

Nonlinear Rheology of Poly(ethylene-co-methacrylic acid) Ionomers

Tanja Tomkovic and Savvas G. Hatzikiriakos

Department of Chemical and Biological Engineering, The University of British Columbia,
Vancouver, BC, V6T 1Z4, Canada

ABSTRACT

Using a parallel plate rheometer equipped with a partitioned plate, and an extensional fixture (SER), a full rheological characterization of several commercial ionomers has been carried out including the determination of the linear viscoelastic moduli, the damping function and the tensile stress growth coefficient. The experimental rheological data have been fitted to a viscoelastic model (the K-BKZ model). Particular emphasis has been placed on the distribution of the relaxation times to identify the characteristic times such as reptation, Rouse, and sticky-Rouse that is associated with the characteristic life time of the ionic associations.

INTRODUCTION

Ionomers is a class of thermoplastic polymers that contain a small mole fraction of ionic functionalities (up to 15 mol%) covalently connected to the polymer backbone [1]. Recognized class of ionomers include those obtained from semi-crystalline ethylene-methacrylic acid copolymers which are neutralized with various metal ions, such as sodium, magnesium, zinc, calcium [2,3]. Extensive research on linear and nonlinear viscoelastic properties of these ionomers [3–12] reveals the influence of complex microstructure on their properties. On the one hand, free radical copolymerization of ethylene and ionic comonomer, methacrylic acid, generate copolymer with broad molecular weight distribution and long chain branching that has a significant impact

on the rheology. On the other hand, neutralization of copolymer introduces formation of ionic multiplets and clusters, which affect the relaxation processes of ionomers. It is the objective of this paper to study the nonlinear rheology of several ionomers, although the data for one ionomer will be presented here.

EXPERIMENTAL

Partially neutralized poly(ethylene-co-methacrylic acid) with sodium ions, in the shape of pellets, was kindly provided by DuPont (Experimental station, Wilmington, DE, USA). The ionomer examined and presented here contains 19 wt% (7.1 mol%) of methacrylic acid (MAA). More details in [13]. The sample is labeled as E-0.071MAA-0.65Na.

In order to eliminate the influence of moisture, the ionomer pellets were annealed for one week at 75 °C and then allowed to cool down slowly to room temperature by turning off the oven heater. After drying, the sample was fabricated using compression moulding, where the ionomer pellets were sandwiched between two poly(tetrafluoroethylene) sheets. First, the press was preheated to 130°C, and then the ionomer sample was allowed to melt for 15 minutes without applying pressure. Consequently, a pressure of about 10 MPa was applied for 5 minutes, and the sample was allowed to cool down to room temperature. The prepared sample thickness was about 1 mm. It was stored in a

desiccator over CaSO₄ at room temperature before testing.

To study the nonlinear viscoelastic properties of the ionomer sample, the Anton Paar MCR702 rotational rheometer was used, equipped with a cone-partitioned-plate geometry. In comparison with conventional cone-and-plate geometries, the cone-partitioned-plate allows reliable measurements at high shear strains and rates overcoming edge fracture effects. The top part of this type of geometry contains a plate, 8 mm in diameter attached to the transducer (center plate), and a stationary coaxial ring (partitioned plate), which acts as a shield and prevents edge fracture of the sample. Two types of experiments were performed. First, stress relaxation after imposition of sudden step-strain experiments were conducted in the range of shear strains from 0.05 to 10 to determine the damping function. Second, start-up-of-steady-shear experiments at different shear rates ranging from 0.1 to 20 s⁻¹ were performed to determine the viscosity of this material.

The elongational viscoelastic properties were determined using the second generation Sentmanat Extensional Rheometer (SER2) fixture. Ionomer specimens were prepared as films with a specific width of 9.2 mm and thickness of about 1 mm. Uniaxial extensional rheological measurements were performed at three different Hencky strain rates, namely, 0.5, 2, and 5 s⁻¹ at the reference temperature of 140 °C.

RESULTS AND DISCUSSION

Linear Viscoelasticity

Dynamic shear measurements were carried out at 20°C intervals in the range from 120 °C – 180 °C. The resulting storage, G' , and loss moduli, G'' , were shifted to the reference temperature of 140 °C using the time-temperature superposition principle. The master curves of dynamic moduli, G'

and G'' , and complex viscosity $|\eta^*(\omega)|$, of the ionomer, are depicted in Figure 1, along with the fit using the Maxwell model:

$$\tau_{ij}(t) = \int_{-\infty}^t \sum_{k=1}^N G_k \exp\left(-\frac{t-t'}{\lambda_k}\right) \dot{\gamma}_{ij}(t') dt' \quad (1)$$

The obtained parameters of λ_k and G_k found from the fitting procedure are listed in Table 1. From the superposition of G' and G'' the horizontal shift factors (a_T) were calculated, and they were found to follow the Arrhenius equation with energy of activation, $E_a=9.17 \times 10^4$ J/mol.

The damping function

Stress relaxation experiments after the imposition of step strains were performed using the cone-partitioned-plate geometry. The relaxation modulus was measured at various strains from 0.05 to 10 at the reference temperature of 140 °C (Figure 2). The threshold between the linear and nonlinear region was found to be at the strain of 0.2 with the relaxation curves obtained at lower values of strain to be independent of strain (only time dependence).

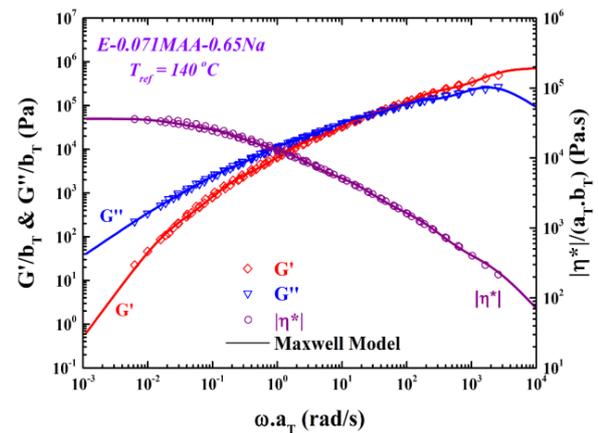


Figure 1. The master curves of the storage (G') and loss (G'') moduli and complex viscosity ($|\eta^*(\omega)|$) (symbols) along with the Maxwell model fit (lines) for the E-0.071MAA-0.65Na melt at the reference temperature of 140 °C using the relaxation spectrum listed in Table 1.

Table 1: Relaxation spectra and material constants given in the K-BKZ model (Eq. 4) for the E-0.071MAA-0.65Na at 140 °C.

Relaxation spectra		
k	λ_k (s)	G_k (Pa)
1	5.26×10^{-4}	4.92×10^5
2	6.58×10^{-3}	1.64×10^5
3	6.05×10^{-2}	5.42×10^4
4	5.80×10^{-1}	1.46×10^4
5	5.28	2.55×10^3
6	43.3	229
Material constants		
n	β	
0.14	0	

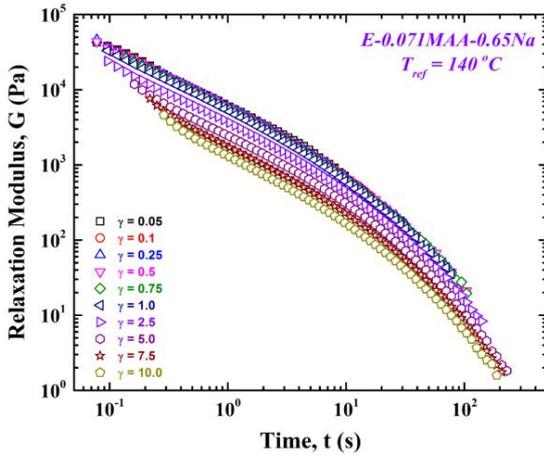


Figure 2. Relaxation moduli after imposition of various sudden step shear strains for the E-0.071MAA-0.65Na melt at the reference temperature of 140 °C

The reduced relaxation modulus for different shear strains obtained by shifting the data of nonlinear to the linear viscoelastic regime is shown in Figure 3 (excellent superposition). The damping function, $h(\gamma)$, is determined by using the following equation:

$$h(\gamma) = \frac{G(\gamma, t)}{G(t)} \quad (2)$$

where $G(t)$ and $G(\gamma, t)$ are the linear and nonlinear relaxation modulus, respectively.

The obtained values of the shift factors that make up the damping function (Figure 3) are fitted using the Wagner damping

function [14] which for simple shear is reduced to:

$$h(\gamma) = \exp(-n\gamma) \quad (3)$$

Good fit of the experimental results was obtained with the Wagner parameter $n = 0.14$, depicted in Figure 4. This parameter is also listed in Table 1.

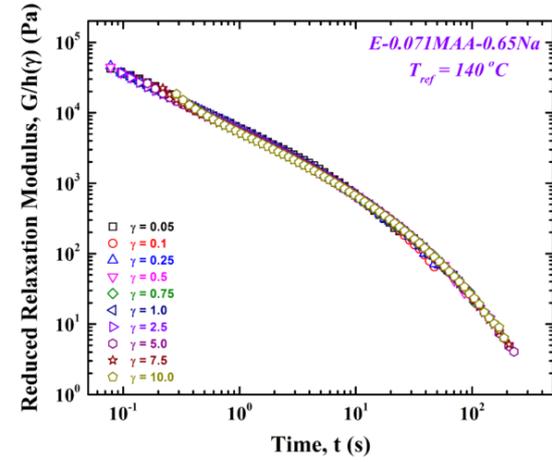


Figure 3. Vertically shifted relaxation moduli at various strains on the linear relaxation modulus to determine the shift factors for the damping function

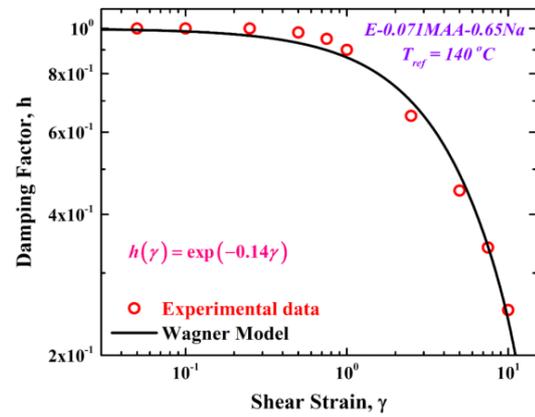


Figure 4. The damping function obtained from step strain relaxation experiments and its fit using the Wagner model.

Start-up of steady shear

Figure 5 shows the experimental shear stress growth coefficient of the E-0.071MAA-0.65Na ionomer at five shear rates from 0.1 s^{-1} to 20 s^{-1} . Solid lines represent predictions of the K-BKZ equation

with the parameters obtained from the previous rheological tests, namely small amplitude oscillatory shear and step-strain relaxation tests. The K-BKZ Equation is written as:

$$\bar{\tau} = \int_{-\infty}^t \sum_{k=1}^N \frac{G_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) \exp\left[-n\left(\beta I_{C_t^{-1}} + (1-\beta)I_{C_t} - 3\right)^{1/2}\right] \left[C_t^{-1}(t') + \theta C_t(t')\right] dt' \quad (4)$$

where λ_k and G_k are the relaxation times and relaxation modulus coefficients, N is the number of relaxation modes, n and β are material constants, and I_{C_t} , $I_{C_t^{-1}}$ are the first invariants of the Cauchy-Green tensor C_t and its inverse C_t^{-1} , the Finger strain tensor. Overall the predictions are satisfactory although the K-BKZ slightly underpredicts the observed overshoots.

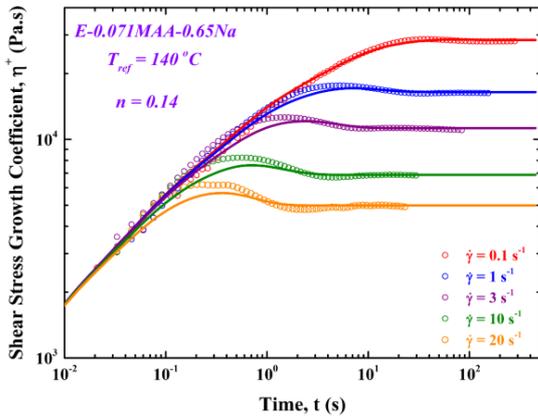


Figure 5. Shear stress growth coefficient at various shear rates for E-0.071MAA-0.65Na at the reference temperature of 140 °C and the prediction of the K-BKZ model (Wagner damping function).

Uniaxial extension

Using the SER2 fixture, uniaxial extension experiments were conducted at the reference temperature of 140 °C at several Hencky strain rates, namely 0.5, 2, 5 s⁻¹. The experimental data were modelled using the K-BKZ model prediction (Eq. 4) using the value of $\beta = 0$ (listed in Table 1). Fig. 6 presents the uniaxial stress growth

coefficient, η_E^+ versus time with predictions of the K-BKZ model (solid lines). Strong strain hardening effects can be observed which are due to the strong ionic interactions. Relatively rapid increases of the elongational viscosity is observed which the model misses to capture accurately.

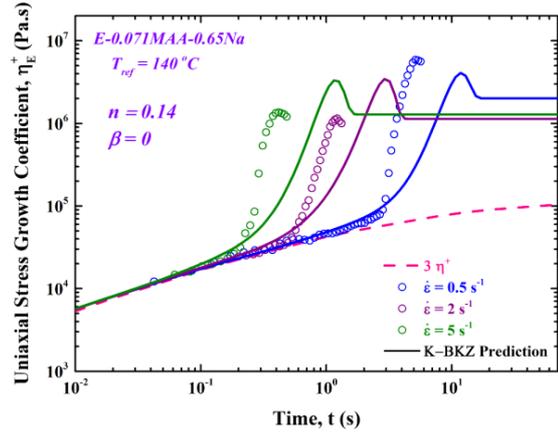


Figure 7. Uniaxial stress growth coefficient for E-0.071MAA-0.65Na and the K-BKZ model (Wagner type) fit at different Hencky strain rates at $T_{ref}=140$ °C

Similar results were found for three other ionomers of different compositions (degree of neutralization, molecular weight and molecular weight distribution).

CONCLUSIONS

Several commercial ionomers have been studied rheologically and the experimental results were used to fit the parameters of a K-BKZ model. It was concluded that ionic interactions have a significant effect on the extensional viscosity of the polymers and that K-BKZ can represent their rheological behaviour adequately. Furthermore it was found that the K-BKZ model can predict well the capillary flow of ionomers (no shown here) and therefore it can safely be recommended to be used in more complex flows in polymer processing.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research

Council (NSERC) of Canada. The University of British Columbia is also acknowledged for the 4YF scholarship for one of the authors.

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