Multi-scale reactive extrusion modelling approaches to design polymer synthesis, modification and mechanical recycling

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Kyann De Smit,[a] Tom Wieme,[a,b] Yoshi W. Marien,[a] Paul H.M. Van Steenberge,[a] Dagmar R. D'hooge[a,c]*, Mariya Edeleva[a]*

Reactive extrusion (REX) is an important processing and production technique with applications in the field of polymer synthesis, modification and recycling. A full REX design demands a multi-scale approach recognizing at the molecular scale a wide spectrum of elementary reactions, at the micro-scale viscosity variations influencing the observed kinetics, at the meso-scale multiphase and morphological variations, and at the macro-scale various screw configurations and designs. In the present contribution, an overview is given of the multi-scale modeling tools currently available to fundamentally understand REX processes, targeting a (average) chain length increase, preservation or decrease. Emphasis is on computational fluid dynamics, in general, flow oriented approaches, and classical chemical reaction engineering approaches, addressing both deterministic and stochastic solvers. To highlight the potential of the discussed modeling tools five case studies are included, considering functionalization of (bio)polymers, polymer recycling and circularity.

Introduction

In the last decades, extrusion has become one of the leading technologies for the processing of polymers and the production of polymeric products.[1-3] Extruders are nowadays so broadly employed because they combine several processing operations such as melting, transport, mixing, homogenization, pressure generation, and product shaping into one single equipment. This versatility can be achieved while dealing with highly viscous polymer melts that display Newtonian viscosities between ca. 10^2 and 10^7 Pa s.[4] As extruders are very capable of treating and shaping highly viscous melts, the interest arose to utilize them as reactors for desired chemical modifications. These modifications include the injection of chemicals once the molten state has been reached, explaining the increasing popularity of reactive extrusion (REX) for polymer synthesis and modification. [5-12]

REX is an industrially applied process that involves the main operations steps of conventional extrusion, while simultaneously carrying out chemical reactions. The application scope of REX is extensive, due to (i) excellent mixing and heat transfer capabilities, (ii) the ability for continuous production, and (iii) the combination of both compounding and synthesis in one equipment. Disadvantages can be the need of a rather low residence time and the establishment of a residence time distribution (RTD), complicating REX application with slower reactions and complex blend compositions. REX can also suffer from a lack of cooling capacity, limiting the application range for highly exothermic reactions.

Figure 1 gives an overview of common REX processes, differentiating according to the product target at the (average) chain length level, with the chain length formally defined as the total number of monomer units in a chain regardless of the topology.[5] At this chain length level, one can aim at a chain length increase, a chain length preservation or a chain length reduction. Historically, most emphasis has been on a chain length increase with the most prominent examples being chemical modification by grafting and crosslinking that have virgin pre-synthesized polymer as reactant (first three arrows in yellow middle box in Figure 1).[13, 14] In more rare cases (not shown in Figure 1), the chain length increase is realized by polymerizing (co)monomers thus executing a conventional polymerization reaction in an extruder.[15]

An example of chain length increase is grafting vinyl polymers by controlled radical polymerization techniques using reversible addition–fragmentation chain-transfer polymerization (RAFT) polymerization or nitroxide mediated polymerization (NMP) chemistries.[16] Specific polymers for this grafting are polylactic acid[17, 18] and polyethylene terephthalate.[19, 20]

---

[a] Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, 9052 Ghent, Belgium.
[b] Centre for Polymer and Material Technologies (CPMT), Ghent University, Technologiekpark 130, 9052 Ghent, Belgium.
[c] Centre for Textile Science and Engineering (CTSE), Ghent University, Technologiepark 70a, 9052 Ghent, Belgium.
* Corresponding authors: dagmar.dhooge@ugent.be, mariya.edeleva@ugent.be.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

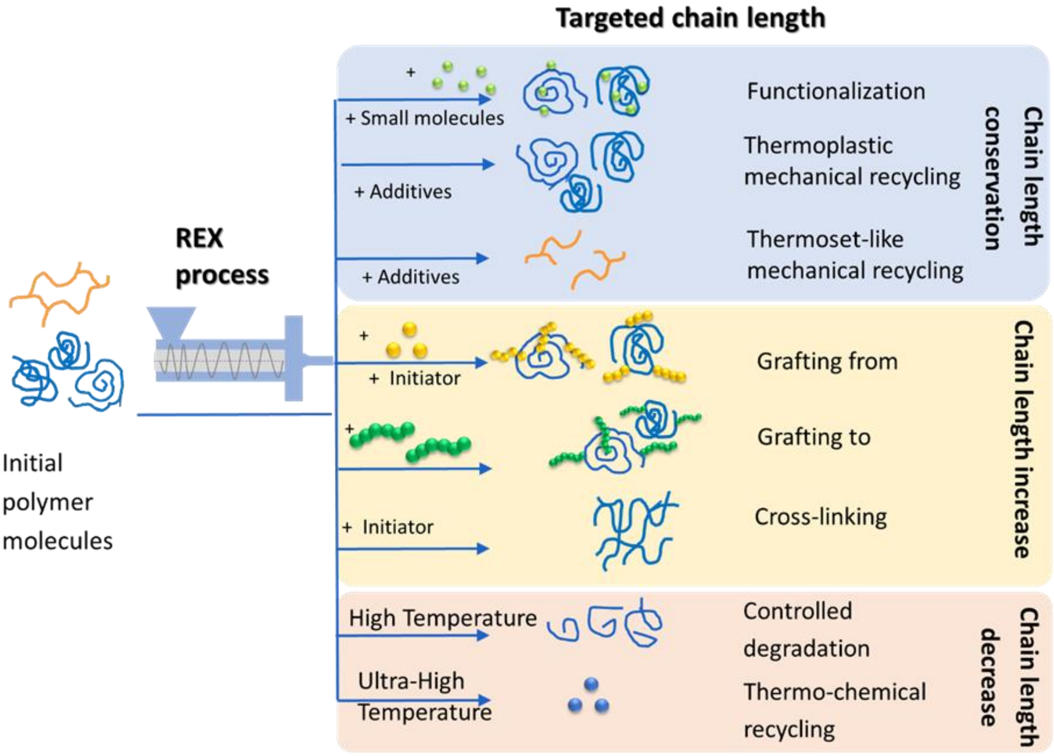


Figure 1: Common reactive extrusion (REX) process and their relation to the (average) chain length at the molecular scale; only cases shown starting from polymer molecules; the added chemicals (above the arrows) are added along the extrusion.

If chain length preservation is the target, one conventionally implies chemical functionalization in REX equipment (first arrow in top blue box in Figure 1). Such functionalization refers to the transformation of functional groups in the original polymer chains into more added value functional groups for the actual application envisaged. An example is the incorporation of maleic anhydride side moieties on polyolefin backbones to synthesize compatibilizers.[21, 22]

More recently there has been also interest to aim at chain length preservation for mechanical recycling applications.[23] A distinction can be made between the mechanical recycling of thermoplastic (second arrow in top blue box in Figure 1) and thermoset-like (third arrow in top blue box in Figure 1) materials. For the thermoplastic materials, the REX environment is utilized to conduct chain length repair and to realize small chemical modifications. The target is to reprocess recycled polymer grains or flakes, minimizing degradation and performing only very limited modifications by for instance adding only extra stabilizer.[23]

For the thermoset(-like) materials, one considers the rearrangement of the advanced chemical building blocks that these materials possess either via a light- or temperature trigger.[24-26] For more large scale objects a temperature sensitivity is more practical so that at elevated temperature one can easily open and reshuffle the dynamic bonds in the network/crosslinked materials (orange macromolecules in Figure 1). Under such conditions more conventional thermoplastic flow can be mimicked and deformations through self-healing can be applied. REX can therefore be used to decrease the (average) cross-linking density and thus reprocess and recycle crosslinked systems.[27] Upon decreasing the temperature a thermoset-like material shape again results, which possesses ideally similar macroscopic properties as the virgin material. This virgin material can be made through REX as well, again showing the flexibility of the extruder equipment. Currently, several dynamic chemistries have been developed and the term vitrimers is often employed.[28-30] A challenge remains to increase the scale-up potential of these dynamic chemistries, highlighting the need to bridge the fields of polymer chemistry and reaction engineering.

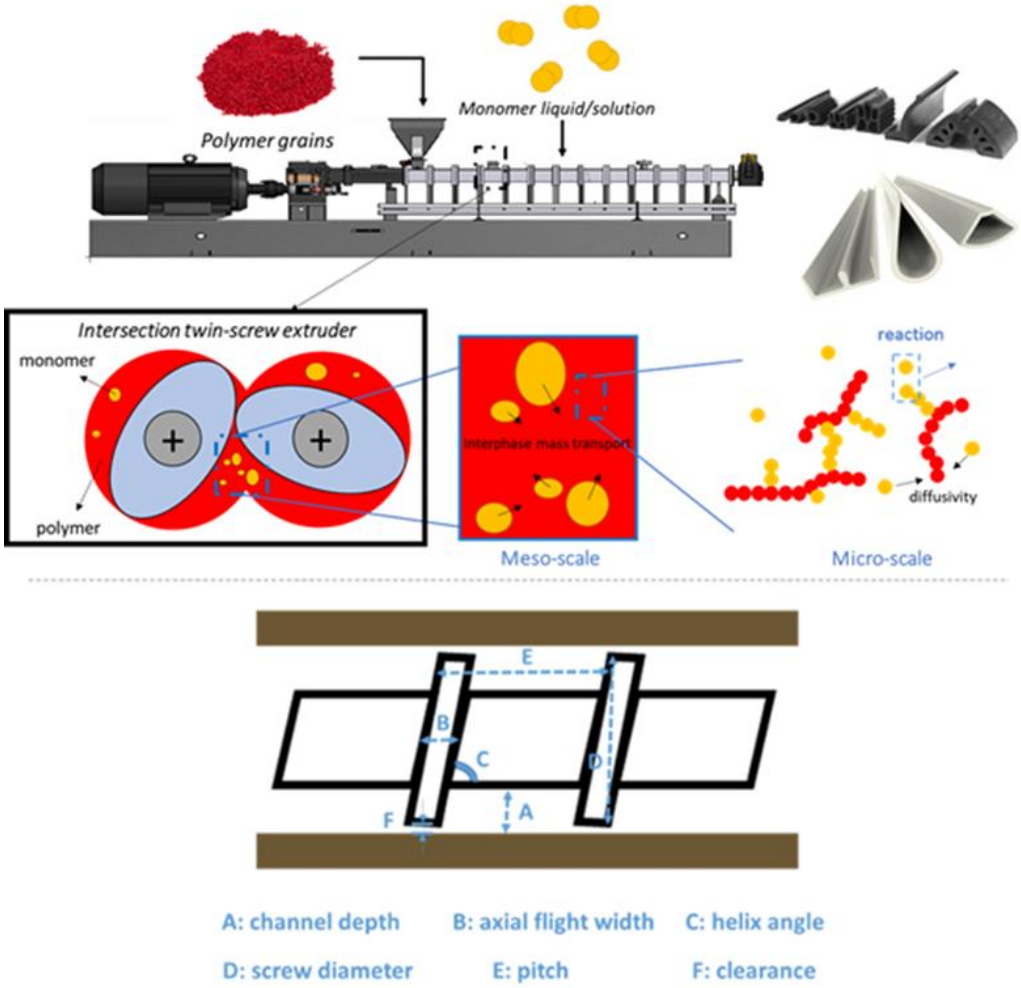


Figure 2: Top: Multi-scale character of reactive extrusion (REX), exemplified via grafting in a twin-screw extruder. The zoom of the macro- or reactor/equipment scale highlights consecutively the meso-, micro- and molecular scale. Bottom: conceptual representation of one screw part, defining typical screw variables.

As shown in the bottom salmon box of Figure 1, REX can also be applied to realize a chain length reduction.[31-33] One can make a distinction between controlled degradation and (thermo)chemical recycling. In controlled degradation, one deliberately induces (limited) fission of certain chains to tune the polymer viscosity toward a target value.[6] In (thermo)chemical recycling one aims at monomer (or oligomer) recovery thus depolymerization. The use of REX technology for these depolymerization processes is most relevant for polycondensation products. It is also relevant for vinyl polymers with a highly selective and fast formation of monomers, e.g. the formation of methyl methacrylate out of poly(methyl methacrylate) at elevated temperature.[34, 35] In contrast, for polyolefin chemical recycling, one often relies on pyrolysis.[36]

For (reactive) extrusion, a differentiation can be further made on the level of the screw configuration, with a main difference being single- and twin-screw configurations. Single screws are widely applied for more general polymer processing tasks, e.g. sheet/profile extrusion, film blowing, filament production,[37-39] while twin screws are used more for compounding and mixing purposes.[40-45] The main advantages of twin-screw extruders compared their single screw counterparts are a better mixing, a self-cleaning effect, the possibility for a modular design of the screws, and the starve fed operation mode, which means that reactant/product streams can be easily removed as the fill ratio is only partial. It is thus not surprising that REX mostly involves twin-screw adaptations as excellent mixing is necessary to obtain a sufficiently homogeneous end product.

It can be claimed that REX is one of the most economical and cost-effective techniques for polymer synthesis and modifications, due to an acceptable investment cost, the possibility of solvent-free processing, the flexibility of scale, and a comparatively small unit size. A dedicated process control is although needed as along the screw(s) there can be a strong variation of temperature, pressure (both drop and build-up), residence time, rheology, and morphology. Optimal REX processing conditions thus not only demand a detailed knowledge of the relation between temperature/pressure and chemical reactions but also an in-depth understanding of the impact of the screw and barrel settings (e.g. screw rotation speed, feeding rate, filling ratio, external heating rate, channel depth, helix angle, flight width, and screw diameter and length) on the mixing intensity to facilitate such chemical reactions.

The complexity of the flow in twin-screw extruders, including physical phenomena such as shear thinning and shear induced heat dissipation, makes REX a challenging process to operate. In this scope, a purely experimental research and design approach is not recommended, as too many process and machine variables exist.[46] Instead one needs to apply model-driven design in combination with experimental validation.

In the current contribution, it is first explained that REX design is ideally performed through multi-scale modeling. An overview is then given of the main (multi-scale) modeling approaches, making a distinction between unreactive and reactive modeling approaches on the one hand, and deterministic and stochastic modeling approaches on the other hand. The advantages and disadvantages of these modeling approaches are in a final step illustrated through five case studies. Both case studies on functionalization and recycling are addressed, considering both oil-based and biopolymers. Attention is also paid to the potential of machine learning tools for REX design.

A bridge is made between the application scope of REX and the historical modeling endeavors that have been undertaken. Even though the amount of reviews regarding REX is quite extensive,[2, 5, 6, 8, 9, 41, 47-49] most reviews have focused on the modeling progress in rather general terms or give an overview of the most important applications, starting from simplified reaction schemes.[3, 46, 50-54] Hence, this review fills a gap in the REX literature giving both an extensive overview of REX modeling approaches, and the most prominent REX applications and chemical modifications. To not overload the discussion main emphasis is on well-defined inlet streams and thus less on more advanced composite material production.

The need of multi-scale REX modeling

As explained above, REX allows to execute a wide range of chemical processes or modifications such as functionalization, degradation, recycling and the synthesis of polymeric materials. REX thus deals with a plethora of reactant and/or product streams so that in general a multiphase description is needed, also bearing in mind melting and solidification stages.

Such multiphase description goes hand in hand with a multi-scale engineering research approach, as exemplified in the top part of Figure 2, dealing with the grafting of virgin polymer backbones (colored in red) with injected monomer molecules (colored in orange). The macro-scale is defined at the equipment, hence, reactor scale. The most essential macro-scale process parameter is the screw configuration, with a definition of its main parameters provided at the bottom of Figure 2 considering two screws. The meso-scale is defined around the interface of the polymer- and monomer-rich phase, as established due to imperfect mixing and possible thermodynamic constraints, and thus this scale addresses interphase phenomena. A further zoom allows to define the micro-scale per (reactive) phase. Specifically for the polymer-rich phase there is at the micro-scale a strong competition of diffusion of molecules and reactions between these molecules, ultimately defining the molecular scale in which species are at reaction distance to perform the actual chemical modifications.[55]

In the last decades, mostly a rise in micro-scale kinetic modeling tools for chemical processes involving highly viscous polymer melts has been witnessed.[56] These developments range from the introduction of completely empirical models to more advanced kinetic models involving chain length dependent scaling laws capturing differences in diffusion modes. On the meso-scale, attention has been paid to a better understanding of mass transport and several physico-chemical parameters such as the micro-scale viscosity in a given phase and solubility limits.[57] For macro-scale modeling, a slow trend can be identified to capture in more detail local velocity field variations.[58-61] Such variations can induce spatial heterogeneity, for instance, a non-uniform distribution of monomer droplets. This is further complicated by the possibility of injecting reactants (e.g. monomer and initiator) along the axial position inside the extruder (cf. top part of Figure 2). Similarly, the pressure and temperature profile can vary along the extruder, with in the case of polymer modification/recycling a melting zone before the actual chemical modification.

A more detailed inspection of the literature for the modeling of the polymer transformation and rheology in single and twin-screw (reactive) extruders reveals that two major approaches or schools of thought can be distinguished. The first approach is computational fluid dynamics (CFD) or thus flow oriented and starts from the solving of the mass, momentum and energy balances for a given geometry. It is inherently a slower approach that is often with singularity and convergence issues for reactive (viscous) systems and restricted in application to specific (extrusion) sections.[62,63] The second approach can be classified as classical chemical reaction engineering and is based on ideal or simplified flow patterns, or cascades of reactors.[52, 64] It allows to cover chemical variations at the micro-scale in much more detail but at one point needs to more pragmatically grasp higher length scale phenomena. In other words, a phenomenological modeling approach is then applied.

One can make a further distinction between one-, two- and three-dimensional (1D, 2D and 3D) models. For example, the first models were 1D with the flow only considered to change in the axial direction of the extruder. Later on also 2D models have been developed taking into account the changes in e.g. both the radial direction of the screw and the axial direction of the screw, the latter alternatively replaced by the unwounded screw trajectory. Such flow patterns are more complex as the relative movement of the screw to the stationary barrel is taken into account. More recently also 3D models have been put forward, for both Newtonian and non-Newtonian fluids, at least for selective zones of the extruder.[65-69] The application of REX multi-dimensional models with polymer melts is although limited. Such processes are generally modeled using the second, engineering approach in which the extruder is either simplified as ideal plug-flow reactors, a cascade of continuously stirred tank reactors (CSTRs) or a network of CSTRs.

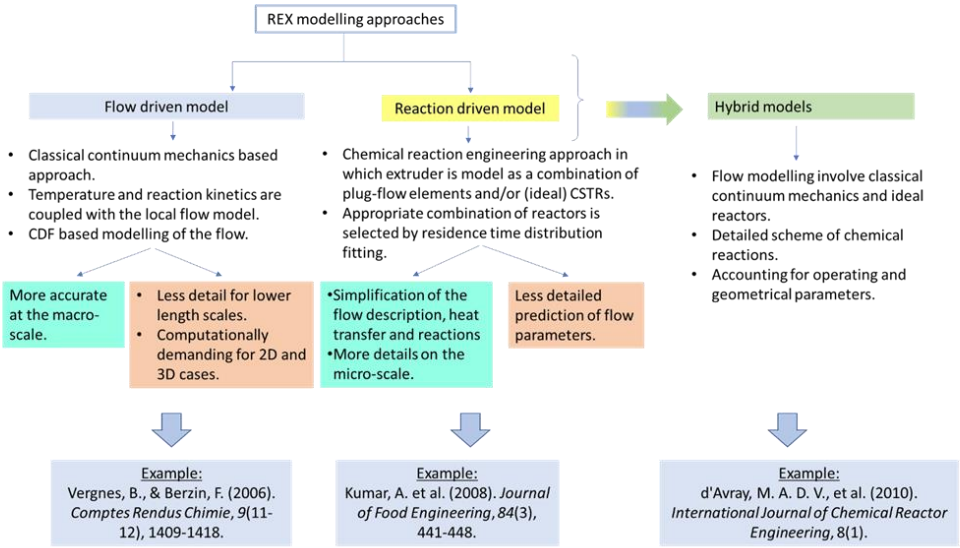


Figure 3: Overview of multi-scale modeling tools for reactive extrusion

It should be further noted that most of the modeling attempts consider a constant temperature. Non-isothermal conditions are more difficult to model, as chain movement and consequently molecular scale flow behavior is a strong function of the local temperature. Depending on the desired accuracy of the model, the effect of temperature can either be introduced by calculating a whole 3D temperature field or a 1D mean temperature that varies in the axial direction. In any case, there is need for better scale-up models.[144]

Multi-scale modeling approaches for design of reactive extrusion

Figure 3 provides an overview of the multi-scale modeling approaches currently available to describe and design REX. Consistent with the previous section, a distinction is made between models that are oriented around (i) flow and (ii) reaction. The former approach, which is denoted in the present work as flow driven extrusion modeling, is strongly interlinked with conventional "unreactive" extrusion. The latter approach, which is denoted in the present work as reaction driven modeling, is the core of the field of chemical engineering and thus puts as essential modeling feature the reactor/chemical conversion nature of the REX equipment. Also mingled approaches exist that are denoted in the present work as hybrid models. In what follows, the main characteristics of the flow driven, reactive driven and hybrid models are put forward.

Flow driven extrusion modeling

The modeling of the conventional extrusion process is often directed towards macro-scale modeling, this with a gradual expansion from 1D to 3D models. As conventional extrusion does not involve (desired) chemical reactions, the smaller length scales such as the molecular and micro-scale are of lower importance.

Because the extruder equipment is large a division in macro-scale sections is highly recommended. The common way is the consideration of separate models for the main sections taking the screw as the main differentiator. This leads to following four sections: (i) the solid transport section, (ii) the melting section, (iii) the melt conveying section, which is also known as the pumping or metering section, and (iv) the extrusion exit unit or die. In any extrusion section, nowadays mostly deterministic numerical methods are being employed such as the distinct element method (DEM) and the finite element method (FEM). In what follows, a concise overview is given of the most important flow driven models for the four main sections of the extruder. The discussion is ended with the mentioning of a global approach for the four sections together.

By far the most studied extrusion section is the melt conveying section (extrusion section 3), which encompasses the final section of the extruder excluding the die. In this section, the material inside the extruder exclusively consists of polymer melt. Thus, the modeling of mass transport mainly involves the correct description of the behavior of non-Newtonian molten fluid for a certain screw configuration. To lower the mathematical complexity, the first models were 1D isothermal Newtonian models to allow for drag and pressure flow contributions.[70, 71] Later on these models have been expanded towards non-Newtonian fluids, first with correction factors starting from the Newtonian solutions. These models initially considered the flow of material through a rectangular channel of infinite width with formally the barrel rotating around a stationary screw. Later on these models have been improved considering 2D and 3D flow with thermal/mechanical coupling. It should be stressed that for the melt conveying section in an extruder, or more general for viscous polymer streams in a given reactor environment, flow driven models accounting for chemical reactions are very rare. Only more recently the first attempts have been made but there the flow modeling is mainly limited to microreactor channels[72, 73] or even basic batch reactors.[74-76]

Benefiting from the progress in modeling the flow, in the conventional melt conveying section, also attention has been paid to the modeling of only the extrusion exit flow out of the die mounted at the end of the extruder (extrusion section 4). For a detailed overview of the modeling efforts, the reader is referred to the recent review of Tang *et al*.[77]

For the modeling of the solid transport zone (extrusion section 1) simplifications have are typically made. This section consists of the hopper and the first few pitches of the screw and the first models describing the conveying of solids in the extruder assumed that the polymer pellets are moved as a solid block.[78-80] This is defendable, at least to a certain degree, if the screw channel below the hopper is completely filled and because the internal friction of the polymer pellets is likely much greater than the friction at the (steel) screw and barrel wall. These types of models have been optimized and refined throughout the years starting from isothermal models with isotropic pressure distributions, ultimately leading to models accounting for the interplay of both physical and geometrical parameters.

Despite that the above mentioned solid-based models have been used and researched intensively for the modeling of the first extrusion section, more recent research has pointed out that relative movements of the granules inside the screw channels can be encountered.[81-84] This has led to the usage of other techniques, mostly DEM, for modeling the transport of solids in a single screw extruder. DEM is a very useful tool for modeling the transport of solids in extruders, with (i) each polymer granule approximated by a rigid sphere and (ii) the interaction of the granules with each other and with the screw and barrel modeled, using simple impulse and frictional forces resulting from collisions.[85] DEM is particularly useful for non-continuum substances, which is why FEM is rarely used for modeling the solid transport section of the extruder. The downsides of the DEM technique are the generally long simulation times and the difficult measurement of some input parameters such as the coefficients of friction and restitution.

The melting section (extrusion section 2), which relates to the description of the melting of solid polymer pellets into a viscous continuous polymer melt, has mostly been studied in a single screw extruder. Experimentally, melting tests have been originally performed using the screw pulling out technique or screw-freezing experiments, in which the screw movement is stopped in full operation and then the screw and polymeric material are cooled down rapidly.

One of the first researchers to obtain a significant understanding of the melting mechanism in an extruder was Maddock.[86] Numerous research has extended the work of Maddock, however, the basic principles remained relatively unaltered, even for the recent field of pellet-driven additive manufacturing or 3D printing.[87, 88] According to Maddock, the melting mechanism of polymer pellets in an extruder is contiguous solid melting or melt removal by drag. According to this mechanism, a layer of polymer melt is formed between the heated barrel and the bulk of the polymer pellets. This film is dragged by the barrel surface and as the film reaches the edge of the advancing flight it is mixed with previously melted polymer. Along the axial direction of the extruder, the portion of the solid polymer pellets gradually decreases and the channel is filled with more and more molten polymer.

The disadvantage of the Maddock model is that a prior melting mechanism of the polymer is assumed, which is likely invalid for all polymer materials, screw geometries and processing conditions, limiting the application range of the melt removal by drag models or making it in certain cases only a qualitative model. Researchers have therefore recently opted to simulate the melting of polymer by solving the conservations equations of mass, energy and momentum, leading to the utilization of FEM/CFD approaches with both 2D and 3D adaptations. [89]

Several research groups have also tried to connect the macro-scale models per section along the extruder. One can aim at a local accurate description of the flow field with high computational cost but from a more pragmatic point of view it is worthwhile to aim at a global description for the whole REX process thus from hopper to die (or reverse). This global approach of modeling (twin-screw) extrusion is essentially a series of simplified (1D) local approaches to obtain a realistic description of twin-screw extrusion whilst decreasing the computational demand. One of the most known global 1D models is the Ludovic© software package.[71] These types of models focus more on the description of flow in the melt-conveying section and use severe simplifications for the other sections. Specifically, for the description of flow in a twin screw extruder, the global model can make a distinction between flow in the C-shaped screw elements and the flow in the intermeshing area between the screws. The flow in C-shaped screw elements has been studied intensively and is typically handled in 1D or 2D. However, the intermeshing area is much more complex which makes a full 3D simulation more ideal. Vergnes *et al.*[90] showed that a simplified modeling approach is still very able to describe the flow in screw elements, but for the description of the flow inside other screw elements such as kneading disks, more advanced 3D simulations might be more opportune.

It is further worthwhile mentioning that the strong side of the flow driven models is the possibility to address dispersive mixing during REX. An example is the work of Komolprasert *et al*.[91] who studied bacterial starch liquefaction. While addressing mixing in rather high detail, the authors approximated the reaction kinetics by a pseudo-first-order reaction. It is further interesting to note that flow driven models can address micromixing effects which are challenging to access with other approaches.[92]

Flow-driven models find application is the description of the polymer synthesis as well as exemplified by Cegla *et al.*[93]

Reaction driven extrusion modeling

To account more in detail for the reactive part of REX one needs to sacrifice the level of flow detail, hence, apply a more phenomenological modeling approach, consistent with classical chemical engineering modeling approaches. Most known is the consideration of series of chemical reactors to represent the overall behavior in the (twin-screw) extruder. Such reactors are typically (ideal) continuous stirred-tank reactors (CSTR's) or plug-flow reactors (PFR's).[9] Depending on the geometry the screw profile is described by a certain number of these reactors that can additionally include backflows. In parallel, kinetic equations for chemical variations and energy balances can be written down to simulate the REX process, either under steady-state or non-steady-state conditions.

It should be stressed that also the reaction driven models still have many assumptions. An example is the nature of the kinetic equations that are generally established under static and isothermal conditions, very far away from the stronger conditions encountered in the extruder. The reactive medium is also often assumed to be homogeneous so that the reagents are supposed to be instantaneously perfectly mixed with the molten polymer. One can although expect that in some cases local mixing should be evaluated and so that mixing efficiency should be at least formally introduced as a parameter in the kinetic equations to account for heterogeneity. In addition, degradation of (polymeric) reactants due to the very high temperatures and the formation of local hotspots is likely but often not accounted for. There is also the possibility of a multiphase REX system, as typically the inlet streams are not based on one composition. Upon dealing with for instance reactive blends the morphological changes are relevant and thus a meso-scale layer should be embedded. The amount of descriptive models for multiphase behavior is although limited and most of them deal with a minor phase dispersed in a matrix of another component. [50, 94]

A distinction can be made between deterministic and stochastic reaction-driven modeling approaches. The majority of research efforts regarding the modeling of reaction driven REX have been deterministic in nature, although stochastic models also exist. Generally, deterministic models focus more on the description of the macroscale properties, while the focus of stochastic models is usually on the accurate description of the microscale kinetics and mesoscale mass transfer phenomena.

Within the deterministic models a key question is the sufficiently accurate representation of the left-handed and right-handed screw elements as CSTRs with possible backflows. Most studies are in agreement for these basic screw elements, however, for more complex elements such as the kneading disks and the die, different approaches exist. Choulak *et al.*[52, 95] only considered a cascade of CSTRs, where both the kneading disks and the die have been linked to CSTRs with flow rate expressions depending on the geometry. Other studies have shown that the flow in kneading disks is significantly different from the flow in conventional screw elements and therefore introduced formal corrections factors accounting for the possibility of upstream and downstream drag flow components. Dies are commonly considered ideal plug-flow reactors in which the residence time is determined by the die free volume and the volumetric flow rate. [96] Note that the deterministic kinetics are also simplified significantly on the chemical level, commonly making use of total reaction rates or very toned-down reaction schemes.

Stochastic models on the other hand focus on the detailed description of the kinetics, micro- and meso-scale phenomena to obtain correct input results for the macroscale process.[54, 97] While deterministic models aim mainly to predict the correct RTD and somewhat less on the (distributed) molecular properties (e.g. grafting density, functionalization degree, average chain length), the current stochastic models do quite the opposite. Most promising are here coupled-matrix based simulations as introduced by De Keer *et al*.[98] and Figueira *et al*.[99] to show the detailed chemical compositions of all molecules, also including crosslinked ones.

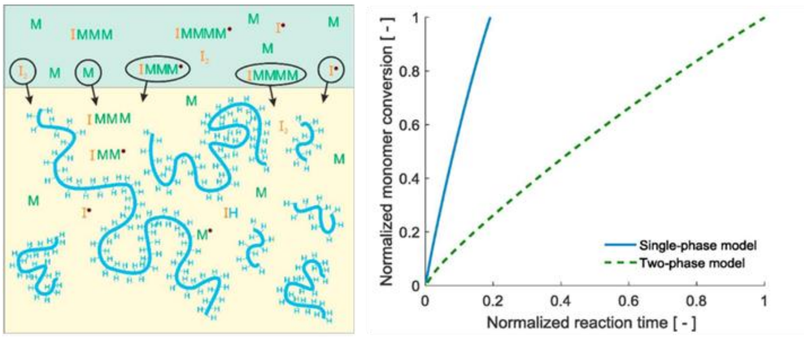
The reaction driven approach has been mostly applied for modification of oil-based polymers. This approach is in contrast rare for starch biopolymers, as the number of reactions can be high and the reaction mechanisms are not always clear. Furthermore, a highly viscous medium affects the apparent reactivity and the diffusion models for (biopolymer) melts under high shear stress are not well established yet. An example of rheokinetic modelling of acrylamide graft copolymerization with starch (related to REX) can be found in work of Bao *et al*.[100] Similarly, Wang *et al*.[101] addressed phase transitions during starch-water interaction even though the authors did not account for flow patterns.

The reaction-driven models can also describe the synthesis of polymers via REX. A key example is the work of Cong *et al.*[93] who described the synthesis of flame-retardant polyurethanes. The authors used the link between the torque and extend of the reaction to increase the relevance of their modeling effort.

Hybrid models

To construct highly predictive models for REX of polymers, a flow model, a heat transfer model and a reaction model should be ideally coupled together. Depending on the approach, i.e. flow driven or reaction driven, the models are typically applied to different processes. An intermediate solution is a hybrid (flow reaction) driven model.[102, 103]

For example, the base for the flow modelling part can be the Ludovic© software, as exemplified by simulations of starch cationization via REX by Tara and collaborators.[104-106] From a rheokinetic point of view, this REX modification is simple as no significant changes in the molar mass of the starch molecules occur. Thus the authors could derive a power-law dependence between the viscosity, and the temperature and specific mechanic energy.[106, 107] For the kinetic model development, the authors used batch experiments and derived a so-called effective kinetic equation which links the reaction time to the degree of substitution.



(a) (b)

Figure 4: (a) Mass transfer for a two-phase system in a reactive extrusion (REX), aiming at free-radical induced grafting of monomer (M) on polyolefin chains using initiator fragments I; (b) relevance of two-phase kinetic model to accurately grasp the REX characteristics by including a theoretical comparison with one phase kinetics for the simplified case of a monomer that adds only one time. Both subfigures are reproduced from Ortiz *et al.* [108] Published with permission of Elsevier, copyright 2022.

For completeness it is mentioned here that a specific version of Ludovic© software has been developed, which accounts for changes in viscosity.[106] In this case more sophisticated chemical processes via REX, e.g. controlled degradation or polymerization, can be simulated more accurately.[106]

The work of Morales-Huerta *et al.*[109, 110] exemplifies the usefulness of hybrid REX models as well. In particular, he authors combined a scheme of 5 reactions and reduced flow equations obtained from simplification of the Navier–Stokes equations to describe the pre-treatment of lignocellulosic biomasses in twin screw extruders. The model allowed for accurate description of the experimental data.

Finally, for the hybrid (and the flow-driven) models, the description of the flow patterns should depend on the construction of the screw elements. For the right-handed screw element the drag flow and the pressure rate leaving reactor can be calculated based on the description of Booy *et al.*[111] A model for the kneading blocks has been proposed by Choulak *et al.*[52] and d'Avray *et al*.[96] Recently, Cegla *et al.*[112] reviewed the flow modelling approaches depending on the screw element geometry and they proposed an improved description of the backflow modelling.

Case studies

To further demonstrate the working principles of the multi-scale models in Figure 3, in this section, five case studies are included. The first two case studies deal with functionalization of the backbones of polymer chains, considering in Case study 1 polyolefins, hence, vinyl polymers, and in Case study 2 starch molecules, thus biopolymers. In the next two case studies emphasis is on recycling of polymers, with in Case study 3 focus on mechanical recycling for (epoxy-amine-acetoacetate based) vitrimers and in Case study 4 emphasis on chemical recycling of polyacrylics. In Case study 5, the relevance of machine learning tools is illustrated.

In each case study, attention is paid to the reaction scheme and the main modeling assumptions are discussed to then highlight typical modeling outcomes. These modeling outcomes are related to specific length scales so that the five case studies together highlight results from the molecular to the macro-scale as defined in Figure 2.

Functionalization of polyolefins: meso-scale interphase transport influencing process intensification

REX is often used for modification of polyolefins A crucial step in REX functionalization and chain length increase is frequently the injection of small molecules in a viscous medium. As mixing is likely non-instantaneous and the time scales for chemical modification are low (e.g. residence times of only a couple of minutes) the likelihood of a multi-phase reactive system is high. A natural question coming forward is whether the functionalization kinetics are altered because of the presence of several phases or one can simply assume perfect mixing and thus one phase behavior.

In this respect, the work of Ortiz *et al.*[108] dealing with free radical induced grafting (FRIG) of polyolefins, either with a monomer that can easily polymerize, thus with significant monomer addition leading to rather high graft lengths, or a monomer that can only participate in one addition, is one of the few modeling studies allowing a deeper understanding of the relation between multiphase composition, and FRIG kinetics and performance. These authors introduced a meso-scale in their multi-scale *k*MC model to explicitly describe if species could be transferred from one phase to the other, as conceptually illustrated in Figure 4(a) with the top green layer being the monomer-rich phase and the bottom yellow layer the polymer-rich phase. Micro-scale parameters have been assessed in a first step under very dedicated in the limit one phase conditions, as achievable through very long mixing times and less severe reaction conditions. In a next step, mass transfer parameters have been assessed under industrially relevant two-phase REX conditions.

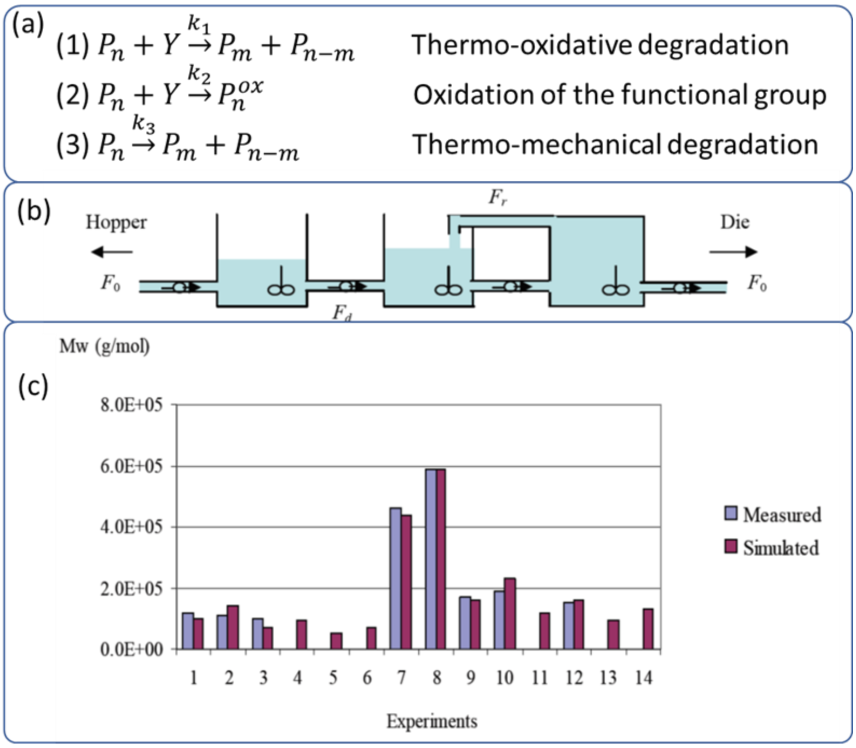


Figure 5. Macro-scale modeling of reactive extrusion, focusing on the oxidation of starch biopolymers (a) Relevant reactions; (b) the reaction driven approach for the melt section of the extruder (F_0 = feed rate, F_d =drag flow, F_r = pressure flow). (c) Comparison of measured and simulated mass average molar masses. Reproduced from d'Avray *et al.*[96] Published with permission of Berkeley electronic press, copyright 2022.

Figure 4(b) shows that a REX functionalization under multiphase conditions displays different chemical kinetics compared to its simplified countercase of one phase conditions. Emphasis is on a monomer (e.g. maleic anhydride) that only adds one time to a polyolefin chain that has undergone hydrogen abstraction. It follows that the (normalized) monomer conversion increases faster in the one-phase theoretical case (full blue line), as the whole reactive system can then witness micro-scale diffusional limitations on termination. In contrast, in the two-phase system, such limitations are not that relevant in the less viscous monomer-rich phase, explaining the lower position of the dashed green line in Figure 4(b). In general, in the two-phase system there is competition between mass transfer and chemical reactions which is absent by default in the one phase model, again highlighting the relevance of the meso-scale consideration.

Macro-scale challenges for chemical modification of starch polymers

Due to the recent environmental regulations, societal challenges and growing environmental understanding throughout the world, renewed efforts have emerged in the polymer industry to develop new products and processes compatible with our environment. The design of biodegradable and bio-based plastics is an appropriate, eco-efficient approach to enhance the environmental quality of many products. [113-116] Up until now, many biodegradable plastics still struggle to compete with petroleum-based bulk products especially in terms of cost-competitiveness and thermo-mechanical properties. To increase their commercial scale-up and competitiveness while still maintaining biodegradable properties, these type of polymers are generally mixed with organic/inorganic fillers. To ensure high product quality, the dispersion and interfacial adhesion between the fillers and the polymer material is of the utmost importance, explaining why REX has emerged as the go-to processing technique for biopolymers. As no solvents are strictly required, REX seems to be even more promising, as natural and biopolymers are hard to solubilize.

Starch being the most abundant natural feedstock for sustainable polymers has been successfully processed by REX for various applications such as enzymatic hydrolysis,[117-119] oxidation,[120] esterification,[121, 122] cationization[123, 124] grafting of the maleic anhydride[13] as well as grafting and blending with synthetic polymers.[3, 125-128] However, optimization and scale-up remain a challenge because of the strong coupling between flow characteristics, rheological behavior, thermal evolution, and reaction kinetics.[129] Additional challenges relate to the modular configuration of the extruders possessing various screw geometries and temperature profiles. From this point of view model-guided optimization at the macro-scale is recommended.

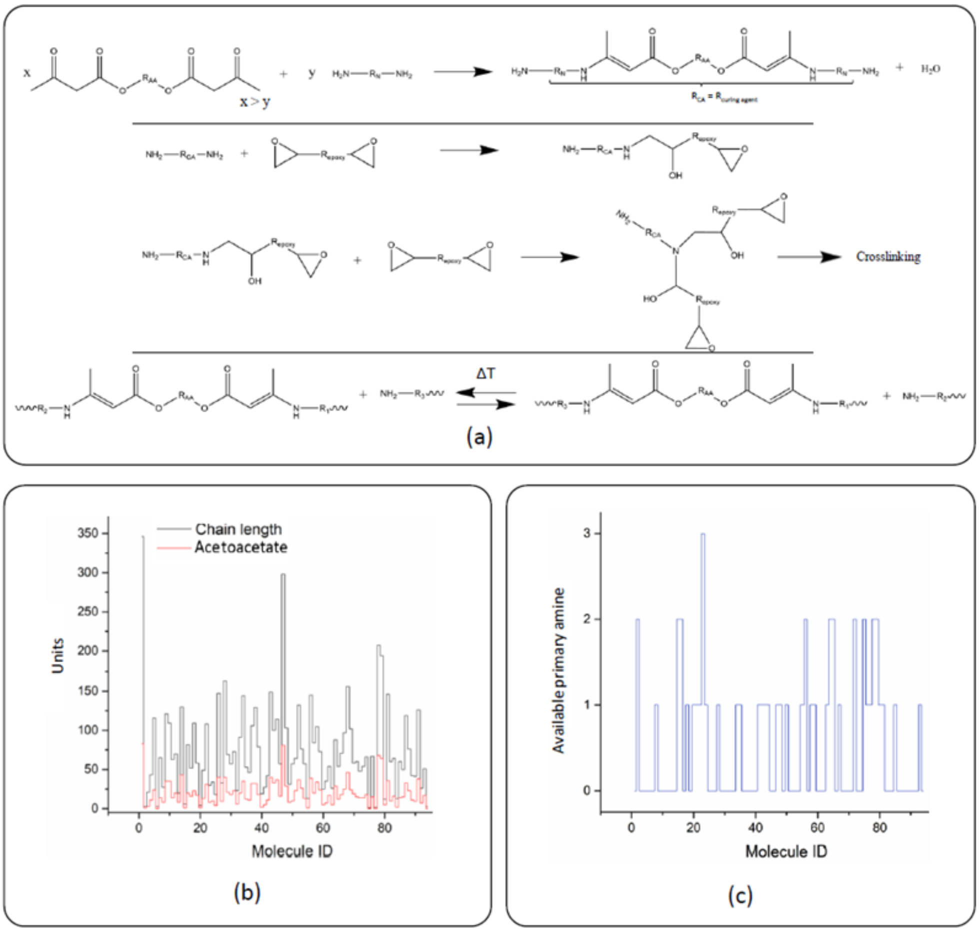


Figure 6: (a) Reaction chemistry of synthesizing mechanically recyclable dynamic networks based on acetoacetate, amines and epoxy functionalities, i.e. vinylogous urethanes vitrimers; (b) and (c) relevance of molecule-to-molecule deviations as modeled through the principles outlined in De Keer *et al.* [98] and the (intrinsic) model parameters and reaction conditions listed in Figure S1 of the Supplementary Information; in b total monomer units (chain length) and number of acetoacetate units per molecule, and in c available primary amines per molecule. Focus on ca. 100 molecules for illustration purposes.

One of the most advanced macro-scale REX models has been described by d'Avray *et al*.[96] These authors presented simulations of the oxidation of starch biopolymers, selecting the deterministic reaction driven approach and the reactions in Figure 5(a). Several chemical transformations occur during this REX oxidation, i.e. polymer functionalization with carbonyl and carboxyl groups, and chain scission. The latter reaction results in a significant change of the average molar mass. Hence, the viscosity changes cannot be neglected as in a typical cationization REX case. [130]

In the model, d'Avray *et al.*[96] addressed flow patterns by taking into account simplified fluid mechanics laws and geometrical parameters, as proposed by Choulak *et al*.[131] More in detail they used CSTR and plug flow ideal reactor models to simulate the screw elements in the extruder with calculation of the drag and pressure flows, as depicted in Figure 5(b). Additionally, these authors accounted for the differences in the flow patterns for the kneading blocks by subdividing the drag and pressure flows into downstream and upstream components. The heat transfer has been modelled by implementation of the energy balance equations for each of the screw elements represented by an ideal reactor model. The kinetics of the chemical reaction has been modeled based on the solution of population balances, allowing to model the evolution of (the averages of the) molar mass distribution (MMD).

The authors obtained an excellent agreement between experimental and simulated residence times, average molar masses of the products (Figure 5(c)), degree of functionalization, and specific mechanical energy, highlighting the relevance of the modeling approach combining a sufficiently detailed reaction scheme with a sufficiently advanced flow model.

Another interesting study is the one of Morales-Huerta *et al.*,[109, 110] who applied a similar approach to d'Avray *et al*.[96] In particular, the authors described an extruder as a cascade of CSTRs, considering a detailed reaction scheme. The flow is described based on Navier-Stokes equations, considering for simplicity isothermicity. Nevertheless, the model provides accurate description of the experimental data under a broad range of conditions, e.g. reagent concentration, temperature, and screw speed.

Mechanical recycling of vitrimers: molecular scale insights in dynamic bond exchanges of crosslinked molecules

A more recent chemistry trend is the introduction of dynamic bonds in crosslinked or network polymers that enable reshaping upon for instance a temperature increase, thereby displaying mechanical recycling potential. In the present case study emphasis is on vinylogous urethane vitrimers, as developed in the research groups of Du Prez and Winne. [28, 132, 133]

As shown in Figure 6(a) (first row), in that chemistry, precursor species are first synthesized by adding an access of bis-amine to bis-acetoacetate, resulting in a curing agent with primary amines as terminal groups and vinylogous urethane bonds that will later serve as reversible thus dynamic bonds. These precursor curing agents are subsequently reacted in the presence of bifunctional epoxy-capped species to form epoxy-amine-based crosslinks. This crosslinking is highlighted in the second and third row of Figure 6(a), making differentiation between the attack of a primary and secondary amine. As acetoacetate-amine-based bonds or so-called vinylogous urethanes are present in this crosslinked system, dynamic exchanges in the form of transamination of the vinylogous urethanes are possible at elevated temperature, as shown at the bottom row of Figure 6(a).

From a chemistry point of view it is worthwhile to explore molecule-to-molecule deviations, as it can be expected that the number of dynamic bonds per molecule matters in the mechanical recycling potential. Figure 6(b) and Figure 6(c) demonstrate that indeed such deviations exist by displaying for 100 molecules (or so-called molecule ID's) the simulated total number of monomer units (black), the simulated number of acetoacetate monomers units (red), and the amount of free primary amine units enabling further exchange (blue). This is theoretically done for a precursor curing agent synthesis with 3000 bis-amine monomers and 1900 bis-acetoacetate monomers at 298 K until 100% yield. The crosslinking synthesis is conducted by adding 2100 bis-epoxy monomers to the curing agent from the previous step at 298 K up to 99% epoxy conversion. The simulation results have been obtained following the *k*MC framework of De Keer *et al.*[98] and the model parameters listed in Figure S1 of the Supplementary Information. The pre-exponential factor for secondary reactions on amines has been increased for model testing purposes. For simplicity intrinsic kinetics are assumed so that simulated deviations are of a pure molecular nature and thus viscosity effects as defined at the micro-scale are still ignored.

It follows from Figure 6(b) that all molecules contain acetoacetate monomer units in quantities relatively identical to the initial ratio of the amount of acetoacetate groups to the total amount of monomer molecules. This makes sense, as all the acetoacetate molecules have reacted in the first step in Figure 6(a), and are thus encapsulated in between amine-bonds. It should however be realized that the absolute acetoacetate amounts differ due to the inherent stochastic nature of polymerization kinetics,[98] leading to various chain lengths. The availability of primary amines in Figure 6(c) is very limited with either no contribution or at most three, highlighting the relatively restricted exchange potential of the theoretical/intrinsic system under investigation as defined by the parameters in Table S1 of the Supplementary Information.

Chemical recycling of polyacrylics: micro-scale chain-to-chain deviations

Opposed to mechanical recycling of polymers one can also conduct (thermo)chemical recycling. For polyacrylics, as shown by recent research,[34] REX is an interesting reactor technology. Most emphasis has been on the chemical recycling of poly(methyl methacrylate) (PMMA) homopolymer, aiming at its transition at elevated temperature into methyl methacrylate (MMA) monomer through the top reaction in Figure 7(a). However, side products, including the formation of so-called heavies and volatile compounds,[134] cannot be avoided.

Not all polyacrylics are although homopolymers and in general a certain comonomer content can be expected in a given chain. Limited variations in the unzipping reactivity are likely within the same monomer family (thus methacrylates) but significant variations are anticipated for another monomer family such as acrylates, as recently highlighted in Moens *et al.*[134] As shown in Figure 7(a), acrylate radicals are in principle of the secondary type and methacrylate radicals of the tertiary type. As secondary radicals are less stable than tertiary radicals one can thus obtain a less facile unzipping for a copolymer with a main methyl methacrylate backbone but also incorporated acrylate units.

Recently, De Smit *et al.*[34] applied coupled matrix-based kinetic Monte Carlo simulations to study the polymerization and depolymerization kinetics of vinyl homo- and copolymer chains. Thanks to the explicit positioning of functional groups or monomer units in the chains, dedicated growth and unzipping pathways are within reach. An essential consideration are diffusional limitations on the micro-scale, specifically during the (co)polymer synthesis phase inducing chain-to-chain-deviations. To further illustrate in the present work the typical output of such simulations, in Figure 7 a comparison is made between an acrylic homo- and copolymer, focusing for simplicity only on two reaction times and the parameters in Table S2 of the Supplementary Information that are merely inputted for illustration purposes.

More in detail, in Figure 7, the unzipping behavior of a PMMA homopolymer and a PMMA copolymer with a small amount of an acrylate comonomer (5%) is dealt with formally considering the unzipping of 1000 homopolymer macroradicals (Figure 7(b) and Figure 7(d)) and 1000 copolymer macroradicals (Figure 7(c) and Figure 7(e)). After a time t_1, starting at time t_0, a significant reduction of the length of the radicals has occurred for the homopolymer (Figure 7(d)), with some radicals even completely unzipped as highlighted by the empty rows. In contrast, for the copolymer (Figure (e)) only a small reduction of the length of the radicals has occurred (limited white spaces).

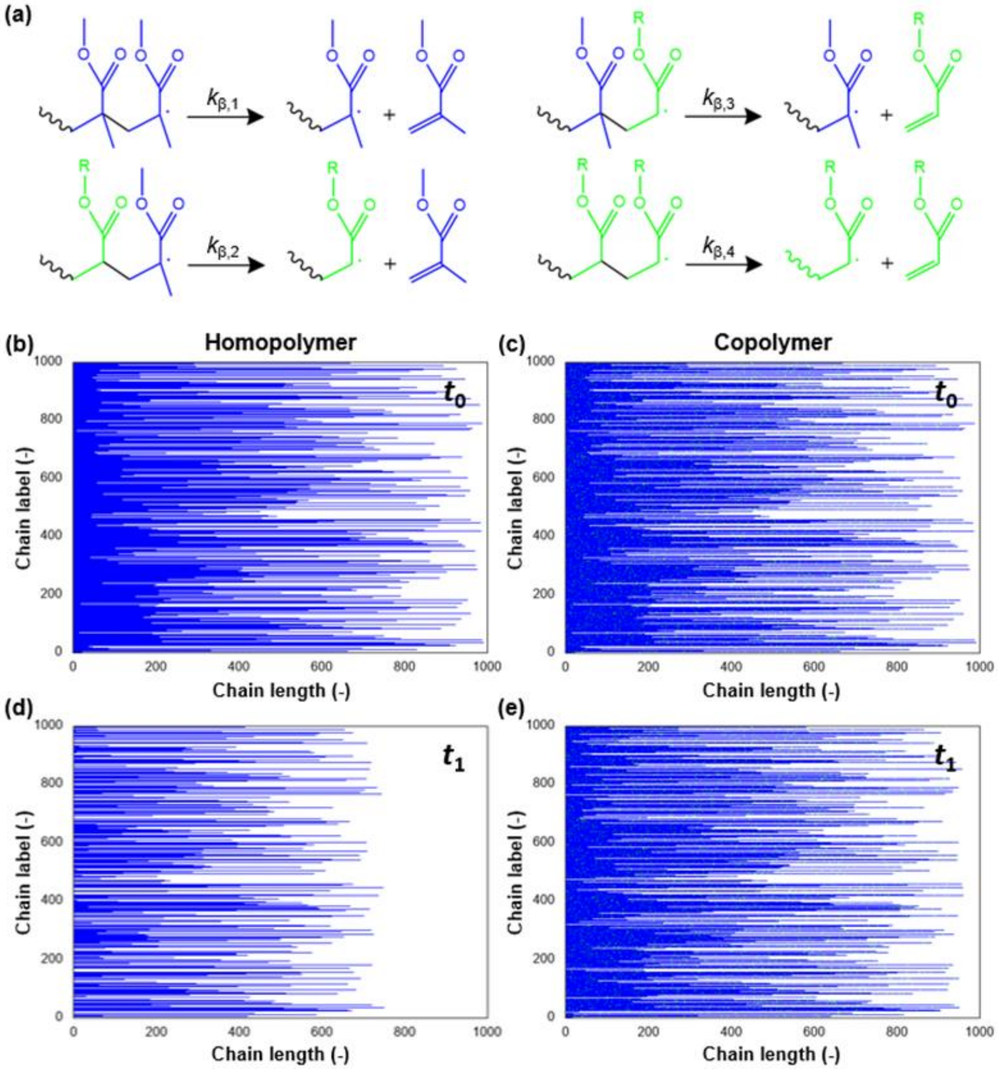


Figure 7: (a) Unzipping reactions for chemical recycling of poly(methyl methacrylate) and a related copolymer including acrylate comonomer moieties with an ester side-chain group R, as discussed in detail in Moens *et al.*[134]; (b-e) Formal visualization of 1000 unzipping radicals at two time stamps t_0 and t_1 using coupled-based kinetic Monte Carlo simulations as applied in De Smit *et al.*[34] (b,d): case of PMMA homopolymer; (c,e) case of PMMA copolymer with 5% acrylate units; blue: MMA unit, green: acrylate unit. Model parameters in Table S2 of the Supplementary Information.

This confirms the retardation that occurs if after the fast unzipping of an MMA-segment a macroradical with a penultimate acrylate unit is obtained. This leads to a β-scission thus depolymerization reaction occurring with a significantly lower rate coefficient ($k_{\beta 2}$ in Figure 7(a)), due to the transition of a tertiary to secondary radical.

Novel trends in optimization of multi-scale models

The four case studies described above show that REX models contain many parameters at different length scales. Hence, the application of artificial intelligence algorithms and artificial neural networks (ANN) can be beneficial as they are applicable for pattern recognition and can handle the non-linearity of the chemical processes.

The very first promising results of combining ANN and reaction driven modeling for the optimization of nylon-6,6 polymerization process through REX have been presented in a series of works by Nascimento and collaborators[135-138] a decade ago. These authors used lab-scale and industrial data for ANN training and then applied the simulations for the process optimization, allowing for a production increase by 20%.

Furthermore, Mehralizadeh *et al.*[139] applied ANN for the optimization of polystyrene and ABS reactive blending. The ANN model has been trained based on the experimental data and the authors aimed at the highest possible tensile properties of the blend while optimizing through non-linear relations the ABS content and REX conditions. Another example of data-driven modelling has been provided by Ibañez *et al.*[140] The authors optimized maleic anhydride grafting to the polypropylene. Despite the limited amount of data the authors could construct a model that relates material properties and process parameters in REX cross-linking. Another example is the work of Teixeira *et al.*,[141] who used the reduced Pareto set genetic algorithm to identify an optimal screw configuration for the cationization of starch via REX. These authors defined conflicting objectives, such as minimizing the specific mechanical energy and maximizing the output and reaction efficiency.

The ANN model can employ both flow and reaction driven model results as input. In a broader context, a new type of hybrid models has been established. This has been demonstrated with reasonable success by Castéran *et al.*,[142] who developed an ANN model combined with flow simulations provided via Ludovic© software. This was done considering experimental data on torque, pressure, engine power, and exit temperature for a REX aiming at the reaction of polyethylene oligomer with a triamine or a sorbitol, while dispersing in a polypropylene matrix.

Another approach is the development of semi-empirical models based on multivariate data analysis.[143] This approach is specifically valuable for in-line process control.

Conclusions

Reactive extrusion (REX) is a versatile technology to synthesize, chemically modify and recycle polymers. Many multi-scale design parameters matter and, in this context, modelling approaches are highly recommended.

Despite that there has been extensive research on developing a quantitative and scientific understanding of the fluid mechanics and transport phenomena that dictate the performance of conventional extrusion machines, limited effort has been devoted to the coupling of fluid mechanics and transport phenomena with polymer reaction engineering thus multi-scale REX design. Most modelling approaches in REX are thus based on a classical chemical engineering approach with reactors in cascades. Nevertheless there is a trend to account for more length scales, specifically the micro-scale with the emerging trend of kinetic Monte Carlo simulations. The above findings have been further illustrated through five case studies.

The current review highlights that bridging polymer chemistry and engineering or in general reaction chemistry and reaction engineering is an added value tool for future design of sustainable processes and scale up.

Author Contributions

All authors contributed equally.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

K. D. S. acknowledges support by the Fund for Scientific Research Flanders (FWO Flanders) through an SBO-project (1SB0619N, 2019-2020). D.R.D. acknowledges FWO through G.0H52.16N. P.H.M.V.S. acknowledges FWO through a postdoctoral fellowship. D.R.D. also acknowledges the Flemish Government and Flanders Innovation & Entrepreneurship (Vlaio) through the Moonshot project P2C (HBC.2019.0114).

Notes and references

1. Lafleur, P. G.; Vergnes, B., *Polymer extrusion*. John Wiley & Sons: 2014.
2. Raju, G.; Sharma, M. L.; Meena, M. L., Recent methods for optimization of plastic extrusion process: a literature review. *International Journal of Advanced Mechanical Engineering* **2014,** 4, (6), 583-588.
3. Raquez, J. M.; Narayan, R.; Dubois, P., Recent advances in reactive extrusion processing of biodegradable polymer-based compositions. *Macromolecular Materials and Engineering* **2008,** 293, (6), 447-470.
4. Young, R. J.; Lovell, P. A., *Introduction to polymers*. CRC press: 2011.
5. Brown, S. B., Chemical processes applied to reactive extrusion of polymers. *Annual Review of Materials Science* **1991,** 21, (1), 409-435.
6. Beyer, G.; Hopmann, C., *Reactive extrusion: Principles and applications*. John Wiley & Sons: 2018.
7. Li, T.-T.; Feng, L.-F.; Gu, X.-P.; Zhang, C.-L.; Wang, P.; Hu, G.-H., Intensification of Polymerization Processes by Reactive Extrusion. *Industrial & Engineering Chemistry Research* **2021,** 60, (7), 2791-2806.
8. Janssen, L. P., *Reactive extrusion systems*. CRC Press: 2004.
9. Cassagnau, P.; Bounor-Legaré, V.; Fenouillot, F., Reactive processing of thermoplastic polymers: a review of the fundamental aspects. *International Polymer Processing* **2007,** 22, (3), 218-258.
10. Thomas, S.; Yang, W., *Advances in polymer processing: from macro-to nano-scales*. Elsevier: 2009.
11. Tzoganakis, C.; Zhu, S., Reactive Extrusion of Polymers. *Encyclopedia of Polymer Science and Technology* **2002**.
12. Crawford, D. E., Extrusion–back to the future: Using an established technique to reform automated chemical synthesis. *Beilstein journal of organic chemistry* **2017,** 13, (1), 65-75.
13. Raquez, J.-M.; Nabar, Y.; Srinivasan, M.; Shin, B.-Y.; Narayan, R.; Dubois, P., Maleated thermoplastic starch by reactive extrusion. *Carbohydrate Polymers* **2008,** 74, (2), 159-169.
14. Moad, G., The synthesis of polyolefin graft copolymers by reactive extrusion. *Progress in Polymer Science* **1999,** 24, (1), 81-142.
15. Zagal, A.; Vivaldo-Lima, E.; Manero, O., A mathematical model for the reactive extrusion of methyl methacrylate in a co-rotating twin-screw extruder. *Industrial & engineering chemistry research* **2005,** 44, (26), 9805-9817.
16. Mohammadi, Y.; Saeb, M. R.; Penlidis, A.; Jabbari, E.; Stadler, F. J.; Zinck, P.; Vivaldo-Lima, E., Toward Olefin Multiblock Copolymers with Tailored Properties: A Molecular Perspective. *Macromolecular Theory and Simulations* **2021,** 30, (3), 2100003.
17. Benvenuta-Tapia, J. J.; Champagne, P.; Tenorio-López, J. A.; Vivaldo-Lima, E.; Guerrero-Santos, R., Improving Recycled Poly (lactic Acid) Biopolymer Properties by Chain Extension Using Block Copolymers Synthesized by Nitroxide-Mediated Polymerization (NMP). *Polymers* **2021,** 13, (16), 2791.
18. Benvenuta-Tapia, J. J.; Vivaldo-Lima, E., Reduction of molar mass loss and enhancement of thermal and rheological properties of recycled poly (lactic acid) by using chain extenders obtained from RAFT chemistry. *Reactive and Functional Polymers* **2020,** 153, 104628.

19. Benvenuta-Tapia, J. J.; Vivaldo-Lima, E.; Guerrero-Santos, R., Effect of copolymers synthesized by nitroxide-mediated polymerization as chain extenders of postconsumer poly (ethylene terephthalate) waste. *Polymer Engineering & Science* **2019,** 59, (11), 2255-2264.

20. Benvenuta-Tapia, J. J.; González-Coronel, V. J.; Soriano-Moro, G.; Martínez-De la Luz, I.; Vivaldo-Lima, E., Recycling of poly (ethylene terephthalate) by chain extension during reactive extrusion using functionalized block copolymers synthesized by RAFT polymerization. *Journal of Applied Polymer Science* **2018,** 135, (42), 46771.

21. Mehrabzadeh, M.; Kamal, M. R.; Quintanar, G., Maleic anhydride grafting onto HDPE by in situ reactive extrusion and its effect on intercalation and mechanical properties of HDPE/clay nanocomposites. **2009**.

22. Fang, H.; Ma, X.; Feng, L.; Wang, K.; Cao, B., Effects of screw configurations on the grafting of maleic anhydride grafted low-density polyethylene in reactive extrusion. *Journal of applied polymer science* **2008,** 108, (6), 3652-3661.

23. Fiorio, R.; D'hooge, D. R.; Ragaert, K.; Cardon, L., A statistical analysis on the effect of antioxidants on the thermal-oxidative stability of commercial mass-and emulsion-polymerized ABS. *Polymers* **2019,** 11, (1), 25.

24. Kislyak, A.; Frisch, H.; Gernhardt, M.; Van Steenberge, P. H.; D'hooge, D. R.; Barner-Kowollik, C., Time-dependent differential and integral quantum yields for wavelength-dependent [4+ 4] photocycloadditions. *Chemistry-A European Journal* **2020,** 26, (2), 478-484.

25. Wu, H.; Liu, X.; Sheng, D.; Zhou, Y.; Xu, S.; Xie, H.; Tian, X.; Sun, Y.; Shi, B.; Yang, Y., High performance and near body temperature induced self-healing thermoplastic polyurethane based on dynamic disulfide and hydrogen bonds. *Polymer* **2021,** 214, 123261.

26. Gordon, M. B.; French, J. M.; Wagner, N. J.; Kloxin, C. J., Dynamic bonds in covalently crosslinked polymer networks for photoactivated strengthening and healing. *Advanced Materials* **2015,** 27, (48), 8007-8010.

27. Fortman, D. J.; Brutman, J. P.; De Hoe, G. X.; Snyder, R. L.; Dichtel, W. R.; Hillmyer, M. A., Approaches to sustainable and continually recyclable cross-linked polymers. *ACS Sustainable Chemistry & Engineering* **2018,** 6, (9), 11145-11159.

28. Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E., Vitrimers: directing chemical reactivity to control material properties. *Chemical Science* **2020,** 11, (19), 4855-4870.

29. Schoustra, S. K.; Dijksman, J. A.; Zuilhof, H.; Smulders, M. M., Molecular control over vitrimer-like mechanics–tuneable dynamic motifs based on the Hammett equation in polyimine materials. *Chemical Science* **2021,** 12, (1), 293-302.

30. Hubbard, A. M.; Ren, Y.; Konkolewicz, D.; Sarvestani, A.; Picu, C. R.; Kedziora, G. S.; Roy, A.; Varshney, V.; Nepal, D., Vitrimer Transition Temperature Identification: Coupling Various Thermomechanical Methodologies. *ACS Applied Polymer Materials* **2021,** 3, (4), 1756-1766.

31. Wolf, S.; Miethlinger, J., Control Strategies for Reactive Extrusion of Polypropylene by Peroxide Degradation A Brief Review and an Experimental Study. *International Polymer Processing* **2021,** 36, (5), 472-498.

32. Tzoganakis, C. Peroxide degradation of polypropylene during reactive extrusion. 1988.

33. Martey, S.; Addison, B.; Wilson, N.; Tan, B.; Yu, J.; Dorgan, J. R.; Sobkowicz, M. J., Hybrid Chemomechanical Plastics Recycling: Solvent-free, High-Speed Reactive Extrusion of Low-Density Polyethylene. *ChemSusChem* **2021,** 14, (19), 4280-4290.

34. De Smit, K.; Marien, Y. W.; Van Geem, K. M.; Van Steenberge, P. H.; D'hooge, D. R., Connecting polymer synthesis and chemical recycling on a chain-by-chain basis: a unified matrix-based kinetic Monte Carlo strategy. *Reaction Chemistry & Engineering* **2020,** 5, (10), 1909-1928.

35. De Tommaso, J.; Dubois, J.-L., Risk Analysis on PMMA Recycling Economics. *Polymers* **2021,** 13, (16), 2724.

36. Dogu, O.; Pelucchi, M.; Van de Vijver, R.; Van Steenberge, P. H.; D'hooge, D. R.; Cuoci, A.; Mehl, M.; Frassoldati, A.; Faravelli, T.; Van Geem, K. M., The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy and Combustion Science* **2021,** 84, 100901.

37. Abeykoon, C.; Li, K.; McAfee, M.; Martin, P. J.; Niu, Q.; Kelly, A. L.; Deng, J., A new model based approach for the prediction and optimisation of thermal homogeneity in single screw extrusion. *Control Engineering Practice* **2011,** 19, (8), 862-874.

38. Sakai, T., Screw extrusion technology--past, present and future. *Polimery* **2013,** 58.

39. Covas, J. A.; Gaspar-Cunha, A., Modelling of flow and heat transfer, mixing and morphology development in plasticating single screw extrusion of polymer systems. **2018**.

40. Utracki, L.; Shi, Z., Development of polymer blend morphology during compounding in a twin-screw extruder. Part I: Droplet dispersion and coalescence—a review. *Polymer Engineering & Science* **1992,** 32, (24), 1824-1833.

41. Thompson, M., Twin screw granulation–review of current progress. *Drug development and industrial pharmacy* **2015,** 41, (8), 1223-1231.

42. Puaux, J.; Bozga, G.; Ainser, A., Residence time distribution in a corotating twin-screw extruder. *Chemical engineering science* **2000,** 55, (9), 1641-1651.

43. Giles Jr, H. F.; Mount III, E. M.; Wagner Jr, J. R., *Extrusion: the definitive processing guide and handbook*. William Andrew: 2004.

44. Bigio, D.; Cassidy, K.; Dellapa, M.; Baim, W., Starve-fed flow in co-rotating twin screw extruders. *International Polymer Processing* **1992,** 7, (2), 111-115.

45. Duan, L.; Spoerk, M.; Wieme, T.; Cornillie, P.; Xia, H.; Zhang, J.; Cardon, L.; D'hooge, D. R., Designing formulation variables of extrusion-based manufacturing of carbon black conductive polymer composites for piezoresistive sensing. *Composites Science and Technology* **2019,** 171, 78-85.

46. Hyvärinen, M.; Jabeen, R.; Kärki, T., The modelling of extrusion processes for polymers—a review. *Polymers* **2020,** 12, (6), 1306.

47. Tzoganakis, C., Reactive extrusion of polymers: a review. *Advances in Polymer Technology: Journal of the Polymer Processing Institute* **1989,** 9, (4), 321-330.

48. Hu, G.-H.; Cartier, H.; Plummer, C., Reactive extrusion: toward nanoblends. *Macromolecules* **1999,** 32, (14), 4713-4718.

49. Hopmann, C.; Adamy, M.; Cohnen, A., Introduction to reactive extrusion. *Reactive Extrusion: Principles and Applications* **2017**, 1-10.

50. Cassagnau, P.; Bounor-Legaré, V.; Vergnes, B., Experimental and modelling aspects of the reactive extrusion process. *Mechanics & Industry* **2019,** 20, (8), 803.

51. Zhu, L.; Narh, K. A.; Hyun, K. S., Evaluation of numerical simulation methods in reactive extrusion. *Advances in Polymer Technology: Journal of the Polymer Processing Institute* **2005,** 24, (3), 183-193.

52. Choulak, S.; Couenne, F.; Le Gorrec, Y.; Jallut, C.; Cassagnau, P.; Michel, A., Generic dynamic model for simulation and control of reactive extrusion. *Industrial & engineering chemistry research* **2004,** 43, (23), 7373-7382.

53. Vergnes, B.; Berzin, F., Modelling of flow and chemistry in twin screw extruders. *Plastics, Rubber and Composites* **2004,** 33, (9-10), 409-415.

54. Enayati, S.; Ayoub, A., Applying Mathematical Optimization To Efficiently Make Better Decisions for Extrusion Technology: State-of-the-Art and Opportunities. In *Biomass Extrusion and Reaction Technologies: Principles to Practices and Future Potential*, ACS Publications: 2018; pp 243-260.

55. D'hooge, D. R.; Van Steenberge, P. H.; Reyniers, M.-F.; Marin, G. B., The strength of multi-scale modeling to unveil the complexity of radical polymerization. *Progress in Polymer Science* **2016,** 58, 59-89.

56. Mastan, E.; Li, X.; Zhu, S., Modeling and theoretical development in controlled radical polymerization. *Progress in Polymer Science* **2015,** 45, 71-101.

57. Aguiar, L. G.; Pessôa-Filho, P. A.; Giudici, R., Mathematical modeling of the grafting of maleic anhydride onto poly (propylene): Model considering a heterogeneous medium. *Macromolecular theory and simulations* **2011,** 20, (9), 837-849.

58. Xie, L.; Liu, Q.; Luo, Z.-H., A multiscale CFD-PBM coupled model for the kinetics and liquid–liquid dispersion behavior in a suspension polymerization stirred tank. *Chemical Engineering Research and Design* **2018,** 130, 1-17.

59. Xie, L.; Wang, Q.-A.; Luo, X.-J.; Luo, Z.-H., CFD Simulation of the Particle Dispersion Behavior and Mass Transfer–Reaction Kinetics in non-Newton Fluid with High Viscosity. *International Journal of Chemical Reactor Engineering* **2019,** 17, (7).

60. Pohn, J.; Cunningham, M.; McKenna, T. F., Scale-U p of Emulsion Polymerization Reactors Part II–Simulations and Interpretations. *Macromolecular Reaction Engineering* **2013,** 7, (8), 393-408.

61. Ghiass, M.; Hutchinson, R. A. In *Simulation of free radical high-pressure copolymerization in a multi-zone autoclave reactor: compartment model investigation*, Macromolecular Symposia, 2004; Wiley Online Library: 2004; pp 443-456.

62. Tang, D.; Marchesini, F. H.; Cardon, L.; D'hooge, D. R., Evaluating the exit pressure method for measurements of normal stress difference at high shear rates. *Journal of Rheology* **2020,** 64, (3), 739-750.

63. Xie, L.; Zhu, L. T.; Luo, Z. H., Computational fluid dynamics simulation of multiscale mixing in anionic polymerization tubular reactors. *Chemical Engineering & Technology* **2016,** 39, (5), 857-864.

64. D'hooge, D. R.; Fantin, M.; Magenau, A. J.; Konkolewicz, D.; Matyjaszewski, K., Two-compartment kinetic Monte Carlo modelling of electrochemically mediated ATRP. *Reaction Chemistry & Engineering* **2018,** 3, (6), 866-874.

65. Tang, D.; Marchesini, F. H.; Cardon, L.; D'hooge, D. R., Three-dimensional flow simulations for polymer extrudate swell out of slit dies from low to high aspect ratios. *Physics of Fluids* **2019,** 31, (9), 093103.

66. Szydlowski, W.; Brzoskowski, R.; White, J., Modelling flow in an intermeshing co-rotating twin screw extruder: Flow in kneading discs. *International polymer processing* **1987,** 1, (4), 207-214.

67. White, J.; Adewale, A., A unified view of modeling flow in counter-rotating twin screw extruders. *International Polymer Processing* **1993,** 8, (3), 210-217.

68. Barrera, M.; Vega, J.; Martínez-Salazar, J., Three-dimensional modelling of flow curves in co-rotating twin-screw extruder elements. *Journal of materials processing technology* **2008,** 197, (1-3), 221-224.

69. Hétu, J.-F.; Ilinca, F., Immersed boundary finite elements for 3D flow simulations in twin-screw extruders. *Computers & Fluids* **2013,** 87, 2-11.

70. Bruschke, M. V.; Advani, S., Flow of generalized Newtonian fluids across a periodic array of cylinders. *Journal of Rheology* **1993,** 37, (3), 479-498.

71. Vergnes, B.; Valle, G. D.; Delamare, L., A global computer software for polymer flows in corotating twin screw extruders. *Polymer Engineering & Science* **1998,** 38, (11), 1781-1792.

72. Nagy, J.; Reith, L.; Fischlschweiger, M.; Steinbichler, G., Modeling the influence of flow phenomena on the polymerization of ϵ-Caprolactam. *Chemical Engineering Science* **2014,** 111, 85-93.

73. Wu, L.; Jia, Y.; Sun, S.; Zhang, G.; Zhao, G.; An, L., Numerical simulation of reactive extrusion processes for activated anionic polymerization. *Journal of materials processing technology* **2008,** 199, (1-3), 56-63.

74. Zhang, J.; Lu, Y.; Jin, Q.; Wang, K.; Luo, G., Determination of kinetic parameters of dehydrochlorination of dichloropropanol in a microreactor. *Chemical engineering journal* **2012,** 203, 142-147.

75. Wei, H.-L.; Liu, S.-E.; Li, G.-X.; Su, Y.-H.; Yan, W.-C.; Luo, Z.-H., Numerical modeling of a microreactor for the synthesis of adipic acid via KA oil oxidation. *Chemical Engineering Science* **2021,** 230, 116208.

76. Guo, X.; Fan, Y.; Luo, L., Residence time distribution on flow characterisation of multichannel systems: Modelling and experimentation. *Experimental Thermal and Fluid Science* **2018,** 99, 407-419.

77. Tang, D.; Marchesini, F. H.; Cardon, L.; D'hooge, D. R., State of the-Art for Extrudate Swell of Molten Polymers: From Fundamental Understanding at Molecular Scale toward Optimal Die Design at Final Product Scale. *Macromolecular Materials and Engineering* **2020,** 305, (11), 2000340.

78. Trippe, J.; Schöppner, V., Modeling of solid conveying pressure throughput behavior of single screw smooth barrel extruders under consideration of backpressure and high screw speeds. *International Polymer Processing* **2018,** 33, (4), 486-496.

79. Potente, H.; Melisch, U., Theoretical and experimental investigations of the melting of pellets in co-rotating twin-screw extruders. *International polymer processing* **1996,** 11, (2), 101-108.

80. Schoeppner, V.; Bruening, F., Development of a solids conveying throughput model for grooved barrel extruders based on discrete element simulations. *Advances in Polymer Processing; Hopmann, C., Dahlmann, R., Eds* **2020**, 50-62.

81. Trippe, J.; Schöppner, V. In *Modeling of the dissipation in the solid conveying section in single screw extruders*, AIP Conference Proceedings, 2019; AIP Publishing LLC: 2019; p 030036.

82. Bastian, M., Melting of Polymer Blends in Co-rotating Twin Screw Extruders. *International Polymer Processing* **2001,** 16, (2), 124-130.

83. Wilczyński, K.; Nastaj, A.; Lewandowski, A.; Wilczyński, K. J.; Buziak, K., Fundamentals of global modeling for polymer extrusion. *Polymers* **2019,** 11, (12), 2106.

84. Bawiskar, S.; White, J., A composite model for solid conveying, melting, pressure and fill factor profiles in modular co-rotating twin screw extruders. *International Polymer Processing* **1997,** 12, (4), 331-340.

85. Michelangelli, O.; Yamanoi, M.; Gaspar-Cunha, A.; Covas, J., Modelling pellet flow in single extrusion with DEM. *Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering* **2011,** 225, (4), 255-268.

86. Maddock, B., A visual analysis of flow and mixing in extruder screws. *SPE J.* **1959,** 383.

87. La Gala, A.; Fiorio, R.; Erkoç, M.; Cardon, L.; D'hooge, D. R., Theoretical Evaluation of the Melting Efficiency for the Single-Screw Micro-Extrusion Process: The Case of 3D Printing of ABS. *Processes* **2020,** 8, (11), 1522.

88. La Gala, A.; Fiorio, R.; Ceretti, D. V.; Erkoç, M.; Cardon, L.; D'hooge, D. R., A Combined Experimental and Modeling Study for Pellet-Fed Extrusion-Based Additive Manufacturing to Evaluate the Impact of the Melting Efficiency. *Materials* **2021,** 14, (19), 5566.

89. Altınkaynak, A.; Gupta, M.; Spalding, M.; Crabtree, S., Melting in a single screw extruder: Experiments and 3D finite element simulations. *International Polymer Processing* **2011,** 26, (2), 182-196.

90. Vergnes, B.; Berzin, F., Modeling of reactive systems in twin-screw extrusion: challenges and applications. *Comptes Rendus Chimie* **2006,** 9, (11-12), 1409-1418.

91. Komolprasert, V.; Ofoli, R. Y., A dispersion model for predicting the extent of starch liquefaction by Bacillus licheniformis α-amylase during reactive extrusion. *Biotechnology and bioengineering* **1991,** 37, (7), 681-690.

92. Tang, H.; Zong, Y.; Zhao, L., Numerical simulation of micromixing effect on the reactive flow in a co-rotating twin screw extruder. *Chinese Journal of Chemical Engineering* **2016,** 24, (9), 1135-1146.

93. Cegla, M.; Engell, S., Application of Model Predictive Control to the reactive extrusion of e-Caprolactone in a twin-screw extruder. *IFAC-PapersOnLine* **2021,** 54, (3), 225-230.

94. da Silva, E. G.; Parnaudeau, P., Comparison of multiphase models for computing shock-induced bubble collapse.

95. Choulak, S.; Le Gorrec, Y.; Couenne, F.; Jallut, C.; Cassagnau, P.; Michel, A., A Complete Dynamic Model for Twin Screw Extruders. *IFAC Proceedings Volumes* **2004,** 37, (1), 239-244.

96. d'Avray, M.-A. D. V.; Isambert, A.; Brochot, S.; Ferchaud, P., Development and Validation of a Steady-State Mathematical Model for the Physicochemical Processing of Biopolymers by Reactive Extrusion. *International Journal of Chemical Reactor Engineering* **2010,** 8, (1).

97. Manepalli, P. H. Stochastic modeling of flow behavior and cell structure formation during extrusion of biopolymer melts. Kansas State University, 2014.

98. De Keer, L.; Kilic, K. I.; Van Steenberge, P. H.; Daelemans, L.; Kodura, D.; Frisch, H.; De Clerck, K.; Reyniers, M.-F.; Barner-Kowollik, C.; Dauskardt, R. H., Computational prediction of the molecular configuration of three-dimensional network polymers. *Nature Materials* **2021,** 20, (10), 1422-1430.

99. Figueira, F. L.; Wu, Y.-Y.; Zhou, Y.-N.; Luo, Z.-H.; Van Steenberge, P. H.; D'hooge, D. R., Coupled matrix kinetic Monte Carlo simulations applied for advanced understanding of polymer grafting kinetics. *Reaction Chemistry & Engineering* **2021,** 6, (4), 640-661.

100. Bao, X.; Yu, L.; Simon, G. P.; Shen, S.; Xie, F.; Liu, H.; Chen, L.; Zhong, L., Rheokinetics of graft copolymerization of acrylamide in concentrated starch and rheological behaviors and microstructures of reaction products. *Carbohydrate polymers* **2018,** 192, 1-9.

101. Wang, S. S.; Chiang, W.; Zhao, B.; Zheng, X.; Kim, I., Experimental analysis and computer simulation of starch-water interactions during phase transition. *Journal of food science* **1991,** 56, (1), 121-124.

102. Banu, I.; Puaux, J. P.; Bozga, G.; Nagy, I. In *Modeling of L-lactide Polymerization by Reactive Extrusion*, Macromolecular symposia, 2010; Wiley Online Library: 2010; pp 108-118.

103. Dubey, S. P.; Abhyankar, H. A.; Marchante, V.; Brighton, J. L.; Blackburn, K.; Temple, C.; Bergmann, B.; Trinh, G.; David, C., Modelling and validation of synthesis of poly lactic acid using an alternative energy source through a continuous reactive extrusion process. *Polymers* **2016,** 8, (4), 164.

104. Tara, A.; Berzin, F.; Tighzert, L.; Vergnes, B., Preparation of cationic wheat starch by twin-screw reactive extrusion. *Journal of applied polymer science* **2004,** 93, (1), 201-208.

105. Berzin, F.; Tara, A.; Tighzert, L.; Vergnes, B., Computation of starch cationization performances by twin-screw extrusion. *Polymer Engineering & Science* **2007,** 47, (2), 112-119.

106. Berzin, F.; Tara, A.; Tighzert, L.; Vergnes, B., Importance of coupling between specific energy and viscosity in the modeling of twin screw extrusion of starchy products. *Polymer Engineering & Science* **2010,** 50, (9), 1758-1766.

107. Tara, A.; Berzin, F.; Tighzert, L.; Moughamir, S., Mesure en ligne du comportement visqueux d'un amidon de blé en cours d'extrusion. Application à la cationisation. *Rhéologie* **2005,** 8, 5-12.

108. Hernández-Ortiz, J. C.; Van Steenberge, P. H.; Duchateau, J. N.; Toloza, C.; Schreurs, F.; Reyniers, M.-F.; Marin, G. B.; D'hooge, D. R., A two-phase stochastic model to describe mass transport and kinetics during reactive processing of polyolefins. *Chemical Engineering Journal* **2019,** 377, 119980.

109. Morales-Huerta, J. C.; Jaramillo-Soto, G.; Manero, O.; Bárzana, E.; Vivaldo-Lima, E., Modeling of Pretreatment and Acid/Alkaline Hydrolyses of Lignocellulosic Biomasses in Twin-Screw Extruders. *Industrial & Engineering Chemistry Research* **2020,** 59, (25), 11389-11401.

110. Morales-Huerta, J. C.; Hernández-Meléndez, O.; Hernández-Luna, M. G.; Manero, O.; Bárzana, E.; Vivaldo-Lima, E., An experimental and modeling study on the pretreatment and alkaline hydrolysis of blue agave bagasse in twin-screw extruders. *Industrial & Engineering Chemistry Research* **2021,** 60, (34), 12449-12460.

111. Booy, M., Geometry of fully wiped twin-screw equipment. *Polymer Engineering & Science* **1978,** 18, (12), 973-984.

112. Cegla, M.; Engell, S., Reliable Modelling of Twin-screw Extruders by Integrating the Backflow Cell Methodology into a Mechanistic Model. In *Computer Aided Chemical Engineering*, Elsevier: 2020; Vol. 48, pp 175-180.

113. Gigmes, D.; Van Steenberge, P. H.; Siri, D.; D'hooge, D. R.; Guillaneuf, Y.; Lefay, C., Simulation of the Degradation of Cyclic Ketene Acetal and Vinyl-Based Copolymers Synthesized via a Radical Process: Influence of the Reactivity Ratios on the Degradability Properties. *Macromolecular rapid communications* **2018,** 39, (19), 1800193.

114. Tardy, A.; Gil, N.; Plummer, C. M.; Siri, D.; Gigmes, D.; Lefay, C.; Guillaneuf, Y., Polyesters by a Radical Pathway: Rationalization of the Cyclic Ketene Acetal Efficiency. *Angewandte Chemie* **2020,** 132, (34), 14625-14634.

115. Tardy, A.; Honoré, J. C.; Tran, J.; Siri, D.; Delplace, V.; Bataille, I.; Letourneur, D.; Perrier, J.; Nicoletti, C.; Maresca, M., Radical copolymerization of vinyl ethers and cyclic ketene acetals as a versatile platform to design functional polyesters. *Angewandte Chemie* **2017,** 129, (52), 16742-16747.

116. Delplace, V.; Guégain, E.; Harrisson, S.; Gigmes, D.; Guillaneuf, Y.; Nicolas, J., A ring to rule them all: a cyclic ketene acetal comonomer controls the nitroxide-mediated polymerization of methacrylates and confers tunable degradability. *Chemical Communications* **2015,** 51, (64), 12847-12850.

117. Govindasamy, S.; Campanella, O.; Oates, C., Enzymatic hydrolysis of sago starch in a twin-screw extruder. *Journal of Food Engineering* **1997,** 32, (4), 403-426.

118. Wu, W.; Jiao, A.; Xu, E.; Chen, Y.; Jin, Z., Effects of extrusion technology combined with enzymatic hydrolysis on the structural and physicochemical properties of porous corn starch. *Food and Bioprocess Technology* **2020,** 13, (3), 442-451.

119. Spinella, S.; Ganesh, M.; Re, G. L.; Zhang, S.; Raquez, J.-M.; Dubois, P.; Gross, R., Enzymatic reactive extrusion: moving towards continuous enzyme-catalysed polyester polymerisation and processing. *Green Chemistry* **2015,** 17, (8), 4146-4150.

120. Mohammadi Nafchi, A.; Moradpour, M.; Saeidi, M.; Alias, A. K., Thermoplastic starches: Properties, challenges, and prospects. *Starch-Stärke* **2013,** 65, (1-2), 61-72.

121. Miladinov, V.; Hanna, M., Starch esterification by reactive extrusion. *Industrial Crops and products* **2000,** 11, (1), 51-57.

122. Ye, J.; Luo, S.; Huang, A.; Chen, J.; Liu, C.; McClements, D. J., Synthesis and characterization of citric acid esterified rice starch by reactive extrusion: A new method of producing resistant starch. *Food Hydrocolloids* **2019,** 92, 135-142.

123. Milotskyi, R.; Bliard, C.; Tusseau, D.; Benoit, C., Starch carboxymethylation by reactive extrusion: Reaction kinetics and structure analysis. *Carbohydrate polymers* **2018,** 194, 193-199.

124. Berzin, F.; Tara, A.; Vergnes, B., Optimization and scale-up of starch cationization in a twin screw extruder. *Polymer Engineering & Science* **2007,** 47, (6), 814-823.

125. Yoon, K.; Carr, M.; Bagley, E., Reactive extrusion vs. batch preparation of starch–g–polyacrylonitrile. *Journal of applied polymer science* **1992,** 45, (6), 1093-1100.

126. Zdanowicz, M.; Schmidt, B.; Spychaj, T., Starch graft copolymers as superabsorbents obtained via reactive extrusion processing. *Polish Journal of Chemical Technology* **2010,** 12, (2), 14-17.

127. Formela, K.; Zedler, Ł.; Hejna, A.; Tercjak, A., Reactive extrusion of bio-based polymer blends and composites-Current trends and future developments. *Express Polymer Letters* **2018,** 12, (1).

128. Raquez, J.-M.; Degée, P.; Nabar, Y.; Narayan, R.; Dubois, P., Biodegradable materials by reactive extrusion: from catalyzed polymerization to functionalization and blend compatibilization. *Comptes Rendus Chimie* **2006,** 9, (11-12), 1370-1379.

129. Jongbloed, H.; Kiewiet, J.; Van Dijk, J.; Janssen, L., The self-wiping co-rotating twin-screw extruder as a polymerization reactor for methacrylates. *Polymer Engineering & Science* **1995,** 35, (19), 1569-1579.

130. Berzin, F.; Vergnes, B., Preparation of cationic starches by reactive extrusion: experiments and modelling. In *Biomass Extrusion and Reaction Technologies: Principles to Practices and Future Potential*, ACS Publications: 2018; pp 67-88.

131. Choulak, S. E. Modélisation et commande d'un procédé d'extrusion réactive. Université Claude Bernard-Lyon I, 2004.

132. Denissen, W.; Droesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E., Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nature communications* **2017,** 8, (1), 1-7.

133. Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E., Vinylogous urethane vitrimers. *Advanced Functional Materials* **2015,** 25, (16), 2451-2457.

134. Moens, E. K.; De Smit, K.; Marien, Y. W.; Trigilio, A. D.; Van Steenberge, P. H.; Van Geem, K. M.; Dubois, J.-L.; D'hooge, D. R., Progress in reaction mechanisms and reactor technologies for thermochemical recycling of poly (methyl methacrylate). *Polymers* **2020,** 12, (8), 1667.

135. Giudici, R.; do Nascimento, C. A. O.; Beiler, I. C.; Scherbakoff, N., Transient experiments and mathematical modeling of an industrial twin-screw extruder reactor for nylon-6, 6 polymerization. *Industrial & engineering chemistry research* **1997,** 36, (9), 3513-3519.

136. Nascimento, C. A. O.; Giudici, R., Neural network based approach for optimisation applied to an industrial nylon-6, 6 polymerisation process. *Computers & Chemical Engineering* **1998,** 22, S595-S600.

137. Nascimento, C. A. O.; Giudici, R.; Guardani, R., Neural network based approach for optimization of industrial chemical processes. *Computers & Chemical Engineering* **2000,** 24, (9-10), 2303-2314.

138. Nascimento, C. A. O.; Giudici, R.; Scherbakoff, N., Modeling of industrial nylon-6, 6 polymerization process in a twin-screw extruder reactor. II. Neural networks and hybrid models. *Journal of applied polymer science* **1999,** 72, (7), 905-912.

139. Mehralizadeh, A.; Derakhshanfard, F.; Tabatabaei, Z. G., Studying the Influence of the Mixing Speed of the Polymer Blend of General-Purpose Polystyrene and Acrylonitrile-Butadiene Styrene with the Applications of Artificial Neural Networks. *Iranian Journal of Chemical Engineering* **2020,** 17, (4), 21-32.

140. Ibañez, R.; Casteran, F.; Argerich, C.; Ghnatios, C.; Hascoet, N.; Ammar, A.; Cassagnau, P.; Chinesta, F., On the data-driven modeling of reactive extrusion. *Fluids* **2020,** 5, (2), 94.

141. Teixeira, C.; Covas, J. A.; Berzin, F.; Vergnes, B.; Gaspar-Cunha, A., Application of evolutionary algorithms to the definition of the optimal twin-screw extruder configuration for starch cationization. *Polymer Engineering & Science* **2011,** 51, (2), 330-340.

142. Castéran, F.; Ibanez, R.; Argerich, C.; Delage, K.; Chinesta, F.; Cassagnau, P., Application of Machine Learning Tools for the Improvement of Reactive Extrusion Simulation. *Macromolecular Materials and Engineering* **2020,** 305, (12), 2000375.

143. Ulitzsch, S.; Bäuerle, T.; Stefanakis, M.; Brecht, M.; Chassé, T.; Lorenz, G.; Kandelbauer, A., Synthesis of an addition-crosslinkable, silicon-modified polyolefin via reactive extrusion monitored by in-line raman spectroscopy. *Polymers* **2021,** 13, (8), 1246.

144. Berzin, F.; David, C.; Vergnes, B., Optimization and Scale-Up of Twin-Screw Reactive Extrusion: The Case of EVA Transesterification. *International Polymer Processing* **2020,** 35, (5), 422-428.