

DISENTANGLED UHMWPE - CONTROL OF CRYSTALLIZATION, CHAIN ENTANGLEMENT AND RHEOLOGY VIA PROCESS CONDITIONS

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An experimental and theoretical study of the impact of alkanes on the degree of chain entanglement during ethylene polymerization to make ultrahigh molecular weight polyethylene (UHMWPE) is presented. Industrially, this type of polyethylene is produced in slurry phase at mild conditions. It is well known that UHMWPE is a polymer with long chains and very high molecular weight, that poses difficulties in terms of processability due to the presence of chain entanglements. In many cases is thus necessary to treat the material in different ways after the polymerization to minimize the degree of entanglements and improve the processability.

The motivation for this work was the observation in an earlier study that using vaporized alkanes (ICA) in the gas phase to control the reactor temperature also produced higher molecular weight polymers with higher degrees of crystallinity than expected, and noticeably higher than the values obtained in the absence of ICA with all other parameters being identical. Given that UHMWPE is produced commercially in alkane slurries, it was decided to proceed with a systematic study comparing slurry and gas phase polymerisations with the same (and different) alkanes. Furthermore, in order to understand the impact of the operation conditions on the in situ entanglements and crystallinity, it was important to find and to develop the appropriate methods of characterization of the reactor powder (as opposed to characterizing melt phase, or dissolved polymer that will lose all trace of its nascent state in the reactor).

To compare the polymerizations on an equal footing, they were run at similar monomer concentrations in the continuous phase. It was observed that gas phase polymerization gives higher activity, however lower molecular weight compared to slurry. In addition, the crystallinity was higher for gas phase than slurry. It was found that running the polymerizations at lower temperatures led to higher molecular weights as expected. Solid state drawability studies showed that gas phase polymerization in the presence of an ICA provides lower entanglement degree than slurry at the same polymerization conditions, and that this effect became more important as the molecular weight of the ICA decreased. From the lamellar thickness measurements in SAXS and WAXS, it was shown that thicker crystalline lamellae that is produced in slurry reactions, and these thicker lamellae also correspond to higher degrees of entanglement. Along with other experimental evidence, this validated our assumption that the higher degrees of disentangled chains are controlled, at least in part, by the crystallization process and by the relative rates of crystallization and chain growth. In addition, the crystallization studies showed that the difference in terms of crystallinity and lamellar thickness is due to the rate of crystallization and crystal formation in both reactions, which is much faster in gas phase, than in slurry. Furthermore, the comparison of different catalysts with different titanium contents showed that the activity has an impact on the entanglement formation, once again reinforcing the idea that the competition between the rate of crystallization and entanglement formation is a critical parameter for entanglement formation.