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Recent Advances in Modern Static Devolatilization

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Summary: The present paper deals with state-of-the-art static devolatilization technology for polymer melts. Recent results obtained by CFD-studies as well as by experimental testing at pilot scale are presented for the devolatilization of technical thermoplasts like polystyrene, poly (methyl methacrylate) and polycarbonate. It is shown that with the correct design of preheater and devolatilization chamber, volatiles like monomers and solvents can be efficiently removed from the polymer melt, both from the economical and technological point of view. As design criteria for the preheater, maldistribution and heat transfer efficiency are explained in detail.

Keywords: devolatilization; heat exchange; maldistribution; residual volatiles; static mixing

Introduction

Efficient devolatilization is a key process step in the production of modern plastics. For mostly environmental and toxicological reasons, remaining monomer and solvents need to be removed from the polymer melt prior to product finishing and packaging. The range of available technologies for this task is wide: from simple flash tanks to complex degassing extruders.[1] However, when it comes to efficiency with regard to residual monomer concentration but also energy consumption, investment costs and space requirements, major differences are found between available solutions on the market.

When it comes to degassing polymer melts, viscosity becomes an important issue as it significantly limits the mass and heat transfer. To evaporate volatiles that are mainly dissolved in the polymer melt, large amounts of heat need to be introduced. If the polymer melt is not completely mixed over the cross-section of the heat exchanger apparatus, hot spots and overheating occur frequently. At the same time, in order to reach low residual monomer levels, creating large surfaces is a prerequisite at elevated viscosities.

The mixing as well as the enlargement of the surface area can be achieved either by dynamic machinery, as for example the screw of an extruder or kneader, or by static mixers. Sulzer Chemtech has developed and constantly been improving over the last two decades static mixing technology for the application in the devolatilization of polymer melts. Its advantages over dynamic mixing technology are evident: no moving parts, hence less maintenance, lower energy consumption, lower investment costs and, last but not least, smaller space requirements. Despite the simplicity of the technology, excellent devolatilization results are obtained.[2] Industrial applications, where this technology has been successfully installed, are, among others, the production of polystyrene, PC, SAN, acrylics and elastomers. Depending on the desired residual volatile content, one-, two- or three-stage devolatilization plants, with or without stripping agent, are installed.

In a recent research study, Sulzer Chemtech investigated the cause and consequences of maldistribution within static mixer heat exchangers for the devolatilization of PMMA and Polystyrene melts. For these investigations, both CFD-simulations

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and pilot testing were carried out and the results compared. Besides the short residence time when applying two phase devolatilization and the resulting low degassing temperatures, another advantage of the static mixing technology is the reduced energy input compared to dynamic devolatilization. As the shear force and heat dissipation is considerably lower than in a dynamic device, delicate polymers that easily change colour (like SAN or PMMA) or optical grade polymers can be safely devolatilized.

Technology

In static devolatilization, volatile components (monomers, oligomers, solvents, stripping agents) are removed only by evaporation from a falling film, strand or foam of a polymer melt. No dynamic apparatuses, e.g. extruders, kneaders, etc. are used for surface generation and heat transfer. The only moving part in the static devolatilization unit is basically the discharge gear pump at the bottom of the vessel, in which the separation of polymer and volatiles takes place. Compared to dynamic devolatilization, static devolatilization is characterized by the following advantages:

- no moving parts or mechanical seals
- minimized leak rates
- easy to install and operate
- large buffer volume if necessary
- lower energy consumption, preheating with heat transfer oil rather than expensive mechanical or electrical energy
- no product degradation due to low shear and uniform temperature and residence time distribution
- suitable for very high viscosities (>10’000 Pas)

In order to reach conditions close to equilibrium and to prevent freezing of the polymer, it is inevitable to heat up the polymer solution to a certain temperature level. Depending on the preheating mode, the evaporation can take place either after the flashing of the solution into a vessel (1-phase preheating) or already during the preheating step (2-phase preheating).

For the evaluation of the devolatilization efficiency, the partial pressure of the volatile component p_i is needed. At equilibrium conditions, the partial pressure of a volatile component i is equal to its vapour pressure in solution. It can be calculated from the vapour pressure of the pure component p_i^0 according to the theory of Flory and Huggins[3] by the formula

$$\ln\left(\frac{p_i}{P_i^0}\right) = \ln \Phi_i + \chi_{ip}\Phi_p^2 + \Phi_p \tag{1}$$

where Φ is the volume fraction of component i and of the polymer p, respectively, and the factor χ_{ip} the Flory-Huggins interaction parameter, which is a system constant (e.g. 0.28 for PS/Styrene).

With $c_i = \Phi_i\, \rho_i/(\Phi_i\, \rho_i + \Phi_p\, \rho_p)$ and $\Phi_p \approx 1$ follows for the equilibrium concentration c_{ie} of component i in the polymer melt

$$c_{ie} = \frac{y_i P_0 \rho_p}{P_i^0 \rho_i \exp\left[1 + \chi_{ip}\right]} = \frac{y_i P_0}{K_{wi}} \tag{2}$$

where y_i is the molar fraction of component i in the vapour phase and K_{wi} the Henry coefficient (according to the law of Dalton-Henry). This equilibrium concentration is the lowest possible residual concentration that can theoretically be achieved in devolatilization. The degree or efficiency of devolatilization can be described based on a comparison between this equilibrium concentration c_{ie} and the actual volatile concentration after the devo step by Equation (3) and (4). Equation (3) is also known as devolatilization efficiency. Unfortunately, it is strongly dependent on the initial concentration $c_{i\alpha}$ and does not include any transport limitation phenomena.

$$E_f = \frac{c_{i\alpha} - c_{i\omega}}{c_{i\alpha} - c_{ie}} \tag{3}$$

For polymer foams, where the diffusion of volatiles depends on many other parameters, the empiric Equation (4) allows a much better evaluation of the devolatilization efficiency.[2] The proportion of $c_{i\omega}$ to $c_{i\varepsilon}$

is related to the system pressure P_0 and a characteristic pressure increase within the foam cells p_B.

$$\frac{c_{i\omega}}{c_{ie}} = 1 + \frac{p_B}{P_0} \tag{4}$$

The parameter p_B depends on cell density, diffusion constants, Henry constants, viscosity, surface tension, pressure, temperature, flowrate and equipment design and needs to be determined experimentally. Equation (4) can then be used to compare different devolatilization systems and designs of apparatuses: The smaller the parameter p_B of a devo system, the more efficient it is.

The setup of a typical static devolatilization unit with two-phase preheating is rather simple (see Figure 1). The polymer solution enters the first preheater H-I where it is heated up, the volatiles begin to evaporate and the pressure decreases drastically (flash) due to the reduction of liquid volume fraction and increase in gas and liquid velocity until the preheaters exit pressure is reached (compare Figure 4 and 5). The resulting polymer foam is then transferred into the first devo vessel V-I, where volatile and polymer phase are separated. Depending on the polymer and the initial volatile concentration, residual monomer levels as low as a couple of hundred ppm can be reached in this first stage without stripping agent. A recent application for static devolatilization systems is the concentration of dilute polymer solutions from 10–30 wt-% to more than 90 wt-% polymer in a single step.

For many applications, however, lower values are required. In a second stage, a stripping agent is added into the melt from stage I by means of a static mixer. The effect of the stripping agent is firstly the reduction of the partial pressure of the volatile in the vapour phase and, hence, of the equilibrium concentration in the polymer melt, and secondly an improved foaming of the melt in the second stage. As the melt does not contain much of volatiles anymore at this point, it does not foam well on its own and the volatiles have to diffuse though thick layers of polymer melt. By adding a stripping agent and thus creating foaming, the surface of the melt can be increased significantly before it is transferred into the second devo vessel V-II. Depending on the polymer system, a second preheater H-II might become

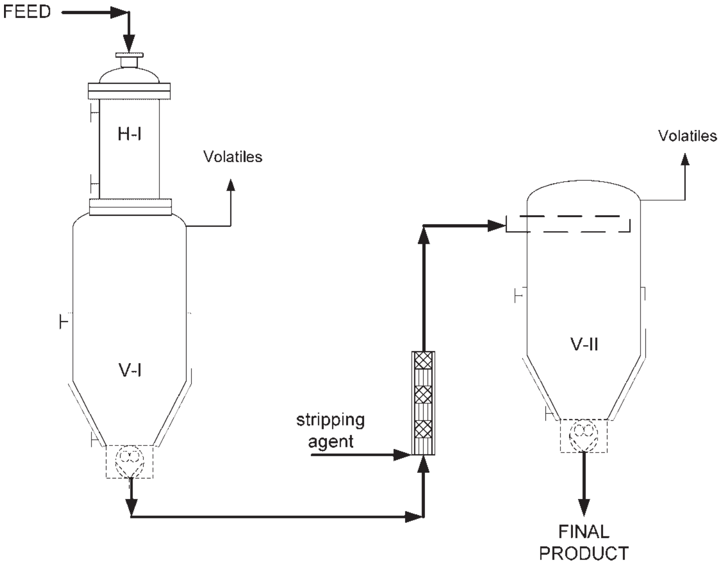

Figure 1.
Standard setup for a two-stage static devolatilization unit with stripping agent.

necessary to bring the polymer melt to a higher temperature level.

In an optimized two-stage devolatilization unit with stripping agent, residual volatile concentrations of 50 ppm and below can be obtained.

Equipment

As visible in Figure 1, a static devolatilization unit consists mainly of three different types of equipment: preheater, devo vessel and a static mixer for the stripping agent. The preheater is one of the most crucial parts concerning its design. In order to adjust the temperature for devolatilization, decrease the viscosity for efficient discharge afterwards and to compensate the heat of evaporation of volatiles, most polymer solutions must be heated up. In contrast to dynamic devolatilization processes, nearly no mechanical energy is introduced into the polymer. The standard heat balance for heat exchangers applies:

$$\dot{Q} = \dot{m}_p cp_p (T_\omega - T_\alpha) + \dot{m}_i \Delta h_i$$
$$= kA\Delta T_m \qquad (5)$$

Due to the high viscosity of the polymer solutions, tube bundle heat exchangers equipped with static mixers have been proven to be most efficient. In an empty tube, the flow profile is strongly parabolic, leading to an overheating of the polymer solution at the walls of the tubes, making the heat transfer less efficient and possibly harming the polymer. The temperature distribution over the tube section is inhomogeneous and fouling might occur in the stagnant film on the tube walls. In Figure 2, the temperature profile of a jacketed tube with and without static mixing elements is compared, both schematically and by a CFD simulation of the temperature distribution for an empty tube and a tube equipped with static mixers. Static mixers improve the heat transfer constant by a factor 4 to 10 by forced radial convection, thus allowing short heating time with homogeneous temperature and residence time distribution. A good dimensioning of the preheater is a prerequisite for an optimal product quality.

Figure 3 shows an industrial scale multitube heat exchanger and a devo vessel with exterior heating coil. The static mixing elements can be manufactured either non-detachable or removable for cleaning purposes. Capacities for this kind of technology range from pilot scale (some kg/h) up to large industrial scale equipment for capacities of 25 t/h and more. The devo vessel can be designed to have a polymer hold-up of up to 1 hour with regard to the production capacity, which means that in an emergency or production problem downstream of the system, the devo vessel can generally buffer polymer from up to one hour production time.

Design Calculations

Contrary to single-phase preheaters, where a standard heat balance is normally sufficient for the design calculations, the

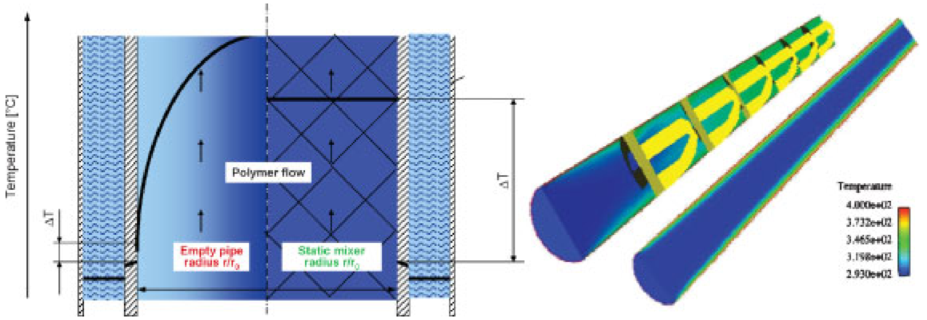

Figure 2.
Comparison of temperature profile in a heat exchanger tube with and without static mixers.

Figure 3.
Tube bundle heat exchanger with static mixers (left) and devo chamber (right).

modelling of two-phase preheaters is highly complex. Since the viscosity and the heat transfer are directly influencing each other and changing over the length of the preheater, it is necessary to program an iteration algorithm for the calculation of temperature, viscosity, residual monomer and pressure evolution over the length of the preheater. This iteration is accomplished at Sulzer Chemtech by an in-house, VB-based program, which is unique in the field. As presented in Figure 4(a) for the example of the one-stage devolatilization of a 50% PMMA solution at atmospheric conditions, this tool allows the illustration of what happens physically during the flashing of the volatiles from the melt: The homogeneous mixture of volatiles and polymer enters the tubes of the heat exchanger. Due to the high pressure at this point, the volatiles stay in solution. For an ideal operation of the heat exchanger, it is important that the evaporation does not begin too early, e.g. before entering the heat exchanger. Therefore, the design pressure drop over the tubes has to be carefully calculated. Within the first zone of the heat exchanger, the polymer solution is heated up. Once the temperature is high enough for the volatiles to evaporate at the given pressure, foaming occurs and the volatiles start to separate from the melt. As a consequence, the viscosity of the melt starts to increase, while the temperature increase is slowed down due to the evaporation enthalpy of the volatiles. Due to high circulation rates the temperature change of the heat transfer fluid is very small. At the exit of the preheater, the melt has reached the pressure level of the devo vessel, i.e. atmospheric pressure in the shown case. The adjustable parameters for the design of a two-phase preheater in order to reach a certain monomer concentration are: the static mixer geometry and variation over the tube length, the tube length, number and diameter, the oil temperature as well as the final pressure in the devo chamber.

The two-phase devolatilization in a tube bundle heat exchanger with static mixing elements can also be modelled by CFD. For this, a grid structure for the static mixing elements is defined as shown in Figure 4(b).

In Figure 5, the results of such a CFD study for the devolatilization of a 50% polystyrene/styrene solution are presented. Clearly visible also from this presentation is the flash point in the first third of the tube length, from where on the liquid volume fraction decreases and the velocity of both liquid and gas increase.

One common phenomenon that can not be predicted by the above mentioned tool is the maldistribution between different tubes of the tube bundle. Maldistribution is known for heat exchangers cooling highly viscous liquids. Figure 6 illustrates cause and effect of maldistribution: due to slight temperature drifts within the volume of the bundle, it can occur that the melt gets slightly cooler in one tube than in the rest of

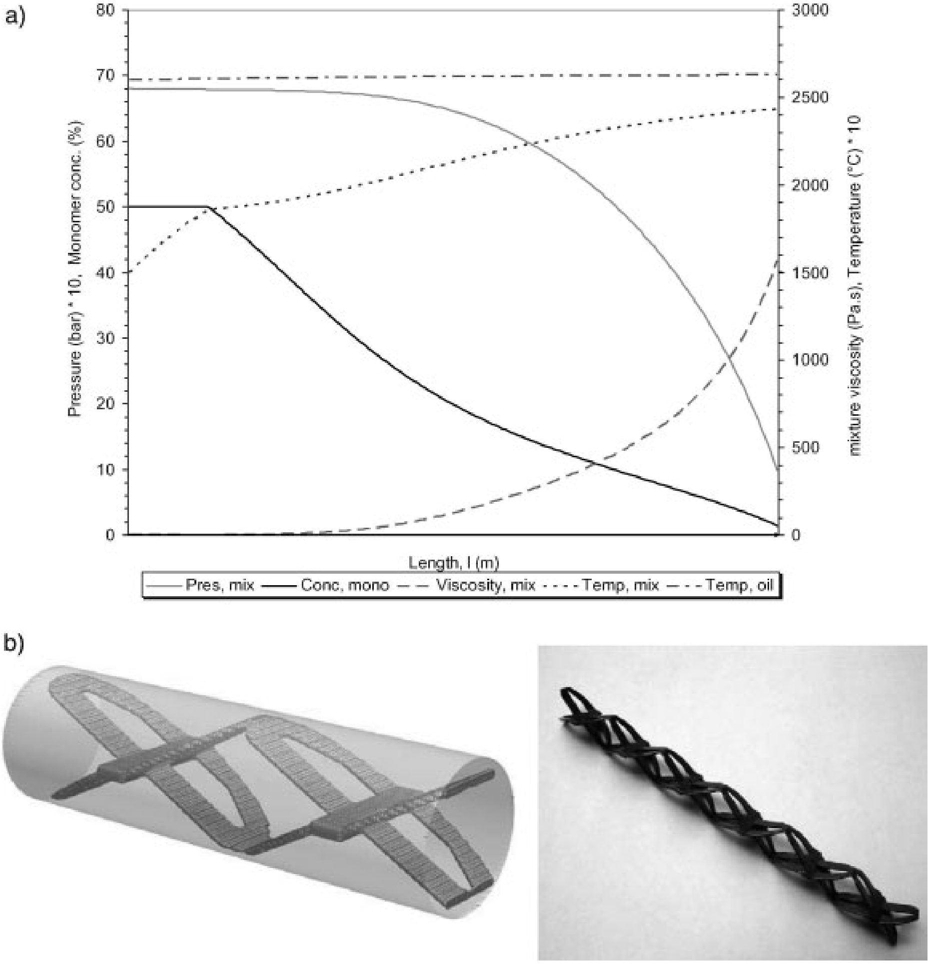

Figure 4.
a): Prediction of temperature, pressure, viscosity and residual monomer evolution in a two-phase preheater over its length for the devolatilization of a 50% PMMA solution; b): Grid structure for the CFD model and real static mixing element.

the tubes, which leads to a drastic increase of viscosity, thus an increase in pressure drop leading to a reduced throughput through the particular tube. This means that the flow through the rest of the tubes is increased and the heat exchanger becomes unstable. In the worst case, single tubes can plug completely, leading to a significant lack of performance of the heat exchanger.

Also in two-phase devolatilization preheaters, maldistribution can occur, yet for another reason. Here, it is not the cooling but the evaporation of volatiles that has a large impact on the mixture viscosity (see Figure 4), which in turn can influence the pressure drop in each separate tube of the bundle. As shown in Figure 7, the pressure drop changes with the flowrate through the heat exchanger for a given design and polymer grade. In a first instance, Δp increases with the mass flow. For each flowrate, there is one pressure drop value that establishes over the tube length. When the throughput is increased further, however, the heat transfer within the preheater is not sufficient anymore to evaporate the same amount of volatiles than before and the viscosity decreases due to the residual

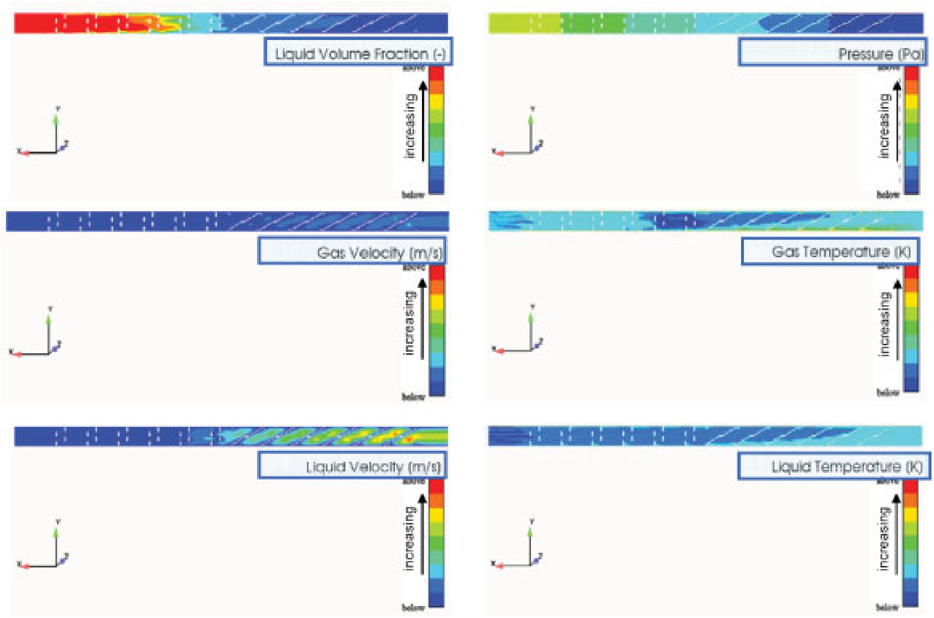

Figure 5.
Results from a CFD-study for the two-phase preheating of a 50% polystyrene solution in a tube containing static mixing elements.

volatiles in the melt. Therefore, the pressure drop decreases as well. If the throughput is increased even further, the evaporation stops and the preheater turns into a mono-phase mode, for which the pressure drop increases again with the flowrate. Within the unstable zone, there are usually several possible operating states, which means that for different flow rates the same pressure drop can establish. Therefore, a small change in operating conditions (temperature, flow rate) can lead to a

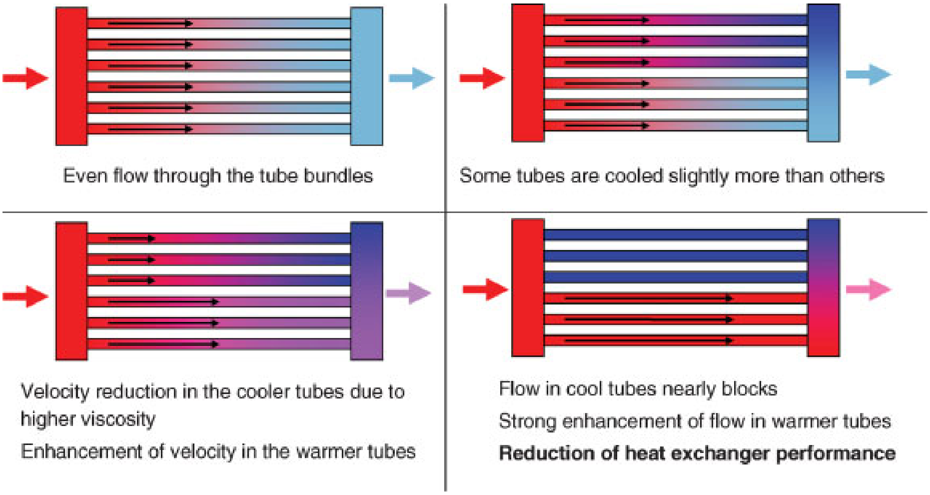

Figure 6.
Illustration of the effect of maldistribution in a two-phase heat exchanger when cooling a highly viscous liquid.

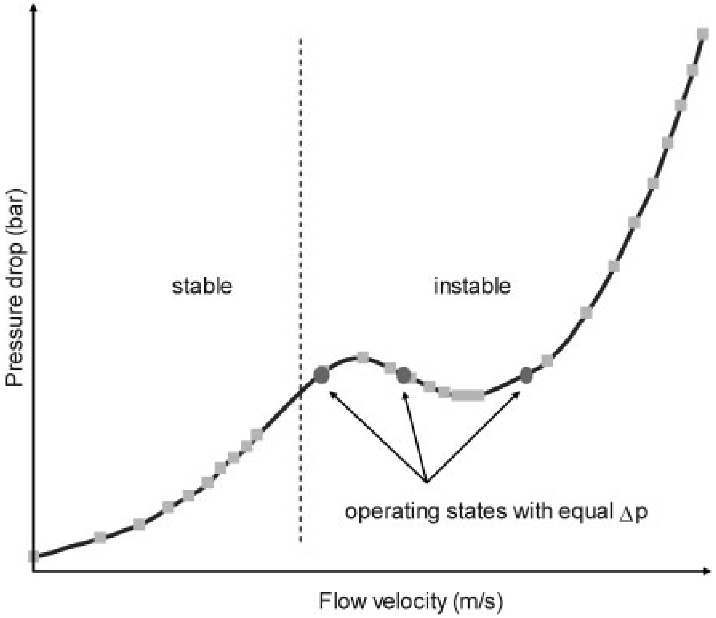

Figure 7.
Pressure drop curve for a two-phase preheater with stable/instable zones.

different flowrate through particular tubes, which significantly lowers the preheater's performance and results in very instable pressure and temperature behaviour. It is, hence, of importance that the design in terms of pressure drop is very well adapted to the required mass flow rates, taking into account possible variations during operation.

Experimental Results

Devolatilization experiments are regularly carried out in the pilot facilities of Sulzer Chemtech in Winterthur. The standard setup for such trials is shown in Figure 8. Usually, the polymer solution is mixed within the plant from solid polymer, which is melted in an extruder, and liquid solvent

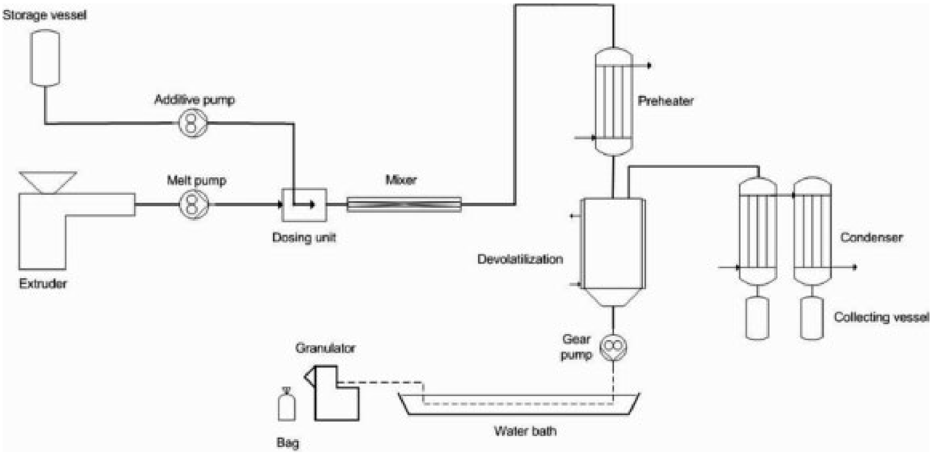

Figure 8.
Pilot setup for devolatilization tests.

Table 1.
List of polymer systems that have been successfully devolatized with Sulzer technology.

Polymer	Volatile	Inlet	Outlet
PMMA	MMA	50%	<1.5%
CPS/HIPS	Styrene	1'500 ppm	<100 ppm
SAN	Styrene	1'800 ppm	80 ppm
	Acrylonitrile	200 ppm	4 ppm
PC	Chlorobenzene	10'000 ppm	50 ppm
PVAC	Vinyl acetate	200 ppm	5 ppm
POM	Trioxane	1'000 ppm	5 ppm
LDPE	Ethylene	4'000 ppm	50 ppm
LLDPE	n-Octane	10'000 ppm	100 ppm
EPDM	Hexane	50'000 ppm	200 ppm

or monomer within a static mixing unit at the desired concentration. The solution is then transferred into a multi-tube preheater and devolatized. The final polymer can be pelletized and the condensed volatiles are collected for analysis. With the presented test rig, a wide range of polymer systems can be examined without major modifications to the setup itself, mostly by choosing the right preheater design and devolatilization conditions. The rig can be equipped as one- or two-stage devo plant.

The following Table 1 contains examples of polymers that have been successfully devolatized by Sulzer Chemtech at pilot scale. Depending on the initial concentration, residual volatile concentrations of some ppm could be reached. In particular for PMMA and SAN, which are very temperature sensitive, the resulting polymer did not show any particular coloration or black spots with regards to the raw material.

Conclusion

Static devolatilization is a simple, old process to devolatize polymer melts, which has been largely improved by the introduction of static mixers and system optimization. The introduction of two-phase preheating has made it possible to use this technology also for sensitive polymers like SAN or PMMA. Moreover, modern calculation methods like CFD and numerical solutions of complicated PDE-systems allow the modelling and optimization of critical equipment, like for example the preheater. These calculations are particularly important for the prediction of phenomena like maldistribution or to determine the ideal process conditions to reach minimum volatile concentrations. With the presented in-house tools, which have been developed with the years of experience, Sulzer Chemtech is capable of carrying out design calculations for almost every devolatilization application and the need for experimental testing could be reduced to a minimum.

The devolatilization down to very low levels of residual monomers has become very important for many different polymers and requires a high efficiency of the equipment so that concentrations close to the equilibrium can be reached. At the same time, the operational as well as the investment costs need to be minimized, in order to make the process attractive for large-scale industrial applications, which is one of the strengths of static devolatilization.

The present paper demonstrates that, with current and future improvements and developments, the field of application for static devolatilization will continue to widen. Maybe also to polymers, which are currently still processed with competing technologies?

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