



High melt strength polypropylene by ionic modification: Preparation, rheological properties and foaming behaviors



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ABSTRACT

In this paper we report a facile process to introduce ionic interactions to polypropylene (PP) based on Zn-neutralization and amine modification reactions of maleic anhydride grafted PP (PP-g-MAH) for the preparation of high melt strength PP (HMSPP). A series of PP ionomers with different structures and ionic properties were synthesized via the choice of the pendant groups, and their effects on the rheological properties were investigated. Increased melt viscosity and elasticity resulting from the ionic interaction and aggregation of the ionic domains were confirmed by both shear and extensional rheological measurements. The rheological behaviors of the PP ionomers share features similar to those of critical gels. Moreover, foaming behaviors of the PP ionomers were investigated by using CO₂ as the foaming agent and compared to that of the original PP-g-MAH. All ionomers show significantly improved foamability. Of the group of PP ionomers, the amine-modified PP ionomers (Zn-AM-ionomer) shows the best foamability due to the combined effects of optimal rheological properties and the underlying favorable interactions with CO₂. These findings provide new insights into the design of high melt strength polypropylenes for foaming application assisted with CO₂.

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1. Introduction

Polypropylene (PP) foams have been attracting increasing interest as lightweight and low cost materials suitable for a variety of applications ranging from protective equipments, insulation, cushions, damping to absorbers for acoustic and electromagnetic wave [1–4]. Foaming by supercritical carbon dioxide (scCO₂) is particularly appealing because of the environmental friendly nature of the process [5]. The key technological constraints in PP foaming process are the low melt strength and narrow foaming

temperature range [6,7], therefore improving the melt strength of PP is highly desired [8]. Great efforts in this direction have been made and various modification methods have been developed, such as blending PP with high melt viscosity polymers, chemical cross-linking and long chain branching [9–13].

We recently developed a new strategy to prepare high melt strength PP by introducing polar groups, such as amine onto the polymer structure [14]. The disparity in polarity between the polymer backbone and the pendant groups may lead to phase separation, and the phase separated polar domains serve as physical cross-links. This resulted in significant changes in the mechanical and rheological properties of the PPs whose behaviors in many ways resemble those of PPs modified by chemical-crosslinking. This physical cross-linking approach presents a viable general strategy to alter the viscoelastic properties of PPs and improve their foamability, due to the characteristic features of reversible equilibrium [15–19] and the potential self-healing ability [20,21] of the physical networks.

Physical crosslinking networks by ionic interactions may present another means to improve the PPs melt strength [22–28]. It

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has been reported that such interactions in a number of polymer systems lead to significant changes of rheological properties [29–39]. Nevertheless studies on ionically crosslinked PPs (PP ionomers) are very limited, and the foaming behaviors of PP ionomers have not been reported. In this study, ionically modified PPs with different degrees of ionic strength and steric hindrance were prepared to investigate the influence of ionic crosslinking on the rheological and foaming behaviors of these PP ionomers. Their effects on shear and extensional rheological behaviors were firstly examined. Moreover, simulation is performed for transient extensional viscosity of PP ionomers over a broad range of extensional strain rate using the modified WM constitutive equation based on experiment results. Furthermore, foaming behaviors of the PP ionomers with carbon dioxide (CO₂) were studied and related to the rheological properties of the PP ionomers and their interaction with CO₂.

2. Experimental section

2.1. Materials

PP-g-MAH (MAH content, 0.3 wt%) was obtained from Ningbo Nengzhiguang New Material Co., Ltd, China. Ammonia (AM, 30% aqueous solution), methylamine (MAM, 40% aqueous solution) and dimethylamine (DMAM, 40% aqueous solution) were purchased from Aladdin. Zinc acetate was supplied by Shanghai Meixing Chemical Reagent Co., Ltd, China. 1,2,4-trichlorobenzene (TCB) and 2,6-di-*t*-butyl-4-methylphenol (BHT) were purchased from Acros.

2.2. Sample synthesis

Fig. 1 shows the schemes for the synthesis of ionically modified PPs. Two types of ionomers were prepared: PP ionomers (Zn-ionomer, structure shown in (a) of Fig. 1) and amine(A)-modified PP ionomers (Zn-A-ionomers, structures shown in (b)–(d) of Fig. 1). Using PP-g-MAH as the precursor, the Zn-ionomer was synthesized (route 1) by hydrolyzing the maleic anhydride groups followed by the carboxylate – zinc ions chelating complex formation. In a typical process ~40 g PP-g-MAH was dissolved in 1500 g of xylene at 130 °C. A stoichiometric amount of zinc acetate in water was added into the solution and the reaction was allowed to proceed for 2 h. The ionomers were then recovered by precipitation in acetone and repeatedly washed with ethanol. Samples were air-dried for 1–2 days first and further dried in a vacuum oven at 80 °C for at least 24 h.

Several types of Zn-A-ionomers (Zn-AM-ionomer, Zn-MAM-ionomer and Zn-DMAM-ionomer) were synthesized via route 2 (Fig. 1) using AM, MAM and DMAM as the amine source, respectively. Typically, 40 g PP-g-MAH was dissolved in 1500 g of xylene at 130 °C. Half of the stoichiometric amount of zinc acetate in water was added into the solution together with 10-fold excess of amines. The reaction conditions and subsequent purification and drying procedures were the same as those for the preparation of Zn-ionomer.

2.3. Structure analysis

2.3.1. Size-extrusion chromatography (SEC)

SEC was performed at 150 °C using high temperature chromatography (Viscotek 350A, Viscotek Ltd.) with triple detectors (a refractive index detector, a four-capillary differential viscometer detector and a low angle light scattering detector). The column used was TSK-gel column (GMHHR-H(S) HT, 300 × 7.8 mm) with TCB as the mobile phase at a flow rate of 1.0 mL/min.

2.3.2. Fourier transform infrared (FTIR) spectroscopy

FT-IR (Nicolet 5700, Thermo Ltd) was performed on thin film samples (100 μm) in a range of 400–4000 cm⁻¹ with a resolution of 2 cm⁻¹. Data were collected and averaged over a total 32 scans.

2.4. Rheological measurement

Shear rheometry were performed on a stress-controlled rheometer (RheoStress 6000, ThermoHaake co.) in nitrogen environment using parallel plate geometry ($d = 20$ mm). Disk specimens were compression molded at 180 °C. Frequency sweep measurements (0.1–628 rad/s) were conducted at 180 °C using a small strain amplitude of 1%. Creep tests were also performed at 180 °C. Small shear stresses between 2 and 5 Pa were adopted to ensure a linear viscoelastic response. At sufficiently long time (2500–4000 s), the deformation rate approaches to steady state and the zero shear viscosity can be determined.

Uniaxial extensional measurements were performed at 180 °C, with a MARS III rheometer (ThermoHaake co.) equipped with a Sentmanat extensional rheometer (SER) universal testing platform (SER-HV-H01 model, Xpansion Instruments). Experiments were run at constant elongational rates ranging from 0.03 to 3 s⁻¹.

2.5. Solubility measurement

A magnetic suspension balance (MSB) (Rubotherm Prazision- messtechnik GmbH, Germany) was used to determine the solubility of CO₂ in the PP-g-MAH and PP ionomers. Measurements were conducted at 157 °C and 23 MPa. Detailed descriptions of this device and experiment procedures used in this study can be found in literature [40]. The mass of dissolved CO₂, W_g was calculated by the following equation:

$$m_g = m_s(P, T) - m_s(0, T) + \rho_g(P, T)\{V_s(P, T)[1 + S_s(P, T)] + V_B\} \quad (1)$$

where $m_s(P, T)$ and $m_s(0, T)$ are the sample weights at the measurement temperature T and at pressure P and zero pressure, respectively; $\rho_g(P, T)$ is the CO₂ density; $V_s(P, T)$ is the sample volume and V_B is the volume of the sample container; $S(P, T)$ is the swelling ratio of sample, which can be calculated by Sanchez-Lacombe equation of state [41–45].

2.6. Foaming by supercritical carbon dioxide (scCO₂)

Batch foaming process was conducted using a high-pressure stainless steel vessel with an internal volume of 150 mL. After placing the sample and purging the system with CO₂, a pre-determined amount of liquid CO₂ was added into the vessel. The vessel was immersed in an oil bath and kept at the targeted temperature and pressure (157 °C and 23 MPa) for 8 h. CO₂ was then quickly released (in ~2 s) to induce foam nucleation and growth. The foam structure was fixed by quickly removing the vessel from the oil bath and placing it into ice water.

2.7. Foam characterization

The foam bulk foam densities (ρ_f) were determined via water displacement measurements following ASTM D792-08:

$$\rho_f = \frac{a}{a + w - b} \rho_{\text{water}} \quad (2)$$

where ρ_{water} is the density of water, a is the apparent mass of specimen in air without the sinker, b is the apparent mass of

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