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Radiation effects on the foaming of atactic polypropylene with supercritical carbon dioxide

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ABSTRACT

Atactic polypropylene (PP) samples with melt flow indices (MFI) of 7.0 g/10 min were irradiated and then foamed with supercritical carbon dioxide ($scCO_2$). A detailed investigation was carried out to understand the effect of radiation on the $scCO_2$ foaming of polypropylene. Variations in the molecular weight, branching degree, crystallinity, and melting and crystallization temperatures of irradiated PP were investigated. The cell diameter, cell density, volume expansion ratio and foaming rate were analyzed in detail under different conditions. It was found that the cell structure of PP foam became more uniform and the foaming temperature window increased to 10 °C. This compares favorably to the 4 °C observed with pristine atactic PP. The best cell morphology was observed at a dose of 30 kGy. The corresponding average diameter and cell density were 16.4μm and 5.7×10^7 cells/cm^3, respectively.

1. Introduction

Polypropylene (PP) foam has attracted increasing interest because of its toughness, light weight, low cost, low electrical conductivity, and higher thermal stability for a variety of applications (Collias et al., 1994; Kumar, 1993; Suh et al., 2000; Xu et al., 2007). PP foam has been applied in insulation, auto industry, electromagnetic wave absorbers, and packaging (Jacobs et al., 2008; Naguib et al., 2005; Zhai et al., 2010). The cell type, cell size, cell density and foaming rate are important to the application of polymeric foam (Doroudiani et al., 1996; Krause et al., 2001; Suh et al., 2000; Wang et al., 2013). Martini and Jane Ellen first reported microcellular polymeric foams prepared using supercritical carbon dioxide ($scCO_2$) as the physical blowing agent (Martini, 1981). Compared to traditional blowing and chemical crosslinking agents, foaming with $scCO_2$ is particularly appealing since $scCO_2$ can be dissolved in the polymer and the foaming process is environmentally friendly (Wang et al., 2013). Since the melt strength of PP is low and the foaming temperature window for $scCO_2$ is narrow, many efforts have been made to improve the melt strength of polypropylene, including cross-linking, grafting, and blending (Hassan et al., 2013; Shukushima et al., 2001; Steller et al., 2006). Radiation cross-linking is broadly used for PP modification and this process involves the formation of three-dimensional structures (Khonakdar et al., 2006) and leads to a significant increase in the melt strength of polypropylene. Cross-linking significantly increases the melt strength and decreases the crystallinity of PP, which can improve its foaming behavior and obtain well-defined cell structure (Gotsis et al., 2004; Stange and Muenstedt, 2006).

PP has a branched methyl group, and thus radiation cross-linking is not easy for polypropylene. In fact, the G-value of scission is higher than in cross-linking with polypropylene (Keyser et al., 1963; Schnabel and Dole, 1963). However, cross-linking can easily be achieved in PP after irradiation by the addition of a cross-linking agent or a long chain branching material (Cao et al., 2011; Cheung et al., 1990; Yao et al., 2009; Ye et al., 2004). In this paper, atactic PP with a melt flow index of 7.0 g/10 min was irradiated at different doses in the absence of a multi-functional cross-linking agent, because irradiation can induce the cross-linking of atactic PP and this will provide a clear comparison of the foaming of irradiated isotactic PP with the pristine PP. The effects of radiation on polypropylene and $scCO_2$ foaming were also carefully investigated. It was found that the foaming behavior of irradiated atactic PP improved greatly and the foaming temperature window was increased to about 10 °C.

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2. Experimental

2.1. Materials

Polypropylene (PP) pellets (atactic, SEP-540) were purchased from LOTTE Chemical Co., (M_w=3. 20×10^5, M_w/M_n=3.96). Their MFI was 7.0 g/10 min at 230 °C with a 2.16 kg weight load, and their density was 0.89 g/cm^3. Carbon dioxide with a purity of 99.5% was purchased from Shanghai Loutang Special Gases.

2.2. Sample preparation

The PP sheet samples were prepared as follows. First, PP pellets were hot pressed at 195 °C and 20 MPa for 15 min to make sheets 2 mm in thickness. Then the sheets were cooled to ambient temperature at a rate of 10 °C/min. Subsequently, the sheets were irradiated with γ-rays, in argon, at environment temperature, at Shanghai Institute of Applied Physics and at a dose rate of 0.0019 kGy/s. The absorbed dose varied from 10 to 40 kGy.

2.3. Gel content measurement

The gel content of irradiated PP was determined by weighing the insoluble fraction of the PP samples. About 0.2 g of irradiated PP was packed in a copper mesh and extracted with boiling *p*-xylene for 96 h at 140 °C, as described in the literature (Wang et al., 2016; Zhao et al., 2010). The solid remainder was dried to a constant weight in a vacuum oven at 65 °C and then weighed. The gel ratio was calculated using Eq. (1), as follows:

$$\text{Gel content}(\%) = \frac{M_1}{M_0} \times 100\% \quad (1)$$

where M_O is the initial weight of PP and M_1 is the weight of the insoluble part.

2.4. Melt flow index (MFI)

The MFI of the original and irradiated PP samples was tested at 230 °C under 2.16 kg of weight using the plastometer (Zwick 4100) apparatus according to ASTM D-1238.

2.5. Molecular Weight Characterization

The molecular weight was measured by high-temperature size-exclusion chromatography (HT-SEC) coupled with a multi-angle laser light scattering (MALLS) detector and a refractive index (RI) detector. The measurement was performed using an Agilent gel permeation chromatography (GPC) PL-GPC 220, (Trichlorobenzene system, PL gel Olexis (300×7.5 mm)) at 150 °C. This gave important information related to the polymer's molecular structure (Otaguro et al., 2010).

2.6. Melting point and crystallization

The thermal behavior of the virgin and γ-irradiated PP was investigated using a NETZSCH STA 449 F3 Jupiter differential scanning calorimeter equipped with a data station. About 10–15 mg of PP samples was put in aluminum pans. The samples were heated from 25 °C to 200 °C in a heating rate of 10 °C/min under argon flow (20 ml/min) and then cooled to ambient temperature. The degree of crystallization was calculated using Eq. (2),

$$X_c(\%) = \frac{\Delta H_f}{\Delta H_{f0}} \times 100 \quad (2)$$

whereΔH_f is the melting enthalpy measured in the heating experiments and $\Delta H_{f0}$is the theoretical enthalpy of 100% crystalline polypropylene (207.1 J/g) (Velasco et al., 2002).

2.7. Supercritical carbon dioxide foaming

The foaming of PP was conducted in an autoclave with $scCO_2$ as the blowing agent. The PP foam material was produced at 20 MPa, 152 °C, and the depressurization rate was 10 MPa/s. The details of $scCO_2$ experimental apparatus were described in a previous paper (Huang et al., 2007; Xing et al., 2008). The batch foaming process used in this work consists of following stages. (1) Formation of a gas/polymer solution, where the molten polymer was saturated by CO_2 at the controlled temperature and pressure, (2) cell nucleation and cell formation after the release of CO_2 from PP, and (3) formation of a stable microporous structure, and cell stabilization in the cooling process associated with the CO_2 depressurization. The whole process of PP foaming in this study is shown in Fig. 1.

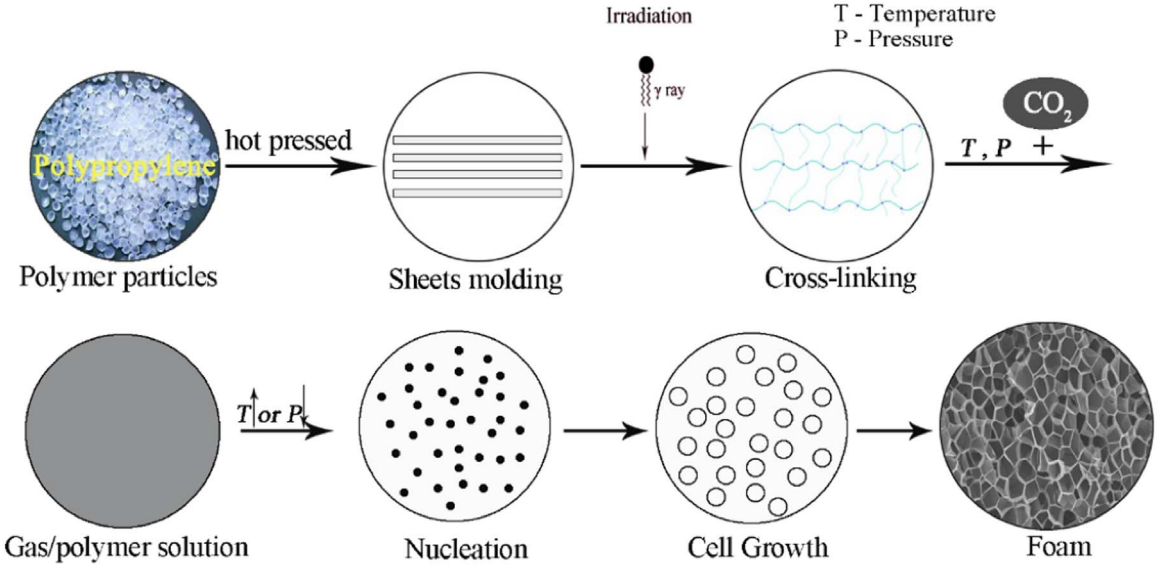

Fig. 1. Schematic of $scCO_2$ foaming of polypropylene.