves of PP and PP composites.

Figure 3: XRD patterns of PP and PP composites.

WAXD. Figure 3 presents the WAXD curves of PP and the PP composites. As shown, PP and PP composites exhibited similar diffraction curves. The diffraction angles (2θ) were strong at 14.1° , 16.9° , 18.6° and 21.7° , which correspond to the α -form monoclinic crystal faces of (110), (040) and (130) and the superposed crystal faces of (111)/(131), respectively. Given the low percentage of fillers, intense peaks of the fillers did not appear. According to Chen et al. (22), the 2θ located at 16° and 21° is for the β -form, whereas that of the γ -form is located at 20.3° . However, the diffraction peaks corresponding to the β -form and γ -form crystals were not observed, which indicates that PP is a typical α -form crystal that does not change with the addition of Q[6], $\text{Zn}(\text{Ac})_2$ and their two compounds.

The XRD pattern peak separation method was applied to calculate the crystallinity (X_c) of each system and the corresponding results are listed in Table 2. The value of crystallinity decreased with the addition of fillers in PP which can be attributed to the heterogeneous nucleation effect induced by the additions. Such an effect destroys the regularity of PP spherulites and diminishes crystallization. Moreover, the molecular chains may be hampered by the fillers, and the formation of orderly crystals may be delayed. A similar observation was reported when clay was used (23).

Table 2: Crystallinities of PP and PP composites.

Sample	X_c (%)
PP	68.7
PZn	66.4
P(Zn + Q)	64.5
PQ	55.1
P(Zn@Q)	59.8

3.4 Crystal morphology of PP composites

POM was conducted to show the crystallization properties of the samples, the micrographs are shown in Figure 4. As we can see, PP generally crystallizes into an isotropic state during melt crystallization, pure PP shows a spherulite with a large size, regular structure and clear boundaries. Adding Q[6], $\text{Zn}(\text{Ac})_2$ and their two compounds significantly decreased the size, increased the number of PP spherulites, destroyed the integrity and blurred the boundaries of such structures. The size and density of spherulites of PQ were the most altered amongst those of the systems tested (Figure 4B–G). For pure PP, the crystallization process involves homogeneous nucleation and the amount of nuclei is relatively limited. As a result, the spherulite of pure PP can grow extremely large under sufficient undercooling. Whereas, the nucleation of the PP composites system can be induced by the heterogeneous nucleation sites provided by the nanofillers. Then, the molecular chains around the nuclei rearrange to form small circular spherulites. Ji et al. (24) proposed that smaller PLA spherulites were observed attributed to the heterogeneous nucleation effect provided by nanosilica. Li et al. (25) also found that the PP composites have smaller size and more uniform distributions of spherulites. Therefore, the introduction of Q[6], $\text{Zn}(\text{Ac})_2$ and their two compounds were proved to obviously improve the behavior of PP crystallization, such as the crystallization rate, crystallinity and micrographs, which may improve the foaming performance of PP composites in the injection process.

3.5 Foaming performance of PP composites

Figure 5 showed the SEM micrographs of the fracture surface, and Figure 6 illustrated the corresponding cell sizes and density. As shown, PP foam exhibited poor cell morphology with a non-uniform distribution at low temperature and big cell sizes at high temperature. With the addition of $\text{Zn}(\text{Ac})_2$, the cell distribution of PP improved at 175°C compared with that of pure PP. This effect may be attributed to the activated decomposition of AC and the cell nucleation effect of $\text{Zn}(\text{Ac})_2$ (26, 27). Unfortunately, with increasing temperature, the average cell size increased significantly, even more so than that of pure PP. This effect occurred because the melt strength of PP decreased with increasing temperature, and the presence of $\text{Zn}(\text{Ac})_2$ exacerbated this change. The cell morphology of the P(Zn + Q[6]) system showed the same tendency as that of PZn. However, the cell morphology of the P(Zn + Q[6])

Figure 4: POM micrographs of PP (A) and PP composites: (B) PZn; (C) P(Zn + Q); (D) PQ and (E) P(Zn@Q).

system with a mass ratio of 1:1 for Q[6] and $\text{Zn}(\text{Ac})_2$ was enhanced as compared with that of PZn at different foaming temperatures. This phenomenon indicated that Q[6] has better nucleation efficiency relative to that of $\text{Zn}(\text{Ac})_2$. The P(Zn + Q[6]) foaming temperature range showed no advantage, compared with that of pure PP except for 175°C. We concluded from the above results that the PP foam can be improved by $\text{Zn}(\text{Ac})_2$ at a low temperature, but increasing the temperature had a further undesired effect.

By adding Zn@Q[6] to PP, the cell morphology was improved in a relatively wide temperature range (180–195°C). However, the experimental system exhibited no superiority at 175°C, because AC cannot be catalyzed at lower temperature without $\text{Zn}(\text{Ac})_2$. When Q[6] was added to PP, the cell morphology was significantly improved within the temperature range of 175–195°C. The optimum cell size of PQ was 24.5 μm at 185°C, and the relative cell density was 1.9×10^7 cells/cm³. These results imply that

the cell structure can be improved by the addition of the Q[6] particles as the nucleating agent. Q[6] manifested the best cell nucleation effect relative to those of $\text{Zn}(\text{Ac})_2$ and Zn@Q[6], and such performance can be attributed to the unique macrocyclic structure and polarizable chemical property of Q[6]. These special characteristics endowed the particles with a high nucleation efficiency.

3.6 Mechanical properties

The tensile properties of neat PP and PP composites are shown in Figure 7 compared with neat PP, the tensile strength for the PP composites increased at 175°C. Meanwhile, the tensile strength for PZn and P(Zn + Q) decreased lower than that of pure PP with the temperature increasing beyond 180°C. Concurrently, the increase in tensile strength was greater in the PQ and P(Zn@Q) than in the

Figure 5: SEM images of PP and PP composite foams.

pure PP. As shown, the cell size and density varied with increasing temperature. The composite systems exhibited similar cell sizes and densities at 175°C. With the

temperature increasing beyond 180°C, the cell sizes of PZn and P(Zn+Q) increased, whereas those of PQ and P(Zn@Q) decreased relative to that of pure PP. The fillers

Figure 6: Average cell diameter (A) and cell density (B) of foamed PP and PP composite.

Figure 7: Tensile strength (A), flexural strength (B) and impact strength (C) for foamed samples.

added to PP can absorb the polymer matrix on its surface and reduce the ability of the foams to deform and stretch (28). However, during tensile testing, large cells were prone to stretch from circular shapes to elliptical ones and then collapsed upon fracturing. Accordingly, the decreased cell size and increased cell density diminished the ability of the cells to deform and further stretch with the applied tensile stress.

The flexural strength versus temperature curves of all the samples are shown in Figure 7B. The flexural strength increased by adding particles to the PP polymer, and this tendency is similar to that of the tensile strength at 175°C. The phenomena of the increased interface interaction between the matrix and particles ultimately reduced the

lower polymeric chain mobility and increased the material rigidity. With the increasing temperature, however, the cell morphologies of PZn and P(Zn+Q) gradually became inferior over that of pure PP. Therefore, the voids in the foams act as stress concentrators that reduce the flexural strength.

The impact strength values for various samples were illustrated in Figure 7C. As shown, adding nanoparticles into the PP matrix improved the impact strength at low temperatures (175–180°C). These improvements originated from the advantages of the nanoparticles in terms of tensile and flexural properties. During impact testing, rigid particles provide increased toughness, improved fatigue life and enhanced energy absorption. Meanwhile,

small cells demonstrated advantages in promoting plastic deformation, cell collapse and absorbing impact energy during the fracture process. Nevertheless, poor cell structure retrogressed at high temperatures (185–195°C). This behavior indicated that the effect was undesirable in terms of tensile strength, flexural strength and impact strength.

4 Conclusions

In this paper, microcellular PP composites with $\text{Zn}(\text{Ac})_2$, Q[6], Q[6]@Zn or a mixture of $\text{Zn}(\text{Ac})_2$ and Q[6] were prepared through injection molding in the presence of the chemical blowing agent AC. We found that the crystallization of the PP composites accelerated, but the crystallinity values decreased. In addition, the size of PP spherulites decreased, but their density increased significantly. These crystallization behavioral changes of PP may be attributed to the heterogeneous nucleation effect induced by the additions. The results showed that the PP composite foaming performance can be improved by $\text{Zn}(\text{Ac})_2$ at a low temperature (175°C), whereas increasing the temperature further disfavored this effect. Q[6] exhibited the optimum foaming improvement effect of PP in a wide temperature range (175–195°C). Adding nanoparticles into the foaming PP matrix enhanced the tensile properties, flexural strength and impact strength at low temperatures while the fillers act as concentrators. However, the cell morphology retrogressed at high temperatures, which indicated that the effect is undesirable in terms of tensile strength, flexural strength and impact strength.

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