

Influence of side-groups on the non-equilibrium dynamics of semi-crystalline polymer films.

Austine A. Mulama^{1*}, Andrew O. Oduor¹ and Günter Reiter²

*mulamaustine@gmail.com, aamukayia@maseno.ac.ke

Introduction

At rapid processing conditions (during preparation or flow), polymers are squeezed/deformed at various length scales and exhibit significantly different properties.

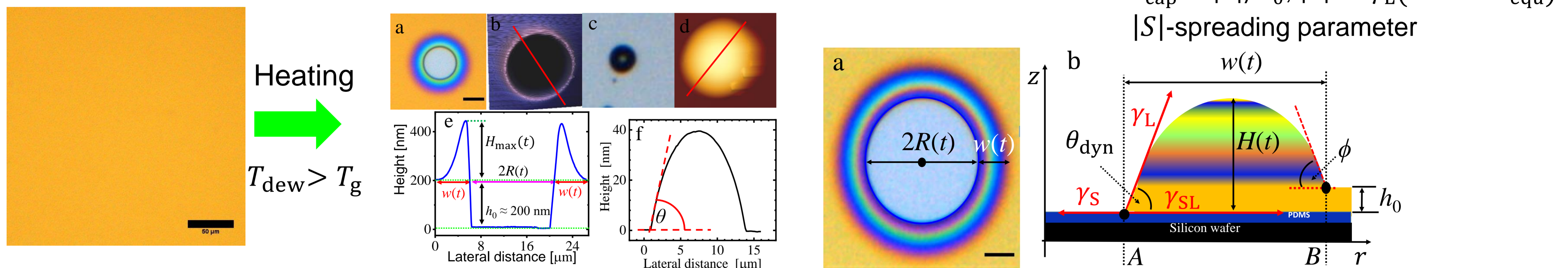
A systematic dewetting experiment in isotactic polystyrene (iPS; side group – hydrogen) and isotactic poly(*para*-methylstyrene) (iPpMS; side group – CH₃) has shown that the dewetting process was so fast that possible phase separation did not occur. Presence of iPS in iPpMS system led to increase in amount of residual stresses, relaxation times and corresponding activation energy possibly due to an increased tendency for the formation of transient clusters in blends with increased iPS content. These transient clusters may require cooperative movement of a higher number of segments. In other words, it is possible to tune the rheological properties of iPpMS system through blending.

Materials and methods

- Samples:** iPpMS: $M_w = 608$ kg/mol; $D = 2.19$; $T_g = 110$ °C; $T_m = 205$ °C; $T_{dew.} = 200$ °C – 280 °C
iPS: $M_w = 400$ kg/mol; $D = 2.8$; $T_g = 95$ °C; $T_m = 220$ °C; $T_{dew.} = 200$ °C – 280 °C

- Spin coating:** Rapid solvent evaporation during spin coating introduces deviations in chain conformations, yielding residual stresses.

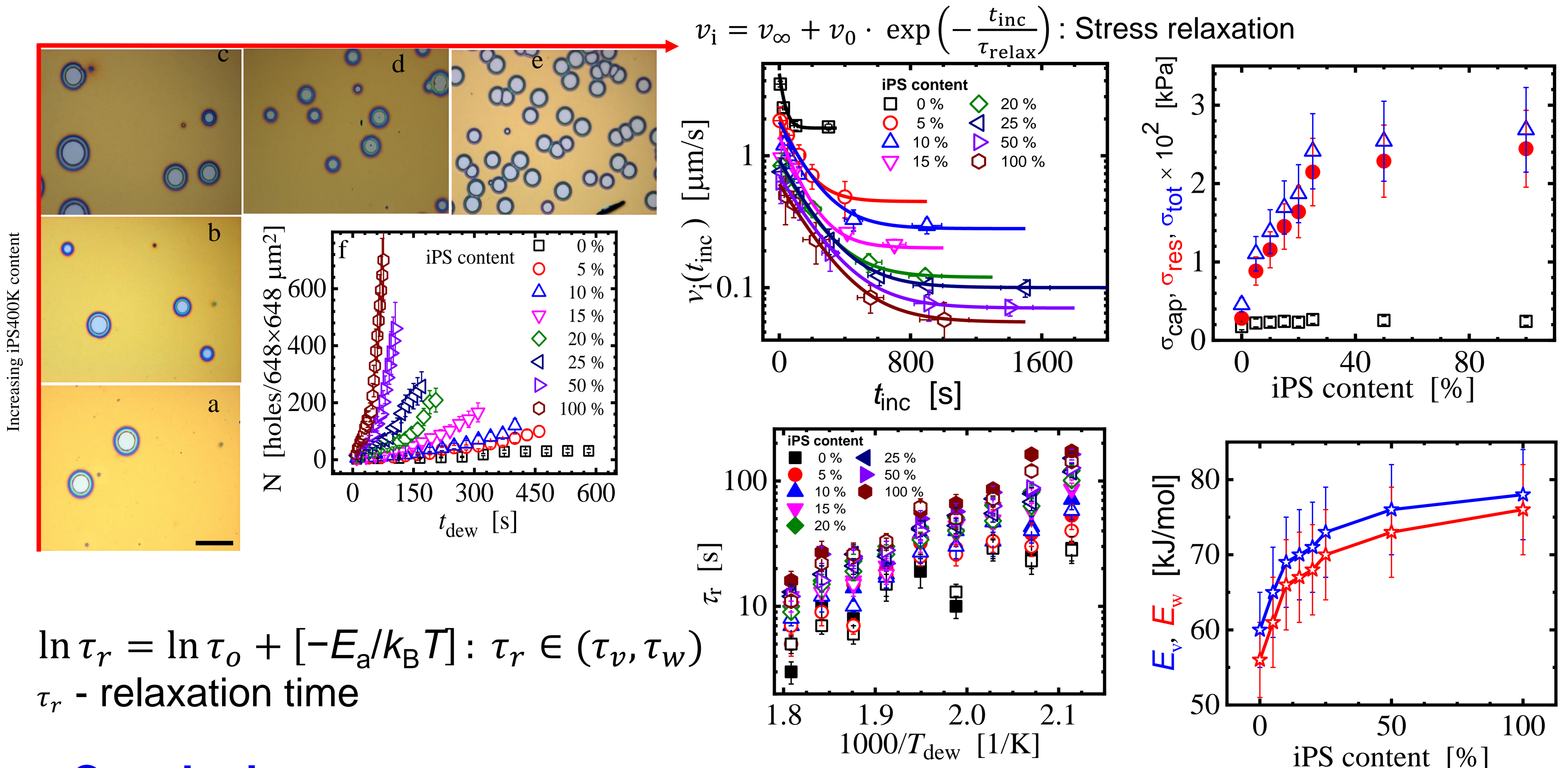
- Dewetting:** Process of retraction of a fluid from an unfavorable surface



Images are for iPpMS films, $h = 200$ nm & $T_{dew} = 220$ °C

Dewetting velocity, $v_{dew}(t_i) = \frac{[R(t_i) - R(t_{i-1})]}{(t_i - t_{i-1})}$ $R(t_i)$ - radius of the hole; t_i - dewetting time ($i = 1, 2, 3 \dots n$).

Results



Conclusion

- Activation energies characterizing the relaxation of preparation-induced residual stresses seem not to be affected by the presence of the side groups. However, in comparison to iPS, iPpMS exhibit reduced energy barrier for flow indicating that the transient clusters of monomers have a short lifetime in iPpMS. Thus, the here presented study demonstrates clearly that systematic dewetting experiments provide a convenient and simple approach for a quantitative determination of rheological properties of thin polymer films.

References

- Mulama *et al.*, *Macromolecules.*, 52(20), 7894-7903, (2019)
- Mulama *et al.*, *Macromolecules.*, 53(20), 9122-9130, (2020)
- S. Chandran & G. Reiter, *Phys. Rev. Lett.*, 116, 088301 (2016)
- Physics & Materials Sci. Dept Maseno University, P.O BOX 333, 40105 Maseno, Kenya
- Physikalisches Institut Albert-Ludwigs Uni-Freiburg Hermann-Herder-Str. 3 79104 Freiburg, Germany

