Synthesis of UHMWPE: Catalysts, Polymers and Co-polymers

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Statement of Purpose: Commercially available UHMWPE has been exhaustively studied. Processing conditions, crosslinking, radical quenching methods and characterization of these materials have resulted in improved properties and wear resistant materials. In arthroplastic application however, the material still fails. In order to design the next level material and starting at the catalyst level, synthesis of a macromolecular system from UHMWPE are introduced. In this report, catalysts previously evaluated and reported for their ability to produce UHMWPE polymers and co-polymers are scaled-up from 4L to 75L and material produced in Kg quantities is made available for properties evaluation.

Methods: Slurry polymerizations were first carried out in heptane (solvent) at incremental temperatures and pressures in a 4 L stainless steel autoclave. Commercially available 5th generation Ziegler Natta catalyst (**^{5}ZN**) were activated with triethyl-aluminum (TEAl); metallocene catalysts (**SCC**) activated with methylalumoxane (MAO) were used for 4L reactor evaluations; scale up of selected metallocene catalysts involved placing MAO activated catalysts on support material followed by polymerizations in a 75L steel reactor. Scavenger was diethyl aluminum (DEAC) or triisobutyl aluminum (TiBAl). Hexene was used as co-monomer in selected polymerizations.

Results: When **^{5}ZN** catalyst was activated with TEAl in the presence of ethylene at ambient to elevated temperatures and pressures, polymers having a range of Mw (>10 x10^6) were produced.

Addition of (MAO) activated metallocene solutions to silica resulted in catalysts having good activity with controlled particle morphology required for fusability. For the 20x scale up, Mw and other physical properties of the polymer flake such as average particle size (APS) and particle size distribution (PSD) were directly comparable. Utilizing two different supported metallocene catalysts was needed to provide a wide range of material (Mw) and more flexible operating conditions than either one could provide individually. Selected single site catalysts were evaluated for processing activity and conditions required for making UHMWPE were compared to **^{5}ZN**. For co-polymer synthesis, a comparison of the kinetics of polymerization for the supported metallocene catalysts in a 75L reactor with and without co-monomer is shown in figures 1 and 2. In general, addition of co-monomer lowered the rate of the reaction and produced polymer having lower Mw (measured by IV) at identical conditions.

Low temperature studies on the 75L reactor using supported metallocenes produced polymers having Mw > 3 x 10^6.

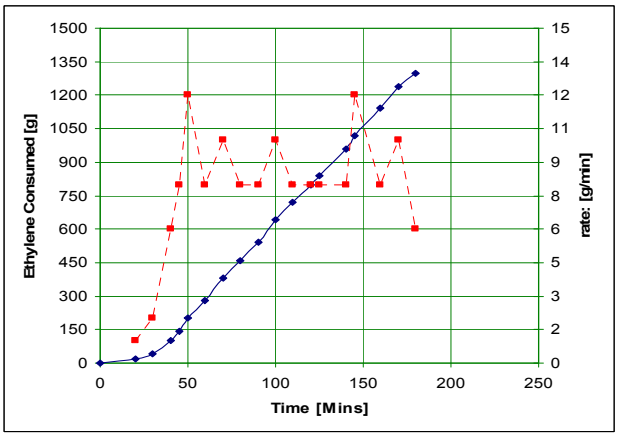

Figure 1. Homo-polymerization with supported metallocene catalyst: 50L heptane, 25°C, 200 psi ethylene; (blue trace is total ethylene consumed)

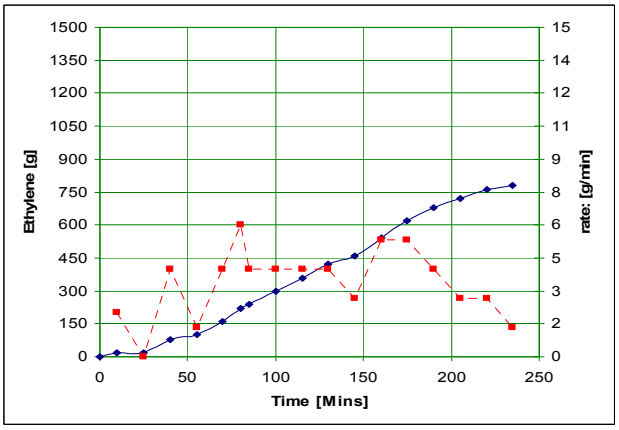

Figure 2. Co-polymerization with supported metallocene catalyst: 50L heptane, 1500 ml hexene, 25°C, 200 psi ethylene; (blue trace is total ethylene consumed).

Conclusions: Unsupported metallocene catalysts were more active than **^{5}ZN**: supported metallocene catalysts were less active than **^{5}ZN** catalysts. Particle size and distribution was controllable and similar for either catalysts and was based on catalyst mileages. Incorporation of co-monomer was similar for scale-up conditions; relative amounts of monomer in the feed to monomer in the product polymer were related and scalable. Polymerization rate and activity for homo- vs co-polymerizations using **SCC** are markedly different. UHMWPE made with supported single site catalysts as homopolymers or co-polymers are being evaluated for material properties.