INVESTIGATION OF CHEMICAL FOAMING AGENTS APPLICATION FOR THERMOSET INJECTION MOLDING

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Abstract

While foam injection molding processes are state-of-the-art in modern industrial plastics processing facilities, the transfer of these technologies to the field of thermoset injection molding has not been investigated. The results presented in this paper outline the potential as well as the challenges of this new technology. While significant weight reductions of up to 20% have been achieved, surface quality and mechanical properties demand further investigation and optimization of the process.

Introduction

The constantly increasing demands on technical plastic parts require a continuous development of materials and processes. An example for this trend is the automotive industry that requires an increasing temperature resistance of the materials in the engine compartment. At the same time, the vehicle weight must be reduced in order to reduce CO2 emissions. The reduction in the weight of the installed subassemblies also has a positive effect on the driving dynamics or the fuel consumption. Therefore, high temperature resistant or stabilized plastics are becoming increasingly important [3]. These can meet the increased demands on temperature resistance and, at the same time, have a significantly lower density than metals (e.g. PA 66 GF30: ~ 1.4 g / cm³, steel: 7.9 g / cm³). Compared to high-temperature thermoplastics, such as polyphenylene sulfide (PPS) or polyetheretherketone (PEEK), which offer high application temperatures with good mechanical properties at the same time [URL 12], thermoset parts are significantly cheaper. This leads to a rising number of thermosets parts in technical series applications [4, 5, 6]. Recent developments both on the materials [6 - 9] and the machine-side in the injection molding of thermosets [10] support this trend. Compared to high-temperature-resistant thermoplastics, however, thermoset molding compounds have a significantly higher density (EP ~ 1.9 g / cm³) [11]. For many applications, especially in the automotive sector, however, a reduction in the component weight is aimed at in order to reduce the vehicle weight and improve the driving dynamics.

While foam injection molding is an established method for reducing the component weight in the processing of thermoplastics, there are no publications on the foaming of thermosets in the injection molding process. The use of foam injection molding processes for thermoset molding compounds (analogous to thermoplastic foam injection molding) could significantly reduce the weight of injection-molded thermoset moldings [1]. In addition, foaming can contribute to a more homogeneous holding-pressure distribution since a pressure is generated in the material itself by the formation of gas bubbles.

In this paper fundamental considerations about the process flow of thermoset foam injection molding are presented. The potential for weight reduction as well as the effects of the foaming process on the mechanical properties are tested using selected material / propellant combinations. The compositions and fillers are selected by means of differential scanning calorimetry (DSC) measurements, which allow an insight to the respective reaction rates as a function of the temperature. Finally, possible applications and perspectives of the new method are discussed.

Theoretical analysis of foaming in thermoset injection molding

For foam injection molding a distinction is made between the chemical and physical introduction of the propellant. During chemical foaming the required gas is produced by the chemical disintegration of a propellant. Physical foaming is based on the metering and dissolved gas in the plasticizing cylinder.

For the foam injection molding of thermosets, the principles known from thermoplastic processing cannot be adopted. The temperature necessary for the decomposition of the chemical propellant in the plasticizing cylinder is only reached in the mold but not in the plasticizing cylinder and no pressure can be maintained in the cylinder due to the absence of a needle closing nozzle. Thus, no gas can be dissolved in the molding compound during plasticizing.

In order to introduce a propellant into the cavity, this must therefore be brought into the cavity in a non-gaseous aggregate state together with the molding material. Figure 1 shows a schematic representation of the thermoset foam injection molding in analogy to thermoplastic processing. The propellant is introduced as a fine-grained powder premixed into the molding compound.
Due to the fact that the thermoset is in the form of a free-flowing molding compound, a homogeneous distribution of the blowing agent can only be achieved by distributive and dispersive mixing in the plasticizing cylinder.

Due to the lack of prior research on the topic, the following process theory was established based on the understanding of the thermoplastics foam injection process and the chemical reactions. When the molding compound is then injected into the cavity, the temperature of the molding compound rises by means of shear heating and heat conduction via the mold wall, and both the gas-forming reaction of the chemical propellant as well as the crosslinking reaction of the thermoset are initiated. The foaming process therefore depends on the ratio of the two reaction rates. However, a homogeneous distribution of the propellant in the material is also assumed decisive. This applies in particular, since, unlike in the case of thermoplastic foam injection molding, a homogeneous distribution of dissolved gas in the molding compound is unlikely. Foam bubbles preferentially form at the locations where blowing agents are present. The propellant is still present as a solid in the initial phase of the reaction and thus performs intrinsically in the function of the nucleus to form a gas bubble.

**Reaction temperatures and material selection**

There is no scientific knowledge regarding the ratio of the reaction rates for the chemical decomposition of the blowing agent and the crosslinking reaction of the molding compound. However, if the gas formation starts too early, the viscosity of the resin is too low and movements of the gas bubbles lead to an inhomogeneous foam structure with large gas bubbles. In the opposite case, the resin has already reacted to a point where the gas can no longer expand. In this case, the foaming process would be inhibited and due to the internal pressure, in extreme cases, mechanical damage to the material could occur. It is therefore assumed that the reactions should take place in the same temperature window.

A molding compound and a corresponding foaming agent with similar reaction temperatures are selected for the further investigation. Epoxidur EP 3582 B MS, of Raschig GmbH, Ludwigshafen, Germany is an epoxy molding material which is filled with glass fibers. The main application areas of this material are in the electronics industry for the insulation of electronic components. Hydrocerol BIF, of Clariant Masterbatches, Lahnstein, Germany is selected as a chemical foaming agent. For use in thermoset foam injection molding, the powdered chemical raw materials are used so that a possible homogeneous mixture of the blowing agent with the molding compound can be achieved. By chemical disintegration of the propellant at a defined temperature, carbon dioxide is released which leads to a foaming of the surrounding material.

To determine the reaction temperatures and heat, the afore-mentioned materials are analyzed in a DSC of the type Q2000 from TA Instruments, New Castle, USA. The measured heat flows are shown in figure 2 for mixtures of the Epoxidur EP 3582 B MS.

The DSC readings illustrate the exothermic reaction of the thermoset as well as the endothermic reaction of the foaming agent. It can be shown that a very good match of the reaction temperature with the decomposition temperature of the Hydrocerol BIF is achieved for the illustrated combination of propellant and molding compound. The addition of 5 or 10 weight % of the chemical blowing agent to the molding compound leads to a reversal of the heat balance of the molding compound. While the pure molding compound exhibits a slightly exothermic reaction, the endothermic behavior of the chemical propellant predominates when mixed. Due to the good match between the reaction temperatures and the exothermic crosslinking reaction, which counteracts the endothermic reaction of the blowing agent, this combination is selected for this first consideration of the thermosetting foam injection molding.

**Experiment setup and execution**

In order to determine the achievable reduction in weight and the resulting mechanical properties, an injection molding machine Allrounder 370A-600 by
Arburg GmbH + Co KG, Loßburg, Germany, is used. The injection molding machine is equipped with a thermoset aggregate \( (D = 30 \text{ mm}, L/D = 15) \) for the processing of granulated molding compounds. For the investigation of the process plates with a 4 mm thickness and an surface area of \( 80 \times 80 \text{ mm}^2 \) are produced.

A mixture of the abovementioned Epoxidur EP 3582 B MS (hereinafter EP) and hydrocerol BIF (hereinafter BIF) is used as the foamable material. Mixtures containing 10% by weight BIF and pure EP are used for the analysis. The mixtures are mixed manually until an optically homogeneous molding compound is formed.

In order to investigate the influence of the processing parameters on the foam formation, a design of experiment is used. Table 1 lists the varied parameters and their stages. In this first study, the mold temperature, which determines the crosslinking and reaction behavior, as well as the cylinder temperature, which influences the required energy for the initiation of the chemical reaction, are varied.

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>0</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Nozzle [°C]</td>
<td>100</td>
<td>95</td>
<td>90</td>
</tr>
<tr>
<td>Temperature Mold [°C]</td>
<td>170</td>
<td>175</td>
<td>180</td>
</tr>
</tbody>
</table>

All other process parameters are not being varied and remain constant. The settings are given in Table 3. To determine the required shot volume, the change-over point is gradually increased for each parameter until the foaming can no longer compensate the reduction of the shot volume. The last setting that produces completely filled parts is used for the investigation.

Table 3. Machine parameters for the production of thermoset specimen

<table>
<thead>
<tr>
<th>Parameter</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Dosing Volume</td>
<td>32 cm³</td>
</tr>
<tr>
<td>Injection Speed</td>
<td>15 cm³/s</td>
</tr>
<tr>
<td>Change-over point</td>
<td>5 cm³</td>
</tr>
<tr>
<td>Holding Pressure</td>
<td>- (no holding pressure applied)</td>
</tr>
<tr>
<td>Curing Time</td>
<td>80 s</td>
</tr>
<tr>
<td>Back Pressure</td>
<td>50 bar</td>
</tr>
<tr>
<td>Screw Speed</td>
<td>30 1/min</td>
</tr>
</tbody>
</table>

Ten test specimens are produced for each test point and weighed after removal of the sprue with an automated milling machine. From five of the test specimens, tensile bars of the type 1 BA according to DIN EN ISO 527-2 are produced by milling and tested on a tensile test stand type Z010 from Zwick GmbH & Co. KG, Ulm, Germany. The tensile bars are taken from the sample plates in the middle and in the flow direction.

**Achieved weight reduction**

When the determined weight is averaged over all test points, the compact plates have an average weight of 50.1 g. By foaming, the weight of the foamed plates can be reduced to 45.2 g. An average weight reduction of 10.8% is thus shown. However, this is associated with a comparatively large deviation of \( \sigma = 3.4 \text{ g} \) for the foamed plates (figure 3).

![Figure 3. Comparison of the average weight of the foamed and compact specimen](image)

The analysis shows that the tool temperature of the investigated influencing factors has the biggest influence on the structural weight. Figure 4 shows the determined effect variables and the corresponding p-values. An effect is assumed to be significant if the p-value is below 0.05. In summary, it can be stated that with compact components only a small influence of the process parameters on the component weight exists. The mold temperature has a significant influence on the weight of the test specimens, both for the compact and for the foamed components. However, the direction of the effect is reversed by the foaming of the material and the effect is significantly higher for the foamed test specimens. A significant effect of the cylinder temperature near the nozzle is not found. However, if both the cylinder temperature and the tool temperature are increased, an interaction occurs. This indicates that higher mold temperatures accelerate the reaction of the molding compound more than the decomposition of the foaming agent. Thus, a low tool temperature can be used to reduce the weight of the specimen.
Influence on the mechanical properties

The tensile tests show an average Young’s modulus of the compact tensile bars of 14.905 MPa. A strongly reduced modulus of elasticity of 10.815 MPa is found in the foamed test specimens. Due to the comparatively high spread of the measured values in the determination of the E-module, no significant effects of the process parameters on the E-module can be found.

The average breaking stress of all compact tensile bars is 61.9 MPa with a standard deviation of 4.2 MPa. Figure 5 shows an overview of the observed effects. As a result of foaming, the technical fracture stress is reduced to an average of 33.4 MPa. At the same time, the deviation of the measured values increases to 9.4 MPa. The analysis of the effects of the process parameters also shows that by increasing both the tool temperature and the cylinder temperature, the breaking stress can be increased significantly.

Considering the elongation at break (see Figure 6), a clear reduction of 0.63 % in the case of compact test specimens to only 0.35 % for the foamed specimens is shown. Here as well, the use of high cylinder and tool temperatures leads to a greater elongation and thus better mechanical properties of the foamed test specimens.

Figure 4. Influence of the process temperatures on the weight reduction.

Influence on the elongation at break.

The reduction of the mechanical characteristic values of the test specimens by the foaming can partly be explained by the reduction of the load-bearing material by the foaming of the material. The amount of the reduction in the mechanical properties, however, goes beyond the amount of the reduction of the component weight. Overall, the measurements on the foamed test specimens show a high standard deviation of the measured values. This scattering is a strong indication that inhomogeneous foam formation is present. This can be attributed to an insufficient homogenization in the plasticizing cylinder. To further investigate this assumption a microscopic analysis of the foam structure in the center of the tension bars was conducted. Figure 7 shows the morphology of a compact (left) and a foamed specimen (right). A foam structure is clearly visible in the foamed part with single bubble sizes up to 100 µm. Also streaks of bubbles have been found in the specimens. While it is not proven, that these streaks are responsible for the reduction of the foamed parts mechanical properties, it is a likely explanation.

Figure 5. Influence of the process temperatures on the stress at break.

Figure 6. Influence of the process temperatures on the elongation at break.

Figure 7. Foam structure and streaks in foam injection molded thermosets.

Foam induced holding pressure

In addition to the reduction in weight, the course of the internal pressure of the mold could be measured by a pressure sensor close to the gate. One of the measured pressure profiles is shown by way of example in figure 8.

SPE ANTEC® Anaheim 2017 / 670
It can be shown that a pressure of approx. 60 bar is build up in the cavity after the filling phase has been completed and without holding pressure provided from the injection molding machine. This is due to the gas production of the propellant and is believed to act uniformly in the cavity. It can therefore be used in order to achieve a flow length independent holding pressure effect.

**Conclusion**

The foaming of thermosets in the injection molding process offers the potential for a significant reduction in the weight of components made of thermoset molding compounds. First findings suggest that for the successful implementation of chemical foaming the coordination of the reaction temperatures of the thermoset system and the chemical propellant is essential. The achieved weight savings with approx. 10% compared to the compact components are already in an economically interesting area. However, for the industrial implementation of the process, it is first of all necessary to develop further process understanding and to optimize the process management, in particular with regard to the mechanical properties. The preparation of the molding compounds should be addressed, since the results so far indicate an inhomogeneous distribution of the chemical propellant in the material. In addition to the expansion of the determination of the results and a systematic investigation of the influence of the reaction temperatures on the process, it is therefore the goal of future research to develop a processable material, which has a foaming agent included during the material production. This material could establish an economically feasible foaming process with sufficient mechanical properties.

**References**


