ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium on Chemical Reaction Engineering

20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

A multiphase model for reactive processing of polyolefins through grafting

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Highlights

- A reactor and kinetic Monte Carlo model are combined to describe grafting of vinyl monomers onto polyolefins.
- Phase segregation due to incomplete solubility of the monomer is accounted for.
- Fundamental description of mass transport between monomer- and polymer-rich phase.
- Design process conditions to control grafting yield and selectivity are evaluated.

1. Introduction

Post-polymerization functionalization of polyolefins allows to impart enhanced properties to these conventional polymers. The most common industrial synthesis route is free-radical induced grafting. Typically, this process involves the treatment of molten polyolefin chains with a source of free radicals and a vinyl monomer. During this process, the primary free radicals abstract hydrogens from the backbone of the polyolefin, creating mid-chain macroradicals (MCRs). These MCRs can add to the double bond of the vinyl monomer, creating grafting points through a grafting "from" process. However, the action of the primary radicals is not selective and they can also add directly to the double bonds of the vinyl monomer, generating homopolymer radicals. Nevertheless, the latter radicals can still contribute to further functionalization if they recombine with MCRs, generating grafting "to" points. On the other hand, phase segregation in the reactive mixture could arise due to the incomplete solubility of monomer and chemical initiator in the polyolefin. The monomer-rich phase will produce mainly homopolymer chains, whereas grafting points and homopolymer will be brought about in the polyolefin-rich phase. The identification of the optimal process conditions that help increase the level of grafting and reduce the extent of homopolymerization becomes crucial for the better performance of this type of reactive processing.

2. Methods

At LCT, the kinetics of free-radical induced grafting of vinyl monomers onto polyolefin was recently modeled by means of the kinetic Monte Carlo (kMC) technique, assuming perfect macromixing (single phase model) and isothermal conditions.[1] The kinetic model allows for the first time to describe all relevant reaction characteristics, such as monomer conversion, grafting selectivity and yield, as well as important microstructural properties, such as grafting "from", grafting "to", crosslinking density, number of grafts and crosslinks per individual chain, and the chain length distribution (CLD) of homopolymer, polyolefin and every individual grafted chain on the polyolefin. For modeling the hydrogen abstraction reaction events, a mass-weighted CLD for the polyolefin is employed for the kMC sampling. Depropagation of the vinyl monomer is also considered, due a reaction temperature close to the ceiling temperature. The kinetic model accounts for diffusional limitations on the micro-scale, based on the "parallel" encounter pair model to evaluate the apparent rate coefficients.[2] The self-diffusion coefficients are calculated using the free-volume theory.[3]

In the current contribution, the kinetic model is combined with a reactor model to allow for the simulation of the grafting kinetics in reactive processing environments. The extended model particularly accounts for phase segregation, due to the incomplete solubility of monomer, initiator and solvent in the molten polyolefin. This leads to the formation of two phases, one rich in monomer (Phase I) and one rich in

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polyolefin (Phase II). Initially, Phase I contains the monomer, the chemical initiator and the solvent. On the other hand, Phase II is only composed initially by the molten polyolefin. The reactants and products formed in Phase I can be transferred to Phase II. The mass transfer takes place until the saturation point in Phase II (given by the solubility of the components in the molten polyolefin) is reached. It is assumed that the polyolefin is not transferred from Phase II to Phase I, due to the low affinity of non-polar long chains with more polar compounds. Hence, the reaction steps involving polyolefin only occur in Phase II. Reactions steps involving low-molar mass species can occur in both Phase I and II. The mass transfer over the interface is accounted for based on fundamental principles.

3. Results and discussion

The feasibility of the extended model has been successfully explored. A parametric sensitivity analysis for the partition coefficients (Phase II versus Phase I) and overall mass transfer has been specially carried out. A typical result is shown in **Figure 1**, displaying the fraction of monomer reacted in Phase II as a function of the initial monomer amount and typical partitioning values for the monomer. An initial high monomer amount leads to a high overall reaction rate but to low levels of monomer consumption and grafting in Phase II. This is a consequence of the different reaction paths and effective reactivities undergone in the two phases. Due to the high mass fraction of polyolefin in the reaction recipe with respect to the other components, the monomer concentration in Phase II is very low, in comparison with the concentration maintained in Phase I, where only homopolymerization takes place. Thus, the effective propagation rate in Phase I is higher than the effective propagation and grafting rate in Phase II, and this effect is enlarged for higher initial monomer amounts and lower partition coefficients. Moreover, the strong diffusional limitations present in Phase II can reduce the apparent values for the kinetic parameters. The extended model can also be applied for multiple temperature zones and injection points.
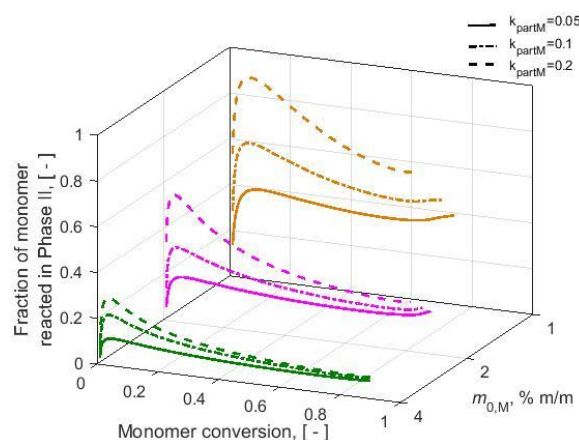
Figure 1. Effect of initial monomer mass fraction and monomer partition coefficient (Phase 2 versus Phase I) on the fraction of monomer reacted in Phase II, which contains the polyolefin chains that need to be functionalized.

4. Conclusions

A novel simulation tool to describe the kinetics during reactive processing of polyolefins has been successfully developed, accounting for phase segregation and partitioning. A design of the initial monomer amount is shown to be crucial.

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