Molecular scale-driven upgrading of extrusion technology for sustainable polymer processing and recycling

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Abstract

Our polymer material and processing industry heavily relies on single- and twin-screw extrusion technology. To facilitate a circular economy technological upgrades, bridging experimental characterization techniques and the predictive power of modeling and software tools, are although indispensable. The current work highlights engineering challenges and solution strategies to make (reactive) extrusion technology more sustainable and reliable. Molecular scale driven case studies are included dealing with (*i*) energy and residence time optimization, (*ii*) the enlargement of the pool of polymers to be processed or synthesized (*e.g.* biopolymers and more well-defined compatibilizers), and (*iii*) polymer recycling applications, both chemical and mechanical. These case studies consider linear, branched as well as crosslinked polymers.

Keywords

polymer circularity; durability; screw optimization; 3D printing; reactive extrusion

1. Introduction

Extrusion technology, as shown in Figure 1, is one the main engineering tools for the polymer material industry, dealing with (*i*) polymer chemical modification, *e.g.* the synthesis of compatibilizers via so-called reactive extrusion technology (REX) [1-5], [3*]; (*ii*) polymer processing in final shapes, *e.g.* wind turbine blades [6]; (*iii*) polymer synthesis and blending, *e.g.* multifunctional and composite materials formulations [7-10], and the fabrication of amorphous solid dispersions [11]; and (*iv*) polymer recycling, *e.g.* mechanical recycling of films or chemical recycling of easy-to-unzip polymers [10,12]. The market share for extrusion-based processes in the polymer community is thus high with for mechanical recycling of polymer waste even a highly dominant role as possible through variations in screw settings, number of screws and screw types.

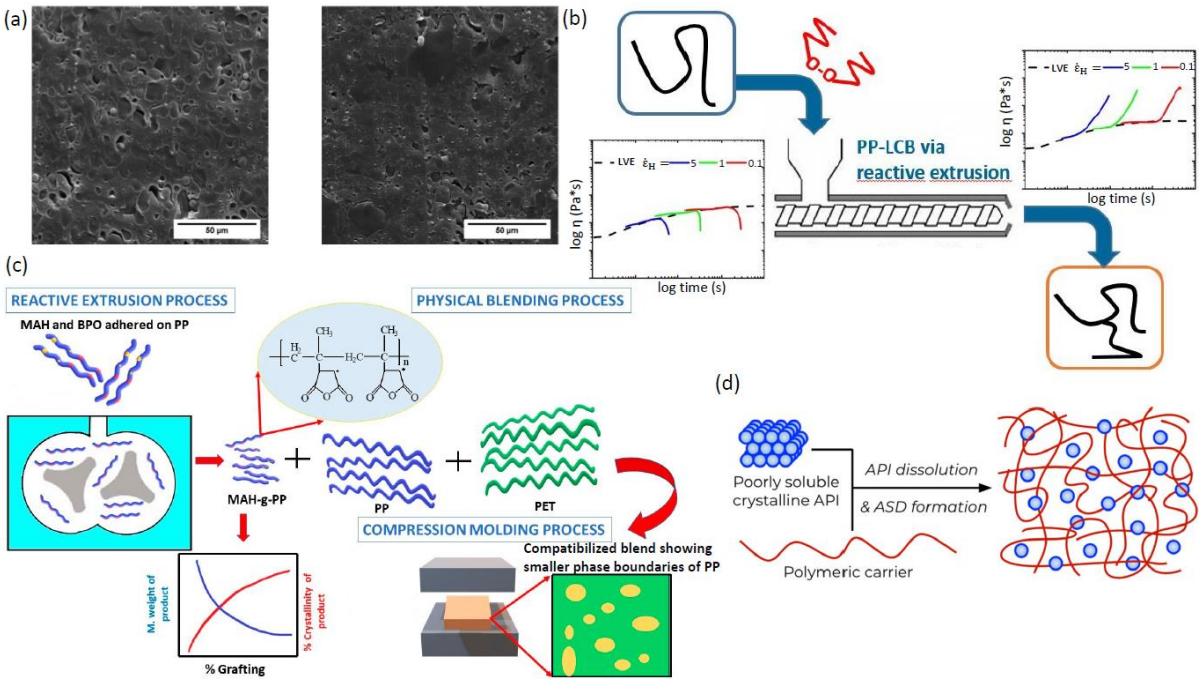

Figure 1: Examples of the beneficial use of (reactive) extrusion technology for high-end applications, with in (a) composite fabrication via chemical modification and/or blending [13], (b) chemical modification via polymer grafting for long chain branching [14], (c) compatibilized blend design [15], (d) production of amorphous solid dispersions for pharmaceutical applications [16].

Societal challenges regarding the efficient use of energy and raw materials, while maintaining an excellent human life standard, require innovation and improvement of the current (reactive) extrusion technology for polymer engineering purposes. Sustainable challenges, as addressed in this work, are (*i*) the use of less external energy to deliver extruded products, thus process intensification; (*ii*) the

enlargement of the pool of polymeric blends that can be homogeneously processed with excellent final properties, *e.g.* biopolymers allowing the replacement of oil-based applications; (*iii*) the increase of the flexibility to manufacture various final shapes, *e.g.* by improving layer-by-layer processing techniques such as extrusion-based additive manufacturing [17]; (*iv*) model-based process design of (reactive) extrusion technology recognizing the molecular scale, specifically the complex interplay of molecular diffusion and chemical reactions defining the chemical build-up of individual chains. In any extrusion step or passage, degradation reactions should be at least addressed, which depending on the polymer type and processing conditions lead to either increases or decreases of the chain lengths of the polymer molecules.

The way forward to tackle the aforementioned challenges is the smart combination of experimental characterization techniques, and engineering software or modeling tools sufficiently recognizing the key phenomena at every length scale, ranging from the molecular to the application or macro-scale. In what follows, the strength of this combination is illustrated via 3 case studies: (i) the coupled mapping of the residence time distribution (RTD) and molar mass distribution (MMD) for mechanical recycling of quasi-linear polymers (polymers with at most intermediate branching levels); (ii) the model-based blend design for novel biopolymer based materials; and (iii) the in silico tailored decrosslinking of quasi-network polymers (polymers with at most intermediate branching and crosslinking levels), thus at first sight less recyclable polymer streams.

2. Coupled design for mechanical recycling with quasi-linear polymers

One of the most important parameters in (reactive) extrusion is the RTD, which is the fractional distribution of times molecules reside inside the equipment [18,19]*. Experimentally, as highlighted in Figure 2a, the RTD is usually determined via a tracer which is added in small amounts to the hopper mixture and followed at several gates, at least one corresponding to the die exit unit [20]. The analytical techniques can range from optical methods, magnetic susceptibility methods, electrical methods to even γ-ray detection methods, which can be executed both in-/off- or on-line.

Complementary, several modeling efforts have been made to predict the RTD inside an extruder [10,21-24]. A detailed calculation is non-trivial as many phenomena at different length scales are active, such as highly viscous conditions inducing macro-scale concentration/mixing gradients and micro-scale diffusional limitations, complex shear rate dependencies of macroscopic properties due to (macro)molecular variations (*e.g.* degradation), prior compounding meso-scale heterogeneities, a wide range of geometries for the screw/barrel configuration, 3D temperature profiles, shear-induced dissipation, solid-melt/liquid phase transitions, and filling rate and screw speed variations. Many modeling studies are therefore simplified, focusing on the prediction of the RTD assuming ideal mixing conditions (*e.g.* a series of identical reactors) and ignoring chemical modifications, the latter more acceptable for highly stabilized polymer processing [11] [25,26]* Recent contributions have *e.g.* been made by Castéran et al. [25]*, Bochmann et al. [11], La Gala et al. [27], with interesting reviews by Hyvärinen et al.[28], Lewandowski et al.[26]*, Tang et al.[29], and De Smit et al.[10] mostly dealing with controlling the melting efficiency and the pressurization to overcome the pressure drop over the die. Upgraded simulations have been reported employing global kinetics but these are still non-generic and too lumped regarding the representation of the molecular scale.

For the profound understanding and designing of multiple extrusion passes during repetitive mechanical recycling (*e.g.* at 150-250 °C), specifically with lower or unknown stabilizer amounts, chemical modifications as well as RTD changes need to be although accounted for. In case chain repair is aimed by the addition of chemicals, *e.g.* crosslinking agents, a detailed model output based on reactive modifications is desired even more. Hence, most interesting for future mechanical engineering design are modeling tools grasping molecular variations for any processing/reactor unit size for a wide range of chemical reactions, accounting for the distributed nature of polymer molecules. Interestingly, recent coupled matrix-based kinetic Monte Carlo (CMMC) simulations [19,30,31] allow to track molecular variations in a given 3D (macro-scale) unit. The innovative use of CMMC, in which reactions and mass transfers are sampled for individual molecules per distinct mixing 3D region/phase/compartment in an extruder (or general unit), allows to predict the distributed properties per slice of the RTD. An observed

(total) property can thus be explicitly calculated as a superposition respecting variations in molecular structure (*e.g.* chain length or molar mass) and processing conditions (*e.g.* RT).

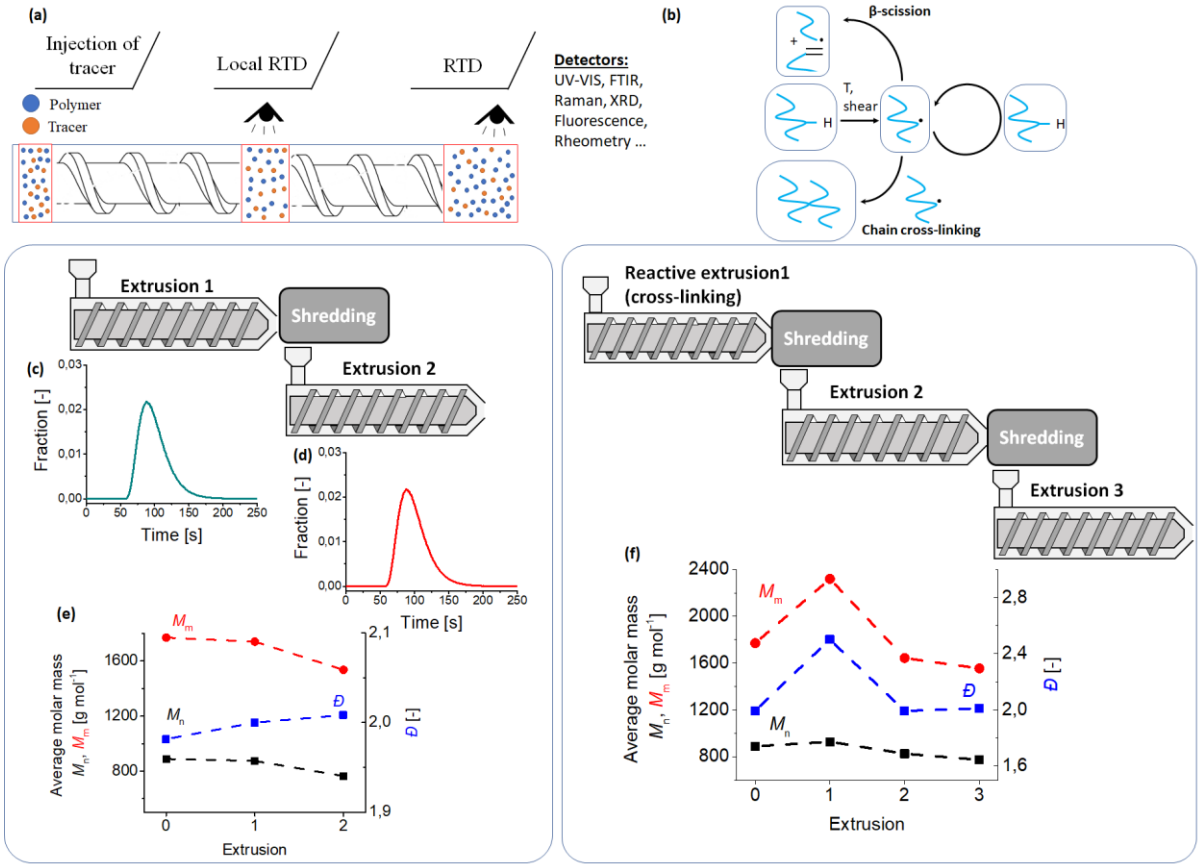

Figure 2: (a) Experimental techniques for measurement of the residence time distribution (RTD); (b) examples of degradation reactions during extrusion-based processing (more detailed overview in Ceretti et al. [32]); (c-e) modeled RTDs and molecular properties (M_n, M_m, and dispersity $Đ$) during single and double pass extrusion of poly(lactic acid), hence, for the virgin production and the first mechanical recycling at 463 K. (f) modeled molecular properties (M_n, M_m, and dispersity $Đ$) during reactive extrusion with the cross-linking agent, mechanical recycling with de-crosslinking and further mechanical recycling of poly(lactic acid) at 463 K. Kinetic modeling parameters and extrusion (screw related) parameters for all modeling results from De Smit et al. [19]*

De Smit *et al.*[19]* already illustrated the CMMC strength for extrusion-based polymer modification in which maleic anhydride is grafted onto polyethylene (PE) precursor chains. Notably the CMMC tool can also be applied for polymer processing or recycling including thermal and (thermo)mechanical degradation of the polymer. The quantification and correct prediction of the degree of degradation is important for polymer processing and mechanical recycling as it determines the final properties of the polymer material. The most common degradation reactions are fission and scission reactions (Figure 2 (b)), decreasing the average chain length (or molar mass), and crosslinking increasing the average chain length. For example, Figure 2(c-h) highlights the simulated impact of melt conditions on a single and

double passing, selecting poly(lactic acid) (PLA) as polymer both in the presence and absence of crosslinking agent (CA). Consistent with previous work, [19]* 5 compartments are considered to represent the extruder and all model parameters are literature-based [19]*. Dynamic but controlled variations for the number average molar mass (M_n), mass average molar mass (M_m) and dispersity ($Đ$) are witnessed. Note that this division in compartments also allows to include discrete energy calculations, considering molecular scale bound energy variations and large scale flow parameters and screw settings.

The further strength of modeling tools lies in their combination with machine learning and artificial intelligence (AI) algorithms. Most emphasis has been on the combination with deterministic software. For example, Castéran et al. [33] connected Ludovic© software with AI to optimize the reactive extrusion of maleic anhydride functionalized PE, comparing regression techniques. Recently, data-driven modeling [34] has been applied for recycling of PE to mimic the main process outputs with acceptable agreement but still a basic representation of the molecular scale. Another AI-based example is the optimization work of Takada et al. [35] for blending of polyphenylene sulfide with elastomer. Ibañez et al. [24] in turn compared ML techniques to model the link between material and process parameters for parts obtained by reactive polymer extrusion. The reviews of Rajendra and Brahmajirao [36] and Rajendra et al. [37] further indicate that the number of AI modelling techniques applicable for systems with high dynamics such as extrusion is growing. However, the highest predictive nature would be obtained in case the AI algorithms for process intensification rely on training with models embedding specifically the molecular scale in high detail. Such type of training will only be possible in the near future as the field of *e.g.* CMMC is as such very new.

3. Blend design for novel biopolymer-based alternatives

The current environmental polymer waste problems have led to growing concerns about our dependence on finite fossil resources. This has caused a growing interest in developing bio-based sustainable materials, aiming at partly or even fully replacing oil-based synthetic plastics by biopolymers. Biopolymers are materials derived from biological sources and are accompanied with several

advantages such biodegradabilty, non-toxicity, and renewability, and they can upon proper tailoring be characterized by physicochemical properties comparable to those of conventional polymers.

Among the various types of biodegradable products (Figure 3a), PLA is currently by far the most commercially developed both for conventional processing and additive manufacturing (AM) [38,39]. In terms of recycling, mechanical recycling is the most applied for PLA and its reinforced blends (*e.g.* with polyhydrohyalconates (PHAs)), as it is superior to chemical recycling in terms of the use of resources and energy efficiency [38,40]. However, mechanical recycling causes downgrading which eventually results in a recycled PLA material with a lower quality than the original PLA (blend/composite) [41-45], with the end-of-life options (for bioplastics in general) summarized by Fredi and Dorigato as well as Sikorska et al. [46-49].

Moreover, starch (polysaccharide-)based materials are gaining increased attention, being renewable and abundantly available via various plant sources such as corn, potato, rice, cassava and starchy foods such as peas [8]. Also here blending is needed to increase the final properties and control the water-sensitivity [50,51]. Ideally, thermoplastic starch (TPS)-based materials are supposed to be collected and composted in a specialized facility. In practice, due to the small quantities of TPS packaging currently on the market, TPS is discarded with the general waste and ends up in the landfill, leading to uncontrolled methane emissions [52]. Additionally, the disposal of (bio)degradable materials in the general waste stream can have a negative effect on the material properties after mechanical recycling of the conventional polymers, *e.g.* PE [53]. The model-based design of the recycling routes for these types of plastics is therefore of high importance, but requires more basic molecular scale training as limited chemistry and transport parameters are known for the less studied class of biopolymers

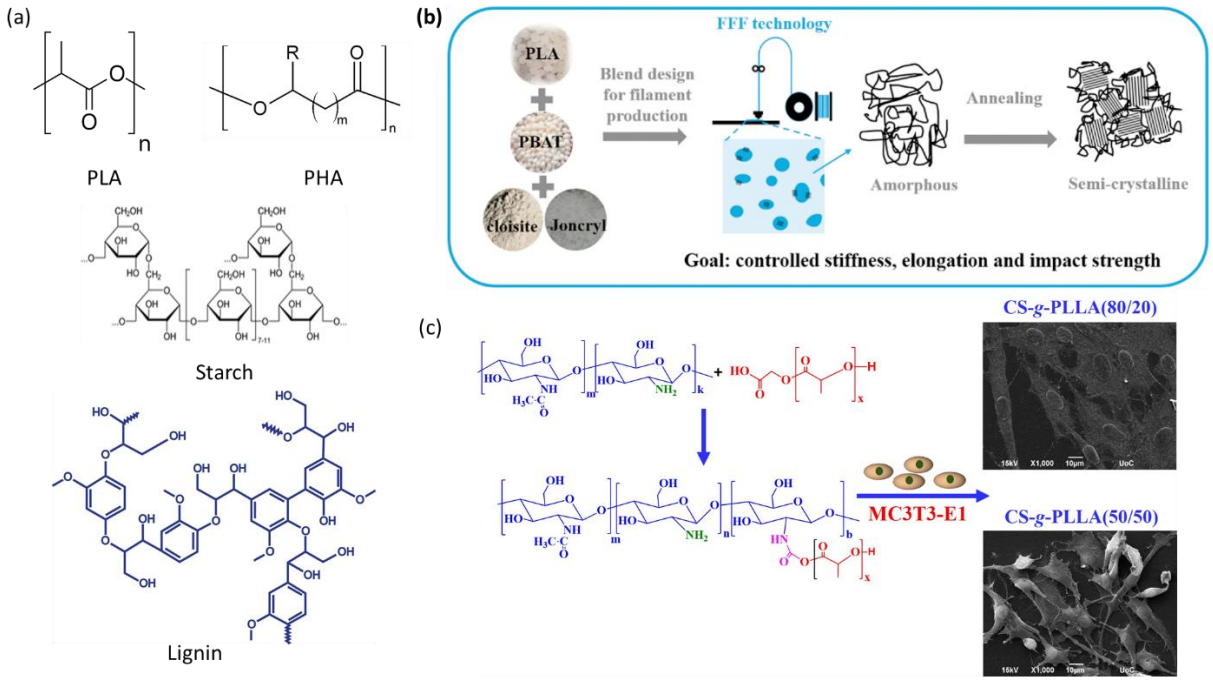

Figure 3: (a) Examples of biopolymers currently used for extrusion-based processing; (b) PLA-based blending strategy as exemplified by Wang et al. [54] and Kaliva et al. [55]

The field of TPS mechanical recycling is still in its early stage with on the one hand these polymers and their blends not designed for recycling, and on the other hand such blends degrading slowly in the environment eventually contributing to microplastic formation [56]. Promisingly, several current studies reveal a high mechanical recycling potential. Peres et al. [57] *e.g.* showed that mechanical and rheological properties remain the same after 5 to 10 extrusion cycles for PE/TPS blends. Oliveria et al. [58] in turn investigated thermal reprocessing of polypropylene/poly(butylene adipate-co-terephthalate/TPS blends, even finding the improvement of the mechanical properties after 7 single screw extrusion cycles. Furthermore, Tavanaie and Ghahari [56] studied the mechanical recycling of commercial PP/TPS blends in a single screw extruder, highlighting a slight decrease of the viscosity after 5 reprocessing cycles, although the mechanical properties remained unchanged. Additional research is however needed to generalize the trends from the above contributions, specifically the potential of reactive extrusion for bio-based polymer product developments is worthwhile [59,60].

Note that many other biopolymers are interesting to explore as well. Key examples are polybutylene succinate (PBS). [61-65] In any case, the model-based approaches presented in the present work can be applied, provided that the model parameters are trained.

4. Recycling for cross-linked and (quasi-)network polymers

Thermoplastic (quasi-linear polymer) materials are prone to thermal and/or oxidative degradation, and creep. Sufficient crosslinking improves the thermal stability and mechanical properties, such as impact strength, tensile strength, stress cracking, and resistance to creep [66]. Several crosslinked polymers therefore exist, with a broad range of applications, as shown in Figure 4.

However, crosslinking increases the melting temperature tremendously, the crosslinked polymers cannot be (easily) mechanically recycled since they do not (easily) melt. In several cases, the polymer undergoes only softening, and in extreme cases the melting temperature is above the decomposition temperature, with in the limiting case of highly crosslinked thermosets often the statement 'recycling the unrecyclable" [67]. Very interesting is again a reactive extrusion with interesting approaches being (*i*) (dedicated) degradation of polymers using chemicals (Figure 4b); (*ii*) ultrasonic energy treatment (Figure 4c); and (*iii*) chemical modifications inducing controlled dynamic behaviour at the polymer level (Figure 4d), *e.g.* the formation of vitrimers. A challenge still remains the identification of the most interesting route for a general purpose, also bearing in mind the potential of chemical recycling. A key question is the identification of the threshold crosslinking degree (*e.g.* for rubber-(like) materials) still controllable via extrusion technology.

The use of chemicals to de-crosslink plastic material has been mainly researched for silane crosslinked PE (XPE). The decrosslinking of XPE is found to be successful using supercritical alcohols in single and twin-screw extruders. Still, more research is needed in this field regarding to the influence of different parameters such as temperature and pressure in the extruder, the amount and kind of alcohol, the screw geometry, and the structure of crosslinked polymer. [68]*

Research of ultrasonic decrosslinking using extruders is mainly focused on peroxide XPE and crosslinked polyurethane foam (PUF). For example, Moon et al.[69] recycled PUF using an ultrasonic extruder to re-crosslink afterwards by adding virgin polyol and isocyanate. These authors show that the use of a higher amplitude results in a lower gel fraction, since more crosslinks could be broken due to higher acoustic pressure [14]. In follow-up work, Moon et al. [70] confirmed this relevance of the

amplitude for a bio-based feedstock. The research group of Isayev also studied ultrasonic recycling of XPE, dealing with variations in the ultrasonic amplitude, flow rate, screw design, and molecular structure [71-73].

(a)

Polymer	Application(s)	Crosslinking degree
PE	Wire insulation, piping for hot water distribution	Low
PMMA	Dental industry, coatings, solar cells	High, low
PS	Lenses, adsorption material	Low, high
PU	Mattresses, insulation	Low, high
PA	Tubes of solar-thermal integrated collector storage	Low, high
PET	Fibres, foams, bottles	Low

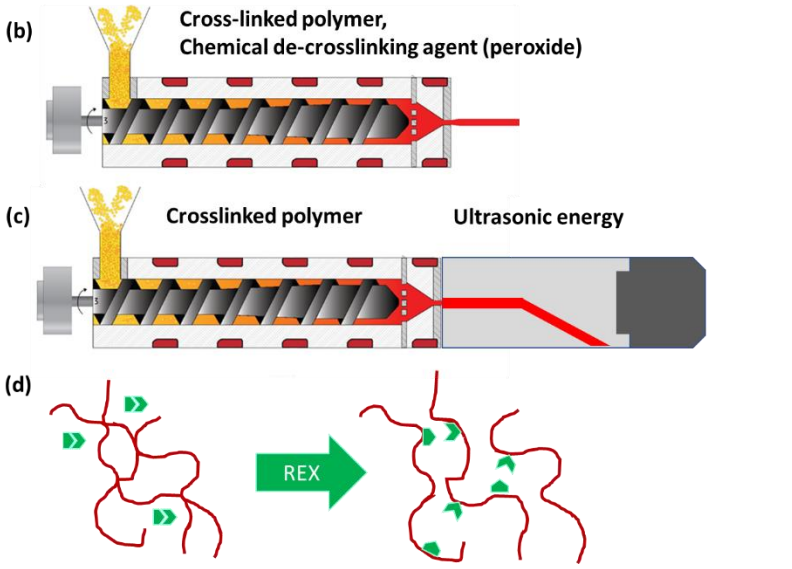

Figure 4: (a) Applications of crosslinked polymers; (b)-(d) de-crosslinking approaches involving reactive extrusion (REX): (b) controlled degradation in the presence of chemicals, (c) ultrasonic decrosslinking, (d) fabrication of vitrimers.

Research on dynamic networks and vitrimers is very recent and still dominant by design at the chemistry level. Such polymers contain crosslinks which can be reversibly opened under external stimuli such elevated temperature and (laser) light (at a specific wavelength) [67,74-76]. In closed configuration, these polymers have the material properties of crosslinked polymers, but in open configuration they can be recycled via traditional routes. Figure 4d specifically relates to the recycling of crosslinked polyesters, as exemplified by Wang et al. [77]** and Yue et al. [78]. In any case, the modeling tools developed for conventional processing and recycling can also be applied for vitrimers, as recently illustrated by De Smit et al. [10] using CMMC.

Conclusions

Extrusion and reactive extrusion are important techniques for the sustainable production of polymeric materials and the circular treatment of plastic waste. A key need is the full recognition of the molecular scale variations, as degradation and repair reactions codetermine the potential of every extrusion-based recycling technique. Purely experimental this is a very tedious task. It is recommended to combine experimental and modeling techniques to incorporate the design starting at the level of the molecular composition and topology. The current work specifically has shown that CMMC can be a powerful engineering tool via several case studies.

As a molecular driven model-based design approach can be made generic applicability is expected in the near future for both linear, branched and crosslinked polymers, also exploiting the potential of biopolymer-based application for (reactive) extrusion technology.

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Introducing artificial intelligence (AI) for extrusion-based proces control using a determinisitic mainframe. The challenge is now to apply such AI embedding also for stochastic frameworks delivering more molecular detail.

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