Polyglycerol esters demonstrate superior antifogging properties for films

As a result of their multifunctional properties and harmless nature, polyglycerol esters are widely used in many applications in the food and cosmetic industries. They notably function as emulsifiers, dispersants, thickeners, solubilizers, spreading agents, or emollients. More recently, new industrial applications based on polyglycerol esters have been developed. This includes their utilization as antifogging and antistatic additives, lubricants, or plasticizers. Dr. Valérie Plasman, Dr. Thibaud Caulier and Dr. Noel Boulos of Solvay discuss the use of polyglycerol esters as antifogging additives in polyolefin and PVC films. This application has been very popular in Asia for many years, and is now of growing interest in Europe and the United States.

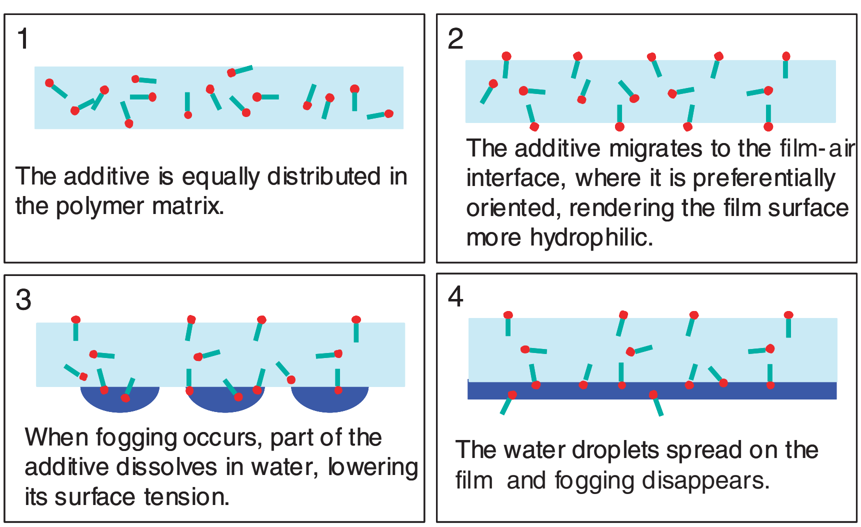

Figure 1: Mode of action of an antifogging additive.

If water or moist air is trapped in a closed system, condensation droplets (fog) form on the inner surfaces when the temperature cools down below the dew point. This phenomenon is a big issue in fresh food packaging and in greenhouses.

For this reason, the development of plastic films with improved antifogging properties is of growing importance. This can be achieved either by spraying an antifogging agent on the surface of the film, or by incorporating an antifogging additive in the polymer matrix.

Compared to surface treatment, the use of additive technology is usually preferred as it provides a longer lasting antifogging performance, and reduces significantly the amount of antifogging agent that is in contact with the packaged food or cultivated plants.

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Figure 2: Use of antifogging agents in agriculture.

In food packaging, films with good antifogging properties offer a more attractive display of the packaged products and enhance their shelf life. Antifogging films are also used in greenhouses where they allow better light penetration, enhancing photosynthesis that improves yields (see Figure 2).

Antifogging additives are typically surface-active products made of two main parts: a hydrophilic head and a lipophilic tail.

Examples include sorbitan esters, polyoxyethylene esters, glycerol esters, and more recently, polyglycerol esters.

When incorporated in a polymer film, the antifogging additive migrates from the matrix to its surface, decreasing the interfacial tension between the polymer and the water droplets. As a result, the droplets spread across the surface of the film.

Therefore, the role of the additive is not preventing water deposition on the film, but condensing it in an invisible continuous thin layer. The mode of action of antifogging additives is illustrated in Figure 1.

Selecting antifogging additives

There are several factors that affect the choice of antifogging additives. Firstly, desirable antifogging properties depend upon the intended application. For fresh food packaging, a fast migration of the antifogging additive to the surface of the film is desirable, but there is no requirement for a long-term antifogging effect. On the other hand, a slow migration rate of the additive and a long lasting antifogging effect are of critical importance in ‘plasticulture’ applications. Another key issue in the choice of the antifogging additive is its compatibility with the polymer matrix.

Other important factors include its stability during film production and its influence on the other properties of the film, for example mechanical properties. A compromise between the antifogging performance and these factors will determine the final selection of the appropriate additive.

Polyglycerol esters

Polyglycerols are highly biodegradable polyols consisting of glycerol units linked by an ether linkage (see Figure 3).

Polyglycerol esters may differ widely in composition, depending upon their production process and raw materials. In the following discussion, we will only refer to polyglycerol esters that are based on Solvay Diglycerol and Polyglycerol-3 (Solvay manufactures high purity polyglycerols but not their esters).

Diglycerol is a product of 90% minimum purity. This allows the manufacture of distilled monoesters, similar to distilled monoglycerides. These distilled monoesters cannot be obtained from lower purity polyglycerols.

Polyglycerol-3 typically contains a minimum 80% di-, tri- and tetraglycerol, by contrast to a polyglycerol manufactured by the traditional glycerol condensation process, which has a broader oligomer distribution (see Figure 4).

This extremely low content of residual glycerol contributes to the superior surface activity of Polyglycerol-3 esters vs. typical condensation polyglycerol esters.

Solvay polyglycerols are clear transparent liquids that are colourless (Diglycerol) or slightly yellowish (Polyglycerol-3), producing esters of reduced colour compared to less pure polyglycerols.

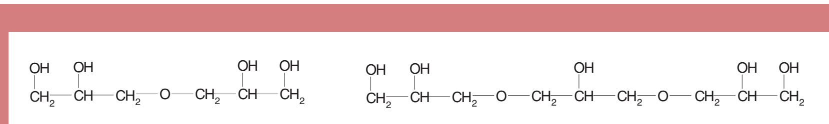


Figure 3: Structures of di- and triglycerol.

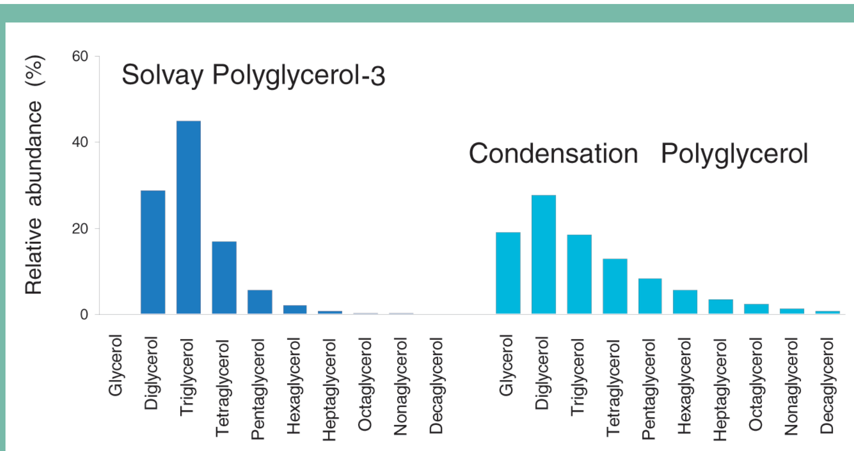
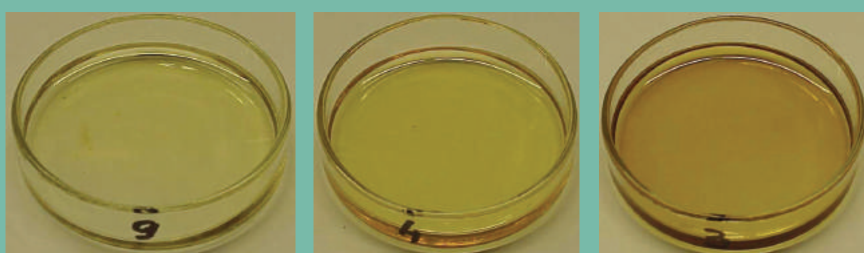


Figure 4: Comparison of the oligomeric distributions of Solvay Polyglycerol-3 and a typical condensation polyglycerol (average MW = 250 g/mol).



Polyglycerol-3 monooleate | *Sorbitan monooleate (SPAN 80)* | *Polyoxyethylene sorbitan monooleate (TWEEN 80)*

Figure 5: Comparison between monooleates of Polyglycerol-3, sorbitan and polyoxyethylene sorbitan. Appearance after 10 minutes at 250°C (under air).

Thermal stability

Compared to glycerol esters, polyglycerol esters are less volatile, which reduces the evaporation of the additive during extrusion.

Polyglycerol esters also exhibit a higher thermal stability than glycerol esters, sorbitan esters or polysorbates, which lowers the possibility of discoloration during film processing.
Figure 5 illustrates the discoloration of sorbitan monooleate and polyoxyethylene sorbitan monooleate compared to Polyglycerol-3 monooleate after 10 minutes at 250°C in air.
The superior thermal stability of Diglycerol and Polyglycerol-3 esters compared to the equivalent glycerides can be traced back to the higher heat stability of the corresponding polyol (Figure 6).
The low content of glycerol in both Diglycerol and Polyglycerol-3 further enhances the thermal stability of their esters compared to condensation polyglycerols

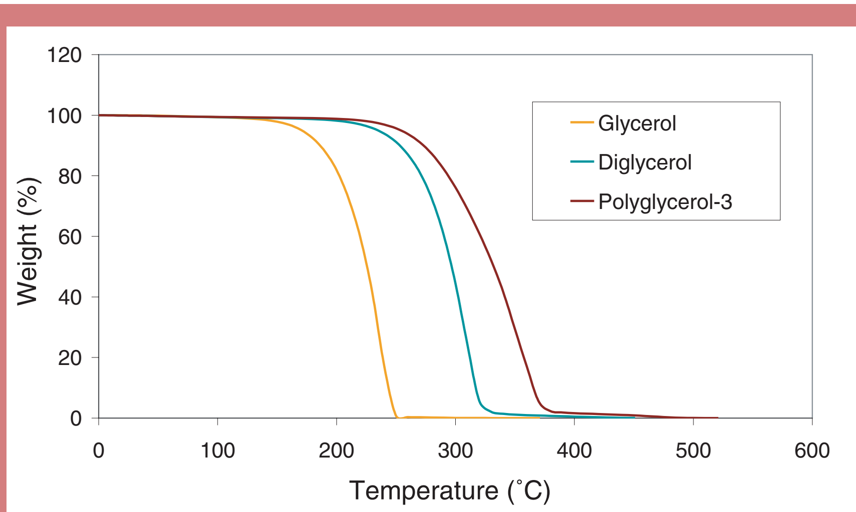
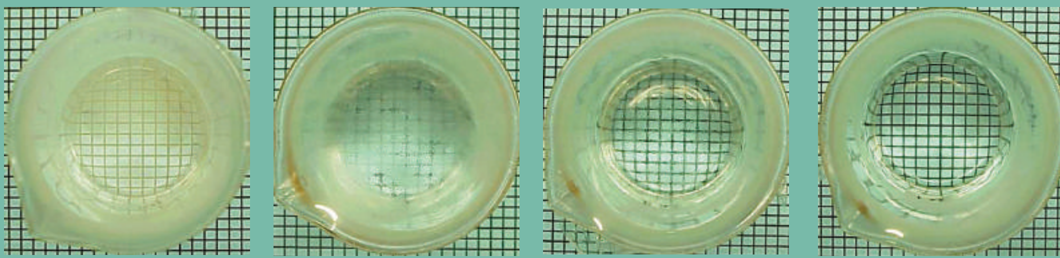


Figure 6: Thermogravimetric analysis of polyglycerols (under air).

Antifogging properties

The best polyglycerol fatty acid esters for polyolefin and PVC food wrap films are the monolaurate and the monooleate esters.
In this example, the antifogging properties of polyglycerol esters in food wrap packaging films were assessed by the following test:
Various esters were incorporated in ethylene-vinyl acetate (EVA) films.
Beakers containing water at 20°C were then covered with the films and kept in a climate chamber at 10°C.
Fog was visually assessed as a function of time. Properties of EVA films containing no additive, 1% glycerol monooleate, 0.5% Diglycerol monooleate, or 0.5% Polyglycerol-3 monooleate were compared (Figure 7).
After a few minutes, Diglycerol and Polyglycerol-3 monooleates at 0.5% w/w concentration were found to be more effective than the corresponding distilled monoglyceride at 1% w/w concentration.
The advantages of polyglycerol monooleates versus the corresponding monoglyceride were confirmed by a visual assessment after a longer period (minimum 5 hours), as well as by contact angle measurements (see Figure 8).
The angles between droplets of water and the films containing the Diglycerol and Polyglycerol-3 monooleates were found to be substantially smaller than those of the corresponding glycerol derivative.
Diglycerol and Polyglycerol-3



No additive | 1% Glycerol monooleate | 0.5% Diglycerol monooleate | 0.5% Polyglycerol - 3 monooleate

Figure 7: Appearance of EVA films after 5 minutes.

monostearates are examples of antifogging agents that are slow migrating and UV resistant, and are therefore good choices for plasticulture applications. These esters impart excellent antifogging properties to polyolefin and PVC films.
Due to their compatibility with other additives, polyglycerol esters can be used alone or combined with other esters for optimal antifogging performance.

Other uses

As with many other antifogging agents, polyglycerol esters also have antistatic properties because the water film that forms on the polymer surface reduces its resistivity.
Polyglycerols as such (not esterified) are used as plasticizers in starch based biodegradable thermoplastic compositions. Their lower volatility and higher thermal stability, compared to glycerol (Figure 6) or sorbitol, allows easier processing (less evaporation and higher processing temperatures).
Polyglycerols or blends of glycerol and polyglycerols are claimed to have better plasticizer properties than glycerol alone in polyvinyl alcohol films (PVA).
Diglycerol esters, such as diglycerol tetraacetate, have been described as good plasticizers for cellulose acetate and, more recently, for polyester resin compositions based on polylactic acid.
Due to their amphiphilic character and their high thermal stability, polyglycerol esters can also be used as lubricants. This is particularly suitable for food handling equipment since many polyglycerol esters are allowed for food use in many countries.

Conclusions

The use of Diglycerol and Polyglycerol-3 esters as antifogging agents is increasingly popular, especially in polyolefin and PVC films. Of particular interest is the opportunity to manufacture tailor-made polyglycerol esters, which would be specially designed with regard to the polymer matrix and the application.
The excellent antifogging properties of polyglycerol esters are due to their controlled migration rate in the polymer, their optimum surface-active properties, their high thermal stability, and their compatibility with various polymers and additives.
Their biodegradability and acceptance for food use in many countries make them particularly suitable for incorporation in films for food packaging and agriculture, or as lubricants for food equipment.

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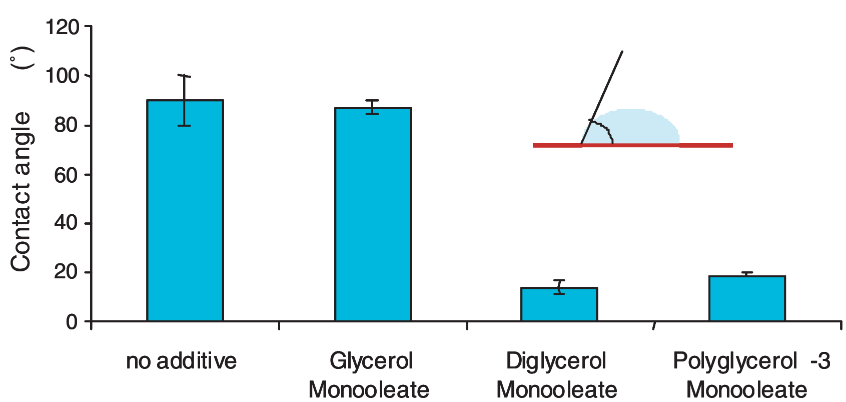

Figure 8: Contact angle measurements between water droplets and the EVA films.