High thermal insulation and compressive strength polypropylene foams fabricated by high-pressure foam injection molding and mold opening of nano-fibrillar composites

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ABSTRACT

Polypropylene (PP) foams with a thermal conductivity of as low as 36.5 mW m^{-1} K^{-1} are fabricated by high-pressure foam injection molding followed by mold-opening with CO_2 as a blowing agent. Regular PPs are not suitable for foaming due to their poor melt strength. To improve melt strength, the in-situ fibrillated blends of PP/polytetrafluoroethylene (PTFE) are prepared using a regular co-rotating twin-screw extruder. The micro-morphology characterized by SEM shows that fibrillated nanoscale PTFE fibers disperse very well in PP matrix. The DSC, dynamic shear rheology, and extensional rheology measurements demonstrate that the in-situ fibrillated PTFE fibers can significantly improve crystallization, visco-elastic performance, and strain-hardening behaviors, respectively. All these factors confirm that PTFE fibers are very effective to improve melt strength and thus foaming ability of PP. The foam injection molding results show that the PP foam's cell size reduces by nearly one order of magnitude while its expansion ratio increases by approximately three times in presence of PTFE fibers. Compared to PP foams, PP/PTFE foams show significantly improved thermal insulation performance due to the increased expansion ratio, as well as unique cell wall structures with micro-holes and/or nano-fibrils. Moreover, it demonstrates that smaller cell size leads to improved compressive strength.

1. Introduction

In recent decades, world energy consumption has increased more than two times from 1973 to 2014 [1], where the share of total world energy production from fossil fuels is up to 81.4%. The burning of fossil fuels releases billions of polluting emissions, damaging the environment [2]. Renewable energy is an efficient solution to the pollution, but it contributes only 19.2% to the global energy consumption reported by REN21 of 2016 [3]. In this context, energy conservation through enhancing energy efficiency shows great potential to achieve global energy sustainability. Thermal insulation materials play a pivotal role in energy conservation [4], of which the most commonly used ones are mineral wools, fibreglass, cellulose, and polymeric foams. These common insulation materials present a typical thermal conductivity of higher than 35 mW m^{-1} K^{-1} in the absence of special insulation gas at standard conditions. Although silica-based aerogels exhibit much better thermal insulation performance than common insulation materials, their application are still very limited due to high cost, difficulty of

processing, intrinsic brittle feature, as well as toxic substances involved in their fabrication procedures [5].

Among common insulation materials, polymeric foams currently ranking second wide applications exhibit many superior properties, such as better insulation, easier handling and installing, lower cost, and no water absorption [5–8]. General technologies to fabricate polymeric foams include batch foaming, bead foaming, foam extrusion, and foam injection molding. Among these technologies, foam injection molding introduces several advantages, such as a shorter cycle time, less material usage, greater dimensional stability, and lower energy consumption [9]. Moreover, it has potential to produce porous products with improved mechanical properties. However, the traditional foam injection molding process can only produce foams with small expansion ratios, typically < 1.5-fold [9–11]. To achieve excellent thermal insulation foams, a large expansion ratio is essential to minimize the heat transfer contributed by solid conduction [12]. To increase the foam's expansion ratio, high-pressure foam injection molding [13,14] with mold-opening was developed [15–17], which can not only increase

expansion ratios but also improve mechanical performances including fracture toughness, impact and compressive strength [18,19].

Polypropylene (PP), a common semi-crystalline polymer, has become the second most important plastic with a global market share up to 19% by 2020 [20], due to its superior robustness to chemical and moisture attack, mechanical performance, manufacturability, recyclability, and versatile applications. In particular, foamed PP exhibits remarkable impact strength and toughness, durability, and strength to weight ratio [21,22]. Due to its unique and advantageous characteristics, PP is an ideal candidate to prepare high-performance thermal insulation foams combined with excellent mechanical properties. However, pure PP generally exhibits low melt strength and weak strain-hardening behavior due to its linear structure of molecules as well as the crystalline phase [23,24], which leads to a poor foaming ability. One solution is to modify the polymer chain by cross-linking or long-chain branching, which can remarkably enhance the strain-hardening response yet accompanying with high cost of manufacture [25,26]. Another solution is to improve crystallization using nucleating agents because crystallization helps to improve the melt strength and thus foaming ability of PP. A variety of nucleating agents such as nano-/micron-sized talc [27], clay [28,29], and silica [30,31], as well as fibrils (e.g. cellulosic fibrils [32], and polytetrafluoroethylene (PTFE) fibrils [33]) have exhibited excellent potential on improving PP's crystallization and hence foaming ability. Rizvi et al. [34,35] have revealed that PTFE fibrils can dramatically increase the bubble density of PP foam by up to three orders of magnitude in foam extrusion process. The mechanism is that the in-situ fibrillated PTFE fibrils create physical networks of entanglements in PP matrix, resulting in significantly enhanced strain-hardening behavior and melt strength. However, to the best of our knowledge, there is few studies involving the PP/PTFE's foaming behavior in high-pressure foam injection molding with mold opening.

In this study, the in-situ fibrillation process based on a twin-screw compounding was conducted to prepare nano-fibrillar PP/PTFE composite with improved melt strength and foaming ability. To clarify PTFE fibrils' role in the crystallization behavior of PP, the non-isothermal crystallization of PP and PP/PTFE composites were investigated by a differential scanning calorimeter (DSC). Furthermore, the dynamic frequency sweep tests, dynamic temperature sweep tests, and extensional viscosity tests were implemented using a rheometer to study the effect of PTFE fibrils on the rheological performance of PP melt. Moreover, thermal conductivity and compressive strength were measured to evaluate the performance of PP/PTFE foams prepared for thermal insulation applications. The mechanisms of cellular structure's effect on thermal conductivity and compressive strength were discussed. The prepared PP foams showed excellent thermal insulation performance with a thermal conductivity of as low as $36.5 \text{ mW m}^{-1}\text{K}^{-1}$.

2. Experimental

2.1. Materials and sample preparation

The polymer used was a linear isotactic polypropylene (Novatec-PP FY4), a commercial homo-polymer supplied by Japan Polypropylene Corporation, with a MFR of 5 g/10 min (at 230 °C/2.16 kg load). Polytetrafluoroethylene powders, Metablen-PTFE A-3000, were supplied by Mitsubishi Rayon. The blowing agent used was supercritical CO_2 with a purity of higher than 99%, which was purchased from Linde Gas Inc.

Four PP blends with various PTFE weight concentrations of 100/0, 99/1, 97/3, and 95/5 were prepared. A co-rotational twin-screw extruder, manufactured by Toshiba Machine Co. Ltd. (Trade name: TEM-26SS), was used for compounding. The temperatures from the hopper zone to the die were set to be 50 °C, 160 °C, 180 °C, 200 °C, 200 °C, 200 °C, 200 °C, 200 °C, 200 °C, 200 °C, and 190 °C, respectively,

as shown in Fig. S1 of the supporting information. Compounding run at a discharge rate and a screw speed of 20 kg/h and 200 rpm, respectively.

To prepare samples for dynamic frequency sweep tests and dynamic temperature step tests, PP/PTFE composites in pellet forms were molded to round plates (i.e., Φ25 mm × 1.2 mm) by hot compression. To prepare samples for extensional viscosity tests, the composites were molded to rectangle shapes (i.e., 10 mm × 18 mm × 0.7 mm), with a duration of 4 min at 180 °C.

2.2. PP/PTFE blends morphology characterization

A scanning electron microscope (SEM, JEOL 6060) was used to characterize the morphology of PP/PTFE composites. To observe the morphology and dispersion of PTFE fibrils, the sample was cryogenically fractured in liquid nitrogen, and the fracture section was then exposed to the xylene bath for 2 min at 130 °C. Since xylene can dissolve the PP matrix while preserve PTFE fibrils which can thus be observed clearly. Thereafter, the samples were dried after being cleaned by acetone. Finally, the etched section was coated with a 10–20 nm layer of platinum using a sputter coater for SEM observation. The SEM images were analyzed to acquire the cellular structure information of foams using the software, Image J.

2.3. DSC characterization

A differential scanning calorimeter (DSC-Q2000, TA instruments), was used to measure the endothermic peak caused by crystal dissolution, for investigating the crystallization processes of the PP/PTFE blends. In a typical measurement, a small amount of material (around 10 mg) was first packaged with an aluminium pan and cap, and then put into a chamber filled with nitrogen. First, the blend was heated from 25 °C to 230 °C at 10 °C/min, and kept in the isothermal condition of 230 °C for 5 min, to eliminate the thermal history of the blends. After that, the melt was cooled to 25 °C at 10 °C/min, and thereafter heated to 230 °C again at 10 °C/min, to attain the thermal properties of the blends. To finish the measurement, the blend was cooled to 25 °C at 25 °C/min.

2.4. Rheological characterizations

The dynamic frequency sweep experiments were conducted using a rotational rheometer, ARES, TA Instruments, to characterize the rheology behaviors of PP and PP/PTFE composites. To identify the strain limits of the linear viscoelastic regions, all dynamic strain sweep tests were implemented at a pre-set strain of 1% over a frequency range from 0.1 rad/s to 100 rad/s at 190 °C. The dynamic temperature step tests were also conducted to analyze the rheological behavior of blends as the temperature decreased from 220 °C to 100 °C at 2 °C/min with a frequency of 0.63 rad/s.

Extensional viscosity of the PP/PTFE blends was conducted using the same rheometer equipment (ARES, TA Instruments) to examine whether the strain-hardening behavior occurs in the presence of PTFE fibrils. In measurement, the extension rate was set at three levels: 0.01 s^{-1}, 0.1 s^{-1}, and 1 s^{-1}, and the temperature selected was 170 °C. For each condition, experiments were repeated by at least three times, and the average values were reported.

2.5. Mold-opening process and conditions

A 50-ton Arburg Allrounder 270 injection molding machine, equipped with a Mucell SCF delivery system (Trexel Inc., Massachusetts), was used in experiments. The mold used was a two-plate one with a fan gate and a rectangular mold cavity (132 mm 108 mm × 3.2 mm). Fig. 1 illustrates the schematic of MOFIM procedures. First, polymer/gas solution in barrel is injected to fill mold