"What Criteria of Production Lines in Polyester Manufacture have a determining Influence on Melt Purity and Quality?"

Contents

(Author: Dr. Ulrich K. Thiele; published by 3. Kunststoff-Symposium 15. & 16. September 1999, Gneuß Kunststofftechnik GmbH, Internet: www.gneuss.de, E-mail: gneuss@gneuss.de;)

Introduction

In the most different fields of polymer manufacture and processing, no topic has influenced work in such a lasting and durable manner as melt purity and the correlation concerning its processibility has. Often, it is not possible to give any clear answers or quick solutions because of the complex influence factors. Finally, criminological feeling is necessary in order to gain control of the causes of inhomogeneities occurring suddenly or very slowly and of the problems observed in the processing and application fields.
Today, the criteria of a production line for polyester manufacture - which have a determining influence on melt purity, in particular - are to be checked, taking the concluding sentence of Mr. Stibal (EMS-KF) up which he expressed during the lecture he gave three years ago on the same occasion; he namely required that all lines should be built and operated in order to "avoid that disturbing particles build up in the course of process".

Raw material handling and conveying

If one considers the topic on the whole, raw material purity plays an important part with polymer purity. With glycol or also with DMT, it is relatively easy, still, to remove the greatest part of inhomogeneous deposits by filtrating within a fineness range between 1 and 2 µm at the manufacturer's or when filling the line. However, transport, storage and conveying of terephthalic acid present enough possibilities of contamination. Furthermore, there is no easily manageable method of analysis, up today, with regard to the determination of insoluble deposits of terephthalic acid – an exciting task for Research and Development. PTA contamination is noticed, at the soonest, during the filtration of pre-polymers. Regarding the prevention of PTA contamination, the transport of this material in special silo vehicles or in 20-m^3-containers with PE inliner proved to be very worthwhile. It generally applies that the smaller transport packaging is, the bigger the level of contamination is. The discharging devices for 1-ton-bags, especially, which are often built very simply, represent intake ports for contamination.

By the way, this also applies to the filling of polyester pellets. What is important, for pellet handling, is the kind and the conception of the conveying. Although the low-speed, the dense phase or the pulse conveying has now gained ground as a standard, high-speed conveying can still be found at manufacturers' and processors'. Tests of dust built up in high-speed conveying have shown a 1000 to 10,000 times higher level of contamination.

The regime of product control – Line and process design

Plug flow and absence of dead spots

When designing a polymer line theoretically, it is always tried to obtain a melt dwell time in the respective devices which is as short as possible and to come closer to the dwell time distribution of a plug flow. With regard to the technical realisation, compromises are made for diverse reasons, these being far away from theory. In this way, valves, pipe bends, welding seams, static mixers, inlet and outlet supports on reactors and filtration equipment, in particular, present possibilities for dead spots to build up in which polymer melt is not transported or only too slowly.
Depending on the local pressure, the existing temperature and the real dwell time, all kinds of conversion products can then build up – starting from a modified, gel-like melt up to dehydrogenised and carbonised products as well as highly-cristalline and highly-polymeric substances. In this case, close co-operation between the machine manufacturer and the polymer chemist is necessary so that design and functionality can match together. Besides the flow-suitable, geometric design of the interior spaces, determining minimum and maximum shear rates, defining the suitable surface finish of inner surfaces as well as the right kind of mix and distribution of additives and catalysts, especially, represent centres which may enable inhomogeneities to build up.
The question regarding the surface finish of the reactor internal walls and pipes is disputed again and again. Practice has shown that manufacturers and processors of polymer for thin films/sheets and filaments in the higher viscosity field such as finisher and melt channel downstream of the filter consider polish to be advantageous for polymer quality.

Temperature control and heating

It is elementary knowledge that too high temperatures or a too high delta T – especially when using electric heating – involve the risk that reduction products and inhomogeneities build up. It is much less known that polymer freezes in the wall area – due to a bad distribution of the heating media and locally limited thermal bridges – and that it may be transformed into highly crystalline and highly polymeric, insoluble materials. Through the load reversal in the throughput or through slight temperature variations, parts of these deposits loosen again and are introduced into the product flow as inhomogeneities. Since this kind of melt contamination is still formable at the usual melt temperatures between 280 and 290°C, it can be retained from filters only with difficulty. This is a problem, which now and then causes anger in spinning mills.

Oxygen

As far as the development of insoluble and infusible products in the polyester process is concerned, oxygen plays a particular part. It is a known fact that, in the vacuum area of lines, the introduction of oxygen leads to a discoloration of the melt and that it also supports, locally, the development of coal-like products. In this field, experienced polyester manufacturers know how important it is to test leakage from time to time and to maintain vacuum sealing systems.
However, the effect of oxygen in the field of ester interchange or esterification is sometimes underestimated, and it is not yet commonly held to carefully free glycol, terephthalic acid and additives from the solute oxygen already in the storage bins and to inertisize them with nitrogen.
Whereas oxygen rather causes a yellow colour in the melt area, it causes a grey colour in the pre-stages rich in glycol.
A recently published work on this topic [S.M.Aharoni, Polymer Eng. Sci., 38 (1998)7, Page 1039-47] shows how this functions; what is interesting to note is that oxygen first oxidises parts of the reaction mass to carbon monoxide which, in its turn, then reduces the existing trivalent antimony to metal. Thus, the b-value gives some information on the oxygen concentration in the polymer part, and the L-value can explain the oxygen introduction in the monomer part of the polyester line.

Build-up of inhomogeneities through additives

Polyester manufacture makes catalysts, stabilisers and additives necessary. During the ester interchange process, based on DMT and ethylene glycol, the catalysts get blocked once the ester interchange reaction is finished, this being due to phosphoric stabilisers.

During the esterification of terephthalic acid with ethylene glycol, the antimony compounds used as a catalyst – such as antimony triacetate or antimony trioxide, for example – is already present in many cases. In order to improve thermal stability, phosphoric stabilisers are today added with increasing frequency, too, for reaction. One should not forget to mention the additions of cobalt compounds and optical brighteners or colouring agents which are necessary for dying and are added to the process before polycondensation.
These additives often have, besides their forced effect, unwanted secondary reactions which can cause the formation of deposits or precipitations.
Familiar deposits include, for example, antimony phosphate, cobalt phosphate or metallic antimony. These particles appear later on in the product as haze or grey tinge, or they become negatively noticeable through the blocking of the polymer filters and spinpacks.
Here is the secret of the formulation and the process - the know-how of polyester manufacturers. Because of the partly unknown influences on the whole chain of further processing, experienced producers distance from familiar recipes only with great caution.

Another “difficult” area is the addition of titanium dioxide pigments as dulling agents and processing aids. In this context, it has to be mentioned that only a highly-efficient treatment (for example grinding on a pearl mill, centrifuging and filtering of the TiO_2 suspension)
can prevent the formation of agglomerates. A filtration is in no case suitable for the removing of defects or problems in this process stage.

Pelletizing

An often unknown and neglected source of filterable contamination comes from the cooling water of pelletizers. The requirement, which dictates to use only, distilled or deionized water in the automatic cooling water circuit, is often not taken seriously in the rough production everyday life. Since the newly built-up surface of pellet grains – with the free COOH final groups - is an excellent ion exchanger, the hardness causing salts contained in the cooling water, like calcium or magnesium, are admitted with a high affinity. During processing, later on, calcium or magnesium salts can frequently be seen on the filter screens.

Production regime

A line intended for polyester manufacture can never be designed and built in such a way that it could be avoided to generally exclude that inhomogeneities – caused by arbitrary interventions in the production regime - build up. In this case, a high-quality standard is guaranteed through the knowledge and experience potential of the line operators and through the foresight of the line constructors. The throughput variations of a continuous line, especially, can be named as a source of inhomogeneities. These can take place either at a constant process temperature or with a reduced or an increased reactor content (dwell time change) or with a constant level of filling and at an adjusted temperature (change in the reaction speed). Experience has shown that level changes at a constant temperature are easier to manage, true, but that an operation with a constant level of filling is less susceptible to lead to a formation of inhomogeneities.
The maintenance regime, which was already mentioned with regard to the oxygen tightness, has a great influence on product purity. Sealing packages and sealing fluids of shaft sealing and valves are also an often-recurring cause of introduced contamination.

The philosophy of filtration

The facts related up to this point prove that measures which make it possible to avoid that inhomogeneities are introduced or that they build up are of prime importance in order to obtain high-quality products. Based on the great number of possibilities and on experience showing that technical systems quite considerably differ from the theoretic thoughts and goals regarding product handling, from time to time, the filtration of raw, intermediate and final products from polymer manufacture is however an effective and necessary tool enabling to adjust melt purity on a high and regular level. Since fitting and operating filtration equipment always means costs and since, furthermore, polymer is affected through filtration under certain circumstances, building and operating filtration systems is always adapted individually to the respective production.

Textile polyester

With regard to the manufacture of polyester for spinning and film manufacture, a concept has proved to be worthwhile, consisting in carrying out filtration already on prepolymer in the low-viscosity area. In this case, one should work with the highest possible filtration fineness. As far as candle filters or disk filters are concerned, the filtration surface has to be enlarged according to the increasing fineness in order to be able to maintain useful life and pressure differences. The volumes of the filter pots, which increase so strongly, are counterproductive. They increase the dwell time of the melt and involve the risk that dead spots develop. As a compromise, one frequently works with a filtration fineness of 20 μm, which makes wondering what the sense of this filtration is.
Alternatively, continuous melt filtration – such as the prepolymerfilter SFT offered by Gneuß Kunststofftechnik makes it possible to realise filtration fineness of 6 μm and even finer with very short dwell times in the filter. In connection with this filtration system, a great number of other technical and cost-efficient advantages can be cited. The polymer chemist being first of all interested in the possibilities of process optimisation.
It is thus easy to recognise that all precipitation or deposits which are sporadically introduced into the process or which build up in the process via catalysts, stabilisers, additives and raw materials, can immediately be monitored and valued on the filter through the variations of the built-up pressure. In this context, for example, the following questions are interesting:

What effect does a catalyst type modification or a manufacturer change have? For example, a change from antimony triacetate to antimony trioxide?

What influence do the kind of solution, the catalyst concentration and the preparation of the catalyst solution have on the filtration capacity of polymers?

What influence does the order of addition of the formulation components have?

Do the kinds of stabilisers (and the points where they are added) have any influence?

Are the colouring agents or optical dyes dissolved properly?

Are the addition conditions of additives optimal from a technical point of view?

It is true those quality problems due to scaling on the reactor walls, or too high additive concentrations due to an insufficient mix are trivial, but since they occur repeatedly they can lead to an unrecognised impairment of polymer quality.

With regard to the filtration of polymer melt before spinning, it should be distinguished between direct spinning and extruder spinning
In the case of direct spinning, spinning machines are often grouped, for cost reasons, in the same titre area and equipped with a central filter. Filtration is then carried out after a heat exchanger (if necessary). In this case, too, it is candle filters which are principally used, these being designed as double-filters for the filter change, without melt interruption. The filtration fineness is here approx. 20 µm, with a trend to reach 15 µm.
In the case of extruder spinning, filtration is carried out depending on the titre area; however, quite different attitudes regarding filtration can be observed from processor to processor. Taking the current pressure on production costs into account and considering the trend towards finer titres, a pre-filtration of melt will generally gain ground, with time, in this field too.
In this context, the pressure-constant and automatically working melt filtration equipment "RSFgenius" of the Gneuß Kunststofftechnik offers as well for the direct spinning process as for extrusion spinning a technically matured solution. To reach a long pack live time of spinning packs the recommended filtration fineness of the melt stream before entering the spinning beam is 10 µm.

Bottle polyester

Since a filtration takes place only rarely in preform manufacture and since visible fish eyes and/or black particles automatically lead to quality complaints, the central melt filtration is here set up after the finisher. Since the mechanical load of a melt is much lower in the bottle manufacture – compared to spinning – and since microscopic deposits have no disturbing effect on the bottle manufacture, one has done, up to now, without an ultra-fine filtration of the pre-condensate. Black particles which can be found in transparent polymer and which are bigger than 60 µm can already be recognised with the naked eye. That is the reason why a filtration fineness of 30 - 40 µm is recommended and sufficient for this application.

Analysis of melt purity

What is important for the valuation of melt purity is reproducible analysis methods. For this, the differently carried out filtration test methods always give relative results, which are only rarely well comparable. Thus, producers and processors must work out a wide database with a standardised method and use internal standards for control measurement. The analysis procedures, of which some are mentioned, are as differently structured as the chemical and physical variety of melt inhomogeneities is wide.

→ Filtration test
→ Melt filtration value with standard screens
→ Size distribution of inhomogeneities
→ Filterability of a polymer solution
→ Measurement melts residue quantity of polymer melt or polymer solution

→ Optical methods
→ Particle size distribution in the melt (e.g. Flow Vision)
→ Film: visual observation, video camera, and automatic picture recognition
→ Film/sheet surface topography
→ Laser scattering on films/sheets, moulded bodies and solutions
→ Filaments and fibres: inclusions, broken ends of fibres
→ Haze measurement on the moulded body, in the solution, on the film
→ Agglomerates, microscopic
→ Sedimentation on solutions with ultra-centrifuges

Generally, the waiting periods between the presence of inhomogeneities in the process of manufacture and the analytical verification are still too long today. Here, there is much space for an effective on-line analytical measurement.
In spite of all optimism regarding the necessity of an analytical determination of melt purity, it must be admitted, unfortunately, that the production tests in spinning, film stretching and bottle blowing can scarcely be replaced by an analytical consideration, especially high speed spinning processes and high performance BOPET film.

Summary

Quality and purity of a polymer depend on a great number of factors, which are connected, to a great extent, on the design and construction of a polymer line as well as on their operation.

In order to be successful, it is reasonable to consider and handle melt purity on the whole. Here, procedures and technologies to avoid contamination are equal to efficient filtration methods.

In polymer manufacture, filtration cannot serve to eliminate process defects. It is however necessary to maintain, continuously, the quality of a polymer melts at a high level and to remove the deposits which can sporadically be observed in practice.

Selecting suitable filtration systems is stimulated through new developments. The monomer filtration in a fineness range of 6 µm, with a continuously working filter of Gneuß Kunststofftechnik, can be mentioned as an example.

The existing analysis methods in order to assess melt purity are relative and, in any case, adapted to the special needs of polymer manufacturers and processors. However, they do not replace – even today – the superior processes of necessary processing tests.