

Feature

Optimizing packaging performance through polymer choices. Part II. The relationships of chemical structure with morphology and rheology

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This article looks at the way in which certain characteristics of polymers, such as molecular weight, molecular weight distribution and long-chain branching, affect their flow properties, or rheology, and their molecular arrangement in the solid state, or morphology.

In Part I, which was published in the August issue of *Food, Cosmetics and Drug Packaging*, we discussed some fundamental principles of polymerization chemistry, as they relate to the resulting polymer structure. In particular, we looked at molecular weight, molecular weight distribution and long-chain branching.

Here, in the second instalment, we will consider the effect of these characteristics on the flow properties, or rheology, and the molecular arrangement in the solid state, or morphology. These effects will then lead us, in the final instalment — scheduled to be published in the December 1999 issue — to end-use characteristics which we can expect from various polymers, and how to choose the correct polymer for a specific packaging application.

Visco-elasticity

One of the first concepts to discuss in relation to structure of the polymer is how that structure affects the visco-elasticity. A rubber band is elastic because the molecules are chemically bonded together by cross-links. When the rubber is deformed, the cross-links keep the molecules from slipping past one another, and energy is stored. Because the cross-links are chemical bonds, the elasticity never relaxes unless bonds are broken.

Visco-elastic materials obtain their elasticity from molecular interactions that come about from associative forces. These interactions act as 'pseudo-cross-links', but they can relax under stress. A mental picture is that of a plate of starchy spaghetti. Where the strands of spaghetti cross, they

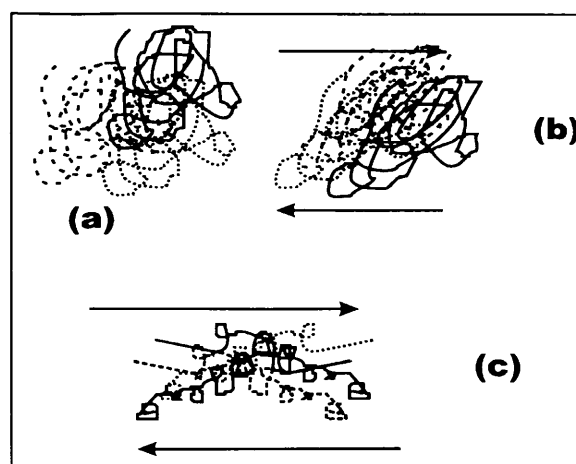


Figure 1. Molecules in the shear-field: at rest (a); low shear (b); and high shear (c).

interact, but the interactions can slip. If there is a larger quantity of water around the strands, the interactions are weaker.

Polymer molecules can interact by attracting one another through weak associative forces, hydrogen bonding, or ionic interactions. All of these will relax under stress and over time. The visco-elastic nature of polymers exhibits itself in both the melt and the solid state. For semi-crystalline polymers like polyethylene, and copolymers, the visco-elastic nature of the solid is rather restricted because the crystallites act as cross-links.

When processing a polymer into a shape, the usual first step is to melt it. In the melt, the polymer molecules are in the form of random coils that are entangled with one another. A visualization of this is shown in Figure 1(a). This diagram can be described

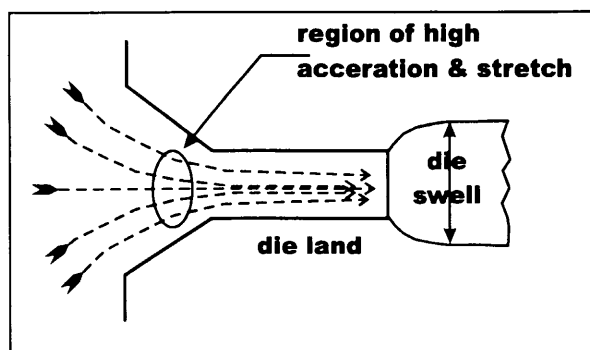


Figure 2. At the entrance to a die land, the flow is accelerated dramatically as the walls converge. The flow-time through the die land is not long enough to allow relaxation, and the melt will try to recover the elastic energy when the shear stresses are relieved after the melt exits the die.

most accurately as a visualization of the melt at rest, or under very little shear.

When the melt is caused to move, as in the flow through a pipe or die, the polymer melt is subjected to shear. That is, the flow-field is not uniform because there is a velocity gradient extending from the pipe's walls to the centre of the channel. Therefore any molecule of finite size has various parts moving at different velocities. This causes the molecules to be distorted as shown in **Figure 1(b)** and **Figure 1(c)**. This is caused by the shearing action of the flow.

Depending on the length of time that the melt is subjected to the shear field, and the magnitude of the velocity gradient, the molecules may become oriented more and more parallel to the flow [Figure 1(c)]. In order for this alignment to happen the molecules must slip past one another. If there are large side groups, hydrogen bonding, ionic bonding, or long-chain branching, the ease of 'slipping past' is greatly reduced. When this situation exists, energy is stored in the melt as elastic energy. Because the interactions between the chains are brought about by associative forces, rather than real cross-links, these interactions can gradually relax and the elastic energy will dissipate. However, accelerating flows in polymer processing will store elastic energy.

At the entrance to a die land, the flow is accelerated dramatically as the walls converge (**Figure 2**). The flow-time through the die land is not long enough to allow

relaxation, and the melt will try to recover the elastic energy when the shear stresses are relieved after the melt exits the die. This is the explanation for the phenomenon known as 'die swell'. This phenomenon also causes an added pressure drop at the entrance of the die as the energy is stored. This added pressure drop is used to measure the elastic characteristics of a polymer.

The more long-chain branching, or the higher the molecular weight, the larger the elasticity of a polymer. Low-density polyethylene (LDPE) produced by the autoclave process is an example of such a polymer with long-chain branching and therefore visco-elastic character.

High-density polyethylene (HDPE) can possess elasticity mainly because of its molecular weight. Low molecular weight HDPE would have very little elasticity. Some types of HDPE may have more elasticity than others because of small amounts of long-chain branching developed during 'pelletization' and/or compounding of additives. Those polymers which are made with catalyst systems that leave terminal unsaturation, will react in this manner.

Visco-elasticity and processing

Visco-elasticity can also have a negative side. It can cause melt fracture, which comprises the melt distortions which are often referred to as 'shark skin'. When the stresses become too high, the melt will begin to oscillate from side to side. It is these oscillations that cause melt fracture. Melt fracture can limit production rates when using very elastic melts.

A related characteristic is the melt strength. This is very important in processing and it is required for the ability to blow a bubble-shaped structure from film, or for the parison to remain on the die of a blowmoulding machine until the moulds close.

Melt strength can come from either very high molecular weight, or from melt with a large number of molecular interactions, like those described in the discussion of elasticity. When a polymer does not have good melt strength it will not produce a stable blown film bubble. Also, the parison will not maintain the correct shape for blowing a bottle. Melt strength is measured by determining the elongation viscosity,

which is related to, but different from, the shear viscosity.

Melt viscosity

Melt viscosity is related to molecular weight and to the molecular weight distribution of the polymer. For polymers above a critical molecular weight, the melt viscosity is related to the weight average molecular weight to the power of 3.4 ($M_w^{3.4}$), as shown in **Figure 3**.

The molecular weight distribution affects the non-Newtonian character of the viscosity. Narrow molecular weight distribution polymers have a viscosity behaviour that is nearly Newtonian. That is, the viscosity is nearly constant.

For polyethylene melts, the viscosity behaviour is non-linear over part of the flow-range. In **Figure 4**, examples of Newtonian and a typical non-Newtonian behaviour are shown. As the molecular weight distribution broadens from 2 to as high as 20 for some types of polyethylene, the melt-flow curve becomes steeper in the non-linear region. This increase in slope represents a behaviour that is more non-Newtonian in nature. The explanation for this behaviour is that the lower molecular weight polymer molecules have a lower viscosity, and therefore act as lubricants for the larger molecules. As the flow-rate increases the apparent viscosity decreases.

From this discussion, one can begin to deduce that, for a given molecular weight, a broader molecular weight distribution causes the apparent viscosity to decrease as the shear-rate (flow-rate) increases. This is a benefit to processing because the power required by the extruder is less for a lower apparent viscosity. However, because the elongational viscosity is related to the shear viscosity, a lower viscosity material may not have enough melt strength for processing. Therefore, one is always faced with the trade-off of properties.

Morphology

As mentioned in Part I of this series of articles, morphology is the arrangement of molecules in the solid state. It refers to the amorphous and crystalline regions, their sizes and their orientation.

The type of morphology that one gets from a polyethylene melt is quite different depending on whether the melt is quiescent

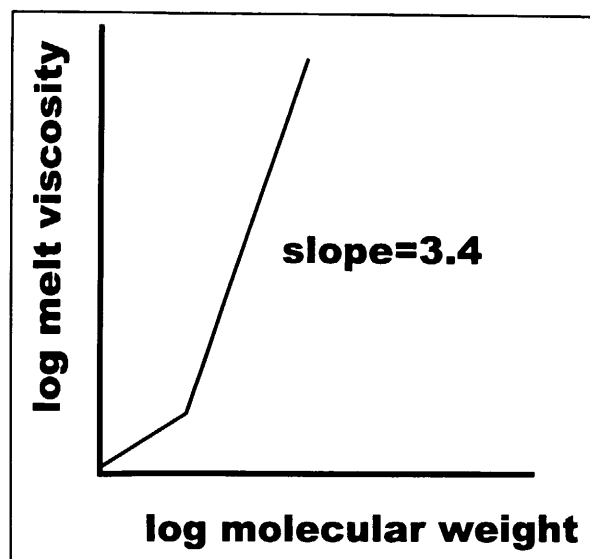


Figure 3. For polymers above a critical molecular weight, the melt viscosity is related to the weight average molecular weight to the power of 3.4 ($M_w^{3.4}$).

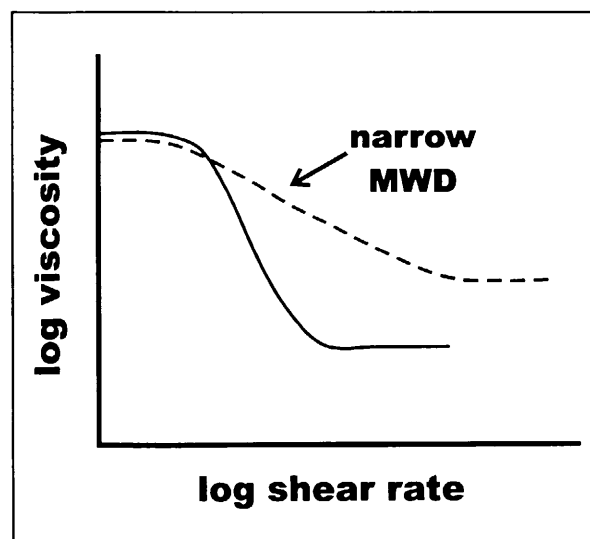


Figure 4. Flow curves: examples of Newtonian and a typical non-Newtonian behaviour.

or under strain, as crystallization occurs. In films, the melt is always under strain during the crystallization process. Whereas in an injection-moulded part there will often be two regions of crystallization. The region near the walls is often under strain during crystallization, while the interior of the part may be quiescent during crystallization.

There is another aspect of the process of crystallization that must be addressed in order to gain an understanding of what the

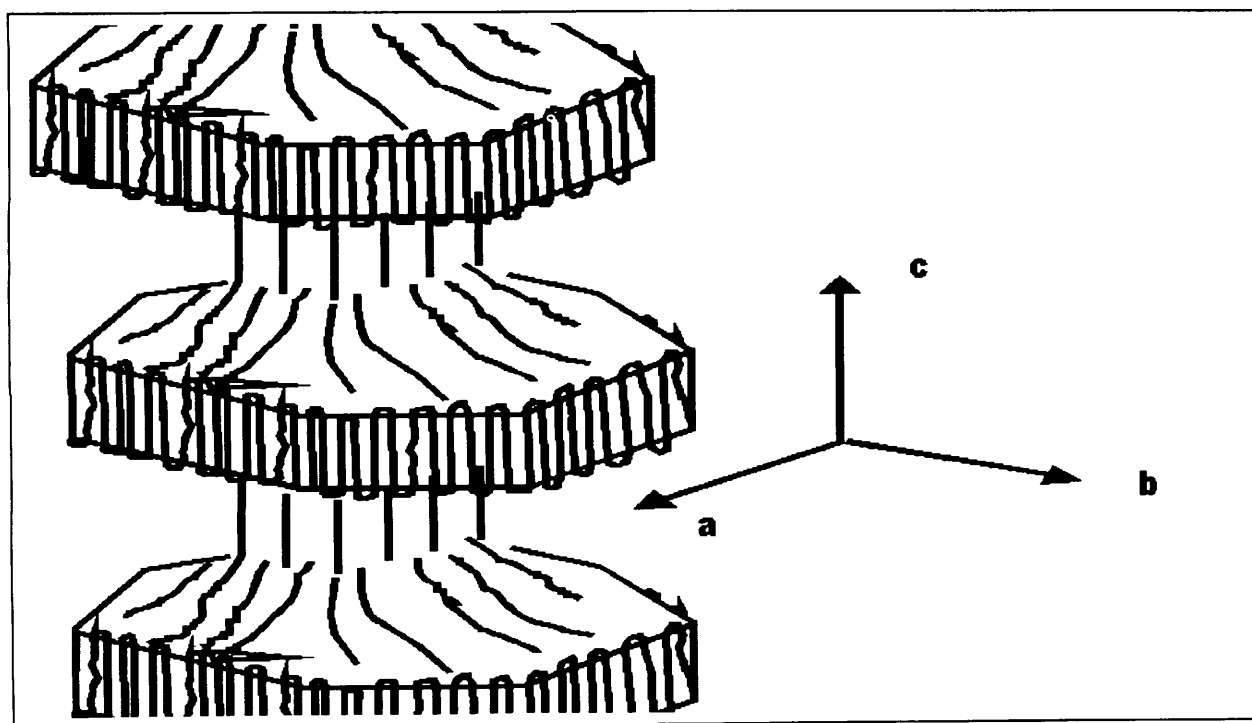


Figure 5. A diagrammatic representation of a microscopy image, showing a backbone of extended chains, onto which epitaxial growth of lamellae has occurred.

morphology might be. This concerns whether or not the crystallization occurred under nearly isothermal conditions. Most of the time one can assume that nearly isothermal crystallization occurs, even in thin films. Literature sources on non-isothermal crystallization of polyethylene films show that the heat of crystallization released is, in many cases, enough to keep the temperature nearly constant during the crystallization process. This means that the critical issues are the level of strain in the melt during crystallization and the temperature gradient across the material. Non-isothermal conditions do affect the amount of 'frozen' strains.

In any crystallization process the polymer molecules must slip through the melt and arrange themselves in the ordered loops of the lamellae. If there is a branch point, or a side group such as vinyl acetate, this will not fit into the crystal lattice and will be rejected. Most chains only develop about four continuous folds into a crystallite before being interrupted. This is because the process depends on a period of time for the group to pull itself from the melt, while another molecule starts to fit itself into the structure.

For polymers with regular repeating, small side branches, such as polypropylene,

it is possible to find a way to pack the side group uniformly close enough to form a crystallite. However, this demands that the stereo-regularity is sufficiently high enough. That is, a change from isotactic conformation of the monomer to syndiotactic would cause rejection of that portion of the molecule from the crystallite. Therefore, molecular structure is very important to crystallite formation.

High molecular weight and long-chain branching both mean that molecules have more trouble moving through the melt to get into the ordered structure. Crystallization goes on from the time the proper temperature is reached for it to commence until the melt is frozen. At that point some of the macromolecules are not in crystalline order, but form an unordered amorphous phase.

In a crystallization process that occurs under strain, the morphology is described as a row of nucleated lamellae. The images that have been presented in the literature from transmission electron microscopy, or scanning electron microscopy, show a backbone of extended chains, onto which epitaxial growth of lamellae has occurred. A pictorial representation of this structure is shown in **Figure 5**. The extended chains are

higher molecular weight chains that have been oriented in the direction of the flow through the die. The lamellae are made up of lower molecular weight species that relaxed more rapidly. For this ordered growth to occur on the extended chain backbone, the chains must slip through the melt, as discussed above. Therefore, the structural characteristics that retard movement through the melt, such as high molecular weight, long-chain branching, and other factors, are important to how fast the materials can reach a crystallized state.

Lamellae are described by an a-axis, b-axis, and c-axis. The c-axis is along the molecule. The b-axis is the growth direction. Obviously, the a-axis is the direction left over. The stress on the melt has been shown to control the orientation of the crystallites relative to the machine direction for films and sheet. High-stress flows cause what is referred to as c-axis orientation along the machine direction. This would mean that in Figure 5, the machine direction would be oriented vertically.

Since one of the critical parameters for films is the permeability, this orientation characteristic is important. Permeation can not occur through the crystallites, so one would want to have the c-axis oriented in the thickness direction of the film to obtain maximum barrier properties. This sort of orientation never occurs, but one can get a random orientation of the lamellae under the right choice of polymer and processing conditions.

Characterizing a polymer

The critical measure for characterizing a polymer is not the crystallization rate, but the elastic relaxation rate, as measured by rheological means. The reason crystallization rates are not always an accurate predictor, should be obvious from the previous discussion. The rate is affected by molecular weight, molecular weight distribution, strains on the melt, and the degree of 'undercooling'.

Normal crystallization measurements are accomplished at a nearly quiescent state. Furthermore, not all rheological measures of relaxation are necessarily sufficiently accurate. Therefore, careful measurement techniques are needed to determine these parameters correctly. These measures are typically the province of the polymer manufacturer, but a discussion of the

methods used is worthwhile in accessing the validity of their data.

In the next part of this series, we will explain how morphology affects end-use properties such as strength, stiffness, transparency and permeability.

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