Supplementary material for 'Brittle fracture in associative polymers: the case of ionomer melts'

1 Crack propagation profile at $T = 80$℃

Sequence of images of PTMO-Na ionomer filament undergoing uniaxial extensional deformation at a constant Hencky strain rate, $\dot{\epsilon} = 1\ s^{-1}$ and $T = 80$ ℃. The time specified is the time remaining to achieve complete brittle fracture of the filament.

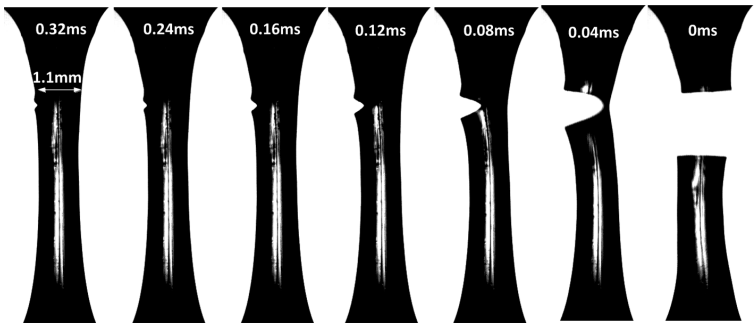

Figure 1: Crack propagation of PTMO-Na ionomer at $T = 80$℃, and $\dot{\epsilon} = 1\ s^{-1}$

Images of PTMO-Na ionomer filament showing multiple crack propagation.

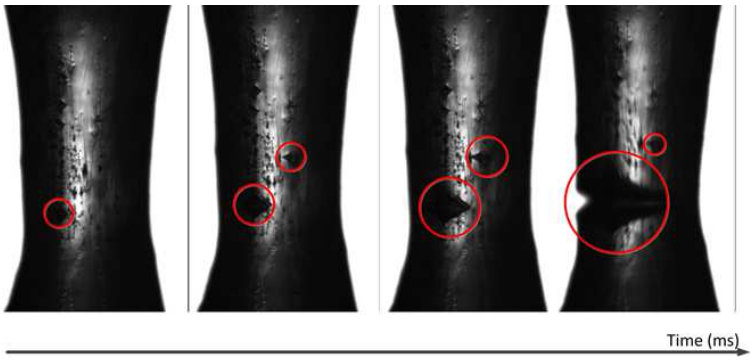

Figure 2: Sequence of images showing multiple cracks during stretching of PTMO-Na filament

2 Estimation of surface tension from parachors

Parchors signifies a function of chemical composition and is a useful means of estimating surface tension.[1] It can be represented by the following formula:

$$\gamma = \left(\frac{P_s}{V}\right)^4 \tag{1}$$

where γ is surface tension, P_s represent additive group contribution values and V is the molar volume.[2] For PTMO-Na ionomer $P_s \approx 2004.8\ (cm^3/mol)(erg/cm^2)^{1/4}$ as,

$P_s = 44 \times C + 75 \times H + 15 \times O + 1 \times S + 1 \times Na + 5 \times doublebond$

$P_s = 44 \times 9 + 75 \times 15.5 + 15 \times 19.8 + 1 \times 49.1 + 1 \times 54.8 + 5 \times 17$

$\rho \sim 0.994\ g/cm^3$[3] at $T = 20$℃ which gives value of molar volume $V = M/\rho = 903.4\ cm^3/mol$ for molar mass $M = 898\ g/mol$. Temperature dependence of surface tension is obtained using the following formula:

$$\gamma = \rho(293)\left(\frac{\rho(T)}{\rho(293)}\right)^4 \tag{2}$$

3 Estimation of surface energy from Eq. 12 in manuscript

Using Eq. 12 in the article, values of surface energy can be obtained and are plotted in Figure 3 along with the values of surface tension estimated in the above section.

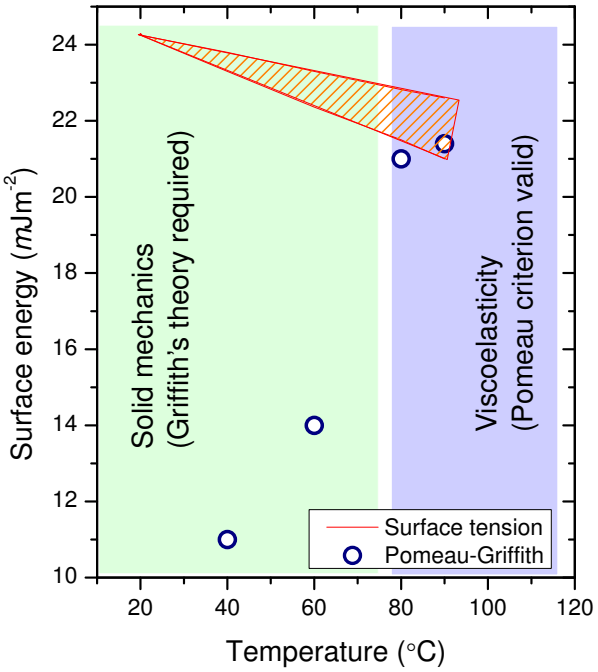

Figure 3: Surface tension as a function of temperature obtained using parachors shown in hatched region where the upper limit represents values assuming 0.25% decrease in density per 10 ℃ temperature increase[4] and the lower limit represents values assuming 0.5% decrease in density per 10 ℃ temperature increase. Open symbols represent estimate of surface energy using Griffith's theory by assuming energy barrier to be overcome by thermal fluctuations k_BT

References

[1] Agrawal, A. Surface Tension of Polymers. 2005.

[2] Quayle, O. R. The Parachors of Organic Compounds. An Interpretation and Catalogue. *Chem. Rev.* **1953**, *53*, 439–589.

[3] Chen, Q.; Tudryn, G. J.; Colby, R. H. Ionomer dynamics and the sticky Rouse model a). *J. Rheol.* **2013**, *16802*, 1441–1462.

[4] Kwok, D. Y.; Cheung, L. K.; Park, C. B.; Neumann, A. W. Study on the surface tensions of polymer melts using axisymmetric drop shape analysis. *Polym Eng & Sci.* **1998**, *38*, 757–764.