Reactive polymer processing and design of stable micro- and nanostructures

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Abstract

Reactive processing is an alternative and promising method to produce micro- and nanostructured polymeric materials with controlled structure. Using this method it is possible to take advantage of the knowledge on reactive systems (polymerization, modification and blending) that have been conducted during processing. Thus, this chapter shows the potential of this technique to prepare micro- and nanostructured polymeric materials.

Key words: reactive processing, copolymers, blends, modification, polymerization, compatibilization, nanostructures.

Micro- and nanostructures

Introduction

Micro- and nanostructured materials are materials with a microstructure that has a characteristic length scale in the order of a few micro/nanometers. The properties of these materials deviate from those of conventional ones. This deviation results from the reduced size and/or dimensionality of the nanometersized structures.

An outcome of solid state physics and chemistry is the insight that most properties of solids depend on their microstructure, i.e. the chemical composition, arrangement of the atoms (atomic structure) and the size of the solid in one, two or three dimensions. Thus, changes in the properties of a solid will be noticed if one or several of these parameters are changed. However, if it is not possible to control the structure at atomic level, the desired properties can also be obtained by designing the micro- and nanostructure at the molecular level.

Polymeric systems that exhibit unique properties can be directly attributed to the presence of structural entities having dimensions in the micro- and nanometer range. Because of the special contribution of these micro- and nanosized entities, this class of polymeric systems can be collectively designated as micro- and nanostructured polymeric materials.

Understanding and controlling the mechanisms of phase separation and micro- and nanostructure formation in polymer systems enables the enhancement of the performance of these materials in several applications. For example, co-continuous blends of high- and low-melting-point polymers where the latter is the major component, have increased thermal and mechanical properties (such as toughness, stress at break or high-temperature creep resistance and similar processability) in relation to the original polymers. Copolymers exhibiting nanostructured phases show different optical properties and enhanced mechanical properties when compared with traditional copolymers.

Preparation methods

In recent years several strategies have been developed to prepare well-defined and predictable polymer structures. The great issue here is that the desired properties and functions are arrived at not by manipulation of the structure at atomic or molecular level, but by designing larger, nanoscopic building blocks, made of complex fluids (i.e., block copolymers, ion-containing polymers, polymer networks) and often of controlled shape (i.e., micellae, dendrimers, stars, combs, disks). The research for such materials will add a new dimension to the available range of properties and functions in polymers and other materials. The challenge is to go back to the conventional processing-structure-property correlations and develop new principles to create structures of controlled length scales, which would result in novel materials with distinct (and unusual) properties. Until now a lot of research has been performed and as a result various routes leading to these new micro- and nanostructured polymers have been reported.

The production of polyolefins with multimodal microstructural distributions in a single metallocene and a single reactor is an attractive method for producing polymers with balanced properties with simpler reactor technology. For example, copolymerization of ethylene and 1-octene carried out with an in situ supported rac-[dimethylsilylbis(methylbenzoindenyl)] zirconium dichloride catalyst produces polyethylene/ α-olefin copolymers with broad and bimodal short chain branching distributions and narrow molecular weight distributions [1].

Polymeric microtubules and nanofibrils have been prepared by depositing a solution of the desired polymer within the pores of microporous template membranes [2]. This method typically entails synthesizing the desired material within the pores of a microporous template membrane. The template membranes employed contain cylindrical pores with monodisperse diameters, which extend through the entire thickness of the membrane. The template method has been used to prepare tubular and fibrillar micro- and nanostructures composed of metals, semiconductors, electronically conductive polymers, carbons, and other materials [2].

Nanostructured polymers are also accessible by the use of lithographic techniques. Imprinting or embossing is a well-known technique to generate microstructures in hard polymers by pressing a rigid master containing surfacerelief features into a thin thermoplastic polymer film that is then heated close to or, more generally, above T_g [3]. Nanoimprint lithography has the potential of high throughput due to parallel processing, does not require sophisticated tools and allows nanoscale replication for data storage [4, 5]. The quality of the nanoimprinting process depends on a number of experimental parameters like T_g, melt viscosity, adhesion of the polymer to the mold, etc. [6]. Nanoimprint lithography has primarily been used to emboss hard thermoplastic polymers. The micromolding and embossing of elastomers has attracted considerable interest as these materials have found important applications in soft-lithographic techniques such as microcontact printing [7,8]. The advantage of microcontact printing is the ability to pattern surfaces chemically at the sub-micron level. The fabrication of $\sim 100\ nm$ surface relief features has proven to be much more difficult, as nanoscale structures easily collapse [9, 10].

Suh et al. [11, 12] used capillary force lithography for patterning a polymer film. When a patterned polydimethylsiloxane (PDMS) mold is placed on a spin-coated polymer film and then heated above the glass transition temperature (T_g) of the polymer, the capillarity forces the polymer to melt into the void space of the mold, thus yielding a negative replica when the mold is removed. In forming polymer micro-to-nanostructures by capillary force lithography, dewetting of polymer films was observed when the void space of the mold was not completely filled with the films.

Dewetting is also a convenient way of creating ordered micro- and nanostructures. Higgins and Jones [13] investigated the effects of surface topography on polymer dewetting by casting poly(methyl methacrylate) films on glass substrates that are roughened directionally by rubbing. They observed an anisotropic dewetting, the period of which is in accordance with that of the directional rubbing. They showed that the dewetting pattern follows the substrate pattern period, leading to the formation of droplet arrays.

The structuring of the topography of polymers by plasma treatment can occur at micrometer and nanometer scales and can influence adhesion, optical and wettability properties of the materials. These topography modifications are of great interest to the biomedical (contact lenses, implants) and optical industries (reflection, absorption) [14].

Electrospinning has been shown to be an effective method for the production of structured polymer fibers with diameters in the range from several micrometers down to tens of nanometers, which are of considerable interest to various kinds of applications [15].

Phase separation of polymers into lamellar structures has been used to generate $50-100\ nm$ thick periodic layers with different refractive indices, which can be achieved from solution casting. Block copolymers comprising two (or more) flexible, chemically incompatible and dissimilar blocks, e.g. poly(styrene) and poly(isoprene), can be microphase separated into a variety of morphologies with nanometer-scale dimensions. This self-assembly process is driven by an unfavorable mixing enthalpy and a small mixing entropy, while the covalent bond between the two blocks prevents macrophase separation. The microphase separated morphology that is formed (spheres, lamellae, inverse spheres and several more complex shapes) depends on the polymers used and on their volume fractions [16]. When the morphology can be controlled and turned into a useful structure, phase separation of block copolymers can be a powerful tool to fabricate nanostructures without additional lithography and processing steps.

Solid-state mechanical alloying, wherein the constituent polymers are mixed as solids at cryogenic temperatures, has been successfully used to prepare blends of thermoplastics with nanoscale morphology [17-19]. The dramatically reduced chain mobility in solid-state multicomponent systems effectively prevents phase separation during blending and promotes the formation of nanoscale morphologies. Mechanical alloying generally refers to the high-energy ball milling of two or more dissimilar materials to produce homogeneous alloys at the molecular or atomic level and is responsible for the ongoing development of novel metastable and nanostructured inorganic alloys possessing interesting mechanical, optical, magnetic, and electronic properties [20,21]. High-energy milling of polymeric materials subjects the blend components to a complex deformation field in which shear, multiaxial extension, fracture, and cold-welding develop concurrently.

Recently, it has been demonstrated that noncovalent bonds can be used in constructing block-copolymer-like molecular complexes [22-24] called supramolecules, which serve equally well as building units of nanostructures. Such noncovalent bonds include hydrogen bonding, ionic interactions, coordination complexation, and charge-transfer interactions. These supramolecular routes for block-copolymer-like architectures provide not only a new option to create nanostructured materials, but also a fascinating means to design 'smart' materials that respond to external stimuli or conditions [25,26]. Direct formation or cleavage of supramolecular complexes under a desired condition can thus be a basic strategy to develop materials with several tunable morphologies in the bulk.

An alternative and promising method to produce micro- and nanostructured polymeric materials with controlled structure is by reactive extrusion. Using this method it is possible to take advantage of the knowledge on polymerization, modification and blending via reactive extrusion that has been progressively accumulated. Thus, this chapter will show the potential of this technique to prepare micro- and nanostructured polymeric materials.

Reactive extrusion

The role of reactive extrusion

One of the significant advantages of the extruder over batch reactors is to guarantee a continuous reactive bulk process, e.g. high viscosity solvent-free reactive systems. Actually, reactive processing combines polymer processing and chemical reaction. Consequently, very specific conditions such as high viscous medium ($\eta \sim 10^3 \ \ Pa$.s), high temperatures ($T \sim 250^\circ C$) and short residence times ($t \sim 1 \ \ min$) can be found in this type of process.

Actually, reactive extrusion is now being viewed as an efficient means of continuously polymerizing monomers and/or modifying polymers. Particularly, co-rotating and counter-rotating intermeshing twin screw extruders proved to be a good technical and economical solution for reactive processing of thermoplastic polymers. The numerous possible advantages of using the extruder as a reactor can be described as follows:

- Fast and continuous process - productivity
- No solvents necessary - environmentally friendly
- Good mixing and transport of high-viscosity media
- No torque limitations for high-viscosity reactive media
- Chemical modification and/or compounding in a single step
- Possibility to process complex formulations (filler, plasticizer, etc.)
- Removal of side products, or monomers, by efficient devolatilization
- Turning of residence and reaction times by modular screw profile.

However, there are also some drawbacks in using an extruder as a chemical reactor, which are actually the counterparts of the main advantages:

- Limited number of accessible chemical reactions:
- Fast kinetics - very limited residence times (<60 s)
- High conversion and selectivity necessary for industrial applications
- No exothermal reactions (poor heat transfer), especially for extruders of large diameter
- High viscosity leading to possible strong viscous dissipation, which could induce side reactions (thermal degradation, for example)
- Complex geometry and coupled phenomena (mass and energy transfers, viscous dissipation, extent of reaction, etc.) leading to the development of complicated software for processing control
- The extruder is an expensive 'black box':
- Few sampling possibilities
- In-line and on-line analytical control are still limited, even after intensive research
- Free volume (4.5 liters for an extruder with a diameter of 58 mm)
- Difficulties in scaling up complex formulations to industrial extruders.

Generally, polymer reactive processes are very complicated to design and control, since one has to deal with several highly non-linear coupled phenomena. For example, the flow generated by screw rotation in an extruder is basically laminar, but very difficult to simulate due to its non-steady-state nature. Furthermore, molten polymers may be non-linear and their properties may change along the processing machine (spatial and temporal evolution) due to mixing and/or chemical reaction evolution. All these transport and chemical phenomena are coupled at least to the temperature and composition dependence of the transport properties (viscosities, diffusion coefficients, etc.). The fundamental aspects in reactive processing have been recently reviewed by Cassagnau et al. [27]. However, reactive processing can be used for a number of reactive systems, such as chemical modification of molten polymers, bulk polymerization, reactive blending of immiscible polymer blends, in situ polymerization and/or crosslinking of one of the two phases.

Reactive processes

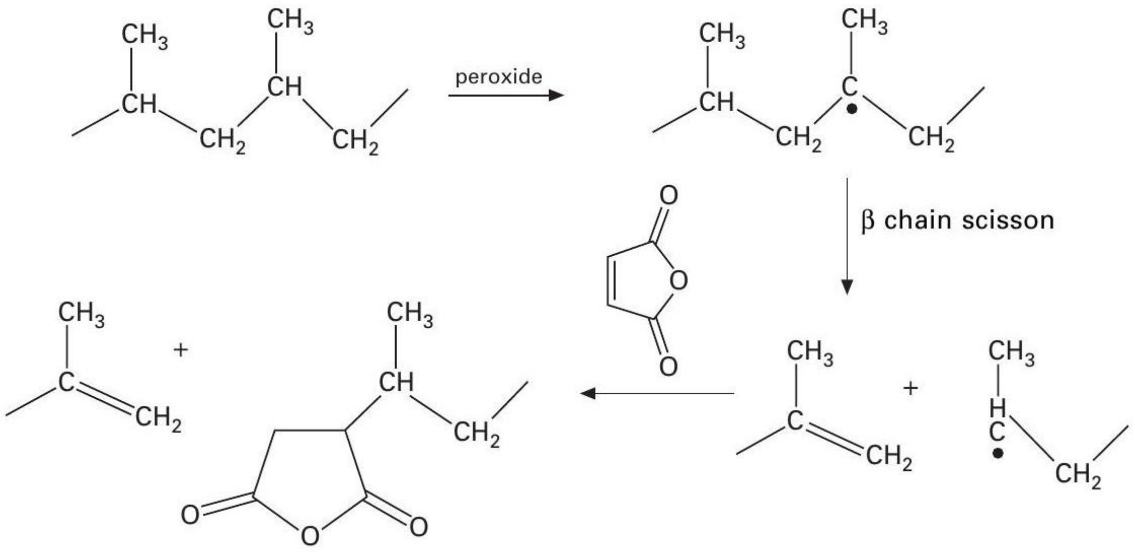
One of the first books on reactive processing was published in 1992 by Xanthos [28]. Xanthos divided into six categories the types of reactions that can be performed by reactive extrusion: bulk polymerization, graft reaction, interchain copolymer formation, coupling/crosslinking reactions, controlled degradation and functionalization (functional group modification). Actually, reactive extrusion is an important post-reactor technology to functionalize non-polar polymers, or to adjust the functionality of polar polymers to specific applications and properties. In the domain of polymer blends, functionalized polymers are currently employed to improve the compatibility and adhesion between immiscible polymers by a process called reactive blending (see Sections 18.3.1 and 18.3.2). However, new applications emerge, such as the synthesis of nanostructured copolymers and blends (see Section 18.3.3: New copolymers). Functionalization can also be used in post-processing operations to graft, branch and crosslink polymers.

Grafting

The conversion of non-polar polymers, such as polyolefins, into material modified to contain post-functionality by reactive extrusion has been extensively reported in the open and patented literature. A major part of the relevant review by Moad [29] on the synthesis of polyolefin graft copolymers by reactive extrusion deals with the synthesis of polyolefins with reactive functionality (grafted maleic anhydride, fumarate and maleate, glycidyl methacrylate, hydroxethyl methacrylate and methacrylic acids). One of the most common examples of polymer modification is the grafting of maleic anhydride (MA) onto polyolefins. Plenty of works have been published in the literature on maleation of polyolefins. Thus, it is unrealistic to report exhaustively the bibliographic references on free radical functionalization of these polymers in the melt. As recommended above, those interested in synthesis and structure of modified polyolefins can refer to the review of Moad [29]. Indeed, most of the attention has been given to the initiation of the reaction by peroxides, since the process produces a successful reactive compatibilizing agent for polyamide/polyolefin blends, or for layer polyolefin adhesion (polymer/polymer or polymer/metal). In contrast with polyethylene, polypropylene (PP) degrades very fast by chain scission when treated with peroxides at high temperature in processing machines (Fig. 18.1). This explains the abundant literature on MA grafting onto PP and the strategies to control the competition between the grafting reaction and chain scission. In general, two strategies are usually developed in order to control the side reactions of degradation at high temperature. The first one intends to modify the chemical mechanisms by using a co-agent (styrene, toluene, furan, etc.) to promote the formation of a stabilized radical able to prevent chain scission, while the second focuses on the processing parameters to minimize the impact of processing conditions on side reactions.

It must be pointed out that regarding grafting reactions initiated by organic peroxide, grafting of vinyl alkoxysilanes onto molten polymers is the most common and oldest example of a graft reaction performed in an extruder. Nowadays, these grafted copolymers can be hydrolyzed to produce crosslinking polymers.

Transesterification reactions can also be developed as, for example, the chemical modification of ethylene-vinyl acetate (EVA) copolymer in molten conditions. To promote new functionalization of EVA (hydroxyl groups), or EVA crosslinking, Bouilloux et al. [30] and Lambla et al. [31] reported the transesterification of EVA in the presence of paraffinic alcohols and basic catalysts giving the corresponding ethylene-vinyl alcohol copolymer. More recently, Bounor-Legaré et al. [32] investigated EVA crosslinking through ester-alkoxysilane interchange reactions.



18.1 Grafting of maleic anhydride on polypropylene and β-scission reaction of the polypropylene chains.

Bulk polymerization

Reactive extrusion is known as an efficient process of continuously polymerizing monomers. Various investigations on the use of twin-screw extruders for bulk polymerization were reported. One early published example of bulk polymerization in an extruder is the polymerization of ε-caprolactam [33]. This pioneering work was followed by various investigations [34-39]. Furthermore, the living anionic polymerization of styrene in a co-rotating twin-screw extruder was investigated by Michaeli et al. [37-40] and Gao et al. [41].

On the other hand, various investigations were reported on the bulk polymerization of acrylate monomers in extruders. Stuber and Tirrel [42] and Ganzeveld and Janssen [43] investigated the homopolymerization of methyl methacrylate (MMA) and n-butylmethacrylate, respectively, using an intermeshing counter-rotating twin-screw extruder. Jongbloed et al. [44] studied the homopolymerization of n-butylmethacrylate and the copolymerization of n-butylmethacrylate with 2-hydroxypropylmethacrylate. More recently, Berthet et al. [45] reported the production of poly(butyl methacrylate) by reactive extrusion, for the manufacture of optical fibers.

Several studies have been devoted to the synthesis of thermoplastic polyurethane (TPU) in an extruder. The first fundamental work was probably that patented by Frye [46], Rausch and McClellan [47] and Quiring and Niederdellmann [48]. Hyun and Kim [49] and Lu et al. [39] studied the reactive extrusion of TPU in a single-screw extruder. Similarly, Bouilloux et al. [50] and Ganzeveld and Janssen [51] performed TPU polymerization in a counter twin-screw extruder with different objectives. In any case, an important aspect that is generally missed out by authors is the depolymerization reaction of the urethane at temperatures above $150^{\circ}C$. The presence of this reaction may hinder extrusion efficiency. Recently, Verhoeven et al. [52] investigated this important aspect in TPU reactive processing. Ring opening polymerization (ROP) of cyclic monomers in extruders has been recently investigated. Although poly(ε-caprolactone) (PCL) is currently produced using a batch process, several studies have been reported on CL polymerization in twin-screw extruders. Patents by Narayan et al. [53-55] disclose a reactive extrusion process to manufacture PCL. Gimenez et al. [56, 57] investigated the bulk polymerization of ε-caprolactone initiated by tetrapropoxy titanium, in a co-rotating twin-screw extruder. Kim and White [58] conducted the CL
bulk polymerization in a twin-screw extruder using aluminum triisopropoxide initiator. They described an extensive experimental investigation of the molecular weight reduction during processing, which was attributed to the mechanical degradation of PCL chains. Raquez et al. [59] successfully carried out the polymerization of ε-caprolactone and 1,4-dioxan-2-one in a co-rotating twin-

screw extruder through a fast single-step process. More recently, Balakrishnan et al. [60] reported an extrusion polymerization process to manufacture three-arm PCL. This polymerization was initiated by aluminum tri-sec butoxide (ATSB) and the objective of this work was to produce PCL with good melt strength properties due to the star structure of the chains. Ring opening polymerization of l-lactide monomers has also been investigated in twin-screw extruders [61-63].

Coupling/crosslinking reactions and interchain copolymer formation have been also investigated in reactive processing, in order to control and stabilize micro- and nanostructures in a polymer material.

Reactive processes for stable micro- and nanostructured morphologies

Reactive blending

Blending of polymers has become a useful technique to produce new polymeric materials with a useful combination of properties, for a relatively low development and production cost [64-69]. As prepared by the physical combination of at least two polymers, most polymer blends are immiscible and have poor physical properties. As for other mixtures, polymer/polymer miscibility is governed by thermodynamic laws [66, 67]. In order to have thermodynamical miscibility, the free energy of mixing ΔG_m should be negative. Since the monomer units are covalently bonded to each other in the polymer chains, the number of ways that they can be arranged in a mixture is limited. Thus, ΔS_m is very small for polymer mixtures and approaches zero in very high molecular weight polymers. Consequently, the thermodynamic law predicts that polymer/polymer miscibility has to result from the exothermic heat of mixing ($\Delta H_m < 0$). A negative heat of mixing results when the interactions between neighboring segments of structurally different polymers are energetically more favorable than the intermolecular interactions between segment pairs. Examples of interactions giving exothermic heats of mixing include hydrogen bonds, dipole-dipole and anionic interactions. However, most polymer pairs are not miscible and compatibilization is necessary.

The main challenge of polymer compatibilization is to produce materials with a stable optimum morphology that maximizes the mechanical performance [69-74]. Poor chemical or physical interaction between two polymers usually implies high interfacial energy and low interfacial thickness. The properties of the interface such as thickness, strength and interfacial tension strongly determine the bulk properties. Therefore, the key to overcome the problems related to the coarse morphology of polymer blends is to reduce the interfacial tension, in order to improve the interaction between the immiscible phases. This can be achieved by adding compounds known as 'interfacial agents', 'emulsifiers', 'adhesion promoters' or, most frequently, 'compatibilizers', to the heterogeneous blends. As a result of compatibilization a fine and stable morphology can be accomplished; the interfacial thickness increases and the interface is strengthened due to interpenetration of the two types of chains across the interface. Several methods can be followed in order to promote blend compatibilization [6-11], such as (a) ex-situ, by addition of a presynthesized copolymer to the components, (b) in-situ, by creating a copolymer during blend preparation, which is located at the interface between the two components, and (c) by stabilizing the dispersed phase via dynamic vulcanization, or crosslinking. Ex-situ compatibilization provides the opportunity for controlling more easily the molecular architecture of the copolymer. However, not only does it require specific chemical routes and reaction conditions, but when the compatibilizer is added to the blend components it is difficult to ensure that most of it actually goes to the interface. In-situ (or reactive) compatibilization requires that both polymers have reactive groups at the interface. It involves the synthesis of a copolymer in situ during blending, which has some advantages over the others. The copolymer is formed at the interface, where it is needed to reduce the interfacial tension between the two phases. As stated above, polymers have been chemically modified in order to improve polymer compatibilization. Due to its reactivity, polymers grafted with maleic anhydride are widely used for compatibilization.

The potential of twin-screw extruders as high-speed continuous reactive blenders has become the driving force behind the present interest in reactive mixing techniques. Reactive extrusion, with the possibility of in-situ synthesis of bock or graft copolymers, sharply increased new developments in polymer blends. For technical and economic reasons, reactive extrusion may provide viable mechanisms for the production of blends with controlled structure and morphology [65-69].

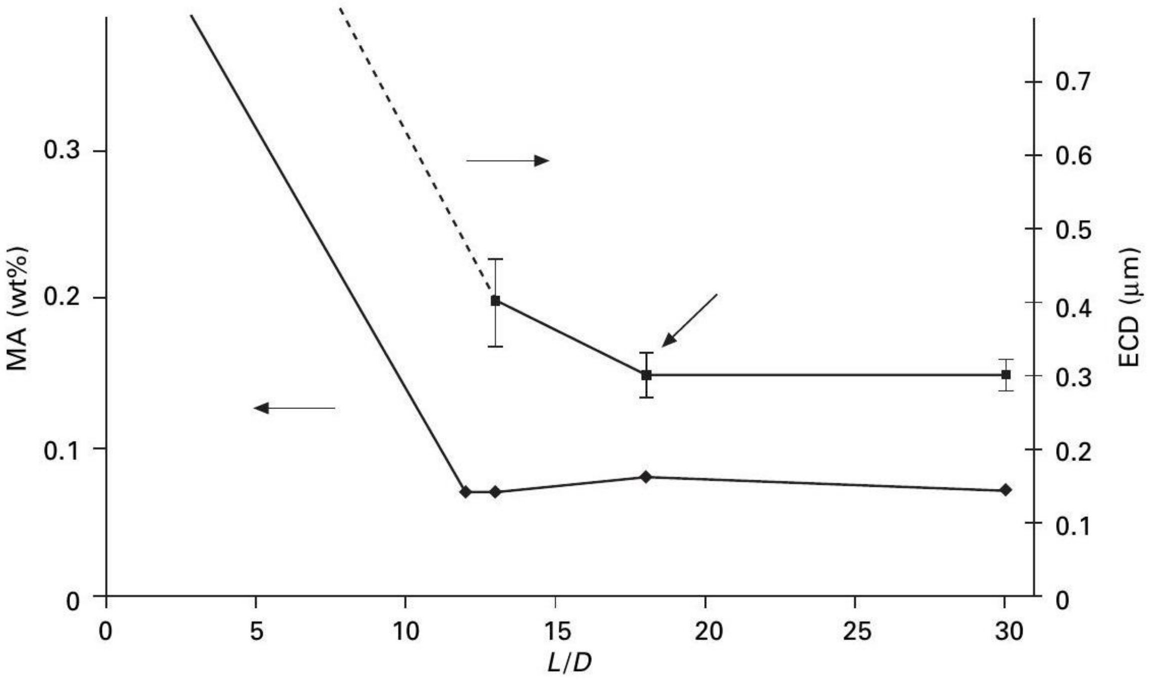
Morphology control is a key parameter for producing polymer blends with superior properties [68]. However, the morphology depends on the thermodynamic and rheological properties of the blend components, as well as on the processing conditions and equipment used. The multiphase nature of polymer blends and the variation of the structure upon processing imply that flow responses may be complex. Thus, during blend preparation not only the parameters controlling homogeneous polymer systems, but also the morphology and its evolution, should be considered. Knowhow on the development of the blend morphology, i.e., the evolution of the blend morphology from millimeter-size particles to micro- and/or nanostructure,
in the final blend in (industrial) processing equipment, such as extruders, is essential.

Several factors influence the morphology development during blending: composition, viscosity and viscosity ratio and processing conditions (screw configuration, time of mixing, screw rotation speed, temperature, throughput, etc.) [75]. However, the number of studies on how morphology actually develops is rather small. There are many important questions concerning this process. There has been much speculation about the mechanisms of particle size reduction and the effect of interfacial reaction on morphology development. Some results have been reported on how the morphology develops as a function of time during blending. Karger-Kocsis and Vergnes et al. [76] reported no significant changes in morphology from 5 to 40 minutes of mixing blends of rubbers dispersed in PP. Favis and Chalifoux [77] prepared blends of PP and PC in a batch mixer and concluded that the most significant changes in morphology occurred during the first 2 min of mixing, when melting and softening of the materials also occurred. Scott and Macosko [78, 79] reported model experiments showing that at short mixing times the phases are sheared into ribbon or sheet structures, followed by a shear and interfacial tension-driven breakup of these sheets or ribbons. Sundararaj et al. [80-82] showed that the most significant morphology development of a polystyrene and polypropylene (PS/PP) blend in a twin-screw extruder occurred in the first two kneading disks of the first kneading section. They also observed sheet structures and demonstrated that after the initial breakup the particle size is not reduced significantly. Moreover, they observed a phase inversion mechanism when the minor component melted or softened at a lower temperature than the major component. Cartier and Hu [83] studied blends in a co-rotating twin-screw extruder and showed that the morphology of polypropylene and polyamide-6 (PP/PA-6) develops very rapidly and that in the case of in-situ compatibilized blends with maleic anhydride modified PP (PP-g-MA) it develops even faster. In the latter case, the size of the dispersed phase undergoes an abrupt reduction from a few millimeters to sub-micrometer levels during phase transition from solid pellets to a viscoelastic fluid. The final morphology is reached as soon as the phase transition is completed.

In systems containing rubber and polyamide/polyesters, the rubber phase is dispersed from millimeter to micrometer level within a few seconds [84]. This means a decrease of the diffusion distance of the polycondensate chains towards the rubber interface by a factor of 10^3 and an increase of the interface by a factor of 10^9, i.e., the rate of interfacial reactions is dramatically enhanced. In the case of PA-6/EPM-g-MA blends, the reaction is so fast that as interfaces are created upon melting, they become immediately covered with PA-6 chains, causing a quick reduction of the interfacial tension and preventing coalescence, which induces a further refinement of the dispersion [85]. In order to study this sequence experimentally, Machado et al. [86] developed an experimental methodology involving the quick collection of material from fully filled screw sections of the extruder. They observed that at the beginning of the melting zone, even though the material is mostly solid, the non-reacted MA content has decreased to less than half of its original value. One L/D later, a fully melted conventional polymer blend morphology is present, with relatively good distributive and dispersive mixing levels, having caused a further important reduction in MA (Fig. 18.2). Before the end of the extruder a stable and controlled morphology was achieved.

The stability of reactively compatibilized blends after the die was studied in PA-6/EPM-g-MA blends by characterization of the morphology and chemical conversion after injection molding and capillary rheometry. Since after being subjected to significant shear the average particle size of the dispersed phase remained constant, it could be concluded that the morphology of the blends was stable and further processing does not change the morphology achieved during compatibilization.

Nowadays, polymer blends prepared by reactive processing seem to play an important role in obtaining micro- and nanostructured polymeric materials. Bayram et al. [87] studied SMA copolymer-PE blends in a Brabender batch mixer and in a twin-screw extruder using as a compatibilizer a PE with reactive epoxy functionality. At 25 % and 50 % reactive PE contents the blends were considered compatible, whereas those with non-reactive PE were incompatible. The blends were characterized in terms of morphology, viscoelastic and mechanical properties. The reactive blends have finer morphology than the non-reactive ones at all concentrations of the modified PE. The reactive blends also have higher modulus of elasticity, tensile strength, and strain at break than the non-reactive blends.



18.2 Chemical and morphological evolution along the extruder.

Poly(butylene terephthalate) (PBT)/poly(ethylene-octene) (PEO) blends containing 1.0 *wt* % epoxy and 0 – 30 *wt* % PEO were obtained by extrusion and injection molding [88]. The observed torque increase showed that epoxy reacted with PBT, leading to a fine and homogeneous morphology up to 15 *wt* % PEO content, which appeared larger and more heterogeneous at higher PEO contents.

Nanostructured glassy-crystalline blends were obtained by reactive blending of poly(methyl methacrylate) (PMMA), or of poly(methyl methacrylate)-b-poly-(*n*-butyl acrylate)-b-poly(methyl methacrylate) (MBM) triblock copolymer, with polyamide-6 (PA) [89]. They found that the nanostructure formation was especially effective for blends based on a triblock PMMA-b-PBA-b-PMMA copolymer. The resulting materials exhibit unique properties such as transparency, creep resistance and solvent resistance.

Alam et al. [90] prepared nanostructured polymer blends via anionic ring opening polymerizations of cyclic monomers in the presence of a pre-made polymer melt, which exhibited a number of special properties over traditional polymer blends and homopolymers. The method consists of in-situ polymerization of macrocyclic carbonates in the presence of a maleic anhydride polypropylene (mPP) matrix and a surface-active compatibilizer (i.e., PC grafted onto an mPP backbone generated in-situ) to yield a micro- and nanostructured polymer blend consisting of a polycarbonate (PC) minor phase and a polypropylene (PP) major phase. They found that by varying the processing conditions and concentration of the macrocyclic carbonate it was possible to reduce the size of the PC dispersions to an average minor diameter of 150 nm .

Stabilized nanoblends of PP/PA-6 were obtained by Hu et al. [91] using in-situ polymerization of ε-caprolactam (ε-CL), in a matrix of PP. In this way, the formation of PA-6 and a PP and PA-6 graft copolymer take place simultaneously in the PP matrix, leading to compatibilized nano-PP/PA-6 blends. The size of the particles of the dispersed phase (PA-6) ranged between 10 and 100 nm .

The same methodology was used by Teng et al. [92], who compatibilized polypropylene/polyamide 6 blends using polypropylene, ε-caprolactam and maleic anhydride grafted polypropylene via in-situ polymerization and insitu compatibilization in a batch mixer. They found that the domain sizes of the polypropylene and polyamide components in the blends could be easily controlled through proper management of the polymerization and compatibilizing reactions during processing.

Dynamic vulcanization

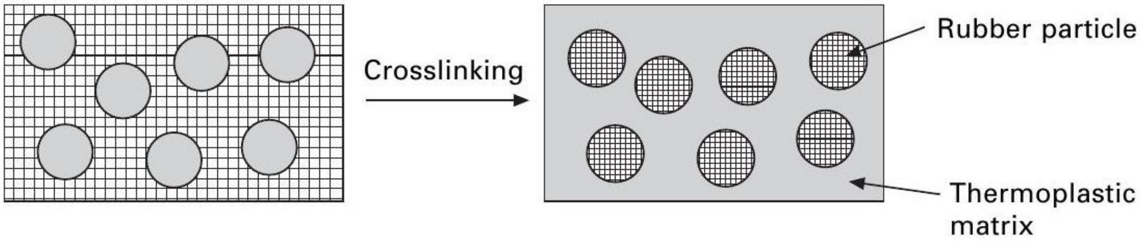
Dynamic vulcanization is a process of vulcanizing an elastomer, during the melt-mixing process, with a non-vulcanizable molten thermoplastic. It has been used as a compatibilization method of immiscible polymer/polymer pairs, being an important way to synthesize polymeric materials with controlled morphology. The process of vulcanization profoundly changes the molecular structure of the rubber: the long rubber molecules (usually having molecular weights of 100 000-500 000) become linked in junctures (crosslinks) spaced along the polymeric chains, with the average distance between junctures corresponding to a molecular weight between crosslinks of about 400010000.

Dynamic vulcanization has been widely used to prepare vulcanized thermoplastics (TPVs), which are a particular class of TPEs. The crosslinking enhances the viscosity and elasticity of the rubber phase and, as a consequence, the final TPV morphology consists of crosslinked rubber particles dispersed in a thermoplastic matrix, even if large amounts of rubber are used (Fig. 18.3).

As a result, TPVs are multi-functional polymeric materials that generally possess the processability of thermoplastics and the elasticity of vulcanized rubber. Crosslinking during blending is essential for producing TPV products with optimum properties. In comparison to simple, non-crosslinked blends, TPVs have enhanced elasticity and oil resistance. In addition, dynamic vulcanization is a way to disperse rather large amounts of elastomer in the thermoplastic matrix, resulting in TPVs with a low hardness, and to prevent coalescence, resulting in a refined morphology. TPVs are characterized by sub-micron scale morphologies and excellent physical properties.

Even though the commercial TPVs are based on an ethylene-propylenediene (EPDM) rubber and polypropylene (PP), other types of rubbers and thermoplastics have been used, such as polyethylene (PE), polystyrene (PS), polyamide (PA), ethylene-vinyl acetate copolymer (EVA) and natural rubber (NR).

Several crosslinking agents (curing systems) are employed to crosslink the EPDM phase in PP/EPDM blends. Each and every crosslinking system has its own advantages and disadvantages. The most used are activated phenolformaldehyde resins, commonly known as resols, and peroxides.



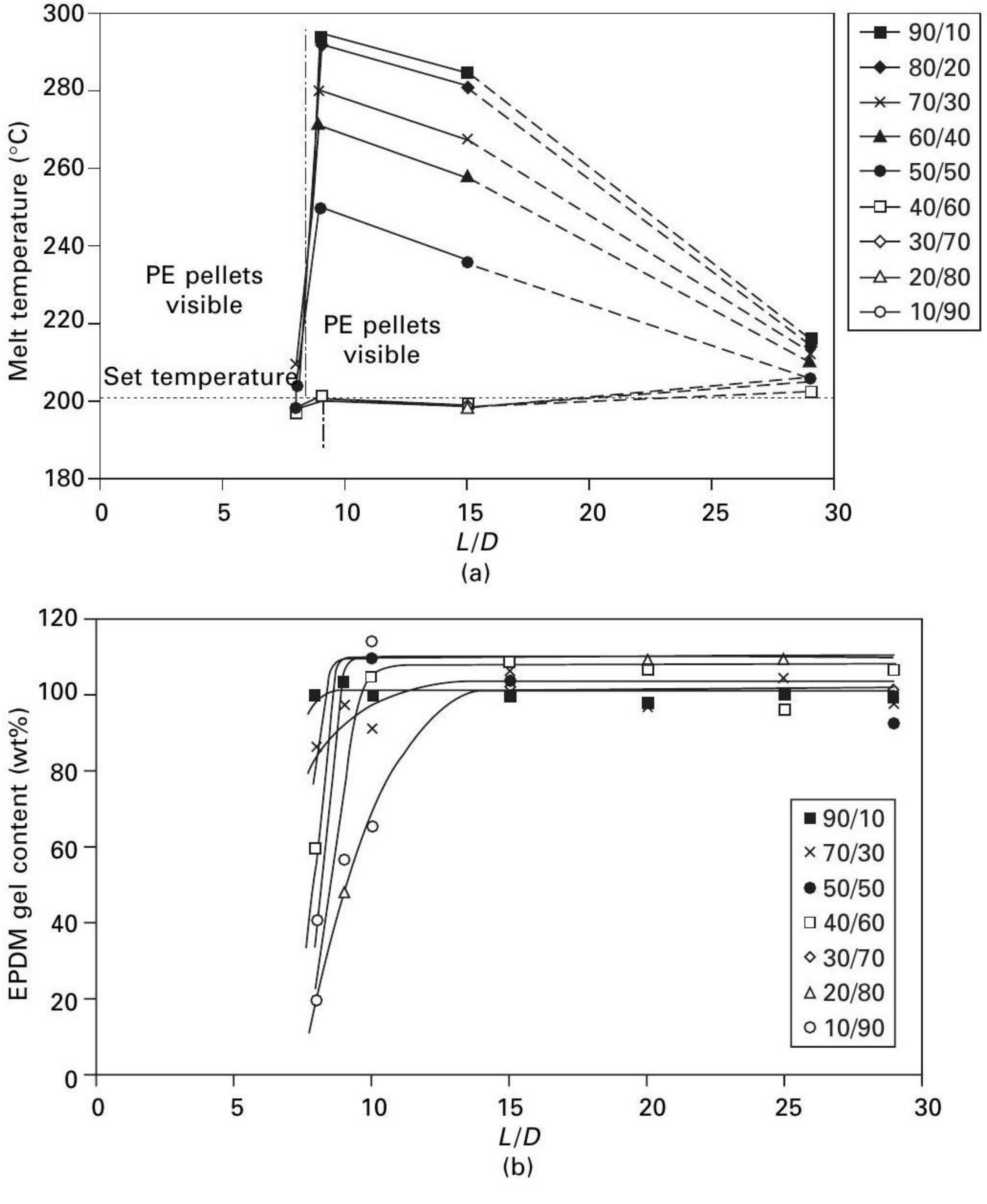
18.3 Morphology development during dynamic vulcanization.

As stated above, the basic parameters controlling the properties of polymer blends are the achieved morphology, the composition, the mixing conditions, the properties of individual phases, the interfacial tension, the viscosity ratio and the elasticity ratio. In the case of TPVs, the curing system and the degree of crosslinking also have an effect on the properties [93-96]. Since the appearance of TPV blends in the field of polymer science in the 1980s, several patents and publications have appeared. Most of these publications are based on works done with an internal mixer and only a few have studied the processing-morphology-property relationships of TPV blends produced in a twin-screw extruder [97]. Cai and Isayev [98] studied the dynamic vulcanization of copolyester/nitrile rubber blends by using various mixing techniques such as internal mixing, open mill mixing and twin-screw extrusion. They showed that better performance characteristics are obtained with the last of threse techniques.

Machado and Duin [99] investigated simple blending and dynamic vulcanization of EPDM/PE blends using the resol/ ¿ $SnCl_2$ system studied in an extruder. From the samples collected along the extruder axis it was observed that crosslinking of the EPDM phase to high levels occurs already when the PE phase is not yet fully molten (Fig. 18.4a and b). This study showed that dynamic vulcanization in extruders proceeds quite differently from that in batch kneaders, where melting, mixing and crosslinking are separated in time. In extruders mass and heat transport, melting of the thermoplastic, morphology development (including dispersion and phase inversion), distribution and dissolution of (crosslinking) chemicals and crosslinking of the rubber do not occur as independent phenomena, but mutually and/or continuously interact.

The effect of dynamic vulcanization on properties was studied by Huy et al. [100], who showed that dynamic vulcanizates exhibit large reversibility and small residual strains and that, in general, the mechanical properties of dynamic vulcanizates differ significantly from those of the blends with a non-crosslinked rubber phase. Nakason et al. [101] prepared various TPVs using different crosslinking agents; it was found that TPVs with phenolic resin showed higher tensile strength, elongation at break and tendency to recover from prolonged extension.

As shown in Fig. 18.3, the most common and desired morphology in TPVs is a dispersed elastomeric phase in a thermoplastic matrix. This morphology is initially made of droplet particles of thermoplastic when the rubber is present as the major component. At the initial stages of dynamic vulcanization, a co-continuous structure can be generated, and, as the degree of crosslinking increases during mixing, the rubber is fully dispersed in the matrix [102]. Research has been performed to understand the mechanism of morphology development during TPV preparation in order to be able to control the morphology and, consequently, the properties.



18.4 Preparation of EPDM/PE TPVs with crosslinking along screw axis: (a) melt temperature; (b) EPDM gel content [99].

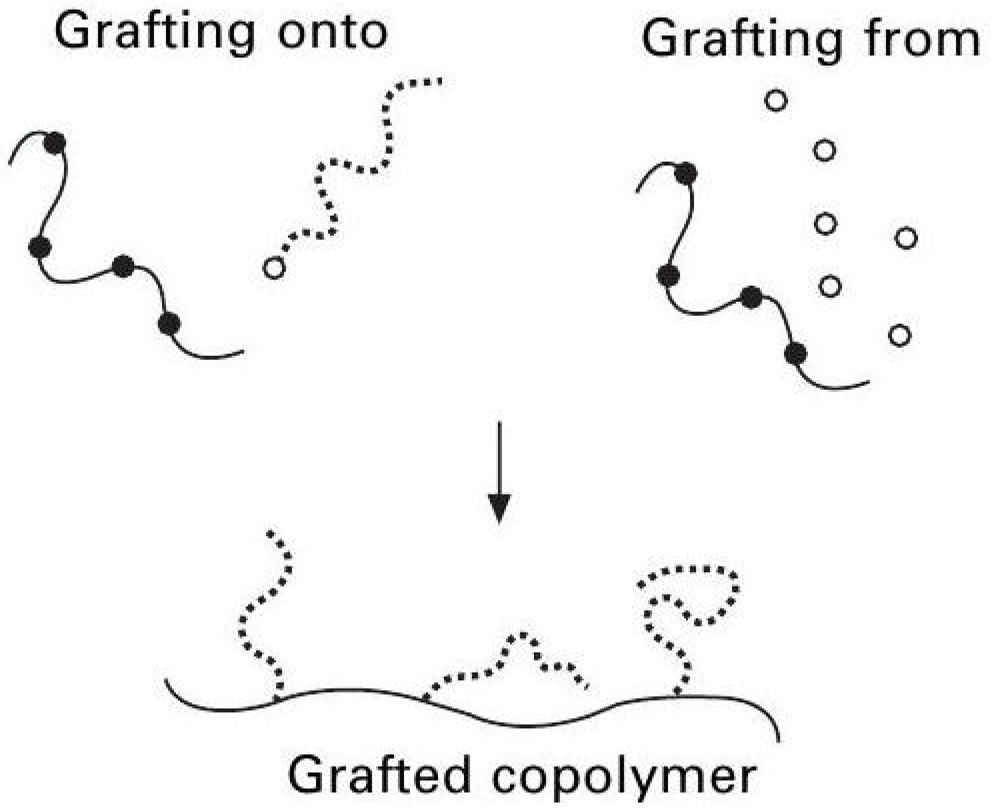
Joubert et al. [103] investigated the preparation of a TPV based on a copolymer of ethylene and vinyl acetate (EVA) and polypropylene (PP) as thermoplastic phase in a batch mixer to get a better understanding of the dispersion mechanism and of the phase inversion of the EVA major phase during its dynamic vulcanization into the PP minor phase. The crosslinking reaction is carried out through a transesterification reaction between ester groups of EVA and alcoxysilane groups of the crosslinker agent, tetrapropoxyorthosilicate. They concluded that the characteristic time of crosslinking must be of the same order of the time of mixing, that better mechanical properties were obtained when a progressive phase inversion occurred and when it was controlled by rheological aspects and transient morphology equilibrium of the two phases. A similar study was performed by Verbois et al. [104], aiming to get a better understanding of the dispersion mechanism of EVA in the major phase during its dynamic vulcanization in the presence of PP in the minor phase. This paper deals with the correlation that exists between the evolution of the two-phase blend morphology and the extent of the crosslinking reaction on the elastomer phase during the elaboration of a TPV. From the gel content and morphology analyses, the authors showed that the correlation between the evolution of the two-phase blend morphology and the crosslinking reaction conversion was almost the same for tailoring of the TPV in the internal mixer and in the twin-screw extruder.

New copolymers

Classically, three main ways of synthesizing block or graft copolymers are reported in the literature:

1. Living copolymerization
2. Chemical modification by post-polymerization
3. Coupling between two appropriately functionalized polymer chains.

Figure 18.5 illustrates schematically that approaches (1) and (2) can be associated with the 'grafting from' method, and approach 3 with the 'grafting onto' method. This illustration of grafted copolymer synthesis, however, is as simple as the reality of the synthesis is complicated. Reaching this structure by reactive processing, which means at high temperature, under shearing and usually in a highly viscous medium, is very challenging. However, the research interest in terms of materials applications attributable to the potential nanostructuration and the importance of reactive processing in terms of industrial applications explains the abundance of literature on this subject.



18.5 Synthesis of grafted copolymers.

Living copolymerization

There has been active research on homopolymerization by reactive extrusion since the 1960s, but investigations on copolymers have been conducted only since the 1990s and covers various types of reaction. Indeed, reactive extrusion is an attractive route for polymerization or copolymerization, because of its numerous advantages. In this section, this will be illustrated through the main chemical reactions (ring opening, anionic copolymerization, etc.) and the efforts developed by several research groups to deeply and fundamentally benefit from breakthroughs in processing to obtain nanostructured copolymers. We will also underline the difficulty in controlling the stability of the structures under normal processing conditions, since for example and according to the reactivity ratio and side reactions, such as transesterification, often evolve towards random copolymers.

Historically, in 1993, Michaeli et al. [40, 105] described the manufacture of polystyrene (PS) or the styrene (S) and isoprene (I) copolymers in a twinscrew extruder through anionic living bulk polymerization initiated by secbutyl lithium. They demonstrated the possibility of copolymerizing the styrene in an extruder even at a temperature over $200^{\circ} C$. They reported that the sequential feeding of monomers produced a diblock copolymer whereas the simultaneous feeding of monomers produced a random copolymer.

Gao et al. [41] discussed the mechanism of living anionic polymerization of a novel styrene-b-butadiene block copolymer in a co-rotating intermeshing twin-screw extruder. They particularly explained the difference of reaction mechanism between a conventional batch reactor and the twin-screw extruder. Since the twin-screw extruder is partially filled, butadiene, mainly in the gaseous phase, occupied the unfilled part of the barrel. Thus, a small part of the butadiene that diffused in the polymer melt polymerized immediately. As a result, S-B diblock copolymer or S-B-S triblock copolymers are formed, whereas as the reaction conditions in the extruder are different, multi-S-Bblock copolymers are obtained. These experiments were recently completed [106] with a numerical simulation of the reactive extrusion for the block copolymerization of S/B in co-rotating twin-screw extruders highlighting this complex reaction associated with diffusion considerations.

The ring opening copolymerization of various cyclic monomers such as lactams, lactones, 1,4-dioxan-2-one, lactides and carbonates in a twin-screw extruder has also been widely studied due to the reaction kinetics being compatible with the process conditions (high monomer conversion in a very short range of time at high temperature, good control of the structure through the judicious choice of the polymerization initiator). The great interest in these copolymers is also based on their potential to participate in the development of biodegradable polymeric materials.

For example, Raquez et al. [59, 107] recently published a review on specific homo- and co-polymerizations carried out by reactive extrusion. In particular, they showed that in approximately 2 minutes, $100\,\%$ of conversion is obtained at $130^{\circ}C$ with $Al\left(O_{\sec}\ Bu\right)_3$ as initiator for the copolymerization of ε-caprolactone with 1,4-dioxan-2-one. A very interesting point observed is the increase of the copolymerization yield with the increase of the molar fraction of ε-caprolactone within the copolymer increases. Kim and White [58, 108, 109] described the influence of screw speed, feed rate and monomer over initiator ratio on the evolution of the copolymer structure and molar mass based on ε-caprolactone and lactam. They particularly focus on polyamide-based copolymers such as poly(lauryllactam-block-caprolactone), poly(caprolactam-block-caprolactone), poly(caprolactam-block-caprolactoneblock caprolactam) and poly(lauryllactam-block-caprolactone-blocklauryllactam). They demonstrated that the order of monomer addition is very important. Indeed, in the reactive extrusion process, the growing reactive species must be able to initiate quickly the second monomer fed into the second hopper for the block copolymerization. For example, when they fed the lactam into the hopper and the caprolactone sequentially into the second hopper, a lactam-caprolactone block copolymer was obtained. However, when they fed caprolactone firstly into the first hopper and then lactam into the second hopper, the extruded product was a mixture of poly(ε-caprolactone) and lactam monomer. The respective block length of the copolymer can be adjusted by controlling the feed rate of each monomer during the extrusion.

Chemical modification by post-polymerization

The second way to prepare block or graft copolymers through the 'grafting from' method consists in polymerizing a monomer in an extruder in the presence of functionalized prepolymers or polymer (end- or pendant-functional groups initiating the monomer polymerization). Most of the monomers employed in the literature are the same cyclic monomers as those mentioned before. However, a few papers deal with other types of structure, such as macrocyclic carbonates.

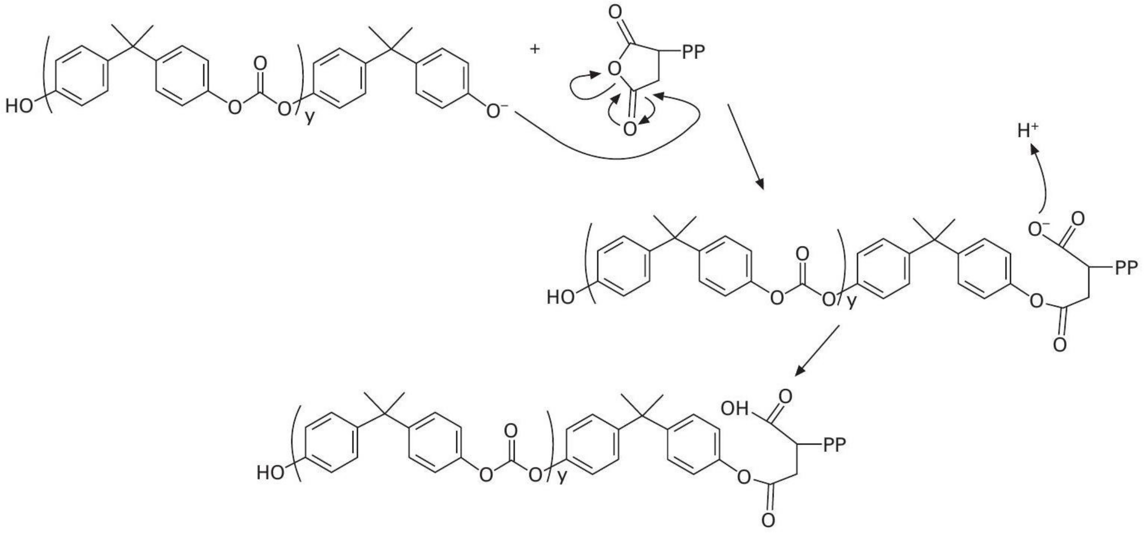
Polymerization of caprolactam was carried out in situ in the presence of an isocyanate-terminated telechelic poly(tetramethylene ether) glycol (PTMEG) [110]. Analysis of the polyetheramide triblock copolymer showed that the conversion of caprolactam is around 95 %, which is close to the equilibrium conversion of caprolactam. Zuniga-Martinez and Yanez-Flores [111] also polymerized ε-caprolactam in the presence of a linear prepolymer of poly(etheresteramide) presenting acyllactam end groups. More recently, Rached et al. [112] developed a new macroinitiator (α,ω-dicarbamoyloxy caprolactam PDMS) for the anionic ring-opening polymerization of lactams. By adjusting the molar ratio of lauryl lactam to macroinitiator, a series of triblock copolymers, PA12-b-PDMS-b-PA12, were obtained with increasing molar weight of the PA12 hard blocks.

Concerning the ring opening polymerization of lactide, Jacobsen et al. [63] developed first the possibility to produce these biodegradable aliphatic polyesters by reactive extrusion. They studied also the possibilities to extend this polymerization process to lactide based block copolymers through the use of prepolymerized hydroxyterminated poly- ε-caprolactone or polyethylene glycol. No significant influence on the propagation of the polymerization reaction of lactide during reactive extrusion is noticed in presence of these hydroxyl species. Stevels et al. [113] reported also the polymerization of Llactide initiated by either a hydroxyl-terminated poly- ε-caprolactone (PCL) or a polyethylene glycol. Our own group was also concerned with the opportunity to obtain block copolymer from poly(bisphenol A carbonate) and ε-caprolactone monomer [114]. The polymerization of ε-caprolactone from a phenoxy titanium end-group created by in-situ exchange reaction between carbonate function and *n*-titanium propoxyde was carried out (Fig. 18.6). High extrusion temperature leads to random copolymers due to transesterification side-reactions, whereas a decrease of temperature after the incorporation of the *n*-titanium propoxyde leads to block copolymers.

The ε-caprolactone monomer was also used in the synthesis of graft copolymers. For example, Becquart et al. [115, 116] functionalized a poly(vinylalcohol-co-vinylacetate) by grafting small poly- ε-caprolactone from the in-situ polymerization of the lactone ring. The hydroxyl groups are the point of initiation of the polymerization but also sites of alcoholysis reactions, leading to a distribution of the poly- ε-caprolactone along the initial polymer backbone. Transfer reactions and the specificity of some initiators to synthesized grafted copolymers of EVA and EMA with ε-caprolactone, cyclic butylene terephthalate (cBT) and lactide by reactive extrusion were also employed. Ti¿ is an initiator judiciously created for its selective properties regarding transfer reactions and therefore grafting, leading to an increase of the grafting efficiency compared to more classical titanium initiators. For example, in the case of in-situ polymerization of cBT in the presence of EVA and the previous initiator, the amount of grafted copolymers was evaluated up to 30% in weight. Ultrathin sections of 50 nm treated with ruthenium tetraoxide revealed by TEM the presence of fine and well-dispersed PBT of around 500 nm diameter.

Other cyclic monomers such as lactam and macrocyclic carbonate have been studied. Madbouly et al. [117] investigated the in-situ polymerization of macrocyclic carbonates in the presence of PP-g-MA (Fig. 18.8). They demonstrated that the degree of polymerization decreased with increasing concentration of maleic anhydride. This was consistent with a higher proportion of graft copolymer formed.

Polypropylene was also grafted modified through in-situ polymerization of lactam. Hu et al. [91, 118] first prepared a polypropylene-g-isocyanate macroactivator from 0.27 to $1.34\,wt\,\%$ of the isocyanate (NCO) group. The polymerization of caprolactam carried out in a second step in the presence of NaCl as catalyst revealed that the higher the NCO content in $PP-g-NCO$, the higher is the polymer yield. They demonstrated by selective solvent extraction that $70-90\%$ of the initial weight was pure PP-g-PA6.



18.7 In-situ polymerization of macrocyclic carbonates in presence of PP-g-MA.

Unsaturated monomers have been the subject of only a few studies. For example, Shi et al. [119] studied the grafting copolymerization of acrylic acid and methyl methacrylate by reactive extrusion onto pre-irradiated linear low density polyethylene. However, the rate of grafting is very low and homopolymers are also formed, showing the importance of the monomer solubility in molten polymer. Badel et al. evidenced the same phenomenon [120] by dealing with the free radical grafting of methyl methacrylate onto a poly(ethylene-co-1-octene). Indeed in that last case the grafting rate under normal in processing conditions was less than $20\,wt\,\%$. Willett and Finkenstadt [121] prepared starch-grafted polyacrylamide by polymerizing the acrylamide in an extruder in presence of starch. Conversion of monomer to polymer, graft content, grafting efficiency and polyamide molecular weight were determined. Monomer conversion appeared to be independent of the residence time. These few illustrations provide evidence that many parameters, such as the nature of the reaction, the monomer miscibility in the melt matrix and the processing parameters, could influence the synthesis of copolymers.

Coupling between two appropriately functionalized polymer chains

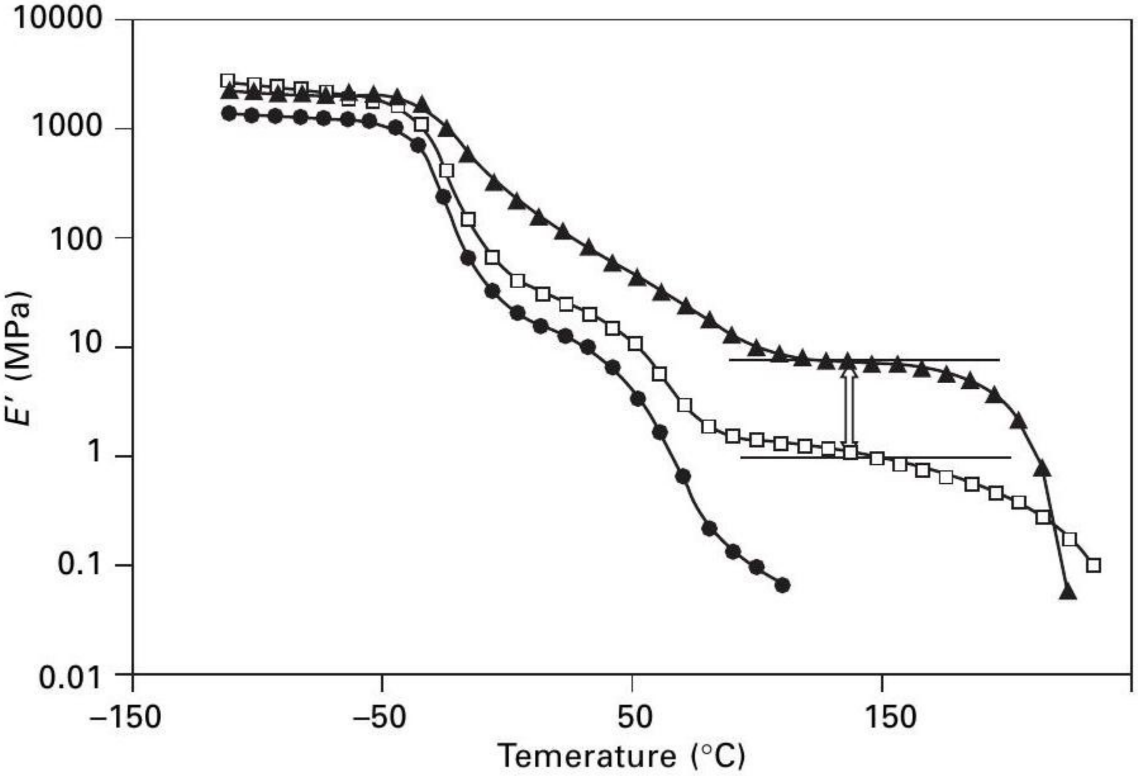
The last method described for block or grafted copolymer synthesis consists in the coupling between two functionalized homopolymers. The main difficulty of this means of copolymer synthesis in the melt lies in the fact that polymer/polymer pairs are generally immiscible. Thus, the chemical reaction occurs at the interface. Paradoxically, the synthesis of copolymers by interfacial reaction stabilizes this emulsion and the formation of a greater quantity of copolymer is then difficult or even impossible. This interfacial reaction leading to the in-situ synthesis of a small quantity of copolymer (1%) should thus be considered as a compatibilization process of polymer blends. Therefore, when the aim is the synthesis of nanostructured copolymers, other parameters have to be optimized in order to increase the concentration of the synthesized copolymer. In this case, copolymers can both arrange themselves at a nanometric scale and also be organized at a larger scale, resulting in a nanostructured material. The nanostructure obtained can be related to the copolymer architecture based in particular on the size and on the molar mass of the sequences of the grafts.

Ideal models, based on the reaction at the interface between two functionalized polymers, showed that initially, the speed of formation of copolymer depends on the reaction speed between two reactive groups of the corresponding chains. The reaction evolution will then be strongly limited by the copolymer formed on the interface [122]. The residual homopolymers must adopt a configuration stretched with low entropy in order to cross the polymer brush. Some studies also highlight an intermediate mode dictated by the diffusion of the reactive chains to the interface, which depends on the chain length and the reactivity of the chemical groups [123-126]. The reaction kinetics also depends on the position of the reactive groups on the chains. The functional groups at the end of the chain react more quickly than those located along the chain [127]. The ends of the chains have a tendency to diffuse to the interface

[128]. Furthermore, a greater quantity of copolymer is formed more quickly at the interface in the case of shorter chains. Thus, in the case of a reaction between two functionalized polymers at the interface, the ideal to obtain high copolymer rates is to use very short funtionalized compounds with a fast reaction [129].

Relevant results were reported by Leibler and his group [129-132] for self-organized materials from grafted copolymers of poly(methylmethacrylate) and polyamide-6 obtained by reactive mixing in molten state [133] on polyolefin-polyamide blends. In this last case, depending on the characteristics of the two polymers, macro- or nanophase separation can be obtained and the analysis of the thermomechanical properties evidenced the appearance of an elastic modulus plateau at around $80^{\circ}C$ (Fig. 18.8). However, the value of this modulus is higher when nanostructures are obtained.

In a work dedicated to the synthesis of graft copolymer PMMA, PA-6 [132] through the reaction between glutaric anhydride randomly distributed along the backbone of PMMA and amino groups from the other partner (PA-6), the influence of the number of graft functionality was studied. High fractions of graft copolymer (35-75 wt%) were obtained, the higher amount being observed by increasing the amount of PA-6 in the blend or the anhydride content on the functionalized PMMA. The molar mass of the homopolymer has a great influence of the stabilization of the morphology. During the grafting reaction between the maleic anhydride function of a random copolymer of ethylene, ethylacrylate and maleic anhydride ($Mn=9300 \; g\cdot \; mol^{-1}$) and the NH_2 end-group of a PA-6 ($Mn=2500 \; g.mol^{-1}$), grafted copolymers formed a co-continuous structure at the nanoscale, which is swollen by the homopolymers without microphase separation. The effect of such nanostructure on the thermomechanical properties was pronounced.



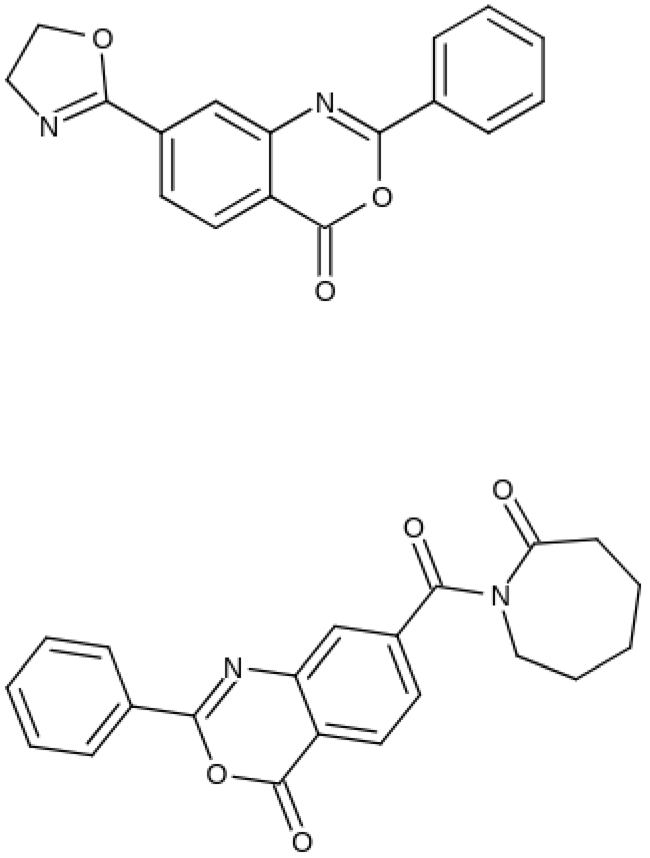
18.8 DMA characterization of macrophase and nanophase separated PA-g-PO compared with parent polyolefin [133].

Taking into account the previous parameters, nearly pure graft copolymer was obtained by Steurer and Hellmann [134] by reactively blending equal amounts of poly(styrene-co-maleic anhydride) and short polyamide 12. Orr et al. [135] employed a very fast cyclic anhydride-aliphatic amine reaction between polystyrene and polyisoprene end-capped with anhydride and amine functions, respectively, to create a uniform morphology with molecularscale self-assembly into cylindrical micelles over the entire sample.

Several authors also reported copolymer formation obtained from (i) anhydride end-functional polyolefins and α-amino polystyrene, (ii) maleic anhydride grafted poly(ethylene-co-propylene) and amine- or carbamate functionalized poly(styrene-co-acrylonitrile) for designing nanostructured blends, and (iii) amino-terminated polyamide-12 and carboxy-terminated poly(butylene terephthalate) [136-141]. In the last case, multifunctional coupling agents had oxazoline and oxazinone reactive groups such as compounds and 2 (Fig. 18.9).

The oxazoline group can react with carboxylic groups and the oxazinone can react with amino or hydroxy groups. This type of reaction was used for the chain extension of AB polyamide and the synthesis of polyamide-polyether block copolymers. Compound 2 can be used as a selective coupling agent for hydroxy and amino group containing polymers (Fig. 18.9).

Whatever the system, the key feature is the precise design of the architecture of the functional homopolymers or copolymers that are to be combined.



18.9 Structure of compounds 1 and 2 .

Equipment

Prerequisites and characteristics

From a practical point of view, the reactive processes studied in the previous sections involve a series of individual steps, such as feeding the components (either together or sequentially), melting them, mixing in terms of distributive and dispersive homogenization, devolatilizing, and working the new polymeric system into a useful physical shape (in the case of reactive extrusion, this usually corresponds to generating pressure flow through a die for subsequent pelletization).

The advantages of using an extruder as a chemical reactor (for polymerization purposes) were recognized in the 1950s [142]. Unlike batch reactors, extruders ensure continuous production and avoid the use of solvents to dilute the viscous polymer. Hence, apart from the obvious environmental benefits, energy savings are obtained from the elimination of solvent heating and cooling, as well as separation steps. A single-screw extruder was then used, as it was assumed that its behavior was similar to that of a plug flow reactor, and so a shorter residence time distribution would induce a narrow molecular weight distribution. Also, the average residence times could be sufficiently high (of the order of tens of minutes). During the 1960s and 1970s the machine was also used for polymer chain breaking and grafting of monomers to polyolefins. However, several authors pointed out that the use of other types of extruders, such as counter-rotating and co-rotating twinscrew extruders, seemed more suitable to the specificities of some chemical reactions, combinations of various types of equipment having also been proposed [143].

Successful reactive extrusion, scalable to industrial production, should involve reactions that are compatible with the general characteristics of extruders [28, 37, 144, 145]:

- The chemical reaction(s) should have low activation energy and be fast, i.e., chemical conversion should be completed inside the extruder; in the case of polymer blending, the polymers should either have a high concentration of reactive groups, or should be highly reactive, to ensure a high conversion into copolymers.
- Both the reagents and the resulting new polymeric system should be stable at the compounding temperatures. Stability of the chemical bonds formed implies also that they should remain unaffected by subsequent conventional processing operations (which involve a new thermomechanical cycle).
- The instabilities that are inherent to the extrusion process should not affect the reaction rate and yield.
- The sub-products of the reaction should be easily removed.

In turn, an extruder is adequate for use as a chemical reactor if it satisfies the following requirements:

- It allows the sequential addition of the ingredients (monomer, polymer, water, solvent, reactant, etc.), which may have distinct physical forms, at different locations along the screw.
- It behaves as a continuous plug flow reactor and is able to work with materials that may present a wide range of characteristics (gas, solid, powder, highly viscous fluid).
- It allows the efficient removal of remaining ingredients or low molecular weight by-products via devolatilization.
- It provides a sufficiently long reaction zone.
- It allows working in an inert atmosphere.

- It creates a thermally homogeneous environment (to avoid side-reactions).
- It provides good interfacial generation, good mixing (as well as mixing control) and efficient heat transfer.
- It guarantees efficient control of pressure, temperature and residence time.
- It is easy to couple to downstream equipment that will shape the final product (generally, pellets).
- It allows the production of diversified polymer systems.

Single-screw extruders are widely used by plastics processors because they are easy to operate and require less investment than more complex machines. Nowadays it is possible to design screws fitted with mixing devices that guarantee good pressure generation and distributive mixing ability. However, their capacity for sequential addition is usually limited. Consequently, they are generally used for relatively simple operations, such as modification of polyolefins with peroxide, or silane grafting [146].

Counter-rotating intermeshing self-wiping twin-screw extruders fulfill most of the above requirements, namely they provide very good control of pressure, temperature and residence time. However, the maximum screw rotation speed is low (usually below 50 rpm), which affects the dispersive efficiency. Copolymerization of styrene- *n*-butylmethacrylate, polymerization of *ε* caprolactam, the grafting of maleic anhydride on polyethylene, the polymerization of urethanes and the radical polymerization of several methacrylates are examples of reactions performed in this machine [147]. Counter-rotating machines of the non-intermeshing type provide excellent distributive mixing at low shear rates, but they have limited pressure generation capacity and dispersive mixing efficiency. They are often used for polycondensation reactions.

Co-rotating intermeshing self-wiping twin-screw extruders have become quite popular for reactive extrusion operations. In general, co-rotating twinscrew extruders have the following features [148, 149]:

- Modular construction, i.e., the geometry of the screw and barrel can be adapted to the needs of a particular system, in terms not only of the feeding sequence of the components, but also of the mixing intensity, average residence time and conveying capacity; by setting an adequate screw profile (which consists in the selection of a number of screw elements from a wide range of units with different geometries), the process engineer can control the location of melting, the number of mixing zones and the corresponding mixing intensity.
- Modularity provides also the capacity to perform, in a relatively wellcontrolled manner, sequential operations such as melt/mixing,

devolatilization and the incorporation of additives and/or fillers once the reactive step is accomplished.

- The operator has independent control over output, screw speed and temperature; this allows the extruder to be operated under starving mode, i.e., the screws work partially filled over a significant portion of their total length, which decreases the mechanical power consumption, promotes distributive mixing and helps to control melt temperature (as viscous dissipation in the mixing zones can be quite important).
- The screws can rotate at high screw speeds (above 1500 rpm), thus ensuring high production rates.
- There is sufficient pressure generation capacity to couple the extruder either to a die and pelletizing equipment (in order to manufacture a compound in pellet form) or, generally via the insertion of a gear pump, to a die and downstream equipment suitable for the manufacture of a final product (this operation is usually known as direct extrusion), for example the reactive spinning of elastomeric polyolefin fibers [150].

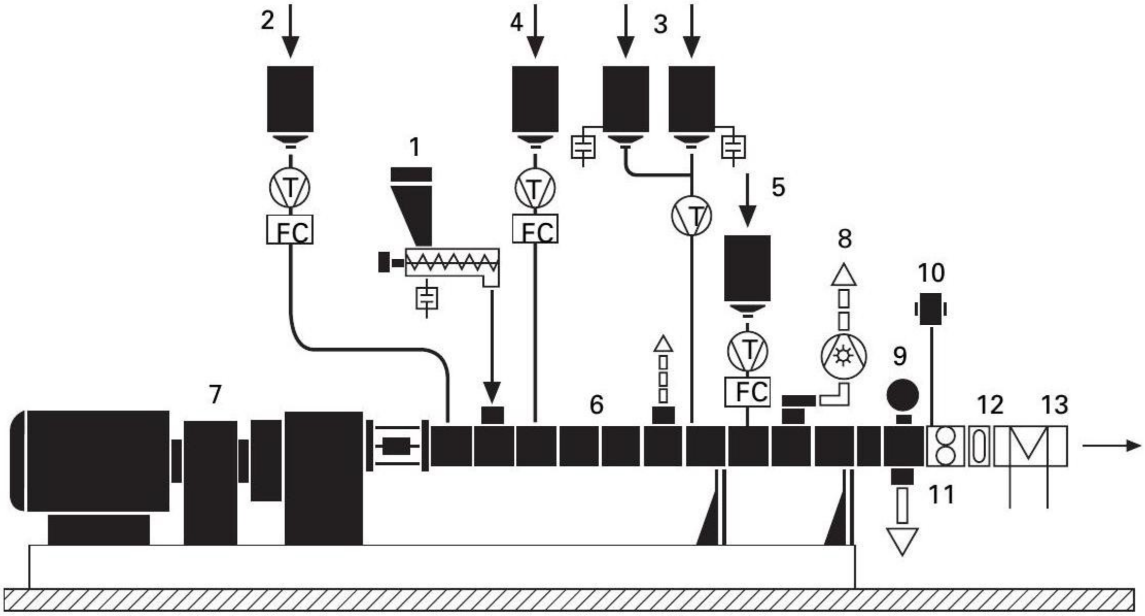
Table 18.1 compares the main characteristics of the types of extruders that are used more often for reactive extrusion (see also [151-153]). The popularity of co-rotating twin-screw extruders is most probably associated with their construction modularity and the knowhow on this technology that has been slowly accumulated by both academia (using small-scale machines) and industry. They can reach high L/D ratios (up to 100, but most commonly up to 50) and the components of the polymer system can be fed by gravimetric or volumetric feeders along the axis. As an example, Fig. 18.10 shows the layout of a machine for the preparation of reactive sealing compounds.

Usually, the screws of a co-rotating twin-screw extruder consist of a series of conveying elements separated by a few mixing zones, which are restrictive in terms of flow conveying capacity and, depending on their geometry, may induce more or less intensive mixing. When the material enters the extruder, it follows a figure-of eight pattern along the helical channels of the partially filled conveying elements. Once the flow meets a restrictive element (typically, a kneading block comprising disks staggered with a negative or neutral angle, or a pair of elements with negative conveying angle), it accumulates immediately upstream, in order to generate the pressure required to continue flowing in the axial direction. The higher the pressure required, the longer the portion of the length of the conveying elements that works fully filled.

Table 18.1 Comparative features of extruders for reactive extrusion

	Single-screw extruder	Co-rotating intermeshing twin-screw extruder	Counter-rotating intermeshing twin-screw extruder	Counter-rotating tangential twin-screw extruder
Output	+++	+++	++	+++
Screw speed	++	+++	-	+++
Pressure generation	++	+¿	+++	-
Distributive mixing	++	+++	++	+++
Dispersive mixing	+¿	++	+¿	-
Breadth RTD	+	+	+++	+
Devolatilization	++	++	++	++
Self-wiping	++	+	++	-
Screw separation	+++	++	-	++
Viscous dissipation	++	+	+++	+++

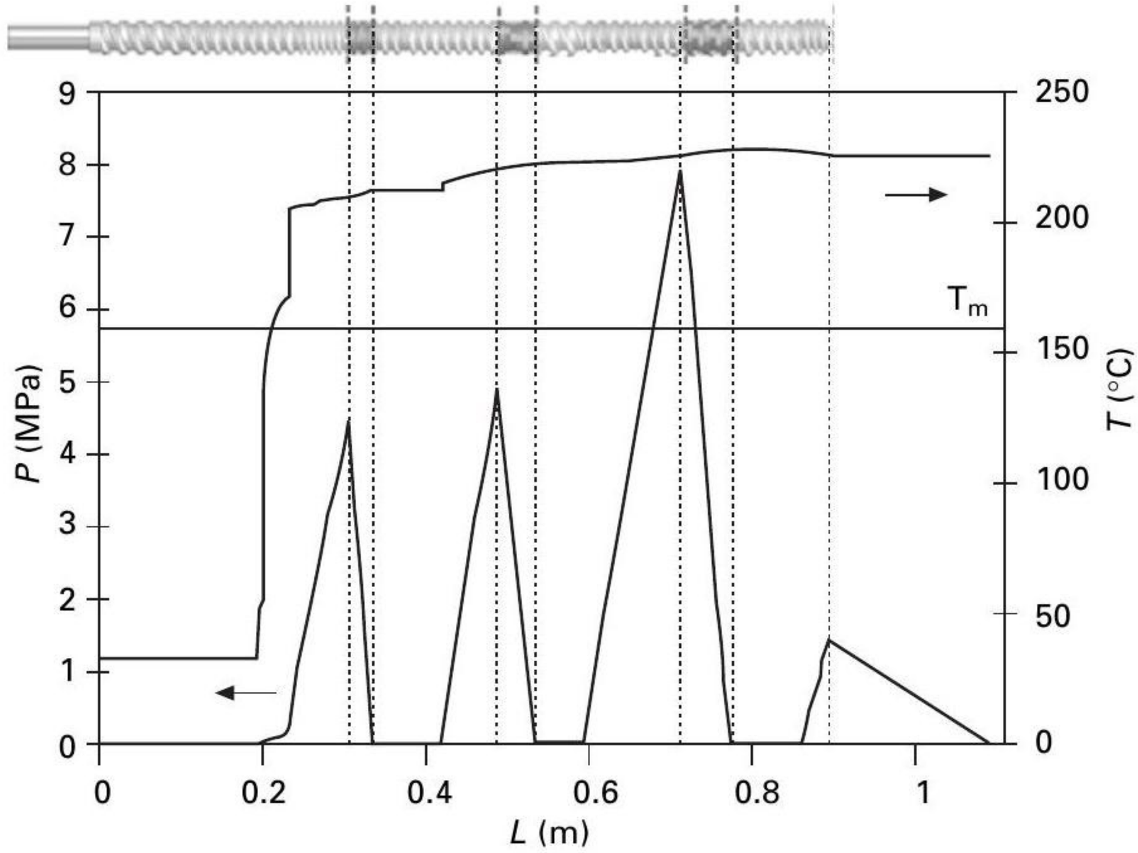
very good; ++ good; + fair; - poor.



18.10 Production of a reactive sealing compound (Coperion: www.coperion.com). 1 aerosil; 2 silicon polymer; 3 silicon oil; 4 crosslinking agent; 5 catalyst; 6 barrel; 7 drive unit; 8 vacuum unit; 9 start-up valve; 10 on-line viscometer; 11 gear pump; 12 screen pack changer; 13 heat exchanger.

Figure 18.11 shows predictions of axial pressure and temperature profiles developing with a screw comprising three restrictive zones, also indicated. Notice the importance of viscous dissipation during flow along restrictive zones.

Restrictive elements create a complex 3-D flow (particularly in the apex region) and induce significant shear and extensional stresses. Thus, depending on their geometry, mixing intensity and/or the occurrence of melting can be controlled. Mixing effects play a major part in reactive extrusion. Since one is usually dealing with high melt-viscosity systems, diffusion-base reactions are dominant, i.e., the machine should generate efficiently interfaces between the components. From a distributive mixing point of view, melt deformation and reorientation are mandatory (and determined by the flow field complexity, average shear rate and time), while dispersion is governed by the intensity and type of the stresses induced (the flow should have a strong extensional component). Table 18.2 shows how the helix angle of conveying elements and the staggering angle of kneading blocks can affect conveying and mixing. Generally, the first restrictive section upstream induces melting, due to the combined contribution of local frictional forces and heat transfer. Melting in a twin-screw extruder is much more rapid, although more complex, than in a single-screw machine. Polymeric components melt and form either matrices or droplets (depending on their concentration and viscosity ratio), which rapidly change in domain size. Simultaneously, solid agglomerates are ground and release smaller aggregates or individual particles. Therefore, in the case of polymer blending, melting has a major effect on morphology evolution.



18.11 Axial pressure and temperature profiles along a co-rotating twin-screw extruder and die [154].

Table 18.2 Effect of the helix angle of conveying angles and the staggering angle of kneading blocks on conveying and mixing ((a) and (b) should not be directly compared)

		Conveying	Mixing		Local residence time
			Distributive	Dispersive	
Conveying elements (helix angle)	Low	+¿	+¿	o	+++
	Medium	++	+	o	++
	High	+++	+¿	o	+¿
	Negative	-	+++	++	++++
(b) Kneading blocks		++	+¿	o	+¿
		+	++	+	++

(staggering angle)	Positive { Low Medium	0	+++	+++	+++
		-	++++	+++	++++

very high; +++ high; ++ medium; + low; 0 nil; - negative.

Scott and Macosko [78] proposed a morphology development model based on these process characteristics.

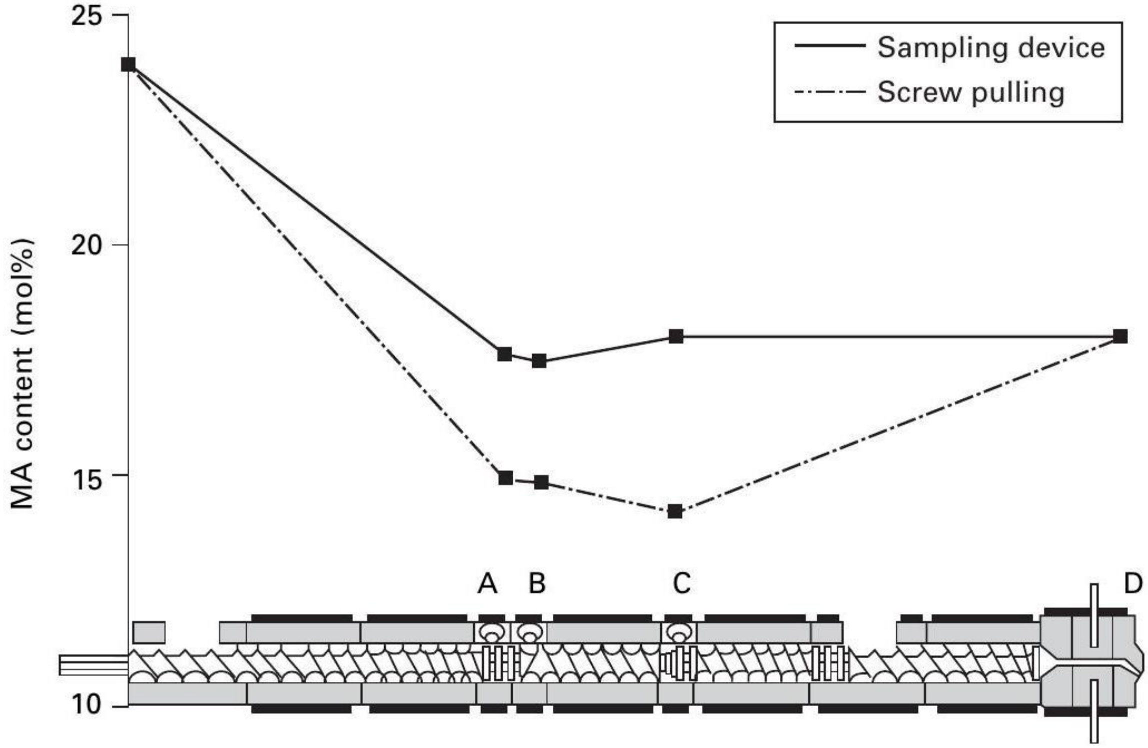
On-line monitoring

Reactive extrusion involves complex mixing processes, chemical reactions and, eventually, morphology development, which should progress along the screw at a pace that depends on local temperatures, residence time, stress levels and velocity fields. Since the extruder is a 'black box', initial research focused on the characterization of the extrudates in terms of reaction products and mechanical and physical performance. Correlations between material recipes, operating conditions and properties were also established. However, it was soon recognized upon performing experimental work in batch-mixing equipment that the thermomechanical environment has paramount importance on the reaction kinetics. Thus, it became evident that practical process optimization would require the detailed understanding of the chemical, rheological and physical phenomena involved in the preparation of a specific polymer system under pertinent thermomechanical conditions, as well as their development along the extruder.

Three approaches have been generally followed:

1. Collect and analyze relevant material specimens. This involves performing Maddock-type experiments [155], i.e., stopping the extruder, chilling the barrel as quickly as possible, removing the die and extracting the screws. This procedure may take several minutes, during which the material does not necessarily freeze sufficiently to prevent chemical/morphological changes taking place, such as coalescence of the disperse phase in polymer blends - thus, it is not surprising that coalescence of the minor phase during the experimental procedure has been reported [156, 157]. This is why some authors pour liquid nitrogen into entry ports [158]. The complexity and extent of these procedures can be minimized with the use of a split-barrel, i.e., a barrel built in two halves, which open like a clam. Other authors proposed the utilization of sampling devices [85, 159, 160] that allow the collection of samples during operation of the extruder. The technique proposed by Machado et al. [85] is particularly effective and simple to apply: the material is detoured from the screw channel through a side hole in the barrel, collected in a small cavity, manually removed and immediately quenched. Various devices can be positioned along the barrel, so that the evolution of physico-chemical processes can be followed.

Consider the reaction of a styrene-maleic anhydride co-polymer (SMA) with 1-aminonaphthalene, which occurs during reactive blending of polyamides and maleic anhydride-containing polymers, and results in the formation of cyclic imide. Figure 18.12 shows the evolution of the chemical reaction along the extruder in terms of MA content, based on samples obtained utilizing the sampling devices and the conventional screw pulling technique. The solid line (sampling devices) shows that imidation takes place mainly in the first part of the extruder, upon melting. By contrast, the long dwell time at high temperature associated with the screw pulling technique induces a decrease of MA content from 23.9 to $14.5\ mol\,\%$, which cannot be justified in view of the $18\ mol\,\%$ measured at the extrudate, which is independent of the sampling technique [161].

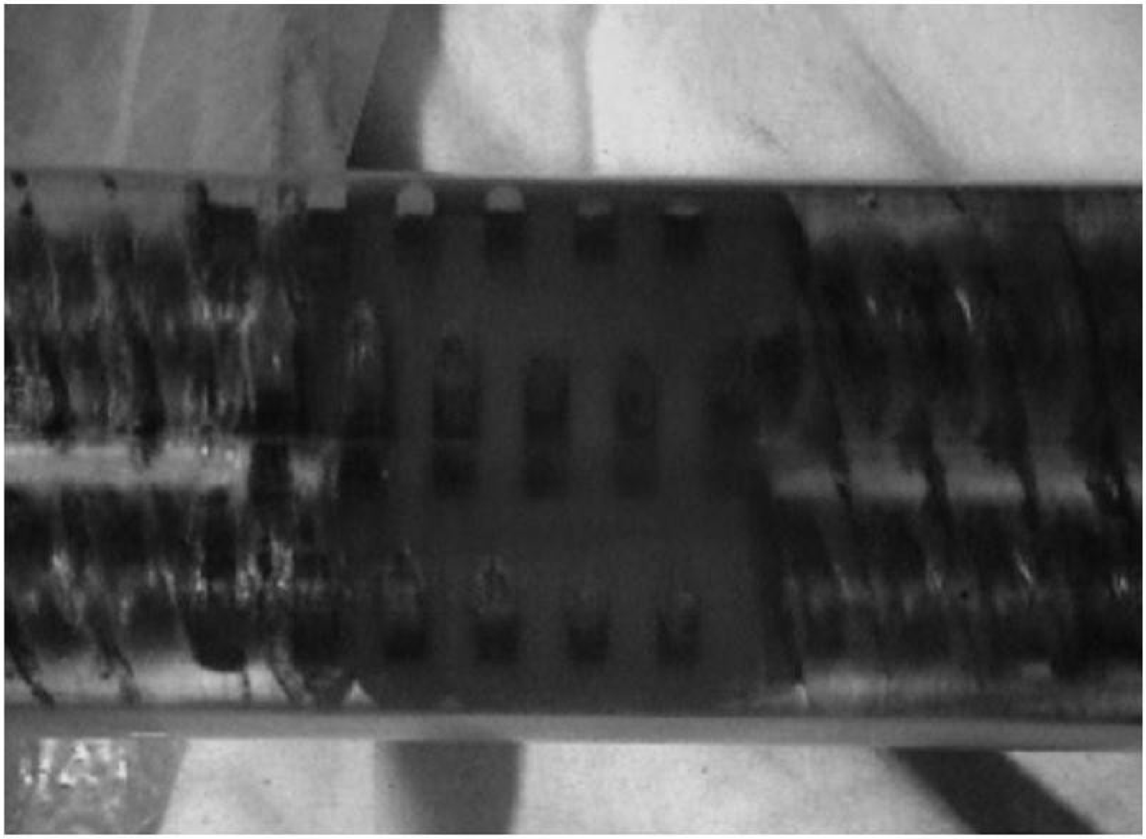


18.12 Evolution of the chemical reaction between SMA and 1-aminonaphthalene from samples obtained using sampling devices and from screw pulling experiments [162].

2. Use visualization techniques. Machining (relatively small) glass windows in twin-screw extruder barrels can provide direct observation of flow, melting and mixing behaviors [152, 162]. Another approach is to manufacture fully transparent barrels and operate at room temperature using highly viscous fluids (as shown in Fig. 18.13, for a 1000 Pa.s oil to which a tracer was added for easier identification of the flow patterns and degree of fill). Recently, miniature cameras were used to follow the melting mechanism in a single-screw extruder [163], the technique being

applicable also to twin-screw machines. All these techniques provide useful information on flow and mixing, but they are of little help in terms of tracking chemical conversion.

3. Develop in-line and on-line monitoring techniques. The concept is ideally suited for reactive extrusion, since it implies the use of sensors to monitor in real time chemical conversion or morphology changes, thus avoiding the use of conventional off-line techniques which, quite often, require the time-consuming preparation of samples. In-line measurements imply the use of probes located in the process without perturbing the main flow stream, whereas on-line techniques usually involve the diversion of a small stream of material - often with the assistance of gear pumps through a specially designed channel containing the probes, this melt eventually merging again with the main melt stream. This is why most on-line devices are positioned between the extruder and the die (so they measure final reaction yields or material characteristics, which are important for process control, rather than evolution of phenomena along the extruder). In fact, generally only in-line techniques using probes with the geometric features of melt pressure transducers can be located along the extruder barrel, unless the latter is modified. The use of both types of probes has been extensively discussed in the literature, a recent review being available [27].



18.13 Flow of a highly viscous silicone oil along a kneading block with a neutral staggering angle.

In terms of reactive extrusion, it is important to monitor chemical conversion, temperature and residence time distribution. In the particular case of polymer blends, it is also important to estimate the main characteristics of the multiphase morphology.

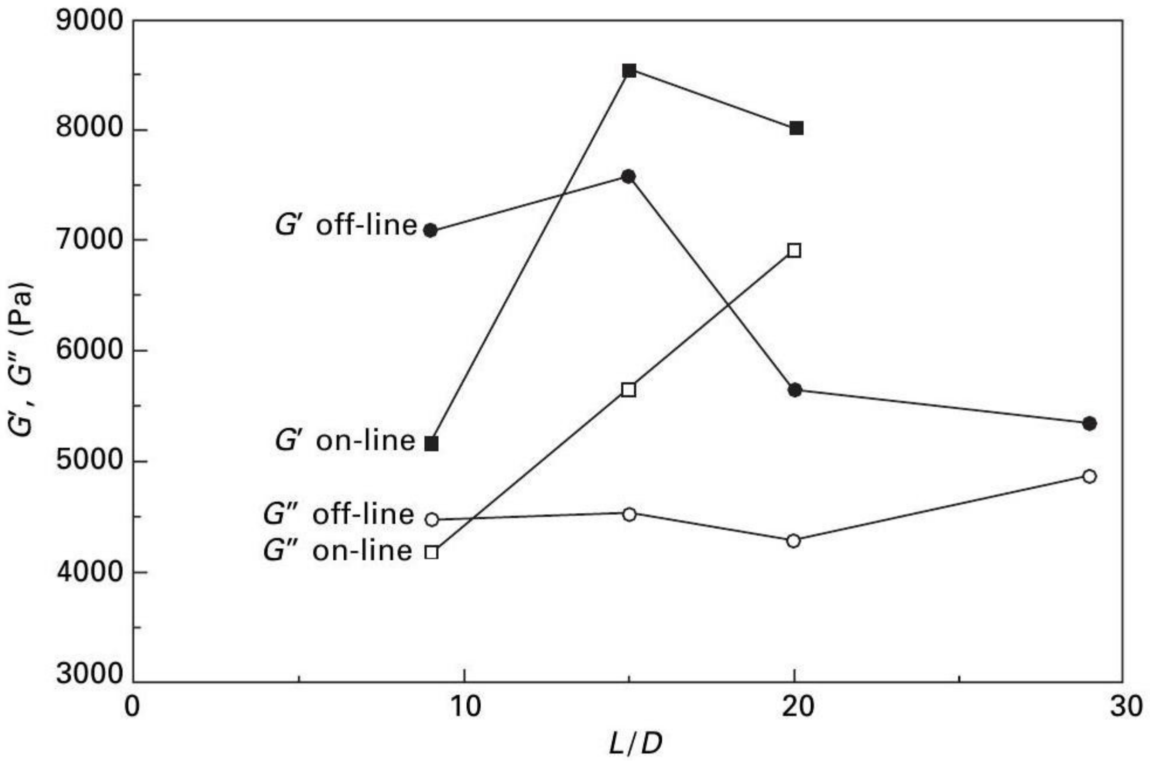
NIR spectroscopy is gaining practical importance for the direct measurement of chemical conversion, particularly since commercial probes became able to withstand the pressures and temperatures typical of polymer processing. The sample is illuminated with a broad band source of radiation in the IR region of the electromagnetic spectrum ($12000-400\ cm^{-1}$) and the concentration of chemical species can be correlated with the absorbance, via the Beer-Lambert law [164]. Other techniques have been used successfully for specific systems, such as MIR (mid-infrared, range from 4000 to $400\ cm^{-1}$) and Raman (usually not the absolute Raman band intensity, but instead the intensity of the spectral band of interest, normalized to that of an internal standard [164]). For example, Haberstroh et al. [165] used attenuated total reflectance (ATR)-FTIR spectroscopy in the mid-infrared range to analyze the monomer/polymer ratio during the polymerization of PA6 using an inline probe mounted in the intermeshing section of the twin-screw extruder.

Measuring the true temperature of the material as it flows along the screw channel or die is extremely difficult. To begin with, due to the high viscosity of polymer melts and the distribution of shear rates across the channel thickness, flow is considerably non-isothermal. Invasive techniques such as inserting thermocouples protruding in the melt affect the flow pattern and induce local viscous dissipation, the readings often being sensitive to where the devices are located (differences of $5^{\circ}C$ can be easily obtained just by rotating asymmetric probes). Obviously, such devices can only be mounted downstream of the extruder. However, measurements of flush-mounted thermocouples are affected by the barrel temperature. Carneiro et al. [166] demonstrated experimentally how readings are insensitive to changes in operating conditions that should induce clear variations in melt temperature. In order to avoid these limitations, temperature can also be measured by fluorescence spectroscopy, ultrasonics and infrared pyrometry, the last two becoming increasingly popular. In the first technique, a temperature-sensitive tracer is added to the polymer and the temperature is measured by monitoring spectral characteristics of the tracer [167]. Ultrasonic sensors transmit ultrasonic waves and receive the echo reflected from the melt, the delay time being converted to temperature via a calibration velocity-temperature relation [168]. However, the signal may be also affected by other variables, such as level and size of suspended fillers [169, 170], which may complicate the interpretation of the results. In infrared pyrometry, in addition to the radiation emitted from the target, the sensor also receives reflected radiation, which is proportional to material temperature. An important issue is the penetration depth of the measurement [171]. Machado et al. [172] reported a simple method of estimating the average melt temperature along the barrel, by sticking a fast response thermocouple into nut-shaped material samples removed quickly from the extruder. The sensitivity of the measurements to changes in operating conditions was satisfactory [166]. Finally, the use of thermochromic materials (i.e., materials that change color at a certain temperature or materials whose fluorescence intensity varies with temperature [173]) could provide an alternative temperature-detection approach, but their potential seems to remain largely unexplored.

The measurement of residence time distribution has attracted intense research over the years, given the wealth of information that it can provide (flow patterns, axial mixing, heat transfer and reaction processes, etc.). Many types of tracers have been proposed, the corresponding detection and measuring techniques having also been discussed: the oldest on-line technique is probably the γ-ray detection of irradiated samples or the change in magnetic susceptibility using iron powder as tracer, but optical methods (light transmittance or light reflectance), ultrasonic attenuation, changes in electrical properties (capacity, conductivity, dielectric constant) and spectrometric methods (infrared attenuation and fluorescence) have also been used [174, 175]. UV/fluorescent tracers and on-line detection techniques seem to be frequently adopted for reactive extrusion since sensors geometrically similar to pressure probes can be used (i.e., measurements can be performed along the extruder), very small amounts (milligrams) of tracer are required to generate a reproducible result, and the tracer can be either pre-mixed or grafted to the polymer [27].

Conventional (off-line) studies of morphology evolution along the twinscrew extruder are generally performed using scanning electron microscopy (SEM) or transmission electronic microscopy (TEM). Several authors coupled a light microscope to a die and obtained digital photographs of the morphology of blends (which could be later studied by image analysis), or coupled a photometer to calculate particle size from the detected light attenuation of the incident light beam [176-178]. A similar strategy was followed by Pinheiro et al. [179], who developed a sensor using polychromatic visible light, based on the fact that transmitted light intensity is reduced due to absorption and scattering by the dispersed particles. Although all these light scattering methods have been used to characterize the morphology of polymer blends mostly at the die or at the die exit, Schlaiter et al. [180] carried out on-line measurements by detouring a flow of molten polymer from the extruder barrel and making it pass through the interior of a glass sphere.

Monitoring morphology can also be performed indirectly, although this requires that well-established correlations exist between the variables to measure morphology. Among the potential advantages of such an approach one may mention the possibility of performing in-line measurements, the location of sensors (able to withstand elevated pressures and temperatures) along the barrel and the reduction of measurement delay times. For example, the analysis of the morphology of polymer blends using ultrasound has been attempted, as different morphologies should give rise to different acoustic properties. However, it was necessary to develop a wave propagation theory for viscoelastic emulsions relating the values of the ultrasonic parameters with concentration, the radii distribution and frequency [181]. Similarly, dielectric spectroscopy at medium frequencies (between 10 Hz and 1 MHz) was used to study shape and co-continuity of the LCP phase with increasing extrusion speed for blends of LCP with PP [182], via the Böttcher-Trukhan relation, which enables the conversion of the dielectric data into values of the particle size. Since rheology is sensitive to changes in morphology, chemistry, temperature and degree of mixing, it reveals a great potential for process monitoring and control. For example, it has been shown that the linear viscoelastic response of non-reactive blends under small-amplitude oscillations can be used to characterize the microscopic material structure [183]. In the case of reactive systems, capillary pressure drop and oscillatory measurements have shown that interfacial adhesion - thus, blend viscosity increases with increasing amounts of copolymer formed at the interface [184]. Several commercial on-line rheometers are currently available, mostly being fixed between extruder and die, and working on the principle of diverting a small stream of polymer that is characterized rheologically via capillary rheometry (or simply, via MFI) and returning this stream to the main flow channel. Efforts at closed-loop process control have also been reported [27, 185]. Studies based on the evolution of the rheological behavior of polymeric systems along the extruder based on on-line measurements are much rarer. A piezo axial vibrator sensor has been manufactured with a shape similar to that of a melt pressure transducer [186]. The device generates an axial oscillation on the sample to be characterized and converts the signal into the rheological moduli $G^{'}$ and $G^{''}$ but data has been reported only for homopolymers. Dogan et al. [187] used ultrasonic velocimetry to measure the velocity profiles and combined the information with pressure drop data, to extract viscosities. Experiments were done in simple tube flow and for polydimethylsiloxane. Covas et al. [188] developed an on-line rotational rheometer that can be inserted between barrel segments of a typical twin-screw extruder and tested it with a compatibilized and an immiscible polymer blend. As illustrated in Fig. 18.14, the results showed that the apparatus was much more accurate in capturing the structural evolutions of the materials along the extruder (a trend towards the increase of the rheological parameters) than analysis performed off-line on samples collected on-line (which are subjected to an extra thermal cycle, for the preparation of disks by compression molding). The same team had previously developed an on-line capillary rheometer, which was used to monitor the evolution of peroxide-induced PP degradation [189].



18.14 Comparison of the linear viscoelasticity of a PA-6/LDPE blend along the extruder at a fixed frequency of $1 \ s^{-1}$ when measured directly on-line, or off-line with samples obtained on-line (with sampling devices) [186].

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