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Technology Tip

Stabilisers, slip and antiblock additives:
their role in polyethylene resins

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Stabilisers, slip and antiblock additives: their role in PE resins

1. INTRODUCTION

Low density polyethylene (LDPE) resins may contain several different types of additives. These are added to enhance the resin properties, and to prevent premature degradation of the polymer. Typically, resins may contain anti-oxidants (for stabilisation), antiblock agents (for open-ability) and slip additives (for CoF control and blocking control). To address the importance of each of these additive types in a formulation, a few basic definitions will be discussed.

Definitions:

1.1 Stabilisation

Stabilisation of LDPE resins is required to ensure that the polymer is protected against degradation. Degradation refers to any process that will alter the molecular weight, molecular weight distribution or chemical composition of a resin, resulting in a product with inferior properties to that of the original virgin polymer. The following factors may lead to degradation:

1. Free radical activity
2. Unsaturation in the resin
3. Thermal abuse of the polymer (during processing or end-use), light exposure

1.2 Coefficient of Friction (CoF) properties (ASTM D18941)

The CoF properties are related to the resistance of the film to the sliding action over another film surface or a metal surface (slip properties). Scientifically, the CoF is defined as the ratio of the force required to move one surface over another to the total force applied normal to those surfaces. Two types of CoF measurements are defined: starting (static) and sliding (dynamic or kinetic). The slip properties are primarily influenced by the base CoF of the polymer, the addition of additives and extrusion and storage conditions. Generally a film with a low CoF (for example 0.2) is referred to as a slippery film, while a film with a high CoF (>0.5) is referred to as a non-slippery film.

1.3 Blocking (ASTM D33542)

Blocking can be defined as the resistance of two films to separation by a peeling force. Blocking is also sometimes described as unwanted adhesion, preventing the separation of two films. ASTM D3354 is the test method typically used to compare blocking performance of polyethylene films. Blocking can be found during both processing and storage. This is especially evident when the surfaces of the films are exceptionally flat- a film with a very high gloss will be more prone to blocking than one with a lower gloss. Blocking itself is initiated by the application of heat or pressure, or both.

2. FACTORS AFFECTING BLOCKING AND SLIP PROPERTIES OF A FILM

The slip and blocking of a film depend on the surface properties. The coefficient of friction and blocking properties of films are mostly critical in determining their suitability in end-use applications. Adding the right amount of performance additives is critical as a too high slip additive level will result in stacking difficulties and also may interfere in lamination and corona treatment processes. A too low slip additive level may result in problems in applications where the film has to move over mechanical parts, for example in automatic converting and packaging equipment.

There are several factors which could influence the blocking and the CoF performance of a resin. These include:

1. Resin density and melt index: generally an increase in the density or a decrease in the MI will result in less blocking and lower CoF values.
2. Additives: antiblock additives will reduce the blocking tendency while slip additives will lower the CoF.
3. Film surface: the smoother the surface of a film, the higher the tendency to block and the higher the CoF.
4. Static electricity: the higher the static electricity, the higher the tendency to block.
5. Extrusion conditions: with an increase in the film temperature when it contacts the nip rollers, the tendency to block will increase. A high nip roller pressure also will result in higher blocking. If the film is exposed to higher temperatures during storage or during wind-up, it also will result in an increase in the blocking tendency.
6. Corona treatment: corona treatment will increase the CoF and also the tendency to block.
7. Film thickness: a thin film requires higher concentrations of slip and antiblock additive for optimum performance.

3. THE THREE MAIN ADDITIVE TYPES IN LDPE RESINS

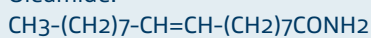
3.1 Stabilisation package

LDPE resins are typically stabilised with a primary anti-oxidant. BHT (butyl hydroxyl toluene) is an example of a primary anti-oxidant that was commonly used in LDPE stabilisation, but this is now being phased out internationally. BHT is a very good anti-oxidant, but it may, however, result in the yellowing of textiles in textile packaging applications. Phenolic stabilisers are currently, mostly used as primary stabilisers. Many LDPE resins also contain secondary stabilisers. These stabilisers are commonly based on phosphate compounds.

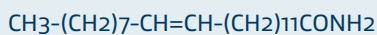
3.2 Slip additives

Commercially, two major types of slip additives are used in polyethylene resins, namely oleamide and erucamide. Several other types are also available (for example steramides) but these additives are not used to the same extent in commercial LDPE and hLLDPE resins. The major difference between oleamide and erucamide is the chain length:

Oleamide:



Erucamide:



The longer chain length of erucamide will obviously have an influence on the migration behaviour (longer molecules take longer to migrate through a substrate compared to shorter molecules). Generally, erucamide has the following advantages:

1. It is more effective than oleamide
2. It is vegetable based (halal applications)
3. It is more stable to high temperatures
4. Less organoleptics

There are however, certain applications where oleamide is preferred due to its faster initial blooming rate.

3.2.1 Mechanism of slip additives

The main purpose of a slip additive is to migrate to the surface of a film, thereby coating the film surface and reducing the CoF of the surface. The slip additive is incompatible with the polyethylene resin, and will migrate until it reaches the surface. Several different types of slip additives, with different levels of compatibility with the polyethylene resin, are available commercially.

In Figure 1 the development of the CoF can be seen as a function of time after extrusion. This migration process is also known as blooming.

The optimum CoF of a film is important. At a too low slip additive concentration, not enough slip additive is available to coat the surface and thereby reduce the CoF. Certain applications, for example form-fill-and-seal (FFS), require a low CoF (around 0.2); while some non-slip shrink applications require a substantially higher CoF to prevent slipping during stacking. If a too high concentration of slip additive is present in the film, it may result in several other problems (e.g. stacking, printing, sealing and corona treatment).

Grades are formulated for a certain target film thickness. A thicker film will require less slip additive than a thin film to lower the CoF value. This is due to the higher surface area to volume ration of the thin film compared to the thick film. It is also important to bear this in mind when formulating blends with formulated and non-formulated (containing no slip additive) LDPE and hLLDPE (linear low density polyethylene) grades.

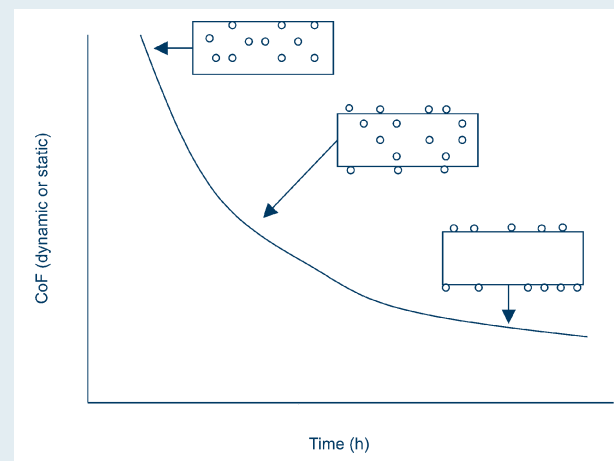


Figure 1: Blooming of the slip additive to the surface after extrusion

In Figure 2 the results of a typical erucamide slip additive optimisation exercise can be seen. The resin evaluated was a 2 MI, 0.922 g/cm³ density LDPE grade, extruded at 30 microns, and conditioned for more than one day at 23 °C and a relative humidity of 50%.

At 30 microns, an erucamide concentration above 400 ppm will provide a constant CoF of 0.1. There is a significant increase in the CoF of the film below 300 ppm. The resin must, therefore, be formulated above 400 ppm to provide a constant CoF of 0.1. Taking into account blending with unformulated LDPE or LLDPE resins, an additional safety factor must be considered.

3.2.2 Migration rate of oleamide vs erucamide

The migration rate of erucamide is expected to be slightly lower than that of oleamide. Actual evaluations were carried out, where the CoF performance of an autoclave resin (formulated with oleamide) and a tubular resin (formulated with erucamide) were compared (Figure 3).

Immediately after extrusion, a film formulated with erucamide may appear to be slightly less slippery than a film formulated with oleamide. (This can also be seen from Figure 3). After 24 hours, full blooming has taken place and the CoF values are comparable.

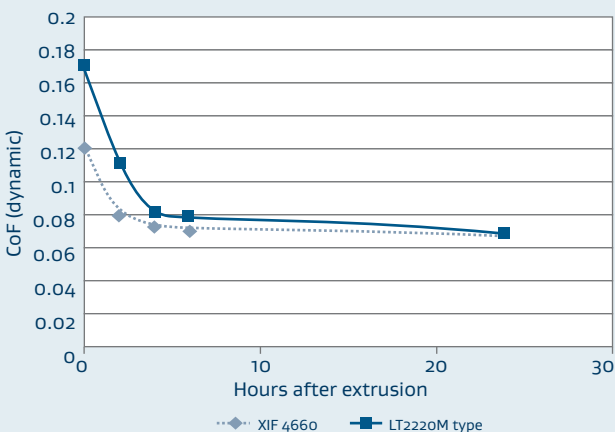


Figure 3: Differences in migration rate between films formulated with oleamide and erucamide respectively (30 microns)

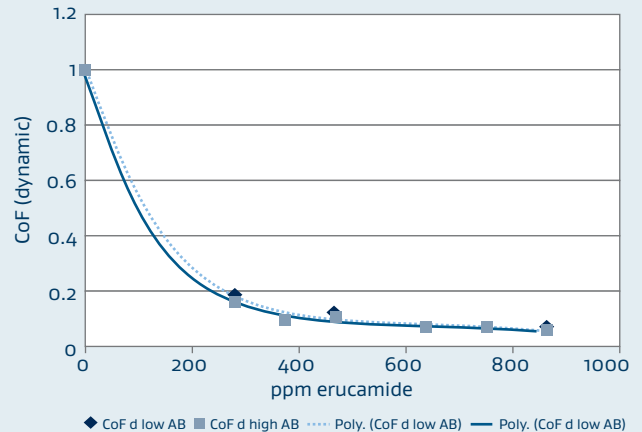


Figure 2: Optimisation of the erucamide level in a 2MI LDPE grade

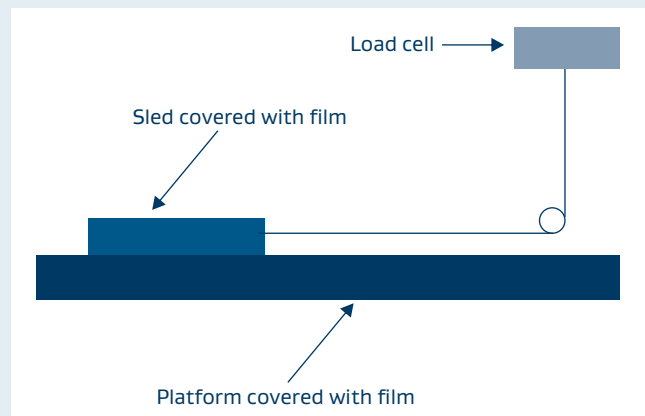


Figure 4: The measurement of CoF properties using a tensile based method.

3.2.3 Test methods for evaluating CoF properties of thin films

Several setups can be used to determine the CoF properties of a film (ASTM D1894). Nowadays, several laboratories use a tensile tester-based method. A typical setup can be seen in Figure 4.

The load cell (on either the tensile tester or the CoF measurement apparatus) measures the force necessary either to start movement of the two surfaces (static CoF measurement) or to keep the two films sliding across each other (dynamic CoF measurements).

3.3 Antiblock additives

The major purpose of the antiblock additive is to “roughen” the surface, thereby preventing intimate contact between two film surfaces. Typically, inorganic materials (silica, talc, diatomaceous earth) are added to polyethylene resins for this purpose. There are two main types of silica additives: natural silica and synthetic silica. Natural silica is cheaper than synthetic silica, but is less effective, and will have a more significant effect on the optical properties of the resins.

3.3.1 Test methods for evaluating blocking and induced blocking

Several test methods deal with the measurement of blocking and induced blocking properties. ASTM D3354 is the standard test method for testing the re-blocking of films. Induced blocking (typically carried out at 50 °C or 60 °C) measures the blocking behaviour of films, pre-conditioned at the above mentioned temperatures.

3.3.2 Mechanism of antiblock additives

The antiblock additive is randomly dispersed in the polyethylene matrix. Different from the slip additive, an antiblock additive particle cannot migrate. The polymer solidifies, above the freeze line height, and some of the antiblock particles will protrude from the surface, thereby preventing close contact between the two film surfaces.

In Figure 5 the effect of higher levels of a synthetic antiblock on the induced blocking properties can be seen. Samples were evaluated at both low and high slip additive contents, as the slip additive will also reduce the blocking behaviour of a film.

3.3.3 Effect of the antiblock additive on optical properties

The optimum concentration of antiblock depends on several factors, including the type of antiblock, particle size of the antiblock, the resin properties and extrusion conditions. Theoretically, a higher antiblock concentration will improve the blocking and antiblocking properties (up to a certain maximum). The downside, however, is the loss in optical properties. In Figures 6 and 7 the increase in haze and the decrease in clarity with an increase in the antiblock concentration can be seen in a 2MI LDPE grade.

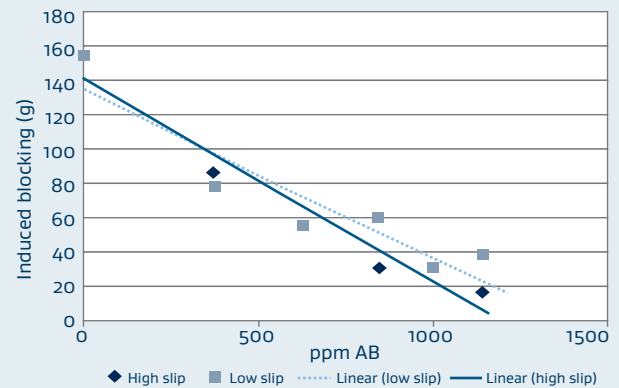


Figure 5: Effect of antiblock concentration on the induced blocking properties of a 0.75MI LDPE resin at high and low slip additive contents

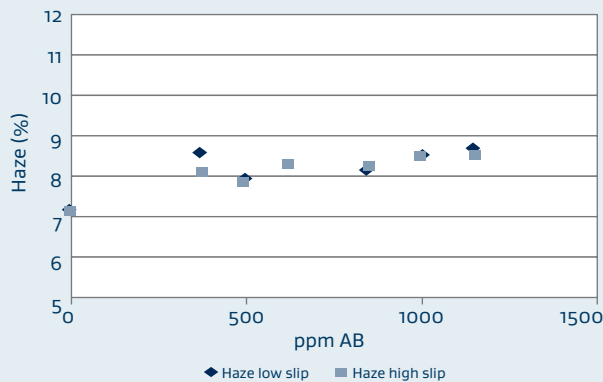


Figure 6: Increase in the haze with an increase in the synthetic antiblock concentration in a 0.75 MI LDPE resin

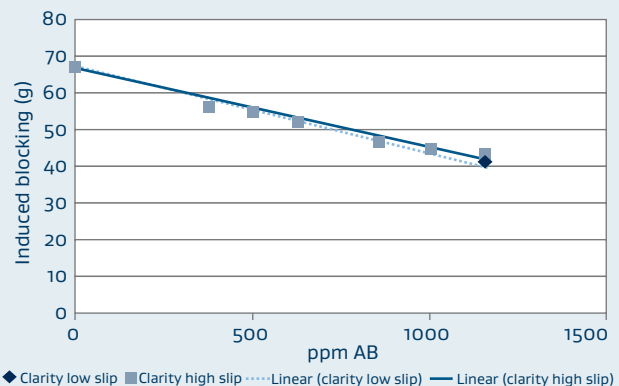


Figure 7: Decrease in the clarity of a 0.75 MI LDPE resin with an increase in the synthetic antiblock concentration

4. CONCLUSION

The performance of LDPE resins is enhanced by the addition of slip and antiblock additives. Optimum levels of performance additives are needed to ensure that the film will perform optimally in a certain application. Generally, LDPE grades are recommended for a certain thickness range. The levels of performance additives are optimised in this range, and using it outside the recommended range, may result in the film either having too much or too little performance additives. This must also be taken into account when formulating blends with hLLDPE or unformulated LDPE grades.

5. REFERENCES

1. ASTM D1894
 2. ASTM D3354
- Croda website (www.Croda.com)

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