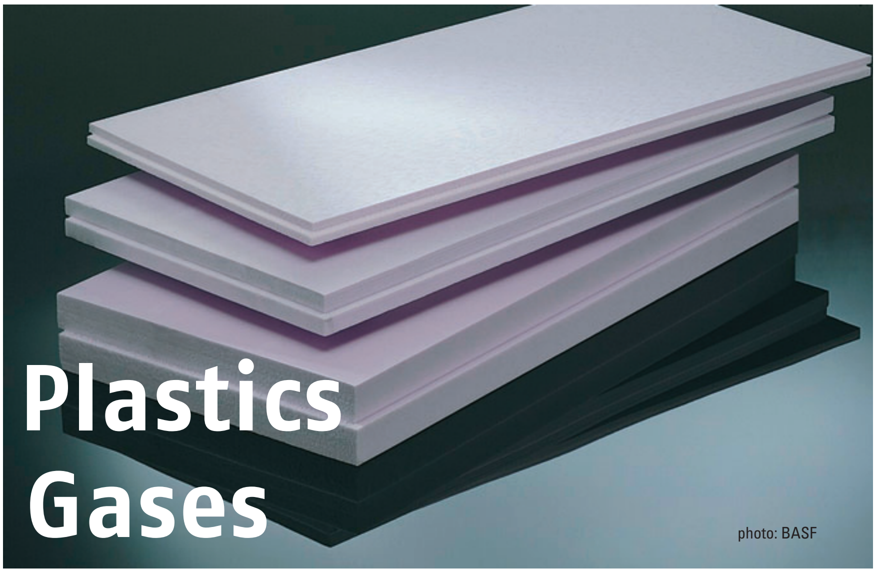

Foaming Plastics with Inert Gases

photo: BASF

Physical Blowing Agents. Inert gases are increasingly being used as blowing agents in the production of foamed plastics. Carefully thought-out supply and metering concepts make it easier for processors to switch to these ecofriendly blowing agents and facilitate gas handling.

ANDREAS PRALLER

The advantages of foamed products are undeniable and have led to their widespread and growing use. In addition to low raw material consumption, they offer positive product properties such as low density, excellent thermal and acoustic insulation, mechanical damping, low water vapour permeability and reduced moisture absorption. Different processes make it possible to produce various types of foam (open- or closed-cell, integral-skin), which are used in many sectors, including packaging, thermal/acoustic insulation and upholstery.

Main Principles of the Production Process

The cellular structure of foamed plastics is produced by so-called blowing agents. Additives such as nucleating agents and stabilisers are also frequently required. Commercially important manufacturing processes are extrusion foaming, in future probably also injection foam moulding, polyurethane foam moulding and the production of EPS foam (expanded polystyrene).

EPS production is a special process for the manufacture of Styropor. The blowing agent debate has not significantly affected this production process. Foaming in injection moulding has been known for a long time and has received new impetus in recent years as microcellular foaming. Both processes will only be mentioned in passing here.

Depending on the process and required density, chemical or physical blowing agents are used to initiate the foaming process. Chemical blowing agents are generally added to the plastic pellets in powder or granule form and decompose at elevated temperatures. Above the specific decomposition temperature of the blowing agent, a gaseous reaction product is released, usually nitrogen or carbon dioxide (CO_2), which acts as a blowing agent. Because undesirable decomposition products can also be formed and chemical blowing agents are often costly, they are used mainly for the production of higher-density materials. Physical blowing agents are metered into the polymer melt during foam extrusion or foam injection moulding, while in polyurethane foam production they are added to one of the starting products. Physical blowing agents can be used to produce the low-density materials that are frequently required.

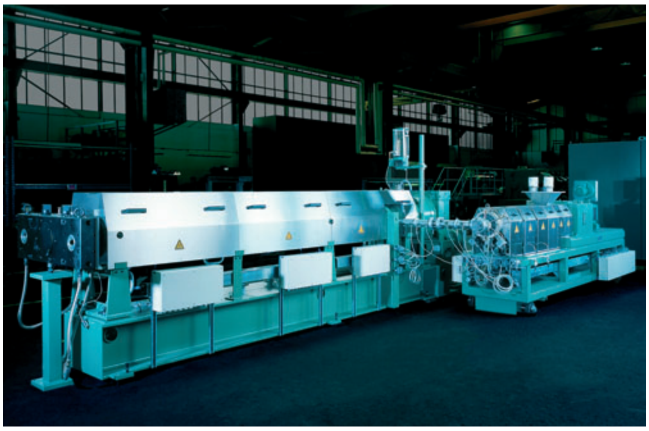

Fig. 1. Foam extrusion machine in tandem arrangement with twin-screw extruder and single-screw extruder (photo: Berstorff)

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In addition, they create a more homogeneous foam structure, achieve better process stability and give rise to substantially lower costs.

Physical Extrusion Foaming

Extrusion foaming machines differ considerably from standard machines. Depending on output rate and the particular product, either a single extruder or two extruders in a tandem arrangement are used. In the tandem machines frequently employed for higher outputs, the primary extruder is used for feeding the blowing agent and homogenisation, while the secondary extruder carries out controlled cooling of the blowing-agent-charged melt (Fig. 1).

A metering pump injects the blowing agent into the extruder under high pressure via an injection valve. The quantity of blowing agent gas injected is directly adjusted to suit the polymer and required foam density. The movement of the screw evenly disperses the gas in the polymer melt. Further homogenisation is achieved by diffusion of the melt/blowing agent mixture. The pressure in the extruder is maintained until the material exits from the extrusion die to prevent premature foaming. At the die exit, the sudden large pressure drop leads to oversaturation of the melt with blowing agent. Foaming starts, i.e. the nuclei already present grow and form the foam bubbles. Nucleating agents increase foam homogeneity, fulfil their nucleating function and promote the formation of many small bubbles. Extrusion is used to produce foamed products for many different applications in the packaging, construction and automotive industries (Fig. 2).

Polyurethane Foaming

Polyurethane foam (PU foam) is produced by the reaction of polyol and isocyanate. Usually, an additional physical blowing agent is added to one of the two reaction components to reduce density. The two reaction components are stored in tanks and recirculated through the system to the mixing head and back to the tanks. Many different additives are used to modify foam properties. The reaction components are mixed in the mixing head and then charged, at which point the chemical reaction starts.

In the continuous process, semi-finished products in the form of slabstock or sheets are made, while in the discontinuous process foamed mouldings are produced by injection moulding.

A distinction is made between flexible foams and rigid foams. PU foams are used, for example, as insulating material, for furniture and mattresses, as packaging or in the automotive sector (Fig. 3).

Fig. 2. CO_2 as a blowing agent – XPS insulation sheets for the construction industry (photo: BASF)

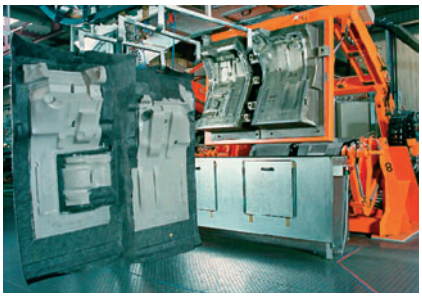

Fig. 3. Carpet for the Mercedes A class produced with CO_2 as blowing agent (photo: Krauss-Maffei Kunststofftechnik GmbH)

Physical Blowing Agents

Physical blowing agents have become established in many applications, especially for low-density products and high foam homogeneity requirements. The choice of physical blowing agent has an important influence on foam quality and the costs of the foamed product. In addition, environmental compatibility is an increasingly important factor.

The Montreal Protocol and its follow-up agreements present a great challenge for the foam producers. Despite the good properties of fluorchlorohydrocarbons and the fact that they are easy to handle, there is worldwide agreement that these blowing agents can no longer be used because of their ozone-depletion potential (ODP). The partially halogenated fluorochlorohydrocarbons are also not environmentally compatible and are already banned in many countries.

The alternatives are hydrocarbons, e.g. isobutane and pentane, and the inert gases, CO_2 and nitrogen. In many cases, CO_2 has emerged as the blowing agent of choice, since it has much higher solubility in polymers than nitrogen (Table 1).

Inert gases offer many advantages:
- environmentally compatible, since they have no ODP and minimal GWP;
- low gas consumption, since they produce a high degree of foaming;
- high cost-effectiveness since they are low-priced;
- non-flammable;

Blowing agent	Chemical formula	Mol weight [g/mol]	Boiling point [°C]	Vapour pressure [bar]	Flammable	ODP	GWP
Carbon dioxide	CO_2	44.0	–56.6		no		0.00025
Nitrogen	N_2	28.0	–195.7		no		
Isobutane	C_4H_{10}	58.1	–11.7	50.53	yes		
Cyclopentane	C_5H_{10}	70.1	49.3		yes		0.00275
Isopentane	C_5H_{12}	72.1	29.0	14.23	yes		
CFC-11	$CFCl_3$	137.4	23.8	15.32	no	1.0	1.0
HCFC-22	CHF_2Cl	86.5	–40.8	151.40	no	0.05	0.35
HCFC-142b	CF_2ClCH_3	100.5	–9.2	49.26	yes	0.05	0.38
HCFC-134a	CH_2FCF_3	102.0	–26.5	96.52	no		0.27

ODP = Ozone Depletion Potential GWP = Global Warming Potential

Table 1. Survey of physical blowing agents

Fig. 4. The high-pressure metering unit compresses the blowing agent to pressures of up to 500 bar

- non-toxic;
- chemically inert;
- they leave no residues behind in the foamed product.

Another advantage is that CO_2 is not specially produced but occurs as a by-product in other production processes. Before it is used as a blowing agent, it is purified, dried and liquefied under pressure.

Foaming with Inert Gases

There are many arguments in favour of using inert gases, especially CO_2. However, the gas is relatively difficult to handle. Liquid CO_2 is a very special blowing agent that differs considerably from other liquid blowing agents. It is normally stored close to the critical point in the boiling state, has a tendency to evaporate and is relatively compressible, which makes metering difficult. In extrusion foaming, precise metering despite varying extruder pressure is a crucial requirement for a uniform foam structure.

Membrane pumps are very widely used for metering liquid blowing agents, such as fluorochlorohydrocarbons in the past and now mainly hydrocarbons. They have been adapted to the requirements for metering CO_2. To prevent metering problems and cavitation damage resulting from the formation of gas bubbles, the gas and pump heads must be very well cooled. A reasonably priced, technically promising alternative is the DSD 500 inert gas metering unit specially developed for this application by Linde AG. This permits extremely accurate metering despite varying counter pressures in the extruder. Nevertheless, there are limits to the use of inert gases. If, as in extrusion foaming, very low densities are to be produced, mainly for polyethylene and polypropylene, hydrocarbons have advantages. CO_2 requires higher process pressures because of its limited solubility and cannot extract so much heat from the foam during expansion, since there is no phase transition from the liquid to the gaseous phase. But an increasing number of products are being foamed with CO_2 and in special cases also with nitrogen. Examples include XPS insulation sheets for the construction industry, foamed polyethylene (PE) films, e. g. for lid seals, foamed PE cable insulation and in some cases polystyrene food packaging. Modified polypropylene can also be foamed with PP to densities of 200 kg/m^3 and lower.

CO_2 in PU Foaming

In PU foaming, the choice of blowing agent depends on the intended end use. Foams for insulation purposes, e. g. insulation sheets or refrigerator insulation, are mainly foamed with pentane because this achieves very good insulating properties.

Through suitable choice of blowing agent, very lightweight foams can be produced. The lowest densities, well below 20 kg/m^3, are obtained with CO_2.

Important products manufactured by the continuous slabstock foaming process with CO_2 are foams for furniture and mattresses, especially low-density foams. In the discontinuous process, products such as carpet backings or other sound-absorbing automotive components as well as car seats are foamed with CO_2.

However, this gas not only allows production of low-density foams but also has other advantages that make it increasingly interesting. Material and production costs are lower, which means a short payback time for investment in the required CO_2 feed systems. In addition, CO_2 improves the mechanical and acoustic properties of the foam and facilitates processing (e.g. reduced urea formation in flexible foams).

In discontinuous production of PU foams, there are various options for feeding the CO_2 blowing agent. A distinction is made between injecting the CO_2 into one of the components, often the polyol, immediately before the mixing head (inline process) and adding it to a reaction component in the day tank (batch process). The batch process is less expensive and suitable for users for whom a constant CO_2 feed is sufficient. In the more technically sophisticated inline process, the user can vary the CO_2 content from shot to shot. For this technology, highly dynamic yet accurate CO_2 metering is required.

High-pressure Metering Pumps

The physical characteristics of CO_2 require a feed and metering concept tailored to specific user needs. Depending on gas consumption and the necessary gas pressure, the optimum concept must be selected on the basis of economic and technical criteria. Special metering pumps are needed, suitable for liquid CO_2 and capable of exact metering at pressures of up to 500 bar. They generally require liquid CO_2 completely free from gas bubbles and, if possible, with a high feed pressure of about 60 bar.

The Linde DSD 500 high-pressure metering unit has demonstrated its suitability for liquid CO_2 and gaseous nitrogen in numerous customer production plants around the world (Fig. 4). It compresses the blowing agent in special, compressed-air driven compressors to pressures of up to 500 bar and meters very evenly despite high fluctuations in counter pressure. This is due to a combination of a patented flow rate control concept and a highly accurate proportional control valve.

The flow rate is controlled extremely accurately and independently of extruder pressure and temperature, even when metering very small quantities. The unit adapts automatically to process pressure conditions. The highly dynamic control valve responds very quickly to process changes. Unlike conventional metering pumps, this pump is not sensitive to gas bubbles in liquid CO_2. Expensive cooling before and in the metering unit is no longer necessary. The metering unit is also suitable for gaseous blowing agents (e. g. nitrogen).

CO_2 Supply and Pressure Boost before the Metering Unit

The DSD 500 metering unit is supported by a complete feed and metering concept. It is possible to use either medium- or low-pressure tanks.

The medium-pressure tank stores the liquid CO_2 under a pressure of max. 80 bar. It is not insulated. To ensure a defined operating condition, the tank is provided with electrical heating and a refrig-

Extrusion foaming

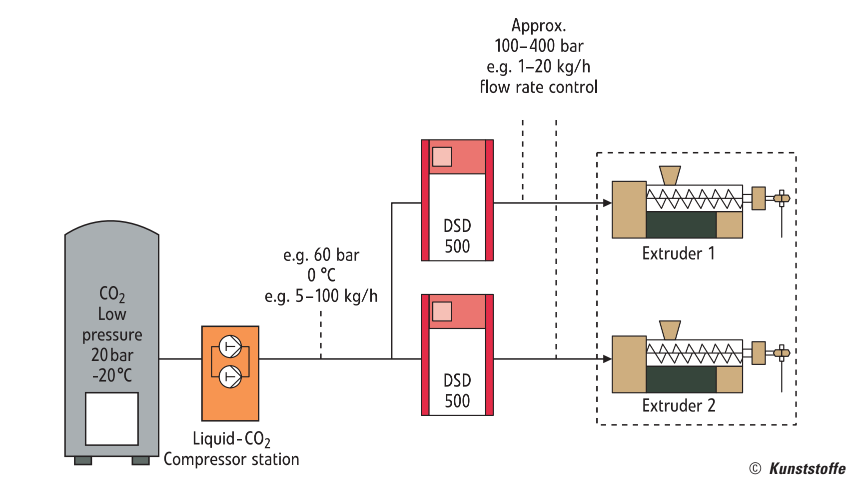

Fig. 5. CO_2 feed and metering concept with compressor station and high-pressure metering unit

eration unit. The temperature of the CO_2 is held constant within a narrow range and so produces a defined tank pressure. This is typically about 60 bar for feeding metering pumps used in foaming.

In the foam- or vacuum-insulated low-pressure tank, the liquid CO_2 is stored at a pressure of about 20 bar and a corresponding temperature of about –20°C. This type of tank offers some advantages over the medium-pressure tank in terms of lower production costs, virtually unlimited storage capacity and high feed reliability.

Although medium-pressure tanks provide the required pressure, the CO_2 is in a boiling state and the liquid tends to evaporate on the way to the consuming unit or at least form gas bubbles. In either case, intensive cooling of the gas before or in the metering pump is required.

It is therefore advisable in many cases to use a low-pressure tank. To provide the feed pressure for the high-pressure metering system, an additional pressure-boosting system is needed on the tank. The cold CO_2 (about –20°C) is compressed to about 60 bar, which causes it to heat up slightly. The temperature of the liquid is however always considerably lower than the boiling point corresponding to the pressure of 60 bar. The metering pump is therefore supplied with a sub-cooled, bubble-free liquid with reduced compressibility.

For pressure-boosting, Linde has developed two different variants specially for CO_2. For continuous PU foaming, a CFA pressure-boosting pump was developed in collaboration with a leading machinery manufacturer. This pump can also be used for high output rates in the slabstock process. With this electrically powered piston pump, CO_2 is compressed to a maximum pressure of 70 bar and circulated through a ring circuit from the CO_2 tank via one or more consuming units back to the CO_2 tank. In this way, the metering pump is always supplied with liquid, bubble-free CO_2.

A compressor has been specially optimised for operation with liquid, cold CO_2. The LCO_2 compressor station DLE 15 is based on this compressed-air-driven piston compressor, which compresses the CO_2 to the adjustable final pressure, generally 60 bar (Fig. 5). By combining this compressor with a CO_2 low-pressure tank, users can gain financial and technical advantages. For example, the liquid CO_2 is provided sub-cooled and bubble-free, i. e. even in sensitive applications, a phase separator or recooling is unnecessary. The flow rate automatically adapts to demand with high flexibility. The investment costs for the gas supply and hence the rental costs for users and the installation costs are considerably lower. The LCO_2 compressor station, unlike other systems, is not sensitive to gas content in the liquid CO_2 on the suction side. For this reason, insulation and recooling are unnecessary.

The concept offers absolute supply reliability, even when transferring CO_2 from tanker to tank. On the suction side, the output and operating behaviour of the compressor station are unaffected by gas bubbles in the liquid CO_2 or pressure variations in the tank, such as occur when filling the tank. ■

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