



Endothermal (white) and exothermal (yellow) masterbatches of blowing agents

Blowing Agent Combination. Also for packagings, weight reduction is one of the main targets of developments for the future. As more and more packagings are getting thinner, also the foaming of packaging materials is on the increase. Unsuitable for foaming until recently, the packaging material PET can now be lighter, thanks to an appropriate combination with a blowing agent. This saves costs and enables environmentally-friendly design.

Stable PET Foaming

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Markets are constantly changing, which is particularly true for the packaging market. Especially for developments in the packaging area, environmental aspects are growing in significance, beside aspects of costs and mechanical properties. The value creation chain of polyethylene terephthalate (PET), for instance, has the great benefit of being excellently suited for recycling. The share of recycled PET today is up to 100 % in packagings. Some of the requirements for packaging materials are posed by trademark owners and supermarkets, and the manufacturers of packaging materials have to meet these demands.

Moreover, the packaging industry is working on new packaging systems, as well as saving raw materials by reducing layer thicknesses and reducing weights. Their target, apart from cost reduction, is to make packagings more eco-friendly. A way to reduce weights is to foam compact materials by using chemical blowing agents in order to save raw (polymer) materials. This opens up new fields of application, too.

Foamed polystyrenes and polyolefines have been established for several years at the packaging market. For PET packagings, the situation is different. Mostly compact, transparent or dyed packagings with a high share of recycled PET are produced

here. However, more and more packaging manufacturers require foamed PET packagings. This means new challenges for film producers, because PET's low melt viscosity, its sensitivity to hydrolysis, and the new types of twin-screw extruders make PET foaming particularly difficult. Additionally, no chemical blowing agent has been available to foam PET until today. How is it possible to foam polyester films, nevertheless? The solution lies in the mechanisms of the chemical blowing agent and its impact on the PET material.

The Benefits of Foaming

Components from foamed plastics have been employed in many areas of plastics industry for more than 35 years. Foaming is an established part of all major technologies of polymer processing. Its great benefit is weight reduction, and thus material saving. With some applications, it even improves the final articles' function. Foamed materials, for instance, have better isolating properties than compact components. In injection molding, a foamed core inside the component can reduce internal stress, shrink marks and warpage. A soft-touch cellular structure can also cause a haptic design effect, for instance in bottles or thermoformed packagings.

When foaming is linked to extrusion, the focus is always on weight reduction. For food packaging films, weight saving is of outstanding importance, because the German "Grüner Punkt" waste management system charges manufacturers for the weights of their packagings. More

weight moreover means higher cost of transport.

Chemical blowing agent: The term mainly refers to gases and low-boiling liquids. It may also mean chemical substances that decompose when submitted to certain temperatures, and lose certain blowing gases then. In both cases, the blowing agent is required to homogeneously disperse in the melt, and dissolve in the polymer matrix. If a melt including a blowing agent leaves the die or nozzle of the processing machine, the pressure in the machine will fall, and the gas will expand into the cooling melt. This produces a foam structure inside the melt.

Most chemical blowing agents are solid organic and inorganic substances. Their solid decomposition residues serve as nucleation seeds. The blowing agent thus easily dissolves in the polymer melt and the foam's cellular structure is refined. An ideal blowing agent should meet the following criteria:

- Decomposition temperature similar to the plastic's processing temperature,
- enabling easy feeding and good distribution,
- having high gas output,

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Blowing agent	Decomposition temperature [°C]	Decomposition products	Blowing gases
5-Phenyltetrazol	220–260	critical, NO _x possible	N ₂
Azodicarbonamide	210–220	smell, semicarbazide, not admitted for food contact in EU	N ₂ , CO ₂ , NH ₃ , CO
Citric acid derivates	200–220	food contact	CO ₂ , H ₂ O
4,4-Oxybis (benzene sulfo hydrazide)	140–165	smell, sulfuric compound	N ₂ , H ₂ O
Sodium hydrogen carbonate	120–150	food contact	CO ₂ , H ₂ O

Table 1. Current chemical blowing agents, as well as their temperatures and products of decomposition

- admitted for food contact,
- being non-corrosive to tools, dies or screws,
- having minor effects on mechanical properties,
- generating no dying or deposits,
- no or minor interaction between decomposition products and polymer.

These properties are required for most processes. However, no chemical blowing agent is able to meet all these requirements at the same time. Chemical agents can be divided into two groups:

- **Exothermal chemical blowing agents** (**Title picture**, yellow) cause heat during decomposition. Typical examples are azodicarbonamide und 4,4'-Oxybis (benzene sulfo hydrazide) (OBSH) und 5-phenyltetrazol (5-PT).
- **Endothermal chemical blowing agents** (**Title picture**, white) absorb heat during decomposition. They comprise e.g. sodium hydrogen carbonate and citric acid derivates.

Table 1 lists the reaction products of the main chemical blowing agents. Exothermal chemical blowing agents and their byproducts may cause smells during processing, and also in the finished product. Some of the solid residues from decomposition are precarious or risky. In Europe, they are therefore prohibited for food contact. The reaction products of commercial endothermal blowing agents are CO₂ and water steam. The two gases form the cellular structure in foamed components. The solid residues are inert salts, which behave neutrally in the polymer. At high processing temperatures, however, the water steam generated may react with the polymer.

Chemical blowing agents are applicable to most thermoplastic materials. It is possible to foam, for instance, the standard plastics PP, PE-HD, PE-LD, PS, ABS, and PVC, and the engineering plastic polyester, such as PET and PBT, as well as polyamide, polycarbonate, and thermoplastic elastomers. The blowing agent must match perfectly with the polymer. The following aspects need to be considered:

	PP	PS	PET	PE-LD
Range of densities [kg/m³]				
– bulk density	900	1,050	1370	914–928
– chemical	350–700	500–700	800–1,100	500–700
– physical	30–100	35–50	–	15–100
Examples of applications				
– chemically foamed	ribbons, convenience-packagings	meat trays, yoghurt tubs, isolating films	meal trays	cooler bag, geo sheets
– physically foamed	fruit packagings	meat trays, tray liner	plates	protective films, seals

Table 2. Applications and density ranges for foamed applications

- The active ingredient is chosen according to decomposition temperature and foam quality.
- The carrier material must be the same as the target polymer, or comply well with it.

With chemical blowing agents, it is usually impossible to use the target polymer as the masterbatch carrier, due to possible decomposition during production. The carrier chosen therefore frequently represents a compromise. This is also why the user can choose from a wide variety of blowing agents, which means the eventual solution is close to specially tailored.

Foam extrusion: Foaming is applied with the following extrusion techniques (**Table 2**):

- Film extrusion (food trays, seals, ribbons),
- sheet extrusion (PVC displays, apparatus engineering, construction),
- profile and pipe extrusion (picture frames, seals, foam core pipes).

If the foamed films are to be used for food packagings, the blowing agent must have food authorization. Most of the endothermal Hydrocerol grades by Clariant do so. The Hydrocerol PEX series was specially designed for extrusion application. The foam structures generated are very fine-celled and cause good mechanical strengths in thermoformed articles. The surfaces are smooth and can be printed. Weight reduction usually ranges from 15 to 30 %.

In foam extrusion, the blowing agent is added to the polymer as a masterbatch or

powder. During the process, the melt temperature makes the blowing agent decompose. This produces the gas-shaped components, which remain dissolved in the polymer, though, due to the melt pressure. If the pressure in this oversaturated melt is reduced to environmental pressure, bubbles are produced, and a foam structure is obtained. This foam structure then enables weights to be reduced by up to 30 %. Foam extrusion is possible on most com-

mercial extruders, if the following preconditions are fulfilled:

- The melt temperature must be so high as to decompose the blowing agent completely.
- Maximum melt pressure must keep the gas in the melt dissolved and prevent pre-foaming.
- Foam qualities are best, if the bubbles are formed only after the material has passed the die (**Fig. 1**).

In co-extrusion, usually the internal layer is foamed. The compact external layer gives the final product its integral structure, and thus the required mechanical properties. The foamed internal layer flows faster, which means the polymers selected and the structure of the layers must be carefully tuned.

Especially with polymers like PET, with a narrow range of processing options, the processing conditions – mainly the temperature course – must be adapted, in order to provide for a stable process.

The Suitable System of Blowing Agents

Endothermal blowing agents, such as citric acid derivates do not fit in with the processing conditions of PET, because their decomposition temperature is approx. 200°C. This is actually too low for the PET, which requires at least 260°C processing temperature. As foaming will start at a relatively early stage, i.e. in the feed zone, the process may become insta-



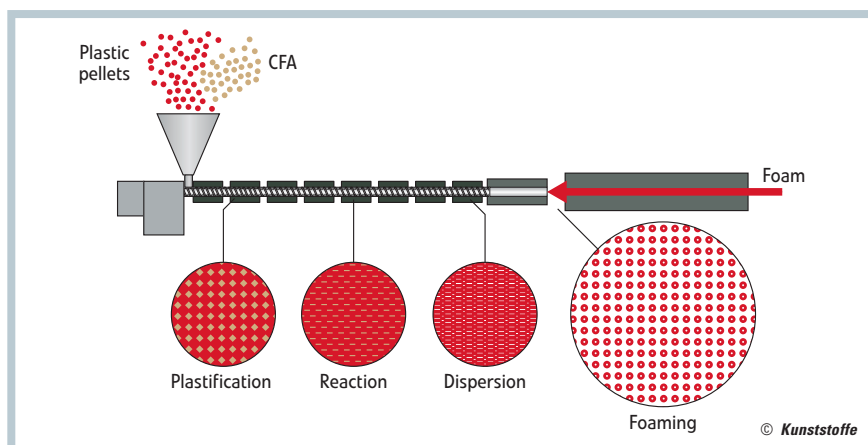


Fig. 1. Graphic presentation of the foaming process (CFA = chemical blowing agent)

ble. When decomposing, the citric acid produces water. This will certainly cause problems, if it gets into contact with a hydrolysis-sensitive plastic like PET. When making an optimum masterbatch of blow agent, designers must consider this.

Clariant's Hydrocerol PEX 5048 is a blowing agent that meets all these requirements and produces a very fine foam structure. The additive masterbatch named Cesa-extend NCA0025531 enables for controlled chain extension.

To enable foaming, PET must be dried or degassed in a prior step. Intrinsic viscosity will otherwise fall rapidly. The same will happen if the melt gets into contact with humidity, during processing. When using endothermal blowing agents, water is obtained as a byproduct of decomposing; it can hydrolyze the polymer chains and thus decompose them. As a result, the melt viscosity is reduced, and the process destabilized. The necessary admission pressure in the die cannot be maintained, melt stability falls, and the produced film sags. The low melt stability also prevents proper dispersion of the foamed bubbles, making them grow unpredictably. This cracks the foam structure and makes surfaces rough. The low

values of viscosity make the film brittle and thermoforming is only possible to a limited extent. Residues from the decomposed short-chain PET can form deposits, drops from the die lip can touch the film and cause holes.

To eliminate these unfavorable effects, chain extenders are employed. They re-link the interrupted polymer chains, and make viscosity rise again. The chain extenders react with the PET's functional groups. The chemical structure and dispersion in the polymer matrix are of major importance with these additives; two mechanisms are possible:

- Purely linear chain extension and
- chain branching: linear and branched extension, cross-linking.

Figure 2 shows a schematic presentation of the reaction between the functional groups of the polyester and the multifunctional terminal groups of the chain extender. The different products of the CESA-extend series – chain extenders and chain branching agent – require different process conditions. Their reactivity is subject to the following parameters:

- Content of humidity,
- reaction time,
- residence time in the extruder,
- dispersion and
- temperature.

These important parameters are subject to the preset values in the overall extrusion line.

When it comes to selecting chain extenders for applications together with endothermal chemical blowing agents, only multifunctional acrylates are suitable, because they are quite insensitive to the humidity produced. In case the reaction with water was too fast, no functional groups would remain to react with the polyester itself. The partial branching also steps up melt strength, which improves foam quality. Figure 3 shows a microscop-

ic image of a foamed PET film. It was produced by employing Hydrocerol PEX 5048 as a blowing agent, and CESA-extend NCA0025531 as a chain extender. The image clearly shows that the foam has a very fine structure and its bubbles are homogeneous.

While manufacturers have been successful for quite some time in foaming pre-dried PET on single-screw extruders, recent trials performed on twin-screw extruders with vacuum drying also revealed very good results. In this case, however, tuning blowing agent, chain extender and temperatures is particularly demanding, so as not to lose blowing gas via the vacuum. If undried PET was used, humidity would emerge into the foaming system, which would then put the PET melt at the risk of reacting with the chain extender. This must be prevented by all means.

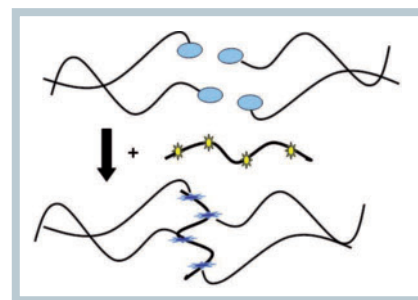


Fig. 2. Schematic presentation of the principle according to which chain extenders act in the PET foaming process

Conclusion

The latest findings clearly show the benefits included in the combination of chain extender and chemical blowing agent used as additives for PET foaming. While degradation of the polyester cannot be avoided, the method counteracts this process, and helps re-gain lost melt stability. Undesired deposits from short-chained polymers can thus be prevented. Final products, e.g. thermoformed articles, maintain their good mechanical properties.

The CESA-extend products improve melt stability, which is their main benefit. Increasingly used on twin-screw extruders with vacuum drying, this combination of additives shows its superiority. ■

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Fig. 3. Microscopic presentation of the foam structure in a PET mono-film (thin cut, amplification 1:100, density 0.87 g/cm³)