Associating Polymers in Extensional Flows: Processing to Performance to Self-Healing

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The addition of associating groups to a given polymer backbone results in improved mechanical, optical, and transport properties over the base polymer. However, typically there exists a trade-off between increases in mechanical properties and the processability of the polymer melt for increasing association strength. In this work we use shear rheology (SAOS) and non-linear filament stretching rheometry (uniaxial extension) to assess the impact of association strength on the processing window of poly(ethylene-co-methacrylic acid) and its ionomer. We show that the longest relaxation time and melt moduli are strongly affected by association strength. Furthermore, in extensional flow, we show that strong associating groups give rise to melt fracture for a wide range of Weissenberg numbers (rates and temperatures) for the ionomer. The fracture envelope is defined using the critical strain and stress at failure, indicating that melt processability in extension is more favorable for an entangled ionomer over unentangled ionomers with similar association strength. We then explore the recovery dynamics of self-healing associating polymers in extension. Because of their dynamic crosslinks, associating networks have the intrinsic ability to recover after damage. We confirm that the waiting time strongly impacts the state of the network before recovery. Furthermore, for entangled backbones, entanglement recovery occurs first, followed by recovery of associations. Also, the Wi at which recovery phenomena are probed strongly affects the measured recovery. Overall, both processability and self-healing can be linked to polymer architecture through several key timescales including: the bare association lifetime, the bond lifetime, and the longest relaxation time. Through this work, we begin to create a framework for highly tailored associating polymers with desirable processing and performance characteristics.