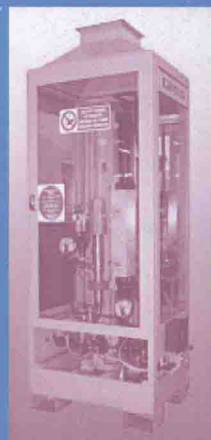
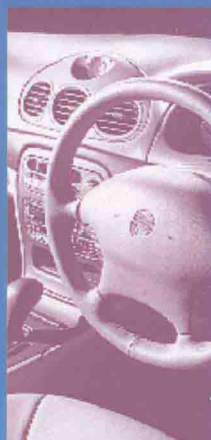


Blowing Agents and Foaming Processes 2006

The 8th International Conference

16th-17th May, Munich, Germany

Conference Proceedings



Blowing Agents and Foaming Processes 2006

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Blowing Agents and Foaming Processes 2006

16-17 May 2006
Marriott Hotel, Munich, Germany

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THE USAGE OF CHEMICAL FOAMING AGENTS IN TECHNICAL POLYMERS

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BIOGRAPHICAL NOTE

Mirco Gröseling graduated in Chemical Engineering from the University of Applied Science in Hamburg, Germany. His major subject was Chemical Engineering. In 1997, he joined the R&D and Technical Service Team for additives of Clariant Masterbatches (Deutschland) GmbH in Ahrensburg, close to Hamburg. Since 2004 he is member for the Technical Service Team for film applications in the packaging market.

Jan-Erik Wegner graduated in Process Engineering from the Technical University of Hamburg-Harburg, Germany. His major subject was Chemical Engineering and Process and Plant Engineering. In 2000, he joined the Technical Service and R&D Team of Clariant Masterbatches (Deutschland) GmbH in Ahrensburg, close to Hamburg. He is responsible for the Development of the Chemical Foaming- and Nucleating Agents HYDROCEROL®.

ABSTRACT

Today, foaming agents are used to produce foamed products of thermoplastic polymers. Several types of thermoplastic resins are foamed commercially. Foaming agents can be either a physical gas or a chemical substance that decomposes in a polymer melt during processing, and releases a gas.

Those chemical foaming agents are offered as a masterbatch and can react either endothermic or exothermic. Due to their numerous benefits endothermic foaming agents are chosen when it comes to foamed food packaging. Their active ingredients are food approved and provide fine foam structures and excellent mechanical properties.

Endothermic foaming agents are quite often used for film applications in food packaging and are well established in polypropylene and polystyrene. But for hydrolysis sensitive technical polymers like polyesters we have a drop of viscosity which creates processing problems and inhomogeneous cell structure.

Special additives like the chain brancher CESA Extend help to increase the melt stability and to optimize the dispersion of the gas and provide a stable process.

This paper will discuss this process and application requirements in detail and present the combination of respective foaming agents together with the chain brancher.

1. Introduction

Foamed thermoplastic articles have been used in the plastics industry for more than 30 years. This technology is applied in all main conversion processes.

The main advantage of foaming is weight reduction and the related material savings. Additionally, in certain applications, the functionality of an article can be significantly increased by foaming giving for example improved heat- and airborne sound insulation properties, if compared to compact parts. In injection molding internal stresses, sink-marks and warpage-effects can be reduced by a foam structure in the core of the article. A cellular structure may also be used as a design-tool in certain applications e.g. soft touch effect in thermoformed trays.

In extrusion weight reduction issue is the main focus. For food packaging films the material cost savings are increasingly important in countries like Germany where converters have to pay duties by weight on disposable packaging [5].

2. Foaming processes

Foaming agents can be either a physical gas or a chemical substance that decomposes in a polymer melt during processing, releasing a gas. In both cases the gas has to be homogeneously dispersed and dissolved

in the polymer melt under pressure. When the melt exits the equipment, the pressure drops and the gas expands the melt, creating a cellular structure inside the core of the polymer.

2.1 Chemical Foaming Agents

Chemical substances that decompose or react by the influence of heat are called chemical foaming agents.

Main benefits in using Chemical Foaming Agents (CFA's) are:

- Weight reduction / raw material saving
- Thermal insulation
- Increase in wall stiffness (sandwich effect)

Solid organic and inorganic substances are used as chemical foaming agents. The solid residues react as nucleator. This leads to a finer cell structure and a better solubility of the gas in the polymer melt.

General requirements to an ideal chemical foaming agent are [1], [3]:

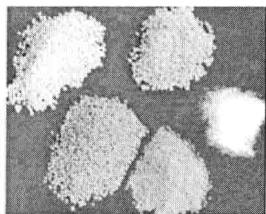
- Decomposition reaction has to be in a defined temperature range, according to the requirements of the polymer used
- Easy mixing and uniform dispersion
- High gas yield
- Approved for food-contact applications
- Should not be corrosive for tools and melt exposed surfaces
- Low influence on the mechanical properties
- No discoloration and plate out of effects
- Minimum or no interaction of byproducts with the polymer

As this variety of properties is demanded in several conversion processes, no chemical foaming agent can satisfy all of these properties. Therefore certain processes often require individual foaming agent formulations.

Chemical foaming agents are divided according to their enthalpy of reaction into two groups:

Exothermic chemical foaming agents (yellow) generate heat during decomposition. Typical substances for this class are Azodicarbonamide and 4,4'- Oxybis(benzolsulfohydrazide) (OBSh) and 5-PT.

Endothermic chemical foaming agents (white), which absorb heat during the decomposition. Typical substances for this class are for example sodium bicarbonate and citric acid derivatives.



Picture 1: Endo- and exothermic CFA's

Table 1 shows the reaction products of the most commonly used chemical foaming agents. The exothermic chemical foaming agents and their byproducts can cause odour during production and in the finished part. The solid byproducts often are critical and even toxic. Therefore the exothermic CFAs are banned when it comes to products that must have food approval.

The reaction products of the most common commercially used endothermic CFAs are CO₂ and water (vapour). Both will form the cellular structure of a foamed article.

The solid residues are mainly inert salts that are neutral to the polymer. This is different for the water that is present in the polymer melt. At temperatures of almost 300°C the water can become an active reactant to the polymer itself. See table 3: Byproducts.

	Dec. temp.	By - products	main gases
5-Phenyltetrazole	220-260°C	toxic	N ₂
Azodicarbonamide	210-220°C	Odour, semicarbazide, banned in food contact	N ₂ , CO, NH ₃ , CO
Citric acid derivates	200-220°C	Food approved	CO ₂ , H ₂ O
4,4-Oxybis (benzenesulfonylhydrazide)	140-165°C	Odour, sulfur derivates	N ₂ , H ₂ O
Sodiumbicarbonate	120-150°C	Food approved	CO ₂ , H ₂ O

Table 1: Decomposition temperatures and byproducts of common chemical foaming agents

Chemical foaming agents can be used for foaming most thermoplastics e.g.

Standard polymers

- PP, HDPE, LDPE
- PS, ABS
- PVC

Technical polymers

Polyesters (PET, PBT)
Polycarbonate
TPE
Polyamides
Polymer blends

Not only a special process but also a special polymer may require an individual foaming agent solution. Using a foaming agent masterbatch, the following parameters have to be considered:

- Selection of the suitable foaming agent substance, based on the temperature range and foam quality required
- Choice of a suitable carrier resin for the final application

The carrier has to fit properly into the matrix of the application polymer. Hence it is most desirable to use the same polymer as a carrier that is also used in the end article. Any possible interactions can therefore be avoided. In PE, such an approach is possible, but using polymers with higher processing temperatures, the reaction temperature of the foaming agent is very soon the limiting factor. Unlike at the manufacture of color- or additive-concentrates, the maximum compounding temperature of CFAs is frequently not higher than 130°C. Is this temperature exceeded, the decomposition of the foaming agent occurs already during the production of the masterbatch. [4]

This is the main cause for comparably high availability of different foaming agent grades. For the end-user this fact reveals the advantage to have a system available that fits perfectly into his process.

3. The Foam Extrusion Process

The main converting processes are:

- Film extrusion (food-trays, sealants decorative ribbons)
- Sheet/board extrusion (PVC-displays, claddings, decking, fencing)
- Profiles and pipes extrusion (picture frames, sealing profiles, etc.)

	PP	PS	PET	LDPE
Density Range				
-density [kg/m ³]	900	1050	1370	914-928
-chemically [kg/m ³]	350 – 700	500 – 700	800 – 1100	500 – 700
-physical [kg/m ³]	30 – 100	35 – 50	-	15 – 100
Typical Applications				
- chemically foamed	Decorative ribbons Food trays, Convenience packaging	Food trays Yoghurt cup Insulation sheets	Food trays	Cool bags
- physically foamed	Fruit packaging	Food trays, Trayliner	-	Protective film, sealants

Table 2: Applications and densities of the most commonly used foamed plastics, Kunststoffe 1/2005 [5]

In film extrusion for food-applications it is crucial that the foaming agent provides a food approval according to the respective legislation which is given for the endothermic HYDROCEROL® grades.

In order to fit the end-users individual demands in extrusion applications, Clariant has developed a foaming agent series called HYDROCEROL® PEX.

Here the converter will find special grades for Packaging Extrusion applications where the thermoforming characteristics of the finished film are a key issue.

HYDROCEROL® PEX series foaming agents produce an especially fine-celled foam structure, enabling thermoforming without surface defects. Density reductions of 15 to 30% are state of the art in standard monolayer as well as in co-extruded applications. These formulations are available for most common packaging resins, such as PP, PE, PS and PET. [1], [2], [6]



Picture 2: Food trays (PE, PS, PET) HYDROCEROL® PEX - food approved grades

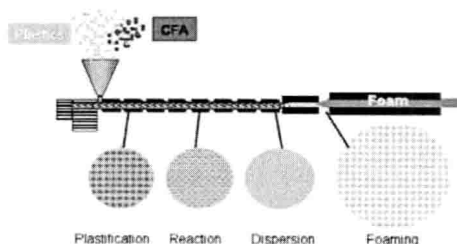
3.1 Process Parameters in Extrusion

In the extrusion of chemically foamed products, the foaming agent masterbatch (or powder) is either mixed or fed together with the polymer. During processing, the temperature of the melt causes the decomposition reaction of the CFA.

Gaseous components are generated and kept dissolved in the polymer melt by the extrusion pressure. The system is an oversaturated gas - polymer mix. The pressure gradient between the extrusion pressure and the ambient pressure at the die exit causes a cellular structure to form within the extrudate – in a similar way as uncorking a bottle of champagne causes the wine to foam. This cellular structure results in density reductions of 15 to 30% in films and sheets and 20 to 40% in pipes, profiles and boards.

Most conventional extruders can be used for foaming, if the following requirements are fulfilled:

- the melt temperature must be high enough to ensure a complete decomposition of the foaming agent
- the pressure of the melt must be kept high enough to keep the gas dissolved in the polymer melt until the melt exits the extrusion die.



Picture 3: Foaming process according to Wiesner [5]

An optimum foam quality will be achieved when the melt exiting the die is free of bubbles and the foaming starts a few mm after the die. This indicates that there is no foaming or expansion occurring already in the die or extruder.

Co-extruded foam products are produced with a foamed inner layer, and solid, compact outer layers. In this case, it is very important to select the proper resin grade. For the outer layer, a "softer" polymer is recommended, while a resin that is somewhat harder is recommended for the inner, foamed layer. The resin selection is key because the foam layer has better flow characteristics (lower apparent viscosity) compared to the solid layer of the same resin. If the layers differ too much in viscosity, this may result in a poor adhesion of the layers.

For polymers with a narrow processing window like PET the processing conditions must be adjusted quite accurately. The most important parameter is the correct die pressure to provide a stable foaming process.

4. New solutions for foamed polyester sheets

Endothermic CFAs like citric acid derivatives do not fit very well to the processing window of PET because the decomposition temperature of 200°C is too low, the foaming starts in the feeding zone and the process becomes unstable.

In 2001 Clariant launched its HYDROCEROL XH series for foaming of high temperature resins. With HYDROCEROL XH 906 a suitable approved endothermic CFA especially for polycarbonate was presented. However, the temperature range of 300°C where the HYDROCEROL XH grades are processed is too high for PET. [4]

Finding a suitable CFA for PET and combine it with additives to improve melt stability is described in this chapter.

4.1 Controlled chain extension with Clariant's CESA® - extend

Ester based polymers like PET are sensitive against hydrolysis. A significant decrease of the intrinsic viscosity (IV) value is the consequence when PET is processed undried or gets into contact with humidity during processing.

A byproduct of most endothermic chemical foaming agents is water and since it is generated during the converting process at high temperatures, a hydrolytic reaction can happen and destroy a part of the polymer chains.

With the lowered IV the viscosity also decreases and the process becomes difficult to handle. The necessary die pressure cannot be kept anymore and the foaming process runs out of control. The melt strength drops down and the film starts sagging. The dispersion of gas in the polymer is not optimized and will create surface defects in the thermoformed sheets. Due to the lower IV the tray can be also brittle.

Moreover, the residues of low molecular weight PET can cause plate out at the die and hence holes in the finished film may form.

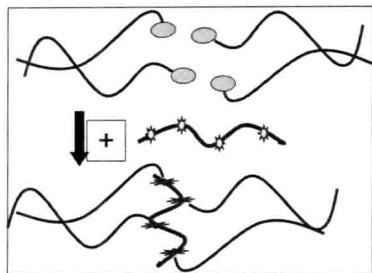
To prevent these negative properties chain extenders are able to reconnect short or broken polyester chains and bring them back to a higher IV level. They are for example based on multifunctional acrylates or carbonylbiscaprolactam which are reacting with the functional groups of the polyester.

The chemistry structure and dispersion of those additives are very important to get the right effect. We are differentiating in two different chain extension processes:

Chain extender – for clear linear chain extension

Chain Brancher – for linear and cross chain extension (branching)

Picture 4 shows the schematic description of the reaction between the functional groups of the polyester ester and the multifunctional groups of the acrylate copolymers.



Picture 4

It has to be respected that these grades of CESA - extend, the one for clear linear chain extension and the one for linear and cross chain extension (branching), Chain extenders or Chain branchers have different optimum processing terms. The reactivity is depending on the following parameters:

- Moisture level
- Reaction time
- Residence time in the extruding unit
- Dispersion

All these parameters are the key factors for successful chain extension and they are depending also on the configuration of the extrusion line.

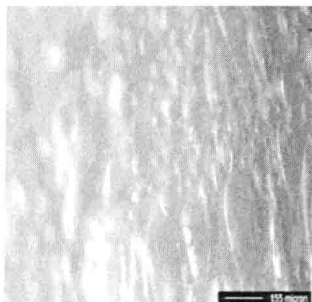
For the use together with endothermic chemical foaming agents only multifunctional acrylates are able to react with the ester groups because they are less sensitive against water. Other chain extenders react faster with the water and do not have any free functional groups left for the main reaction. Another advantage of the multifunctional acrylates is that the partial chain branching enhances the melt strength, therefore stabilizes the extrusion conditions and leads to a better dispersion of the gas, which finally gives a finer and more homogeneous foam structure.

The following table shows the results of an endothermic chemical foaming agent HYDROCEROL® PEX 5048 in combination with a CESA - extend grade for linear and cross chain extension (branching), chain brancher CESA® - extend NCA0025531. The trials were made on single screw polyester film line with pre - dried polyester.

Polyester nature Amorphous	Polyester with 1% HYDROCEROL® PEX 5048	Polyester with 1% HYDROCEROL® PEX 5048 + 1% CESA® - extend NCA0025531
Density = 1,33 g/ml	Density = 0,74 g/ml	Density = 0,74 g/ml
0% Weight reduction	45% Weight reduction	45% Weight reduction
IV 0,79	IV 0,51	IV 0,60

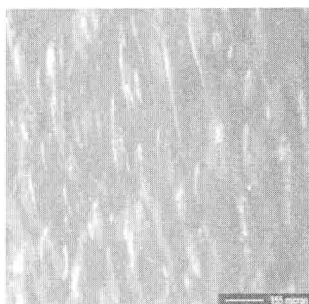
Table 3

Refeing to low the melt strength of the polyester the structure of the gas bubbles is not homogeneous.



Picture 5: Polyester with 1% HYDROCEROL® PEX 5048

The structure of the gas bubbles is more even. Also the surface of the film does not show any defects



Picture 6: Polyester with 1% HYDROCEROL® PEX 5048 + 1% CESA® - extend NCA0025531

4.2 Conclusions

Based on these positive results, it is clear which influence and advantages CESA - extend grade for linear and cross chain extension (branching), CESA® - extend NCA0025531 has in the foaming of polyesters.

It is obvious that the free water of chemical foaming agent causes a significant drop of IV. The processability of polyester films is more difficult to handle because the melt strength is not high enough to provide stable pressure conditions. This means irregular cell structure, plate out on the rolls and less mechanical performance of the film or tray.

The main benefit of using CESA® - extend NCA0025531 is not to increase the IV level of the polyester but to use it as a melt stabilizer.

Finally we can say that CESA® - extend NCA0025531 works as a processing aid, which enhances the effectivity of the foaming agent and stabilizes the process.

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CHEMICAL BLOWING AGENTS – PROPERTIES AND APPLICATIONS

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BIOGRAPHICAL NOTE

Lars Wahlen holds a PhD in polymer chemistry from Hamburg University. His research work there was on LCP and the phase behaviour of polymer blends containing LCP. Afterwards he was offered a post-doctoral fellowship at DSM Research in Geleen (NL), where he studied new ways to reinforce polyamides with hyper-branched aromatic structures. Since 1999 he is responsible for the development of chemical blowing agent preparations and masterbatches at Lehmann & Voss & Co. in Hamburg. He has given presentations about chemical blowing agents on several international occasions.

ABSTRACT

The role of chemical blowing agents in foam extrusion processes will be discussed. The gas that is formed by a decomposition reaction in the plasticizing unit dissolves in the polymer melt because of the pressure level in the extruder. When leaving the die the pressure drops to atmospheric level, the melt becomes oversaturated with gas and bubbles are formed. The melt expands in volume and is calibrated to the desired dimensions. Pipes, sheets, profiles and films can be foamed in this way. Different processing conditions allow control over compact outer layers of different thickness and the foam structure.

1. INTRODUCTION

Polymeric foam applications have reached many fields of every-day life today. The properties of foamed materials are sometimes unique and often very different from the compact material. Because of the gas or air trapped in the polymeric structure, the density of a foamed material can vary from considerably lower (up to 50% reduction) to tremendously lower (95% reduction) than the compact material. Insulation properties regarding heat and noise and mechanical damping are changed dramatically. The price per volume of a foamed material can be lowered considerably. Combined with better mechanical properties per weight this leads to a very advantageous property combination that has proven its potential in many different industries.

2. CHEMICAL BLOWING AGENTS

DEFINITION

Chemical blowing agents are reactive additives that are capable of releasing gases in a chemical reaction that is started by heat during the processing step of plastic materials.

This definition stresses, that blowing agents are reactive additives, which sets them apart from many other additives for plastics, where a certain, well-dispersed concentration in the finished or semi-finished part is necessary to achieve a desired effect (colour, UV-stability, flame retardant property). The blowing agent has to be dispersed in the polymer melt as well, but should then react under normal processing temperatures to form a gas. This gas is the desired "additive" in the polymer or in the final, biphasic product.

Gases or low boiling liquids that are directly dosed into the melt are considered as physical blowing agents, because no chemical reaction is involved in their use. Processes using physical blowing agents are not the main topic of this paper, but will be mentioned on several occasions for comparison. The fundamentals of foam formation are largely the same, once a gas is dissolved in a polymer melt under pressure.

BLOWING GASES

Since the released gas is the desired additive for a blowing agent user, our first look will be into the types of gases that are in use. The gas should be non-toxic, non-flammable and non-corrosive to machinery and polymer. The naturally in the atmosphere occurring gases nitrogen and carbon dioxide have clear advantages. Most chemical blowing agents fall into two groups, one that releases mainly nitrogen and one that produces mainly carbon dioxide. The formation of water vapour is less desirable, because of possible corrosion of metal and the danger of chain scission in certain polymers. Both problems will be addressed in

more detail later. On the other hand the formation of water cannot be easily avoided and trying to do so would limit the choice of substances drastically.

Carbon dioxide and nitrogen are also used as physical blowing agents that are dosed directly into the melt.

SUBSTANCES

The group of nitrogen releasing substances consists of azo compounds, hydrazine derivatives, semicarbazides and tetrazoles. Of each group only one or two substances are of commercial interest. See table 1 for the important substances and some of their properties. Azodicarbonamide is by far the substance with the highest consumption and the most applications.

All these organic compounds are quite reactive and release energy when decomposing to the very stable nitrogen molecule on one hand and other gases or solid residues on the other. A reaction that produces more heat than it needs for activation is called exothermic reaction. This kind of chemical reactions can be started by local heating or a spark, because once a critical amount of substance reacts, enough energy is released to activate the surrounding material avalanche-like. The pure powders should therefore be handled with care, some are classified as dangerous goods or dangerous cargoes.

Table 1: Chemical blowing agent substances

Substance	Decomposition temperature [°C]	Blowing gas	Remarks
Azodicarbonamide (activated)	205-215 (150-190)	N ₂ , CO, NH ₃ , CO ₂	efficient, universal, fine foam, many grades available
Oxybis(Benzenesulfonylhydrazide)	155-165	N ₂ , H ₂ O	Mostly PVC and rubber
Toluenesulfonylhydrazide	105-110	N ₂ , H ₂ O	mostly rubber
5-Phenyltetrazole	215-225	N ₂	only engineering plastics, expensive
Sodium bicarbonate	130-150	CO ₂ , H ₂ O	food approved, coarse foam, cheap
Sodium bicarbonate / citric acid mixtures	130-230	CO ₂ , H ₂ O	food approved, fine foam, many grades available

The other group of chemical blowing agents that has gained commercial importance and is still increasing its market share in the market, consists of inorganic salts that release carbon dioxide and water vapour as blowing gases. Most of these systems are based on sodium bicarbonate / citric acid mixtures. See table 1 for details.

The decomposition reaction of these inorganic compounds is endothermal, more energy is consumed for activation and reorganisation of chemical bonds than is finally released. As a consequence these substances need a continuous energy supply for further decomposition, or they will cool down their surrounding medium (the polymer melt) and the reaction will stop. This effect allows a somewhat better control over the gas formation.

DECOMPOSITION RESIDUES

The solid residues of the decomposition remain dispersed in the polymer melt, where they might have (positive) nucleating effects during cell formation or unwanted effects like discolouring or plaid-out. The percentage of solid residues is typically around 50% of the active component. Related to finished or semi-finished goods the final amount of residues will be below 1% in most cases.

The selection of a suitable substance as a blowing agent involves assessment of possible critical interactions between these residues and the polymer or other additives in a given process. In general it can be said, that those substances that have been successful in the market for longer times already have proven acceptable properties in this respect. Sometimes also special modified grades for reduced plate-out are available. Nevertheless not every chemical blowing agent is suitable for the use with a certain polymer.

LABORATORY METHODS

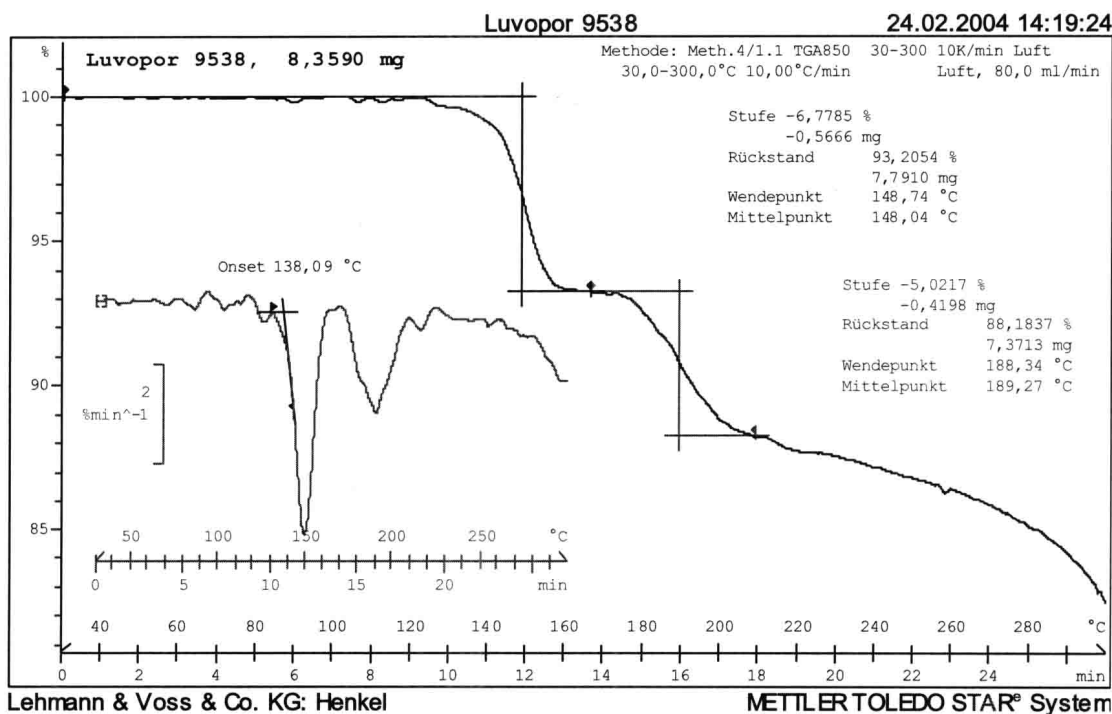
The most important methods to analyse and characterise chemical blowing agents focus on the decomposition temperature, the amount of gas generated and the particle size of the substances. The following methods will be discussed briefly with typical results: thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), direct gas yield measurements and particle size distribution measurements.

TGA

Thermo gravimetric analysis allows the observation of chemical reactions or physical phase transitions that involve the creation or absorption of gases. A small amount of sample (about 5 mg is enough) is weighed into a small sample pan and subjected to a temperature programme in an oven. While the sample is heated (i.e. with 10K/min) the sample weight is constantly measured on a very precise balance. The oven is purged with a constant slow stream of (normally inert) gas to remove volatile substances. After completion of the selected temperature programme a curve (mass versus temperature) can be plotted and the characteristic values onset temperature and mass loss can be calculated (see graph).

For chemical blowing agents the temperature where gas formation starts is determined and commonly referred to as the decomposition temperature. Since the decomposition temperature is a key parameter for the blowing agent customer and dependent on purity or the amount of activators present, it should be fairly constant for a given product and is usually specified. Sometimes more than one decomposition step can be observed, but only the first one is normally reported.

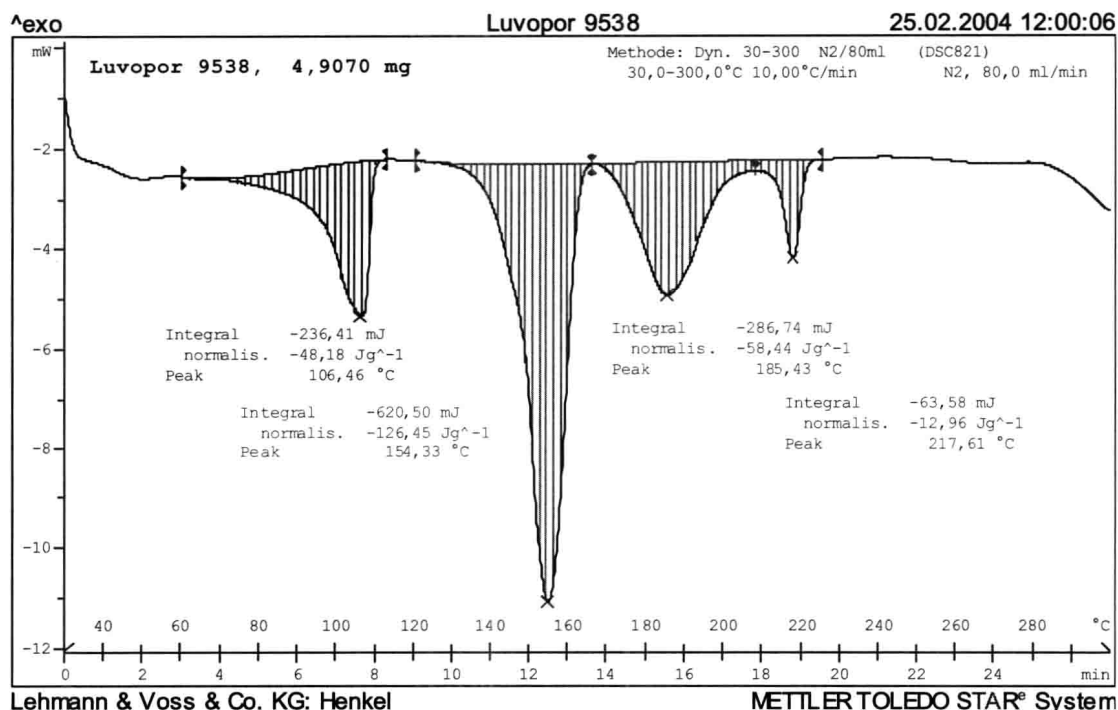
Another value of interest is the mass lost (in %) up to a certain temperature, i.e. 200° or 250°C. The higher the mass loss, the more of the substance has been converted into volatile products during the decomposition. Although this value correlates with the amount of gas produced, it is not possible to compare the gas yield of two different substances with it directly, without knowing the reaction products involved. Nevertheless a constant value for the mass loss of a product from batch to batch is a strong indication for a constant composition, therefore a good value for a specification.



DSC

Differential scanning calorimetry offers another way to characterise the thermal behaviour of a substance. For this method two identical sample pans are needed, one for the sample (about 5 mg), the other one empty as a reference. Both sample pans are put into an oven. Again a temperature programme and a purging gas are applied. In contrast to TGA it is not the sample weight, that is constantly monitored, but the sample temperature. If certain chemical reactions or phase transitions occur in the sample, this is often coupled with energy release or consumption, which will lead to a higher (or lower) sample temperature. The delicate control system of the DSC will notice a temperature difference between sample and reference immediately and compensate it by heating or cooling the sample. The energy used for this compensation will be recorded and can be plotted versus the temperature after completion of a measurement (see graph).

In this way phase transition energies (i.e. heat of fusion) or reaction enthalpies can be determined. The different heat of decomposition of endothermic and exothermic chemical blowing agents becomes obvious in this kind of measurements. The decomposition temperature of a substance measured by DSC can differ slightly from the one measured by TGA, but can also be used for specifications (and cross checked by customers).



GAS YIELD MEASUREMENTS

Direct gas yield measurements are a simple way to determine key properties of chemical blowing agents. Over time several similar methods have been developed. A sample of the material is weighed and heated either dry or under an inert substance like oil. The reaction chamber is connected to a cylinder, where formed gas is trapped either directly or by displacement of water. After decomposition is completed the amount of gas generated can be expressed as ml/g of substance. While easy to implement and perform, this method has several drawbacks: while heating the sample, also the air in the system warms up and expands considerably. This effect has to be eliminated by reference measurements. The resulting gas yield is also dependent on the outside air pressure. This can be compensated by recalculating the values to standard conditions according to the ideal gas law. But even when these effects are accounted for, the determination of the end of the reaction and even more the determination of the beginning (as the decomposition temperature) calls for experienced personnel and a comparison between different methods remains difficult. Generated gas could dissolve more or less in the water or generated water vapour could condensate in cooler parts of the equipment, which makes comparison of results nearly impossible. Standardised methods like TGA or DSC are clearly advantageous for comparability of results and should be preferred for specifications by suppliers and users.