

Feature

Optimizing packaging performance through polymer choice. Part 1. Basic polymer chemistry

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This is the first instalment of a series of three articles which explains how to optimize the performance of packaging through choosing and using specific polymers. In this issue, some fundamental principles of polymerization chemistry, as they relate to the resulting polymer structure, are discussed.

My feature article published in the September 1997 issue of *Food, Cosmetics and Drug Packaging* looked at the optimization of barrier properties through polymer choice and processing conditions. As the number of polymer choices expands, particularly with polyolefins, packaging engineers need to be involved in choosing which polymers are used, rather than leaving this decision to the converter.

As mentioned in the previous article, leaving these choices to the converter can hold back the development of a company, essentially making it a mediocre packaging concern, rather than it being at the forefront. Naturally, this is because the business will rely on the same technology that is being used by many other companies in the market place. However, being directly involved means learning more about topics which are not usually part of a packager's background. I hope that this series of articles will provide some guidelines and mental pictures which will help you to make these choices, and ultimately benefit from them. Subsequent instalments, will cover the effects of chemical structure on the resulting morphology when plastics are processed into packaging materials, and the relationship that exists between final packaging properties and morphology.

Basic polymer chemistry

The discussion presented here will be limited to polyolefins. This is because these are the most widely used packaging polymers, and during the past several years they have advanced the most. In addition, the scope of the discussion also needs to be limited to a manageable size. However, the concepts that

will be covered are applicable to all semi-crystalline polymers.

The basic concept which is to be discussed is that the end-use properties of a plastic packaging material are dependent on the molecular arrangement, or morphology, of the final material. For solidified polyolefins, the macromolecules are arranged into crystalline and amorphous regions as shown in **Figure 1**. The crystalline regions are closely packed, ordered regions, which are similar to crystals of lower molecular weight materials. The major difference is that molecules included in each crystallite or lamella may exit the crystallite after a few folds, and then be in the amorphous region for some period of time before entering the same, or another, crystallite.

In the melt phase, as the material leaves the die, the molecules are in a liquid state, and there is no order. The molecules are usually entangled to some extent, rather like

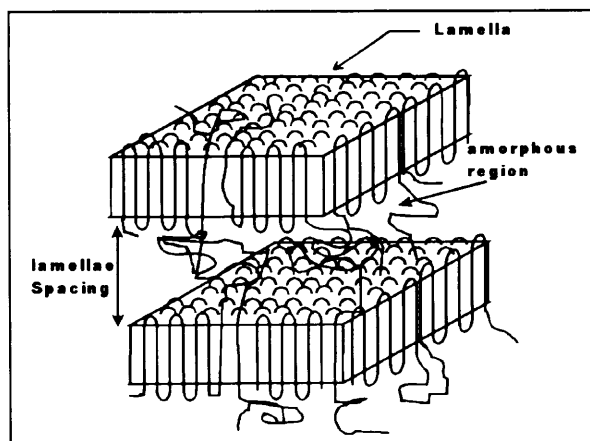


Figure 1. For solidified polyolefins, macromolecules are arranged into crystalline and amorphous regions.

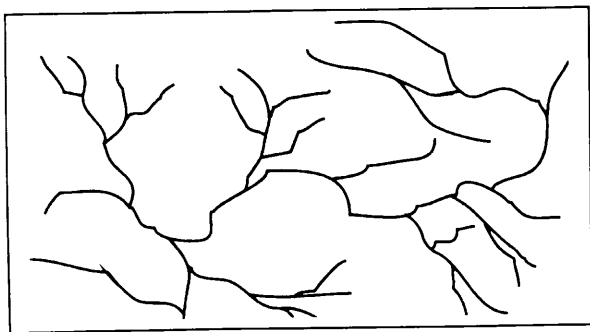


Figure 2. Long chain branching in low-density polyethylene.

spaghetti on a plate. The process by which they are changed from this random, entangled state, to the semi-crystalline arrangement, is controlled on a molecular level by their molecular weight, molecular weight distribution, and their degree of long chain branching. In addition, the processing steps that the melt undergoes contribute to the morphology. Gaining an understanding of all of this detail may seem overwhelming, but it will come together with some practice.

Molecular weight and long chain branching

The next step to master is the concept of molecular weight and long chain branching in polymers. The polymerization process, which causes the monomers to join together into the macromolecules, can be a completely random process, as in the case of low-density polyethylene (LDPE). Depending on the reactor type, autoclave or tubular, the amount of long chain branching in LDPE is slightly different, but there is still a lot of long chain branching, as shown in **Figure 2**. With this degree of branching, it is hard to tell what is the backbone of the polymer and what is a branch.

Also in the polymerization process, chains can be terminated at different lengths. Therefore, polymers are not a single molecular weight as is decane, or other lower molecular weight organic compound. A range of molecular weights is produced, and this range can be measured by size exclusion chromatography. Examples of distribution curves are shown in **Figure 3**. By calculating various averages of this spectrum, it is possible to determine the number average, weight average, and perhaps the z-average molecular weight. (The z-average measures the influence of the higher molecular weight species.)

Chromatography may not be as sensitive to small changes in molecular weight or molecular weight distribution as are the flow characteristics, or rheology of the polymer melt. Actually, chromatography itself tends to be rather sensitive to these changes, but a refractive index detector, which is most often used, is not sensitive enough to molecular changes. Therefore, a more sensitive measure of molecular weight is obtained by doing rheological measurements. Long chain branching is also characterized by using flow measurements.

Melt elasticity

Measuring the extra pressure drop as the flow enters a capillary can be related to the melt elasticity. Polymers with high degrees of long chain branching remain highly entangled and have difficulty sliding past one another, which results in a flow that can store elastic energy like a rubber band. One physical evidence of elasticity is die swell, or the fact that the melt becomes larger than the die opening just after the exit, where the

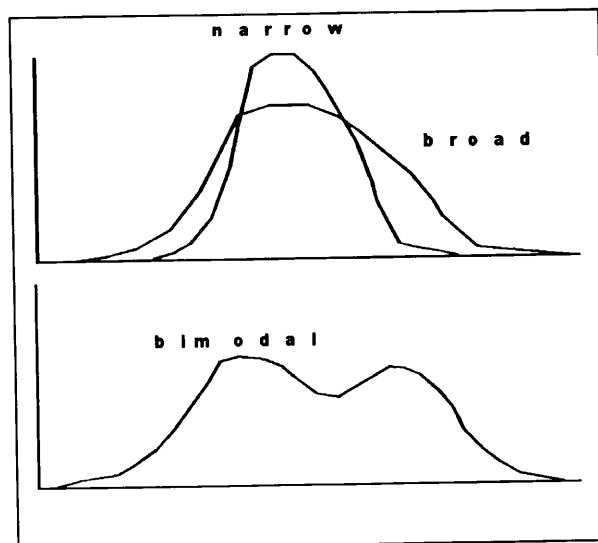


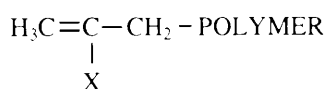
Figure 3. Distribution curves based on data obtained from molecular weight spectra measured by size exclusion chromatography.

stresses have been removed. Melt elasticity is an important measure of how quickly polymer molecules can rearrange themselves into crystallites during cooling of the melt. Highly elastic melts mean large entanglements, and the result is slow rearrangement of the molecules. Highly elastic melts can be a benefit to processing, so one may be faced with the problem of trading one attribute for another.

Catalysts

To gain more control over the polymerization reaction, catalysts are used. The two types that are used in polyolefins are Ziegler-Natta and metallocene types. Both are what are called a stereo-specific catalyst. Their chemical nature causes the monomer molecules to arrange in specific orientations. Ziegler-Natta type catalysts are called heterogeneous catalysts because they have sites that produce different types of molecular structures all on the same catalyst. For instance, with ethylene and its co-monomers — also known as linear low-density polyethylenes (LLDPE) — co-monomer incorporation varies with the type of site. One type of site makes a highly branched, low molecular weight polymer, while a second type of site makes the equivalent of high-density polyethylene, and a third type, the desired LLDPE molecule.

For this reason, when we attempt to incorporate high percentages of co-monomer into LLDPE, the extractables reach unacceptable levels because of the production of highly branched, low molecular weight species. The haze of an LLDPE is slightly higher than would be expected for a given density because of the high molecular weight species. The reason why this is true will be discussed later. Both catalyst systems can be used to make polymer densities ranging from low-density polyethylene to high-density polyethylene. Another feature of these catalyst systems is that when certain metals are used, such as chromium, there is a tendency to make polymer molecules with terminal vinyl unsaturation. A reaction called the β -hydride elimination causes the polymer molecule to look like the structure depicted below.



This vinyl unsaturation can lead to long chain branching during pelletization and compounding. The 'X' in the diagram represents any ligand that would be found in high-density polyethylene or LLDPE.

Single-site catalysts

Metallocene catalysts are also referred to as single-site catalysts because they only have one type of site available and produce only one type of polymer structure. This results

in more uniform incorporation of co-monomer. The uniformity of incorporation of co-monomer allows the production of much lower densities with lower levels of extractables than were previously possible.

Also the single-site nature of the catalyst produces a molecular weight distribution that is narrower than that produced by Ziegler-Natta type of catalyst. The first result of the narrow molecular weight is that the polymer flow characteristics are much closer to Newtonian than those of broader molecular weight polymer. This makes it more difficult to process the material.

LLDPE which is produced using Ziegler-Natta type of catalysts has monomer incorporation that is dependent on molecular weight, and the monomer incorporation decreases as the molecular weight increases. The incorporation also can be non-uniform in its distribution along the chain. This results in portions of the chain that contain a large amount of the co-monomer, while other portions are just polyethylene. This non-uniformity has a major effect on the morphology of LLDPE. These heterogeneous catalysts also produce wider molecular weight distributions than are achievable using metallocene catalysts. The molecular weight distribution is not as broad as that produced by the free radical polymerization used to make LDPE.

Early understanding

When users are first gaining an understanding of the polymers which are being offered by suppliers, it is important to ask about the chemistry: what type of reactor is being used? What type of catalyst is used? Is the polymer intentionally subjected to post-polymerization reactions? It is essential to obtain information on the molecular weight (the number average), and the weight average. It is also important to obtain information on the long chain branching characteristics, even if the polymer is high-density polyethylene (HDPE).

The next instalment will explain how these parameters affect crystallization kinetics, flow properties (rheology), and processing characteristics.

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