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# HIGHLY BRANCHED (ARBORESCENT) GRAFT POLYMERS AS POLYMER PROCESSING ADDITIVES

Mario Gauthier, Firmin Moingeon, Wai Yau Lin, Steven J. Teertstra, and Costas Tzoganakis

*Institute for Polymer Research, Department of Chemistry, University of Waterloo*

*200 University Ave. West, Waterloo, Ontario N2L 3G1, Canada;*

*e-mail: gauthier@uwaterloo.ca*

The processing of thermoplastic materials such as linear low-density polyethylene (LLDPE) in the molten state is limited by a critical shear rate above which the surface of the extrudate becomes rough. Even at relatively low shear rates these defects can occur in the form of *sharkskin*, characterized by a ridged surface. At higher shear rates *cyclic melt fracture*, with alternating smooth and rough extrudate surfaces, is also observed. Fluorinated polymer processing additives (PPA) have been used for many years in polyolefin extrusion to minimize the occurrence of these defects. We investigated a new class of PPA for the extrusion of LLDPE based on fluorinated dendrigraft (arborescent) isoprene homopolymers and copolymers. The usefulness of the fluorinated additives was evaluated by monitoring the presence of surface defects and the extrusion backpressure in capillary rheometry experiments after blending with LLDPE at low concentrations (0.1-0.5% w/w). The results obtained were correlated with the structure of the graft polymers and their fluorine content. Some additives were also derivatized to introduce polar metal-binding functionalities and improve the persistence of the arborescent PPA on the surface of the processing equipment. Branched fluorinated polyisoprenes with a compact structure (side chain molecular weight ≤ backbone molecular weight) performed well as PPA, eliminating surface defects and yielding a backpressure reduction of up to 18% at a concentration of 0.1%. The use of a poly(ethylene glycol) co-additive as an interfacial partitioning agent also led to the complete elimination of melt defects and yielded extrusion backpressure values only 10% higher than the commercial fluoroelastomer additives in some cases. The extrusion performance was improved in all cases by increasing the PPA concentration to 0.5%. The polymers containing metal-binding polar groups allowed the elimination of sharkskin formation, shifted the onset of cyclic melt fracture to higher shear rates, and yielded moderate backpressure reductions.