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

Yan Li b, c, d, Zhen Yao b, **, Zhen-hua Chen c, d, Shao-long Qiu b, Changchun Zeng c, d, *, Kun Cao a, b, ***

a State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
b Institute of Polymerization and Polymer Engineering, Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China
c High Performance Materials Institute, Florida State University, Tallahassee, FL 32310, USA
d Department of Industrial and Manufacturing Engineering, FAMU-FSU College of Engineering, Tallahassee, FL 32310, USA

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 PP 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
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 experimental 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 dimethylamine (DMAM, 40% aqueous solution) 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 2 days.

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 performed 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, Wₔ was calculated by the following equation:

\[ m_\text{g} = m_\text{s}(P, T) - m_\text{s}(0, T) + \rho_\text{g}(\rho, T)\left(V_\text{s}(P, T)\left(1 + S_\text{s}(P, T)\right) + V_\text{B}\right) \]

where \( m_\text{s}(P, T) \) and \( m_\text{s}(0, T) \) are the sample weights at the measurement temperature \( T \) and at pressure \( P \) and zero pressure, respectively; \( \rho(P, T) \) is the CO₂ density; \( V_\text{s}(P, T) \) is the sample volume and \( V_\text{B} \) 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 predetermined 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 (\( \rho_\text{f} \)) were determined via water displacement measurements following ASTM D792-08:

\[ \rho_\text{f} = \frac{a}{a + W - b\rho_\text{water}} \]

where \( \rho_\text{water} \) is the density of water, \( a \) is the apparent mass of specimen in air without the sinker, \( b \) is the apparent mass of
specimen and sinker completely immersed in water, and \( w \) is the apparent mass of the totally immersed sinker. The volume expansion ratios (\( R_v \)) of the foamed samples are defined as:

\[
R_v = \frac{\rho_0}{\rho_f}
\]

where \( \rho_0 \) is the bulk density of the unfoamed materials.

The cell size and density were obtained using scanning electron microscopy (SEM) (Sirion, FEI Ltd). Foamed samples were freeze-fractured in liquid nitrogen and sputter-coated with a thin layer of gold. The cell density (\( N \)), defined as the number of cells per unit volume with respect to the unfoamed polymer, was determined from:

\[
N = \left[ \frac{nM^2}{A} \right]^{3/2} R_v
\]

where \( n \) is the number of cells in the SEM image, \( M \) is the magnification factor and \( A \) is the area of the image.

### 3. Results and discussion

#### 3.1. Characteristic structure of the modified PP ionomers

Table 1 and Fig. 2 summarize the molecular weight (MW) and molecular weight distribution (PI) of the PP-g-MAH and PP ionomers. The MW and PI of all PP ionomers were similar to those of Table 1 and Fig. 2 summarize the molecular weight (MW) and molecular weight distribution (PI) of the PP-g-MAH and PP ionomers. The MW and PI of all PP ionomers were similar to those of
the parent PP-g-MAH, and were not observably affected by the amine-modification/neutralization reactions.

Fig. 3 shows the FTIR spectra of the PP-g-MAH and PP ionomers. The major peak in PP-g-MAH spectrum at 1780 cm\(^{-1}\) corresponded to the anhydride group [26]. This peak was not present in the spectra of any of the PP ionomers, suggesting completion of the neutralization reaction and consumption of the anhydride group. For Zn-ionomer, the bands around 1560–1600 cm\(^{-1}\) were assigned to the carboxylate stretching vibration of the zinc carboxylate. For Zn-A-ionomers, the amide bands (around 1630 cm\(^{-1}\) and 1555 cm\(^{-1}\)) overlapped with zinc carboxylate bands and were difficult to resolve independently [46,47].

3.2. Rheological behavior

3.2.1. Zero shear viscosity

Fig. 4 shows the time evolution of the ratio \(t/J(t)\) for all samples. The zero shear viscosity \((\eta_0)\) was determined according to Eq. (5) and is summarized in Table 2.

\[
\eta_0 = \lim_{t \to -\infty} \frac{t}{J(t)}
\]  

where \(t\) is the creep time and \(J(t)\) is the compliance of the materials.

The zero shear viscosities of the ionomers were several times to orders of magnitude higher than that of parent PP-g-MAH. Since their molecular weights and polydispersities were similar, the substantial viscosity differences can be argued to originate from the two main features in these ionomers: presence of inter-chain ionic interactions and formation of a nanophase-separated structure induced by the ionic aggregates within the materials [29–36,48,49]. The magnitudes of the zero shear viscosities were in the following order: Zn-ionomer > Zn-AM-ionomer > Zn-MAM-ionomer > Zn-DMAM-ionomer. The highest melt viscosity in the Zn-ionomer might be reasonably attributed to the highest Zn concentration and ionic association. On the other hand, steric effect played a role in the Zn-A-ionomers. An increase in the size and number of the pendant groups led to reduced interaction and decrease of zero shear viscosity.

3.2.2. Linear viscoelasticity by small amplitude oscillatory rheometry

Fig. 5 compares the complex viscosity \(\eta^{\ast}\) of the PP-g-MAH and PP ionomers. At low frequency regime (terminal zone), the ionomers showed significantly higher complex viscosity, whose magnitude followed the same order as that observed in creep test, i.e., Zn-ionomer > Zn-AM-ionomer > Zn-MAM-ionomer > Zn-DMAM-ionomer > PP-g-MAH. In addition, the strong shear thinning behavior observed in the ionomers throughout the frequency range also followed the same order. These behaviors were consistent with the strength of the ionic interactions in these materials, and are typical of percolated structures from the physical crosslinks in the ionomers. By comparison, the PP-g-MAH exhibited lower viscosity, and a Newtonian plateau in the low frequency regime.

The differences in linear viscoelasticity of the materials were furthered studied by examining their storage and loss moduli (Fig. 6). The PP-g-MAH showed typical liquid-like terminal behavior, e.g., \(G' - \omega^2\) and \(G'' - \omega\) at low frequencies. On the other hand, all PP ionomers showed more solid-like behaviors with substantially higher \(G'\) and \(G''\). Moreover, the terminal storage and loss moduli of all ionomer exhibited similar power-law type frequency dependency (both \(G'\) and \(G'' - \omega^b\)).

The gel-like behavior and associated network characteristics of the ionomers were analyzed using the critical gel theory developed by Winter et al. [15] According to the linear viscoelastic model for a critical gel, the \(G'\) and \(G''\) can be evaluated as [15,50].

\[
G'(\omega) = S_0 B \cos(n\pi/2) I(1-n)  \quad 1/\lambda_{pg} < \omega < 1/\lambda_0
\]  

(6)

\[
G''(\omega) = S_0 B \sin(n\pi/2) I(1-n)  \quad 1/\lambda_{pg} < \omega < 1/\lambda_0
\]  

(7)

where \(S\) is the gel stiffness and \(n\) (power law index) is the critical network relaxation exponent (\(0 < n < 1\)). \(n = 1\) indicates predominantly viscous behavior, whereas \(n = 0\) indicates elastic behavior. The characteristic time \(\lambda_0\) represents a low cutoff due to glassy behaviors at shorter times or at higher frequencies. \(\lambda_{pg}\) indicates the lifetime of physical junctions. \(I(n)\) is the gamma function.

The measured pair of \(G'\) and \(G''\) for each ionomer was fitted using the above model (data at low frequency, <1 rad/s, were used). The model predictions agreed rather well with the experimental measurements (Fig. 6). Table 2 summarizes the gel stiffness \(S\) and network relaxation exponent \(n\) for each ionomer. The decrease of \(S\) and increase of \(n\) followed the same order observed previously: Zn-ionomer, Zn-AM-ionomer, Zn-MAM-ionomer and Zn-DMAM-ionomer. This suggests that as the strength of the ionic association decreases, the network stiffness and elasticity decreases.
Furthermore, the chain segmental relaxation of the materials was investigated by comparing their crossover frequencies ($\omega_{cr}$). A lower $\omega_{cr}$ indicates lower mobility of the chain segment and longer relaxation time. As shown in Table 2, $\omega_{cr}$ showed the following order: Zn-ionomer < Zn-AM-ionomer < Zn-MAM-ionomer < Zn-DMAM-ionomer < PP-g-MAH. The reduction in the chain segment mobility and increase in segmental relaxation time in the series of PP ionomers is consistent with the previous zero shear viscosity observation and critical-gel analysis.

The series rheological study consistently suggested that the ionic domains (from ionic aggregation and phase separation) caused significant changes of the rheological properties of the ionic PPs. The changes were dictated by the strength of ionic interactions, which were influenced by the ion concentration and steric hindrance. Due to the highest concentration of zinc ions, the Zn-ionomer exhibited the highest zero shear viscosity, highest gel stiffness and lowest network relaxation exponent. In the Zn-A-ionomers, as the steric hindrance increased, the interaction strength decreased with reduction of network characteristics.

### Table 2: Rheological properties of PP-g-MAH and PP ionomers.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\eta_0$ (Pa·s)</th>
<th>$\omega_{cr}$ (rad/s)</th>
<th>n</th>
<th>$S$ (Pa·s$^n$)</th>
<th>$G_e$ (Pa)</th>
<th>Solubility (g/g)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP-g-MAH</td>
<td>1530</td>
<td>244</td>
<td></td>
<td></td>
<td></td>
<td>0.062</td>
</tr>
<tr>
<td>Zn-ionomer</td>
<td>44,000+</td>
<td>71</td>
<td>0.66</td>
<td>1200</td>
<td>10,000</td>
<td>0.067</td>
</tr>
<tr>
<td>Zn-Am-ionomer</td>
<td>25,500+</td>
<td>107</td>
<td>0.73</td>
<td>780</td>
<td>5000</td>
<td>0.082</td>
</tr>
<tr>
<td>Zn-MAM-ionomer</td>
<td>13,300+</td>
<td>154</td>
<td>0.75</td>
<td>500</td>
<td>4000</td>
<td>0.081</td>
</tr>
<tr>
<td>Zn-DMAM-ionomer</td>
<td>8700+</td>
<td>170</td>
<td>0.8</td>
<td>400</td>
<td>2000</td>
<td>0.082</td>
</tr>
</tbody>
</table>

Notes: $^+$ actual zero shear viscosity is higher than the value reported here.

$^a$ Solubility of CO$_2$ in the PP-g-MAH and PP ionomers at 157 °C and 24 MPa.

3.2.3. Uniaxial elongational rheology

The uniaxial elongational viscosity was investigated. Fig. 7 shows the tensile stress growth coefficients for the PP-g-MAH and ionomers under a series of strain rates at 180 °C. For PP-g-MAH, the tensile stress growth coefficients increased gradually with no clear “strain hardening”, typical of a linear polymer. By contrast, all ionomers showed strong stress hardening with the tensile stress growth coefficients rising rapidly above the linear viscoelasticity limit at all elongational rates. Such stress hardening phenomena were direct manifestations of the networked microstructures in the ionomers whose presence and interactions restricted the polymer chain mobility and enhanced the system elasticity.

In light of the similarity on the shear rheological behavior between the ionomers and critical gels, we attempted to predict the transient elongational flow behavior of the ionomers by using the constitutive equation developed by Winder and Mours [15,50]. The WM model is expressed as the following:

$$\sigma(t) = \int_0^t S(t - t')^{-n} \frac{\partial}{\partial t'} B(t, t') dt'$$

![Fig. 5. Complex viscosity ($|\eta^*|$) vs. angular frequency ($\omega$) measured at 180 °C for the PP-g-MAH and PP ionomers.](image)

![Fig. 6. (a) Storage modulus ($G'$), (b) loss modulus ($G''$) vs. angular frequency ($\omega$) measured at 180 °C for the PP-g-MAH and PP ionomers.](image)
where \( \sigma(t) \) is the stress tensor, \( B(t,t') \) is the Finger strain tensor, and \( S \) and \( n \) are the stiffness and relaxation time exponent of the critical gel.

The comparison of the experimental data and model fit is shown in Fig. 7 (solid line). The model under-predicted the tensile stress growth, with larger discrepancy at lower strain rates. The difference may arise from several characteristics unique to the ionomer network structures. In the ionomers, the physical cross-links are the ionic aggregates from the phase separation. They possess finite size and have their own distinct viscoelastic properties, both of which are affected by the ionic strength and steric hindrance, therefore may vary among the ionomers. It is plausible that the elasticity and deformation characteristics of the ionic aggregates would impact the overall behavior of the ionomers. These features are absent in critical gels where the cross-links are covalent bonds from polymer chain strands.

To account for the contribution of the finite-sized viscoelastic ionic aggregates to the ionomers’ transient elongation behavior, we modified the critical gel constitutive equation by adding an additional integral term:

\[
\sigma(t) = \int_0^t (t - t')^{-n} \frac{\partial}{\partial t'} B(t,t')dt' + \int_0^t G_e h(\lambda) \frac{\partial}{\partial t'} B(t,t')dt' \tag{10}
\]

where \( G_e \) can be considered as the long-term elastic modulus of physical cross-links (ionic aggregates); the damping function, \( h(\lambda) = 1/\lambda \) \([2]\), represents the extent of destruction of the physical cross-links by deformation; \( \lambda \) is the principal stretch ratios.

Fig. 7 shows the modified model predicted tensile stress growth coefficients (dotted lines). It captures rather well the transient behavior of all ionomers albeit somewhat over-prediction of the maximum tensile stress growth coefficients. To our knowledge, this empirical model for the first time aims to provide a possible means to take into consideration of the characteristics of the physical cross-links and evaluate their influences on the extensional flow behavior. The model also revealed that the physical cross-links in PP ionomers exhibited considerable strength, characterized by the model parameter \( G_e \) (Table 2). The magnitude of \( G_e \) followed the same order of the strength of the ionic association in PP ionomers discussed previously.

In addition to cause the critical gel behavior discussed herein, the ionic aggregates (clusters) may also contribute to the system viscoelastic properties via a “filler effect”, evidenced by the higher storage moduli of all ionomers than that of PP-g-MAH at high frequencies in the oscillatory measurement (3.2.2). Thus, both the linear and nonlinear rheological behaviors of ionomers reflect two effects that collectively contribute to the highly heterogeneous dynamics of PP ionomers: a network of junctions that give rise to the critical gel behavior and the “filler” effect derived from the cluster properties.

### 3.3. Foamability of the ionomers

From the bubble growth dynamic point of view, rheological factors that impede bubble growth are beneficial in stabilizing the bubble growth \([51]\). Thus with increased elasticity, the ionomers would be anticipated to show greatly improved foamability. To evaluate this, batch foaming was conducted using supercritical \( Co_2 \) at \( 157 \degree C \) and \( 24 \) MPa. Fig. 8 shows the cellular structures of the foams observed by SEM, and Fig. 9 shows the average expansion ratio, cell diameter and cell density. Indeed, the PP ionomers generally showed significantly improved foamability, displaying a higher expansion ratio, higher cell density and more uniform cellular structure than PP-g-MAH.

During bubble growth the polymer experiences biaxial extension \([52]\). While the increase of melt strength helped reduce the matrix failure and foam coalescence and collapse under the stress field, higher elasticity is not always more beneficial because excessive elasticity would result in a matrix with high stiffness and reduced strain-at-break. This leads to the decreased foamability as bubble growth relies on the matrix polymer to undergo substantial strain without fracturing \([53]\). This effect was observed in the foaming of the PP ionomers. For example, the Zn-AM-ionomer had a lower elasticity and melt strength than Zn-ionomer, yet exhibited the best foamability (highest expansion ratio and cell density, and the most uniform cell morphology). Similar phenomenon have been observed in critical gels, in which strong gels are likely to be more brittle than weak ones and may not be deformed to the same extent without fracturing \([37]\). The best overall foamability of Zn-AM-ionomer might be attributed to the good balance between strength and deformability from the moderate enhancement of elasticity. Such behavior was predicted in our previous foaming simulation \([51]\).

\( Co_2 \) solubility might be another contributing factor to the increased foamability. As shown in Table 2, due to the enhanced polymer-\( Co_2 \) interactions \([54–56]\), all three Zn-A-ionomers had substantially higher \( Co_2 \) solubility than the Zn-ionomers, which had solubility comparable to that of the parent PP-g-MAH. The
higher solubility not only enhanced cell nucleation and increased the cell density [55], it also facilitated bubble growth.

4. Conclusions

By utilizing Zn-neutralization and amine modification reactions of maleic anhydride grafted PP (PP-g-MAH), a series of the modified PP ionomers with different strength of ionic associations were prepared. The PP ionomers showed improved melt elasticity, as revealed by a series of rheological measurements. Through the choice of the pendant group, both shear and extensional rheological properties could be conveniently tuned. The shear and extensional behaviors of the ionomers were analyzed by resorting to a critical-gel theory, which satisfactory describes the dynamic shear behavior. Furthermore, a modified Winder – Mours constitutive equation was proposed to include the effects of the ionic domain characteristics of the PP ionomers on the extension flow behavior. The model prediction agreed rather well with experimental results. Finally, foaming of the PP ionomers by supercritical CO₂ was studied. Zn-AM-ionomer showed the best foamability due to the optimal rheological properties and the enhanced solubility resulting from amine–CO₂ interaction. These findings suggest that ionic modification may be a new viable approach to prepare high melt strength PP for foaming with CO₂. Further work should be targeted at controlling the rheological behavior and foaming properties by changing the types of cations, the degree of neutralization, and other factors that are expected to influence the interaction between ion-pairs in polymer chains.

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