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Special Requirements on Compounding Technology for Bimodal Polyolefines and Their Industrial Application

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Summary: This paper describes quality criteria and the optimisation of compounding processes for some bimodal polyolefin grades. Quality criteria and testing methods are different for film grades and coloured grades for pipe extrusion or other applications. Even for comparable polymer grades their producers use different quality criteria which makes the direct comparison of those products impossible in terms of compounding demands. Therefore, the quality checks have to be adapted for optimising a compounding process by special screw designs or operating conditions. Some examples for such an optimisation and the resulting industrial compounding lines are shown. In general this new class of polymers requires an enlarged and specially designed melting zone (i.e. multiple zones) and a longer residence time within the compounder. This leads to either lower throughput for a given machine size or requires a bigger machine for a given throughput.

Introduction

Recent progress in technology of polyolefin synthesis has led to development of a new generation of polyolefin materials with broad, bimodal molecular weight distributions. In contrast to conventional products these bimodal polyolefins are distinguished by a high strength and a good processability. Broader molecular weight distribution leads to bigger potential viscosity difference between low molecular and high molecular fraction. High viscosity ratios complicate any homogenising during a compounding process prior to final processing of the product, causing inhomogeneities consisting of himolecular material which may lead to disadvantages in the product quality.

This requires specially designed compounding equipment and adapted processing conditions during compounding to meet the different quality demands to such products.

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Bimodal Polyolefines

Bimodal Polyolefines (POs) are homo- or copolymers with at least two different molecular weight distributions (MWD) or two chemical compositions, were the combination can be detected in an analytical way.[1] An idealised bimodal MWD and its properties is shown in Figure 1.

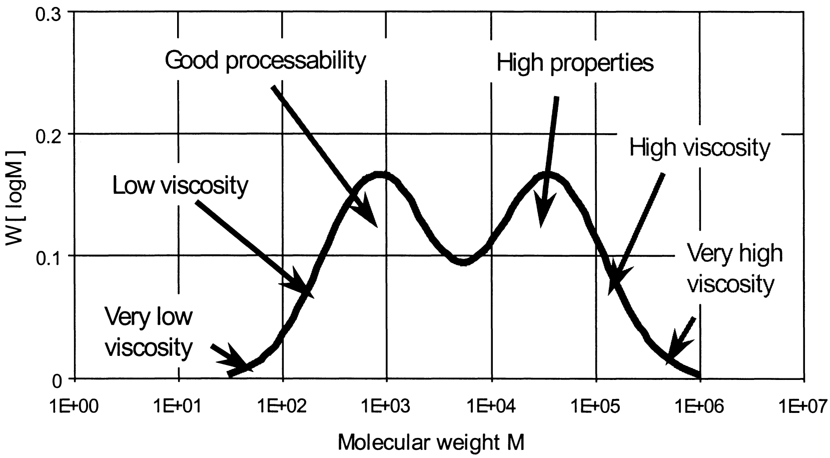

Figure 1. Molecular weight distribution (MWD) and influenced properties.

The low molecular weight polymer leads to a good processability while excellent mechanical properties can be achieved due to the high molecular weight fraction of the „mixture“.

In 1999, the PE 100+ association was launched (http://www.pe100plus.net), BOREALIS, ELENAC and SOLVAY being members of that association. The aim was to promote bimodal polyolefin pipe grades exceeding the excellent properties of PE 100 pipe grades like creep rupture strength, stress crack resistance and resistance to rapid crack propagation. One way to achieve this goal is broadening the molecular weight distribution more and more.

In the meantime ATOFINA and DSM became also member with their pipe grades and ELENAC is now part of BASELL. There exists an ongoing process of continuous improvement for those “high tech” polyolefines.

In general bimodal POs can be produced in two ways: the compounding of two separately produced monomodal POs in an extruder or the use of several reactors in series. The advantage of the multi-reactor system is the possibility of getting a better homogeneity through the combination of molecular weight entities on the same powder particle.[2] However, at some multi-reactor bimodal POs different powder size particles can have different specific melting enthalpy, viscosity and MWDs.[3]

Compounding Characteristics

Bimodal POs do not only show extraordinary good properties, they are also difficult to compound. The high molecular weight parts can cause so called „white spots“ in coloured pipe grades (Figure 2) or „gels“ in film grades (Figure 3).

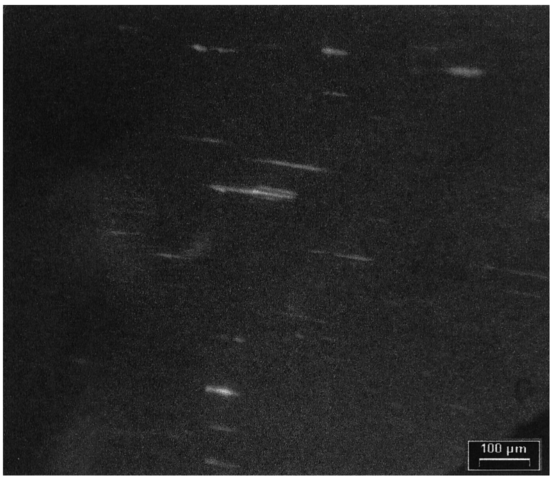

Figure 2. Microtome pellet cut showing „white spots“ in a coloured PE pipe grade.

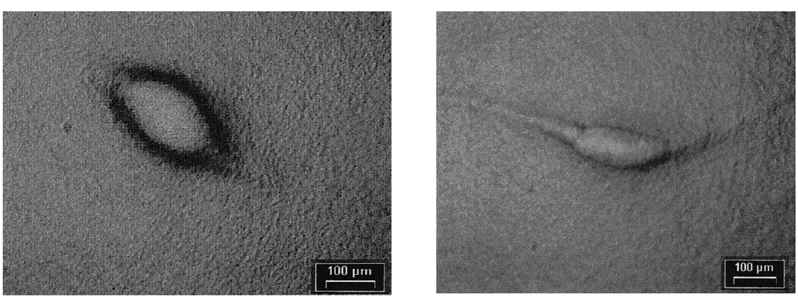

Figure 3. Micrographs showing „fish eyes“ in a PE film.

These inhomogeneities are of high molecular nature, meaning high viscous particles being distributed in a low viscous matrix. Due to this the principle compounding bi- or multimodal POs is more like the compounding of polymer blends than the compounding of monomodal POs with a narrow MWD. Therefore, also the theory of polymer blending can be adapted to get a better understanding of homogenising bimodal POs. The possibility that a high molecular disperse particle can break-up in a low molecular matrix can be described by the critical Weber number for drop break-up We_{crit}.[4]
Figure 4 shows We_{crit} versus viscosity ratio $p = \eta_d / \eta_m$ for simple shear and plane hyperbolic flow. At values above We_{crit} the viscous stress overrules the shape conserving stresses, thus the drop is stretched and finally breaks into fragments.

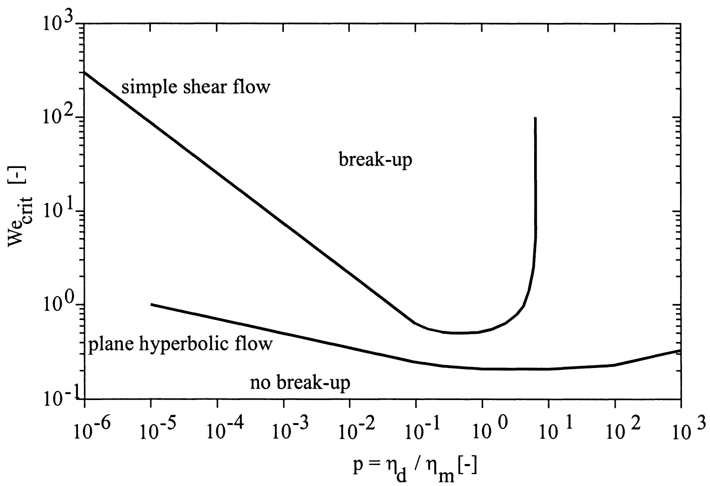

Figure 4. Critical Weber number for drop break-up versus viscosity ratio p in simple shear and plane hyperbolic flow. η_d : viscosity of the dispersed phase; η_m : viscosity of the continuous (matrix) phase.

Like in polymer blends disperse particles cannot be destroyed by mixing if the ratio of viscosity of the disperse gel and the viscosity of the matrix exceeds a certain value. Elongational flow on the other hand is more effective and allows drop break-up in a much wider range of viscosity ratio.
In contrast to polymer blends the goal at bimodal POs is not the dispersion and distribution of the disperse phase, it is the elimination of the disperse phase by mixing in a molecular scale. Due to this the matrix viscosity of bimodal PO can increase with

decreasing „gel“ or „white spot“ content during mixing.[3] Another difference are the possible different break-up mechanisms. In uncompatibilised polymer blends elongated particles break-up due to interfacial stresses[5] whereas in bimodal polyethylene such an effect could not be observed.[4]

This has consequences for the compounding of bimodal POs:

- if the melting section is too strong the viscosity of the matrix can decrease in a way, that it will be impossible to destroy high molecular weight particles in the homogenisation section.
- some extreme high viscous disperse particles can only be destroyed after the viscosity of the matrix has increased due to the integration of moderate high molecular „gels“ into the matrix.

Consequently, a certain energy is required in order to disperse the high molecular gels, but if the energy input is not optimised, the viscosity ratio will increase with melt temperature and further destroying of gels will be impossible.

Quality Demands and Verifications

The homogeneity of a compound is investigated by several different methods for film grades and pipe grades. Film grades are normally judged by investigating gels in a blown film or cast film, while for pipe grades one looks to microtome cuts out of pellets or compression moulded sheets for white spots and pigment agglomerates.

Film grades

Table 1 shows the different applied methods for film evaluation.

There are two methods based on a very limited number of employees who are solely able to perform the quality check. That is a disadvantage, but it is a very fast method.

On the other hand there exist also methods which count the number of gels in different size classes. This methods are much more objective but also more workintensive. Sometimes it is also not easy to differ between polymer gels (which are relevant) and any impurities which may be caused by the laboratory environment.

Table 1. Quality evaluation methods for film grades and their characteristics.

Method	Characteristics
Film rating FAR (internal method)	“Standardized” eye of an employee
Film rate FR	“Standardized” eye of an employee
Classes – method 1	Numbers of hard spots in classifications according to size for different products
Classes – method 2	Numbers of hard spots in classifications according to size for different products

Pipe grades

Also for pipe grades exists a variety of different methods for evaluation of the homogeneity of compounds. They are shown with their characteristics in Table 2.

Table 2. Quality evaluation methods (white spots) for pipe resins and their characteristics.

Method	Characteristics
ISO 11420	• Developed for carbon black distribution in finished product • 6 pellet cuts • The biggest dimension of a particle is judged
GKR	• biggest (not coloured) particle < 0.02 mm² (<150 μm) • 6 cuts (3l/3q) out of a compression moulded plate
WSA	• percentage of not coloured area (whole pellet cut evaluated)
Internal	• blown film-, strand-, cast film evaluation

ISO – rating was established for carbon black – dispersion in end- or semifinished products and allows no particles bigger then 60 μm in its largest dimension. The reason behind is that bigger impurities can create stress concentrations and thus lead to crack initiation and mechanical failure. White spots are not such impurities because they consist of the same material as the surrounding matrix. Furthermore, it creates bad quality ratings when there are already stretched particles present, which will be destroyed during the following processing step.

Nevertheless, sometimes this method is applied also to white spot evaluation in pellets being much more critical then the second method which allows particles up to 0.02 mm².

A very fast method with low standard deviation is based on the amount of uncoloured material in relation to the whole investigated area - **W**hite **S**pot **A**rea (WSA).

Most of the internal methods are shooting for gels or hard points in the range of 100 μm to 200 μm.

The variety of quality evaluation methods for the homogeneity of compounds creates difficulties in comparing different materials directly meaning that the compounding step needs to be optimised for every single grade.

Process Optimisation for Compounding

The first trials to homogenise bimodal polyolefines used a standard screw and process concept being developed for unimodal polyolefines. The screw configuration on a corotating twin screw extruder was comparable simple as shown schematically in Figure 5.

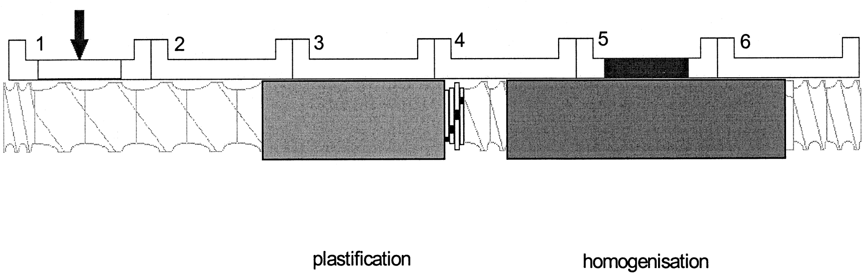

Figure 5. Screw concept monomodal polyolefines.

Working with a short machine consisting of one plastification zone and one homogenisation zone led not to sufficient results as shown in Figure 6.

First it was tried to optimise the given (short) machine for the new product. Therefore, the effect of defined functional zones on the level of homogenisation was investigated.[4] This work led to the development of new mixing elements and combinations of this new elements with standard elements to achieve a good product quality.

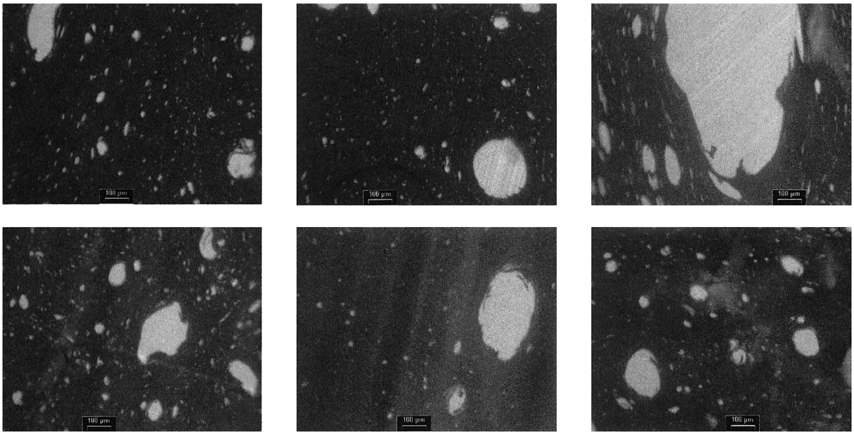

Figure 6. Starting point of optimisation (ISO – rating = 13; WSA = 8 %).

Figure 7 shows the principle configuration of an optimised (short) screw.

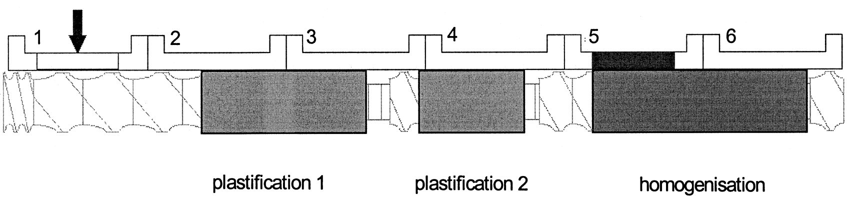

Figure 7. Optimised screw design (short machine).

The screw now is based on two melting zones which uses different new designed elements to avoid unmolten particles entering the homogenisation zone.

Figure 8 shows pellets cuts after the optimised screw design was build in.
The improvement in homogeneity is easy to see. Further improvement can be achieved, but requires also a different machine setup (higher volume and longer screws) and changes also in the drive system (more torque and drive power).

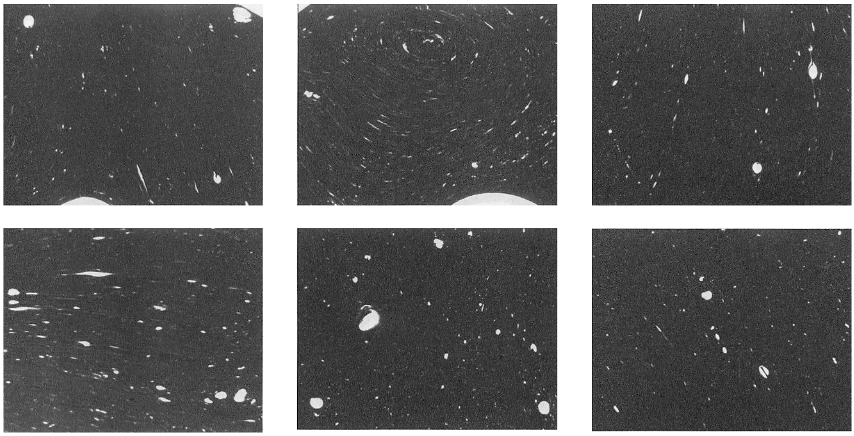

Figure 8. White spots (optimised short screw, ISO – rating = 6,9; WSA = 0,83 %).

Like in blends there exists no general and optimal screw for compounding all types of bimodal POs. The conditions can change with the viscosity, the density, and the heat conductivity of the whole powder or of powder fractions. Furthermore the particle size distribution of the bimodal POs can also be of great importance for the design of the screw configuration. However, experiments have shown that special types of mixing elements and combinations of mixing elements, work effectively in the compounding of most bimodal POs.

Using separated sections for melting and homogenisation, it is possible to achieve a soft but sufficient melting and an effective homogenisation of the product.

Conclusion

Processing of bimodal POs is very much different compared to the processing of mono-modal POs. When compounding bimodal grades, the specific energy input is higher and the throughput lower. However, since the producers of bimodal POs are still developing new products with sometimes extreme MWD's, the producers of mixing devices must also continue developing mixing concepts.

To be able to compare different bimodal PO grades it is necessary to base on objective and identical quality investigation methods.

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