Compounding and Reactive Processing of Polymers

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Abstract: Polymer compounding is an engineering process by which a compound is obtained through proper selection/formulation of ingredients such as reinforcing agents and additives and optimal mixing of the ingredients with the base polymer. Reactive polymer processing signifies that chemical reactions are carried out on purpose and in a controlled manner during polymer processing such as extrusion or in processing equipment like extruders. Sometimes chemical reactions are introduced to compounding operations. Such an operation is called reactive compounding. Today, these processes have established a solid position in the polymer industry as post-reactor technologies and have the common goal of diversifying and/or upgrading existing polymers with reduced costs. They may also allow novel polymer materials to be obtained that could not be made otherwise or in a reasonable fashion.

Keywords: Compounding · Nano-composite · Reactive blending · Reactive extrusion · Reactive processing

Introduction

Most synthetic polymers are made in polymerization reactors. When the end-use properties of a polymer do not meet prescribed criteria, it will not be put back to the polymerization reactor where it is made (in-reactor technology) for further modification. Rather a so-called post-reactor technology will be called upon. There are two main post-reactor technologies: polymer compounding and reactive polymer processing [1]. Polymer compounding is an engineering process by which a compound is obtained through proper selection of ingredients such as reinforcing agents and additives and optimal mixing of the ingredients with the base polymer. By reactive polymer processing, it is meant that chemical reactions are carried on purpose and in a controlled manner during polymer processing such as extrusion or in processing equipment like extruders. Sometimes, chemical reactions are introduced to compounding operations. Such an opera-

tion is called reactive compounding. Today, these processes have established a solid position in the polymer industry as post-reactor technologies and have the common goal of diversifying and/or upgrading existing polymers with reduced costs. They may also allow novel polymer materials to be obtained that could not be made otherwise or in a reasonable fashion. For example, polypropylene (PP) is a very important commodity polymer owing to its low cost, versatile properties and growing commercial applications. However, it suffers from the lack of chemical functionalities, low paintability and dyeability, poor adhesion to metal or glass, *etc.* Compounding of PP with calcium carbonate, $CaCO_3$, leads to a compound with improved rigidity and most likely reduced price. Also, maleic anhydride modified PP improves the adhesion of the polymer with metallic or glass substrates. Such modification is often done directly in an extruder *via* free radical chemistry. This process is typical of reactive polymer processing and more specifically reactive extrusion [2].

Mixing and Mixers

Mixing is a process to put together two or more substances and to achieve compositional homogeneity in a prescribed scale *via* mechanical and thermal actions. Mixing is a core and yet a very

challenging issue in polymer compounding and reactive processing. This is because the thermal and rheological properties of substances to be mixed can be very different. Basically, the main mixing mechanism involved in polymer compounding and reactive processing is laminar mixing. The latter can be of two types: dispersive mixing and distributive mixing. Dispersive mixing is required when a cohesive solid in the form of agglomerates like carbon black, calcium carbonate and organic pigments needs to be reduced in size to the scale of aggregates or even smaller and to be distributed uniformly in a polymer matrix. Dispersive mixing needs stress because a cohesive solid breaks down only when the stress applied exceeds a certain threshold. In a shear mixing dominated mixer, the viscosity of the polymer helps dispersive mixing because the corresponding shear stress is proportional to the viscosity of the matrix and the local shear rate. Distributive mixing refers to the relative spatial displacement of one phase domains in a matrix phase. Thus, distributive mixing requires deformation. Since deformation is always concomitant with stress while stress does not necessarily generate deformation, distributive mixing is always accompanied by dispersive mixing while dispersive mixing does not necessarily generate distributive mixing.

Today, no single equipment is capable of handling all these cases with ease,

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namely, no universal mixer exists for different mixing tasks. However, there are mixers which are more adequate for dispersive mixing and others for distributive mixing. Twin screw extruders and co-rotating twin screw extruders in particular are used the most for polymer compounding and reactive processing operations. This is because such machines have a reasonable balance between dispersive and distributive mixing. More importantly, this balance can be more or less easily adjusted owing to their modular character in terms of barrel and screw configurations. In fact, a screw is no longer made of one block but screw elements. Some of them are more dispersive and others are more distributive, depending on their geometry. It should be noted that mixing in such machines remains very poorly understood. Thus, the mixing performance of such machines depends very much on the operator's experiences and intuition. Engineering principles need to be established in order to predict the mixing performance of various mixers available, to optimize it and eventually to design new mixers.

Polymer Compounding

Compounding involving both non-agglomerate and agglomerate solids has been extensively treated. However, three compounding processes recently developed in the author's laboratory are mentioned: reactive polymer blending (polymer/polymer mixing), pigment compounding (polymer/cohesive organic solid mixing) and nano-composite compounding (polymer/cohesive inorganic solid mixing).

Reactive polymer blending aims at controlling and stabilizing the morphology of immiscible polymer blends by *in situ* formation of a copolymer as a compatibilizer during melt blending in a mixer like a twin screw extruder [3]. Recent results confirm that a reaction between two immiscible and reactive polymers takes place primarily at the interfaces. It is the total interfacial area that dictates the total amount of copolymer formed [4]. Therefore, the rate of copolymer formation depends on the rate of interfacial generation. The latter is related to mixing intensity applied. The presence of a compatibilizer is necessary at the very beginning of melt blending starting from polymer solids [5]. This is because particles formed at the very beginning of the process can be very small and grow in size if no compatibilizer is present or formed in

time. It appears that for most polymer pairs, under typical melt blending conditions, the scale of dispersion of one phase in the other is rarely below 0.1 μm or 100 nm, whatever the compatibilization method used. New processes are developed to achieve nano-scale dispersion of polymer blends [6].

It is well-known that when an organic pigment is added to a polyolefin and high density polyethylene in particular, injection molded articles of pigmented polymer can suffer from severe warping. A new concept is developed to solve this industrially troubling problem [7]. During compounding, the organic pigment is mixed with the polymer together with a small fraction of a derivative of the organic pigment which bears an alkyl group. Such a derivative is located preferentially at the interface between the pigment domains and the polymer and reduces the nucleating ability of the organic pigment. The challenge is that the addition of the organic pigment derivative should not have any side effects on the quality or the end-use properties of pigmented product in terms of color, toxicity, *etc.*

Nano-composite compounding has become a hot topic during the last few years. It deals with the dispersion of fillers with high length-to-thickness ratio such as montmorillonite (MMT) in thermoplastic matrices. MMT is a natural silicate and is in the form of large agglomerates which in turn are composed of many aggregates. An aggregate is made of thin sheets of some 1 nm thick and 1000 nm long and wide. Direct dispersion of MMT in a polymer matrix is thus difficult. This is why most nano-composite compounding processes use pre-treated MMT. A small molecule capable of interacting with MMT *via* ion exchange, such as an alkyl amine, is used for the treatment. The MMT thus treated becomes organophile and intercalated/exfoliated. It can then be dispersed relatively easily in a polymer matrix or a polymerizable monomer such as lactams and epoxy resins. Today it is possible to disperse non-treated MMT in a polymer matrix with a scale of dispersion similar to or smaller than that could be achieved by using pre-treated MMT.

Reactive Extrusion

In a broad sense, reactive extrusion (REX) refers to the use of screw extruders as chemical reactors to deliberately perform chemical reactions of polymers or polymerizable substrate. It is a com-

plex polymer reaction engineering process that combines both the traditionally separated polymer chemistry (polymerization and chemical modification) and extrusion (blending, compounding, structuring, devolatilization, and eventually shaping) into a single process carried out in a screw extruder. The features, advantages and challenges of reactive extrusion compared to classical polymer reaction processes have been discussed in many places [1]. If there is one feature, advantage or challenge which has to be mentioned, it is the absence of solvent/diluent.

Bulk polymerization deals with the conversion of monomers to polymers. Screw extruders are used as polymerization reactors but are far less important than classical polymerization reactors. However, when the features of extruder reactors are used to advantage, novel products can be obtained. A recent example is nano-structured polymer blends obtained by the concept of *in situ* polymerization and *in situ* compatibilization in an extruder reactor [6].

Chemical modification of polymers made by in-reactor technology is an important application of reactive extrusion. Numerous chemical processes have been developed to modify the properties of different polymers. One important chemical process is free radical grafting of vinyl monomers onto polymer backbones. Although free radical grafting can be considered as an old chemical process, the effects of process on the selectivity of the reaction, *i.e.* number of graft per chain and graft number distribution, remain unclear. Recent studies show that a wide variation of graft distribution could be obtained by varying process conditions [8]. Some non-classical free radical grafting processes are being developed in the author's laboratory. Their impact on existing industrial practice remains to be evaluated.

Conclusion

In this limited space, the author wanted to show that although compounding and reactive processing of polymers are widely practiced in polymer industry, room for innovation is big. As long as process fits chemistry and *vice versa*, new processes and innovative chemistries are likely to lead to new products. A few examples were given to make the point.

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The Influence of Branching Architecture on Scission in Modeling Free-Radical Polymerization with Long Chain Branching and Scission

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Abstract: In modeling molecular weight (MWD) and degree of branching (DBD) distribution for radical polymerization systems, assumptions have to be made concerning the length and the number of branches of fragments from scission reactions. The linear-chain approximation with respect to scission kinetics usually applied is shown to be incorrect. A new method is proposed based on a mechanistic model predicting architectures. It is shown that a simple short/long chain fragment scission assumption significantly changes the predicted MWD.

Keywords: Degree of branching distribution · Long chain branching · Low-density polyethylene · Molecular weight distribution · Scission

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Introduction

In models predicting the molecular weight and degree of branching distribution of radical polymerization with long chain branching and scission, the assumptions concerning length and number of branches on fragments are crucial. Here, we focus on the impact of *branching architectures* on scission. Until now, the linear-chain approximation has been employed, which describes the scission of linear chains with branch points (Iedema *et al.* [1], Hutchinson [2]). This article shows, however, that this assumption does not describe scission kinetics of branched molecules correctly. It is proposed that architecture-based scission kinetics, based on our architectures synthesis algorithm, be implemented in the model predicting MWD/DBD. The results of a full implementation are not yet available, but the effect of non-linear scission *i.e.* a preference for short and long chains – on the MWD has been explored. Quite remarkably, the generally observed bimodality in the MWD vanishes with preferred short/long scission.

Here, first the MWD/DBD model is presented, including the most important assumptions being made. Then some examples of the effect of branches on scission statistics are given. Our branched architectures synthesis is briefly described. Finally, the impact of short/long scission is presented and discussed.