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## Introduction to Reactive Extrusion

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Engineering plastics have become indispensable to our daily lives. For several decades, the development of plastics technology to expand the scope of applications for plastics has been marked by “tailor-made” materials as well as by new processing techniques. Today, plastics are used in many applications ranging from plastics packaging and the automotive sector to medical products and they are increasingly substituting metal and ceramic. The success of this class of material is due to its characteristics such as good processability, low density, reasonable price, and especially its adjustable material properties.

The processing chain usually starts with the synthesis of the polymers, which is carried out by mostly petroleum-based monomers. In the field of polymer synthesis, a distinction is made between different polymerization reactions. These include, among others, mass polymerization, solution polymerization, and polymerization in gas phase [10]. Mass polymerization, which takes place in the melt, achieves high throughputs and high purities. However, the reaction rate, which is typically quite slow, results in the sedimentation of polymer chains with high molecular weight. Solution polymerization enables a higher homogeneity of the molecular weight distribution in the mixture because of the use of solvents. However, the solvent has to be removed by an energy-intensive process following polymerization. In addition, the presence of the solvent may produce undesirable side reactions. During gas phase polymerization, the monomers are transferred into a fluid state by an inert gas flow prior to polymerization [10].

Polymerization can be carried out in three different ways: batchwise, semi-continuous, and continuous. The choice of the reaction process influences both the material properties, such as viscosity or achievable molecular weight and the reaction kinetics and the resulting heat dissipation. Although polymerization in a batchwise process allows the production of small amounts of special polymers the batchwise process is less suitable for the mass production of a polymer due to the restricted achievable viscosity. Semi-continuous processes are often used for polycondensate reactions, when either low molecular weight fractions have to be removed to shift the chemical equilibrium or when additives have to be added. The continuous process is characterized by high throughputs

with simultaneously good heat dissipation. The process used influences the residence time as well as the residence time distribution. Typical reactors are the stirring tank reactor, stirred tank reactors in series, and the tube reactor [8].

After the synthesis, the properties of polymers frequently do not meet the requirements for the production of component parts. Therefore, the material properties are specifically adjusted by adding fillers and additives. This takes place in a separate processing step that follows polymer synthesis. Mostly, a co-rotating and closely intermeshing twin-screw extruder is used for this compounding task, in which the polymers are melted and mixed with additives and functional fillers [12]. The additives and fillers can be mixed dispersively and distributively into the melt to achieve homogeneous material properties. The processing during compounding as well as the material composition influence the material properties. The produced material is usually formed as granules, and goes through further processes such as injection molding or extrusion [12]. Alternatively, direct compounding of sheets or profiles is also possible. This saves energy, since the material does not have to be melted again. In addition, the material experiences a lower thermal stress, which enhances the material properties.

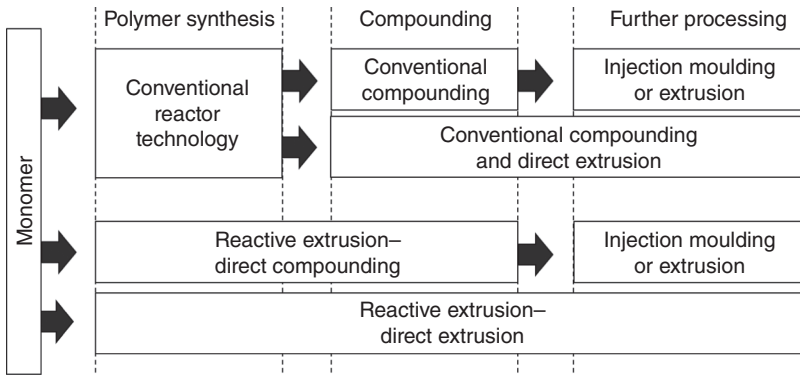
To summarize, the supply chain of plastics processing usually consists of three steps: polymerization, compounding, and further processing. In industrial applications, these three steps are separated in time and space, as each process step is usually performed by a different company with clearly defined areas of responsibilities. At the beginning of the supply chain, the production of polymers is already characterized by inflexibility, as the chemical reactors are generally designed for the production of large amounts of polymers. A typical stirring tank reactor can handle a volume of up to  $50 \text{ m}^3$  [10]. Furthermore, many reactor types are not designed for the handling and mixing of high-viscosity liquids. In such cases, the synthesis of polymers takes place in the presence of a solution, suspension, or emulsion. The removal of the processing aids is complex and reduces the economic efficiency. Therefore, the continuous processing of specialty polymers for specific applications in small amounts ensures efficiency. The raw material manufacturers cannot react rapidly and flexibly to the changing market demands. Thus, it is not possible to satisfy individual customer requirements for small volumes. Therefore, raw material manufacturers produce only few variations in large quantities. This restriction at the beginning of the process chain hinders use in plastics applications that demand more specific characteristics profiles than are currently available. A higher flexibility during polymer synthesis could therefore create a wider range of scope of plastics applications.

In this context, reactive extrusion offers a more flexible alternative to polymerization in the presence of a solution, suspension, or emulsion and subsequent compounding. In reactive extrusion, the co-rotating, intermeshing twin-screw extruder that is traditionally used to melt, homogenize, and pump polymers through dies for compounding, is used for the synthesis of polymers. The extruder, which conveys the reactant oligomer or monomer in solid, liquid, or molten state represents a horizontal chemical reactor. As such, reactive extrusion includes the backward integration of the polymer synthesis into the

compounding process. In principle, all reaction types of polymer synthesis can be realized in the twin-screw extruder, as long as the reaction rate is adapted to the residence time and distribution of the material in the processing machine [4, 7]. The residence time depends on the throughput, the length of the extruder, and the screw design and speeds. An increase of the residence time is possible within certain limits by linking two extruders to a cascade or by using low throughputs and screw speeds. However, this leads to a production that is not economically viable due to low capacity utilization [17].

One advantage of reactive extrusion is the absence of solvents as a reaction medium, as melts with different viscosities can be processed in a twin-screw extruder [7]. The absence of solvents in a conventional reactor technology causes additional issues regarding the removal of excessive heat, as polymer melts show a low thermal conductivity. In comparison, the reactive extrusion enables efficient heat removal due to the large reactor surface in relation to the reactor volume. The use of twin-screw extruders results in a high flexibility, as twin-screw extruders possess segmented barrels, which enable individual heating and cooling of single segments [7, 12]. In addition, the material is heated by the shear energy of the tightly intermeshing screw elements during conveyance and mixing. The introduced shear heating and the external heating provides the required heat for chemical reactions. The screws of a twin-screw extruder also consist of several segments. The geometry of the screw elements may differ depending on the depth between screw flights, the flight thickness, and the direction and degree of flight pitch [7]. Furthermore, mixing elements can be included for different mixing effects. Therefore, both dispersive and distributive mixing are possible. The design of the screw is key for the resulting mixing effect and the shear energy input.

A typical reactive extrusion process involves the following procedure: The reactants are fed through the main hopper into the twin-screw extruder, where the reactants are heated up to start the chemical reaction. The temperature profile, the use of activators and catalysts, and the residence time of the material in the extruder determine the reaction speed and the reaction progress. Consequently, the throughput, the length of the extruder, and the screw speed limit the degree of polymerization. Otherwise, the polymerization can be stopped specifically by the deactivation of reactive end groups to achieve a low viscosity. The addition of solid, liquid, or gaseous reactants is possible at almost any position at the extruder. For example, heat-sensitive additives can be added at the end of the extruder to minimize the residence time, or an inert gas can be added at the extruder feet to protect the process from degradation by atmospheric oxygen. Low molecular components, reaction byproducts and moisture can be removed by vacuum degassing during the reactive extrusion process. The degassing capability is dependent on the residence time, the melt temperature (which influences the viscosity), the diffusion rate, the attainable vacuum, the number of the degassing zones, and the renewal rates of the surface [11]. In addition, the adding of fillers and additives during the reactive extrusion is possible. The excellent mixing effect of the twin-screw extruder enables a homogenous incorporation of fillers. At the end of the extruder the melt is pressed through a die to either form strings that are pelletized, or to extrude directly sheets, films, or profiles. Thus,



**Figure 1.1** Simplified process chain from monomer to the final plastics product [11].

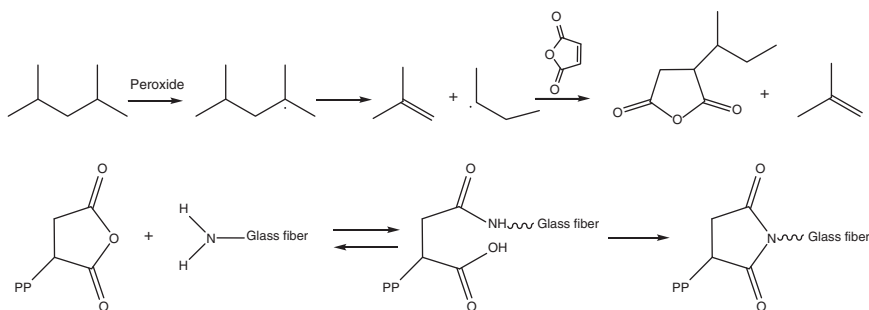
the application of the reactive extrusion shortens the processing chain compared to standard plastic processing (Figure 1.1).

Numerous research projects have demonstrated the possibilities regarding the types of reactions that can be carried out in an extruder [2]. These include the freeradical, anionic, cationic, condensation, and coordination polymerization of monomers or oligomers to high molecular weight polymers. Furthermore, controlled degradation and crosslinking of polymers by means of a free radical initiator for the purpose of producing a product with controlled molecular weight distribution and a higher concentration of reactive sites for grafting are possible. Commodity polymers can be functionalized for the purpose of producing materials to be used in grafting applications. In addition, various properties of the starting material can be improved by grafting monomers or mixture of monomers onto the backbone of existing polymers. Free radical initiators and ionizing radiation can cause the initiation of grafting reactions. Moreover, the formation of interchain copolymers is conceivable. This type of reaction involves combination of reactive groups from several polymers to form a graft copolymer. A final example are coupling reactions that involve reactions of a homopolymer with either a polyfunctional coupling agent or a condensing agent in order to increase the molecular weight by chain extension or branching. Table 1.1 gives an overview about typical types of reactive extrusion [2].

The research work of *Brown* and *Xanthos* gives a detailed overview about reactions that can be carried out in the reactive extrusion [3, 17]. As described earlier, in addition to the reactive extrusion for the synthesis of polymers, the twin-screw extruder provides the possibility of reactive modification as a reaction step after the polymer synthesis in a conventional reactor technique. Existing polymers, for example, apolar polymers, can be functionalized in reactive extrusion to improve compatibility with and adhesion to polar polymers. An overview about the reactive modification for blending immiscible polymers is given in [1, 9]. New functionalities can be introduced to polymers by reactive extrusion with radical polymerization, polycondensation or polyaddition. Furthermore, the viscosity of the product can be adjusted to the requirements of the application by initiated degradation or crosslinking reactions. In the following text, some

**Table 1.1** Possibilities of reactive extrusion.

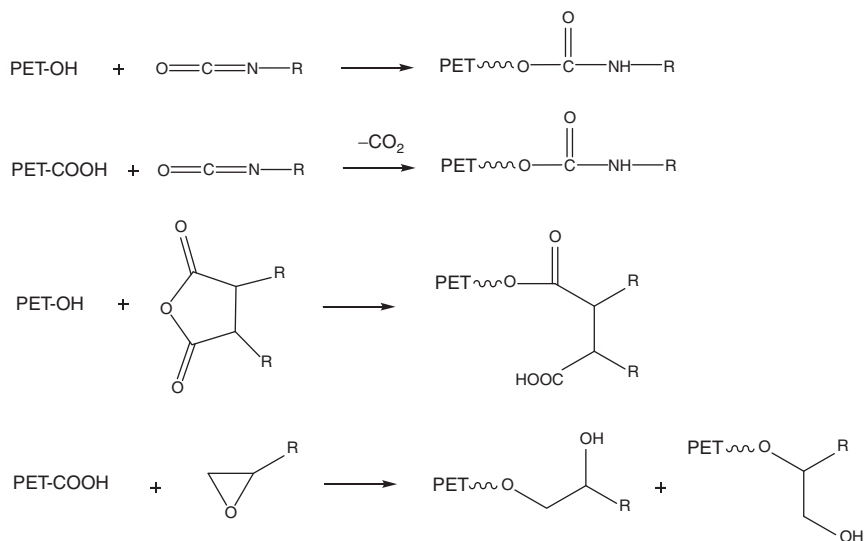
| Reaction type                 | Reactants                                      | Products   |
|-------------------------------|--|--|
| Polyaddition                  | Polyol + diisocyanate + aromatic diamine       | Polyurethane   |
| Polycondensation              | Bishydroxybutyl terephthalate<br>Precondensate | Polyethylene terephthalate<br>Polyamide                    |
| Free radical copolymerization | Styrene + acrylonitrile prepolymer             | SAN  |
| Grafting                      | Polystyrene + maleic anhydride                 | Polystyrene maleic anhydride adduct                        |
| Ionic polymerization          | Caprolactam                                    | Polyamide 6  |
| Anionic copolymerization      | 1,3-Diene + aromatic vinyl compound            | Block copolymers of 1,3-diene and aromatic vinyl compounds |
| Hydrolysis                    | Polyurethane scrap                             | Polyol, amines   |

**Figure 1.2** Modification of PP with MAH and glass fibers [4].

selected examples of polymer modification are presented that play important roles in industrial practice.

Radical polymerization is the most frequently used type of polymerization for the functionalization of polyolefins. Chain shortening, extension, branching or grafting can be achieved by the formation of radicals. Peroxides are usually used as initiators. This method is used for polyolefins, as the lack of functional groups in polyolefins prevents its wide use in various applications. The grafting of polyolefin (e.g., PP) with maleic anhydride (MAH) is one of the most performed polyolefin modifications [13]. Different formulations of MAH-grafted PP are available in the plastics market. MAH-grafted PP is able to achieve good compatibility with glass fibers that are coated with aminosilane (Figure 1.2). Detailed information on the structure and synthesis of modified polyolefins is given in [14].

Polycondensation reactions can also be carried out in reactive extrusion. In a polycondensation reaction, functionalized monomers or low molecular weight compounds react with polymers by release of smaller molecules in a step-growth reaction. Monomers, low molecular weight compounds, or reactive polymers have functional groups such as carboxyl, hydroxyl, epoxy, or amino groups.



**Figure 1.3** Reactions to extend PET chains [4].

Polyethyleneterephthalate (PET) is one of the most important polycondensation products especially in bottle production. The recycling process of PET is very interesting from an economic and ecologic point of view. However, recycled PET often has too low a molecular weight for reuse. Therefore, the industry has developed a discontinuous post-condensation process for increasing the molecular weight of PET. However, the material has a long residence time in the reactor and high temperatures occur. Alternatively, reactive extrusion has been considered. There has been extensive research on the extension of PET chains by functionalized molecules (“chain extenders”) in reactive extrusion [4]. The chain extender can be added during the melting of PET in the extruder. Typical chain extenders are isocyanates, anhydrides, and epoxides that react with the hydroxyl and carboxyl groups of PET [15, 16]. Figure 1.3 shows an example of reactions to extend PET chains.

However, the method of chain extension has also disadvantages. The chain extenders are often toxic substances and therefore the products are not suitable for food applications. Despite the shorter reaction times in the reactive extrusion, the process is more expensive to realize established post-condensation processes to increase the molecular weight of the polymer [4].

To summarize, the reactive extrusion offers many possibilities for flexible and economic production of materials with specific characteristics. In addition, the continuous process, the narrow residence time distribution, and the high flexibility also enable the economic production of small amounts of specialty polymers. The reaction enthalpy, which is set free during many polymerization reactions, can be used to heat up the melt. This allows energetically favorable processes. In spite of the advantages, the reactive extrusion from monomer to polymer plays a tangential role in industrial practice. This is exemplified on the basis of the number of existing twin-screw extruders, which are designed

for the use in the field of reactive extrusion: In the past 50 years, one of the leading suppliers of twin-screw extruders has sold only 87 optimized twin-screw extruders for reactive extrusion. All these plants are designed for the production of thermoplastic polyurethane by using reactive extrusion. These include 43 twin-screw extruders with throughputs between 600–3000 kg h<sup>-1</sup> (ZSK 83–133) and 21 twin-screw extruders with throughputs 200–600 kg h<sup>-1</sup> (ZSK 58–70) [5]. Therefore, theoretically, the production of 250.000 t a<sup>-1</sup> of thermoplastic polyurethanes is possible by a utilization rate of 80%. In 2012, 430.000 t of thermoplastic polyurethane was produced [6]. The reactive extrusion could potentially satisfy nearly 60% of the global market of thermoplastic polyurethane. However, the production of thermoplastic polyurethane is the only example where reactive extrusion is used for polymerization on an industrial scale. It is, of course, possible, that other standard twin-screw extruders are also used for reactive extrusion or that other polymers are synthesized by the use of reactive extrusion in isolated cases. But the present situation indicates that synthesis of polymers with monomers using reactive extrusion is not given much importance in industrial practice. Reasons for this might be the following disadvantages [4]. The limited residence time allows only fast reactions at high throughputs. Nonideal process conditions could cause local high melt temperatures that can trigger uncontrolled side reactions. A further aspect that should be considered is that the use of reactive extrusion demands a comprehensive knowledge about chemical reactions as well as the extrusion processes. The knowledge about these two complex areas is rarely available within just one company. In addition, the company has the responsibility for both the production and the processing of the material, which is a big challenge and not always appreciated by the customer since it limits the exchangeability with the supplier.

However, the addition of compatibilizers during compounding is a common strategy that is adopted to improve the compatibility and adhesion between different polymers or polymers and fillers that is already widespread today. These compatibilizers can initiate chemical reactions. Therefore, reactive extrusion is already employed to a minor extent in many compounding processes. Consequently, reactive extrusion is an essential part of the compounding process and will gain importance in the future, as the potential of blends or fillers depends on the interactions between components, which are in turn influenced by the reactive extrusion process.

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