DEVELOPMENT OF HIGH THERMAL INSULATION POLYPROPYLENE FOAMS BLOWN IN INJECTION MOLDING WITH MOLD OPENING

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Abstract

Polypropylene (PP) foams with a low thermal conductivity (less than 40 mW/m·K) and a low density (0.1-0.2 g/cm\(^3\)) were fabricated by the foam injection molding technology with mold opening while using CO\(_2\) as a blowing agent. PTFE fibrils manufactured by in-situ fibrillation using a co-rotating twin screw extruder were used to improve the melt strength and the strain hardening property. The crystallization behavior and the rheological properties were studied, to demonstrate that the dispersed PTFE fibrils effectively enhanced the crystallinity and, thereby, increased the melt strength, and induced a strain hardening behavior. When foamed in injection molding, the fibrillated PTFE containing PP showed much more improved foaming behavior. The thermal conductivity mainly depended on the expansion ratio of foam, although the quality of the cells (i.e., the size and uniformity) also influenced those properties.

Introduction

Fossil fuels (i.e., coal, oil, and natural gas) contribute 81.4\% of the total world energy production, which release billions of carbon dioxide, together with nitrogen dioxide, sulphur dioxide, and carbon monoxide, resulting to global warming, acid rain, water pollution, and air pollution [1]. Thus, the requirement for efficiency, energy saving, and environmental protection way of energy generation is urgent and significant for the global energy conservation. In this context, energy conservation exhibits great potential to achieve the energy sustainability, especially for the application of thermal insulation materials [2]. Polymeric foams rank second after the mineral wool in the common insulation materials due to its better insulation and lower cast [3].

Foam injection molding is a common foaming technology owing to its short cycle time, less material usage, and less energy consumption, but traditional foam injection molding can only produce foams with low expansion ratio, less than 1.5-fold [4]. To achieve excellent thermal insulation foams, a large expansion ratio is an essential requirement to effectively reduce the contribution of the solid thermal conduction. Based on this requirement, the foam injection molding equipped with mold-opening could be applied to fabricate sandwich-type framework foams with a high expansion ratio [5].

Polypropylene (PP) a semi-crystalline polymer, is the second most important plastic with revenues expected to exceed US$145 billion by 2019 [6], because of its excellent robustness to chemical and moisture attack, mechanical performance, and versatile applications. However, PP’s low melt strength and weak strain-hardening behavior have limited the foaming ability and quality, which is ascribed to the linear structure of molecules as well as the crystalline phase [7]. Introducing crystal nucleating agents to the PP matrix is an efficient approach to improve the melt strength, which includes nano-/micron-sized talc, clay, and silica, as well as polytetrafluoroethylene (PTFE) fibrils [5,8-10].

In this paper, the in-situ fibrillation process was used to enhance the melt strength of PP matrix, and the mold-opening foam injection molding was used to fabricate insulation foams. Additionally, the crystallization behavior and the rheological properties were studied, to demonstrate the effect of dispersed PTFE fibrils on the crystallinity and melt strength of the PP matrix. Furthermore, to investigate the properties of the molded foams, the thermal conductivity and compressive strength were measured, respectively.

Experimental

Materials

The polymer used as the matrix in this study was a linear isotactic polypropylene (Novatec-PP FY4), a commercial homopolymer supplied by Japan Polypropylene Corporation, with a MFR of 5 g/10 min (at 230°C/2.16 kg load). A commercially available polytetrafluoroethylene (Metablen-PTFE A-3000) powder was supplied by Mitsubishi Rayon, with a melt
temperature of 327°C. The blowing agent used was supercritical CO2 with a purity of 99 % (Linde Gas Inc.).

Sample preparation and foam injection molding

Four PP blends with PTFE weight concentrations of 100/0, 99/1, 97/3, and 95/5 were prepared. A co-rotational twin-screw extruder, which was manufactured by Toshiba Machine Co. Ltd. (Trade name: TEM-26SS), was used to compounding the materials. The compounding temperatures from the hopper zone to the die were 50, 160, 180, 200, 200, 200, 200, 200, 200, 200, and 190°C, respectively. The compounding was run at a discharge rate and a screw speed of 20 kg/h and 200 rpm. The melt was cooled to 25°C at 25°C/min, and then the temperature was similar to that of crystallization temperature. Noticeably, the variation of the enthalpy and melt temperature was increased by 10°C, and the crystallization temperature more than 10°C, and the crystallization temperature increased with the increase of PTFE fibrils, which shows that PTFE fibrils effectively enhanced the crystallization kinetics of the solid, and the cell nucleation density was calculated [10].

A 50-ton Arburg Allrounder 270 injection molding machine was used in the experiments, equipped with a Mucell SCF delivery system. The mold-opening foam injection molding procedure is as follows: filling, dwelling or packing, mold-opening, and cooling. The injection pressure and percentage of CO2 were set at 24 MPa and 8 wt.%. The temperatures of melt and mold were kept at 220°C and 80°C, respectively. The injection speed was 100 cm3/s, and the shot size was 60 cm3. The packing pressure was set at 30 MPa. The values of dwelling time were set at 35, 37.5, and 40 s, respectively. The values of mold-opening distance were set at 12, 15, 18, 21, and 24 mm, respectively.

Characterization

The crystallinity of the neat PP and PP/PTFE blends was measured using differential scanning calorimetry (DSC, TA Q2000). The first heating run was to eliminate the effect of thermal history, from 25 to 230°C with a heating rate of 10°C/min, and then the temperature was kept for 5 minutes. After that, the melt was cooled to 25°C at 10°C/min and, thereafter, heated to 230°C at 10°C/min, to attain the thermal properties of the blends, especially for the crystallinity. To finish the measurement, the blend was cooled to 25°C at 25°C/min.

A rotational rheometer (ARES, TA Instruments) was used to investigate the melt strength and strain hardening behavior of the blends. The shear viscosity was measured over a frequency range from 0.1 to 100 rad/s at 190°C. The extensional viscosity was measured with three levels of extension rate, 0.01, 0.1, and 1 s⁻¹, and at the temperature of 170°C.

A water displacement method (ASTM D792-00) was used to measure the density of the PP/PTFE blends and foamed samples. It should be noted that the solid skins of the samples were cut before the measurement. A scanning electron microscope (SEM, JSM-6060, JEOL) was used to examine the foam morphology. Then, the cell size was measured using the SEM micrographs, the average diameter of 100 cells, and the cell nucleation density was calculated [10].

Results and discussion

Crystallization behavior of the PP/PTFE blends

Table 1 summarized the key parameters for the crystallization behavior of neat PP and PP/PTFE blends, such as crystallization peak, enthalpy in the second heating run, melt temperature, and crystallinity. It is found that the addition of PTFE fibrils increased the crystallization temperature more than 10°C, and the crystallization temperature increased with the increase of PTFE fibrils, which shows that PTFE fibrils effectively enhanced the crystallization kinetics of the PP matrix. Additionally, the variation of the enthalpy and melt temperature was similar to that of crystallization temperature with the increased PTFE fibrils. Noticeably, the crystallinity of PP was increased from 36.14 % to 40.18 % by introducing PTFE fibrils.

| Table 1 Key parameters for the crystal behavior of PP/PTFE blends |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | PP-FY4          | PP/1PTFE        | PP/3PTFE        | PP/5PTFE        |
| crystallization peak/°C | 117.82          | 126.94          | 128.19          | 128.89          |
| enthalpy-heating   | 74.82           | 81.61           | 80.68           | 75.38           |
| melt temperature/°C | 163.79          | 165.36          | 166.13          | 165.77          |
| crystallinity/%    | 36.14           | 39.82           | 40.18           | 38.33           |

Rheological behavior of the PP/PTFE blends

Fig. 1 depicts the storage (G') and loss (G*) modulus, complex viscosity (η*), and tangent of the phase angle shift (tanδ) against frequency (ω) for PP and its blends, respectively. It is observed that G' and G* increased at different PTFE concentrations as ω increasing from 0.1 to 100 rad/s in Fig. 5 a)-b). Furthermore, the increments of G' and G* at low frequencies (<1 rad/s) were larger than that
at high frequencies (>100 rad/s), which was resulted from the constraint generated by the spatially linked structure at low frequency [11]. As Fig.5 c) shows, η* values decreased with the increase of ω, since the increasing frequency aligned the fibrils preferentially along the shear direction, thereby decreasing the viscosity. The observation that η* values increased with the increase of PTFE concentration, indicates the formation of PTFE-fibril network structure and its ability to improve the viscosity, especially at a low frequency. Fig.5 d) plots the loss tangent, tan δ, to characterize the elastic response of the polymer melt. The tan δ values decreased with an increase in the fibril concentration, showing a lower viscous/elastic ratio as the fibril concentration was increased.

Furthermore, PTFE fibrils also effectively enhanced the extensional viscosity by nearly one order of magnitude. Fig.6 that the addition of PTFE fibrils improved the PP/PTFE (5 wt.%) measured at a temperature of 190°C and at strain rates of 0.01, 0.1, and 1 s\(^{-1}\). This enhancement in extensional viscosity and strain hardening is attributed to the physical network formed by the flexible PTFE fibrils.

**Foaming behavior and cellular morphology**

To quantitively analyze the role of the dwelling time in promoting foaming ability of PP matrix, the cell sizes and cell nucleation densities in the section which is perpendicular to the mold opening-direction were calculated based on the SEM micrographs. Fig.3 a) plots the cell sizes of neat PP and PP/PTFE blends as a function of the dwelling time, where it is around 3 that the aspect ratio of cell diameter in the mold-opening direction to that in the section perpendicular to the mold opening-direction. The cell size decreased with an increased dwelling time over different concentrations of PTFE. By adding only 1 wt.% PTFE, the cell sizes decreased by one order of magnitude, from around 600 to 60 µm, and as the PTFE concentration increased, the cell sizes further decreased from 60 to 30 µm. PTFE fibrils dramatically promoted the crystallization kinetics of PP matrix, i.e. melt strength, and a higher PTFE concentration more effectively influenced the crystallinity by supplying more crystal nucleation agents, corresponding with the DSC results.
increased with an increase in the dwelling time, and with the added PTFE, the cell densities were dramatically increased by three orders of magnitude, from $10^4$ to $10^7$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$. With an increase in the PTFE concentration from 1 wt.% to 5 wt.%, the cell densities were increased from $10^7$ to $10^9$ per cm$^3$.

To investigate the effect of the mold-opening distance on the cellular morphology, Fig. 4 a) and b) plot the cell sizes and cell densities in the section perpendicular to the mold opening-direction of PP blends with 5 wt.% PTFE over different mold-opening distances, respectively. The cell sizes and cell densities had been kept almost constant around a value with increased mold-opening distance over different dwelling times. To clarify their relation, SEM micrographs were detected in two directions, i.e. parallel (Fig. 5 (a)-(c)) and perpendicular (Fig. 5 (d)-(f)) to the mold-opening direction. Notably, with increasing the mold-opening distance, cells were markedly stretched in the mold-opening direction, by comparing Fig. 5 (a)-(c). However, the cell structures in the section perpendicular to the mold-opening direction were almost the same as shown as Fig. 5 (d)-(f), which was quantitively illustrated in Fig. 4. It indicated that the cell morphology exhibited approximate independence on the mold-opening distance.

**Thermal property characterization of PP and PP/PTFE foams**

Fig. 6 shows the variation of the thermal conductivity of the neat PP foams and the PP/PTFE foams as a function of the expansion ratio. The thermal conductivity gradually decreased with the increase of the expansion ratio for both neat PP and PP/PTFE foams. The minimum thermal conductivity of the neat PP foam was about 60 mW/m·K corresponding to the maximum expansion ratio of 10-fold while the minimum thermal conductivity of the PP/PTFE foam was as small as 36.5 mW/m·K corresponding to the maximum expansion ratio of 18-fold. The dramatically enhanced thermal insulation property of the PP/PTFE foams should be mainly owing to its significantly increased expansion ratio. Notably, PP/PTFE foams had much smaller thermal conductivity than the neat PP foams even under the same expansion ratio. It means that the increased expansion ratio was not the only reason leading to the improved thermal insulation property of the PP/PTFE foams. It is observed from Fig. 6 that a longer dwelling benefited the thermal insulation property of the PP/PTFE foams.

Basically, conduction, convection, and radiation are the three fundamental modes of heat transfer. Heat transfer through foams consists of four contributions, which are gas-phase conduction, polymer-phase conduction, convection, and radiation [12]. The contributions of gas-phase and polymer-phase conduction are approximately proportional to their respective volume fraction in the polymer foams, respectively. The convection could be disregarded owing to the restraint of gas movement inside less than 4-mm cells [13].
Thermal Conductivity

Expansion Ratio

<table>
<thead>
<tr>
<th>Neat PP-DT 42.5s</th>
<th>PP/5wt.%PTFE-DT 35.0s</th>
<th>PP/5wt.%PTFE-DT 37.5s</th>
<th>PP/5wt.%PTFE-DT 40.0s</th>
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<td>60</td>
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Fig. 6 Variation of thermal conductivity of foams with four different PTFE content over an expansion ratio range from 6 to 18 fold

Conclusions

Polypropylene (PP) foams with thermal conductivity as low as 36.5 mW/mK were fabricated by mold-opening foam injection molding for the first time with CO₂ as the blowing agent, combining in situ fibrillation of polytetrafluoroethylene (PTFE) in PP matrix to improve the melt strength. The crystallinity, rheological properties, cellular morphology, together with thermal insulation were characterized, and then, the effect of the processing parameters, the addition of PTFE fibrils as well as the cellular structures were investigated.

The fibrillated PTFE fibrils improved the cell morphology dramatically by enhancing the melt strength, strain hardening behavior, and crystallinity of PP due to their sub-micro fibrillar structure and good dispersion in the matrix, which was represented as the remarkable drop of the cell size by 30 times, from 600 to 20 µm, and the enhancement of the expansion ratio from 10 to around 20 fold, up to 2 times.

The PP/PTFE foams exhibited lower thermal conductivity than PP foams. The decrease of thermal conductivity was mainly resulted in the dramatical increase of the expansion ratio. Additionally, PTFE caused the formation of the micro-holes and micro/nano fibrils in the walls, which further decreased the thermal conductivity.

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References

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