Investigating filler orientation of functionalized thermoset molding compounds during injection molding

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Abstract

Thermoset molding compounds are showing great potentials in applications that demands high temperatures, high media resistance and good mechanical properties. Customized properties such as enhanced heat conductivity or magnetic properties that can be achieved through functionalization are often sought after in the thermoset as well as in the thermoplastic industry. This paper deals with the orientation of magnetic and heat conductive fillers in epoxy molding compounds, which are essential for part design and process control.

Introduction

Higher temperatures and new aggressive media especially in automotive applications leading to increased requirements for the used materials. Commonly used thermoplastics like PA or PBT will face problems at higher temperatures, for which reason expensive materials like PPS or PPA are used. According to [1] materials like epoxy (EP) or phenolic molding compounds (PF) can face comparable or even higher temperatures than PPS at a price in the range of PA or PBT. Also the media resistance of thermosets is superior compared to thermoplastics. Especially EP-materials are showing the best resistance against different chemicals [2], whereas phenolic molding compounds are reaching highest usage temperatures.

However, most probably due to their complicated processing thermosets became a niche material in the plastics industry [3]. In recent year’s thermoset molding compounds underwent some kind of a renaissance under the directive of higher thermomechanical requirements, new aggressive media and demands for high precision of molded parts. Additionally the low viscosity of the materials during processing allows higher filling degrees without the loss of processability compared to thermoplastics [4]. While the influence of the injection molding process on the heat conductivity or the magnetic properties of functionalized thermoplastics was already subject to a number of publications (e.g. [5-8]) scientific work for functionalized thermosets is almost not existent.

This paper deals with the influence of part geometry on the orientation of functional fillers in thermostet molding compounds. The sample-material used for this investigation is an epoxy molding compound.

Background

To increase the heat conductivity or the magnetic properties of plastics, special fillers are added to the polymer. In case of heat conductivity these fillers are divided into electrically insulating and non-insulating. To avoid electric short cuts non-insulating fillers are used, for example aluminum oxide or hexagonal boron nitride (hBN). Typical representatives are shown in Table 1.

Table 1. Different fillers and their typical heat conductivity [9].

<table>
<thead>
<tr>
<th>Filler</th>
<th>Heat conductivity [W/mK]</th>
<th>Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>400</td>
<td>No</td>
</tr>
<tr>
<td>Graphite</td>
<td>150</td>
<td>No</td>
</tr>
<tr>
<td>Boron nitride</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>30</td>
<td>No</td>
</tr>
</tbody>
</table>

For fillers with isotropic properties the heat conductivity of the compound can be calculated by equation (1) according to [10]:

\[
K = \frac{2 \cdot K_M + K_F - 2 \cdot \kappa \cdot (K_M - K_F)}{2 \cdot K_M + K_F + \kappa \cdot (K_M - K_F)} \cdot K_M \quad (1)
\]

where \(K_M\) and \(K_F\) represent the heat conductivity of matrix and filler and \(\kappa\) is the filler content of the compound. Equation (1) enables the engineer to design the part appropriately to the desired functionality. However, by using anisotropic fillers such as boron nitride the orientation of the particles in the part becomes important. For thermoplastic materials a lot of work was done to predict the thermal properties in the different spatial directions. For thermoset materials these associations are still not available and should therefore be part of this work.

For magnetic properties there are similar preconditions. Magnetic fillers can be divided into two different groups: Soft-magnetic and hard-magnetic fillers. Soft-magnetic fillers are used to increase the magnetic
conductivity. Hard magnetic fillers are incorporated to create permanent magnets with more freedom in design of part and magnetic circuit.

For soft magnetic properties a percolation border is existing according to Anhalt [11] and Kirchberg [12] which is comparable to the electric properties of a compound. For hard magnetic properties there is no such percolation found [7], which is in turn comparable to the heat conductivity of filled plastics.

As well as for heat conductive fillers also hard magnetic fillers can be divided in isotropic and anisotropic powders. To keep it simple, anisotropic fillers are showing good magnetic properties in one spatial direction and bad magnetic properties in the other directions. Isotropic fillers have the same magnetic properties in all spatial directions. Important magnetic properties of different fillers are shown in Table 2.

Table 2. Remanence of different fillers used for bonded permanent magnets [13].

<table>
<thead>
<tr>
<th>Filler</th>
<th>$B_R$ [T]</th>
<th>$H_{J3}$ [kA/m]</th>
<th>Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrFe</td>
<td>0.2</td>
<td>170...230</td>
<td>Iso.</td>
</tr>
<tr>
<td>SrFe</td>
<td>0.4</td>
<td>170...240</td>
<td>Aniso.</td>
</tr>
<tr>
<td>SmCo5</td>
<td>1.05</td>
<td>720...1100</td>
<td>Aniso.</td>
</tr>
<tr>
<td>Sm2Co17</td>
<td>1.2</td>
<td>640...960</td>
<td>Aniso.</td>
</tr>
<tr>
<td>NdFeB</td>
<td>1.2</td>
<td>640...1400</td>
<td>Iso.</td>
</tr>
<tr>
<td>NdFeB</td>
<td>1.2...1.4</td>
<td>920...1400</td>
<td>Aniso.</td>
</tr>
<tr>
<td>SmFeN</td>
<td>1.2</td>
<td>740...900</td>
<td>Aniso.</td>
</tr>
</tbody>
</table>

The calculation of the final properties of compounds filled with isotropic magnetic fillers is quite simple, since the filler orientation does not have to be considered. The remanence of the compounds is calculated by equation (2) [7]:

$$B_R = \delta \cdot \varphi \cdot B_{R,Powder}$$  \hspace{1cm} (2)

where $\varphi$ is the filler content, $\delta$ is the degree of orientation and $B_{R,Powder}$ is the remanence of the pure powder. For isotropic powders $\delta = 1$, for anisotropic powders $\delta$ is in the range between 0 and 1.

Materials

The investigations on the heat conductivity have been carried out with commercialized epoxy molding compounds. Three different materials with different fillers have been used: Compound #1 – filled with aluminum oxide and glass, compound #2 – filled with glass and hBN (glass content $> hBN$ content) and compound #3 – filled with hBN and glass (hBN content $> glass$ content).

The investigations on the magnetic properties have been done with experimental compounds only since there are no commercial compounds existing. Therefore a “Blackbox”-Material was used, which contains the resin, hardener, catalyst and accelerator to build the epoxy network. By adding fillers this “Blackbox” becomes and ready for operation epoxy molding compound. The compounding with different magnetic fillers was done at the Leibniz-Institut für Polymerforschung Dresden, Germany. As magnetic fillers a MQA38-14 from Magnequench Inc. and a MF15P from Aichi was used. Both powders are anisotropic NdFeB-powders and have comparable magnetic properties ($B_R \approx 1300$ mT, $H_{J3} \approx 1100$ kA/m and $(BH)_{max} \approx 300$ kJ/m$^3$) [14-15]. Main difference between both materials is their geometry. Whereas the MQA-Material shows a plate-like shape, the MF15P has a more granular shape. The anisotropy direction of the MQA-Material is in thickness direction of the plates.

Experimental

For processing of both the heat conductive and the magnetic material an ARBURG 320C 600-100 injection molding machine was used. The specimen to characterize the heat conductivity is a simple plate geometry (35 x 35 x h mm$^3$) filled via a film gate. The height h of the tool could be varied between 1 and 4 mm.

The thermal conductivity $\lambda$ is calculated according to equation (3)

$$\lambda = a \cdot c_p \cdot \rho$$  \hspace{1cm} (3)

where $a$ is the thermal diffusivity in [mm/s], $\rho$ is the density of the material in [g/cm$^3$] and $c_p$ is the specific heat capacity in [J/g*K]. The thermal diffusivity is measured by means of a NanoFlash447 from Netzsch according to DIN EN ISO 22007-4 [16], the density is determined by the immersion method according to DIN EN ISO 1183-1 [17] and the specific heat capacity is measured via a Perkin Elmer DSC 7 according to DIN EN ISO 11357-4 [18]. The thermal properties were measured in x, y and z direction of the specimens according to Figure 1.

Figure 1. Specimen for measuring of thermal and magnetic properties.
To prepare the magnetic specimens a tool with an incorporated magnetic field was used. The magnetic field could either be provided by a permanent magnet or by electromagnetic coils. The experiments in this work were carried out with an injection molding tool with electromagnetic coils. The magnetic field is necessary to orient the magnetic anisotropic fillers to use the full capacity of these materials. Figure 2 shows a schematic built-up of an injection molding tool with an incorporated magnetic field. The dimensions of the specimens are also 35 x 35 x h mm³ and again h can be varied from 1 to 4 mm.

![Figure 2. Sketch for an injection molding tool with incorporated magnetic circuit provided by magnetic coils.](image)

The magnetic properties are measured with a Permagraph L with the “Electromagnet EP5” from MAGNET-PHYSIK Dr. Steingroever GmbH according to DIN EN 60404-5 [19]. Due to the specimen geometry only the properties in z direction were measured. In general there are four different important parameters to describe a permanent magnet: $B_R$ is the remanence of the magnet and describes the strength of a permanent magnet in absence of an outer magnetic field, $H_C$ and $H_{cB}$ are named the coercivity of a permanent magnet and characterize their resistance against demagnetization in an outer magnetic field. $(BH)_{max}$ is the maximum energy product of the magnet and is a proportion for the stored energy in the magnet.

Since $B_R$ of the bonded magnet is directly proportional to the orientation of the magnetic particles this value will be used to describe the orientation behavior of the particles during the injection molding process of thermoset molding compounds by means of equation (2).

**Results**

**Thermal conductive materials**

The figures 3 to 5 show the results of the heat conductivity for the compounds #1 to #3.

![Figure 3. Results for the heat conductivity in x, y and z direction for compound #1.](image)

For the isotropic aluminum oxide it would be expected that the thermal properties are constant for all specimen thicknesses. However, the thermal conductivity in Figure 3 is changing with increasing plate thickness. This variation might be triggered by the glass fibers added additionally in the compound. The thermal conductivity in z direction increases slightly with increasing thickness whereas the conductivity in x direction decreases accordingly. A total change of 16.1% (z) and 7.7% (x) can be observed.

![Figure 4. Results for the heat conductivity in x, y and z direction for compound #2.](image)

The compound #2, shown in Figure 4, already shows a more distinct behavior with increasing plate thickness.
The heat conductivity in z direction is almost doubled between 1 and 4 mm, the heat conductivity in x direction is simultaneously decreased to around 2/3 of the initial properties at 1 mm thickness.

The strongest dependence on the specimen thickness is shown for compound #3 in Figure 5. Here, the heat conductivity in z direction between 1 and 4 mm varies from 1.5 W/m*K to 4.7 W/m*K, which represents a delta of 220%. The heat conductivity in x direction decreases from 6.8 to 2.8 W/m*K. The breakeven between heat conductivity in flow direction and perpendicular to the flow direction is between 2 and 3 mm thickness. As can be seen for a thermoplastic material filled with hBN in [6], there is almost no difference in thermal conductivity in z nor in x direction between 2 and 4 mm. In terms of heat dissipation from sensible parts this could be an important advantage of thermoset molding compounds.

**Magnetic compounds**

Figure 6 shows the results for the material with 65 Vol.-% MQA-powder (plate-like shaped geometry). It is obvious that the initial magnetic properties (produced without an aligning field) are decreasing with increasing plate thickness. According to the above-mentioned equation (2) the degree of orientation for the 1 mm plates is 0.67 (B_R = 573 mT), whereas for the 4 mm plate it is only 0.48 (B_R = 412 mT). The specimens produced with magnetic field in the cavity do not show this kind of mismatch between the magnetic properties. Still the 1 mm plate shows the best results, however, the results for the 4 mm plate are slightly better than those for the 2 mm plate. With larger cavity thickness the reorientation of the magnetic particles in the cavity becomes easier. Therefore, the magnetic properties converge with increasing magnetic field.

Figure 7. Remanence with and without an aligning field for EP + 65 Vol.-% HDDR.

The results for the material with 65 Vol.-% HDDR-powder are comparable to the results of the MQA-compounds, even though the differences between the different plate thicknesses are smaller. The initial degree of orientation of the 1 mm plate with 0.66 (B_R = 562 mT) is comparable to the MQA-powder. Increasing the plate thickness does not change this initial value as much as seen for the MQA-powder. The initial degree of orientation for a plate thickness of 4 mm is still at 0.58 (B_R = 496 mT). The behavior for the plates produced with 1 T aligning field in the cavity are in good accordance to the MQA-compounds. This means that higher plate thicknesses are leading to a better reorientation of the particles. Due to the small differences in the initial values, the 4 mm plate shows the best results with B_R = 782 mT.

Figure 8 shows the degree of orientation according to eq. (2) of both the MQA- and the HDDR-compounds with...
and without an aligning field applied during the injection molding process.

Figure 8. Degree of orientation according to eq. (2) for the magnetic compounds with and without aligning field.

It can be easily noticed from Figure 8 that the initial orientation for 1 mm specimens is the same between the MQA- and the HDDR-compound. However, for the specimens produced with an aligning field the HDDR-compound is slightly improved. For the 2 and 4 mm specimens the initial values (w/o aligning field) for the degree of orientation for the HDDR-material are higher compared to the MQA-material. Additionally, the total decrease in the initial value for the HDDR-compound is very low. The value for the degree of orientation of the specimens produced with an aligning field is higher for all thicknesses for the HDDR-compound. In general, the values are increasing due to the longer reaction time in the cavity (proportional to the wall thickness). However, the initial orientation of the fillers seems to be the main influencing factor.

Discussion

Since for the heat conductive and the magnetic materials there are two different mechanisms to describe their properties a direct comparison of the filler orientation is not possible. Although there is a linear increase in the particular properties with increasing filler content the thermal properties increase disproportionately as soon as the filler have contact points with each other. For the magnetic properties a contact of the fillers with each other will not change the linear increase, but will restrain the orientation of the fillers in the aligning field.

Even though the mechanism in increasing either the thermal or magnetic properties is different both results are showing a good conformity regarding the influence of the plate thickness on the orientation behavior of the fillers. The results from the heat conductive materials show that there is almost no influence of the plate thickness on the orientation of the particles in y direction. Only in x and z direction of the specimens a significant change was observed. With these results the assumption can be made that the magnetic particles behave in a similar way. This means it is only necessary to consider the particle orientation of plate-like fillers in thermosets as a two-dimensional problem (disregarding the outer limits of the specimen). From a geometrical contemplation of the problem it can be seen that the measured remanence \( B_R \) is depending on the orientation angle \( \alpha \) as shown in (4)

\[
B_R = \cos \alpha \cdot \varphi \cdot B_{R,\text{Powder}}
\]  

where \( \alpha \) is the orientation angle and the other parameters are the same as in eq. (2). Combining both equations leads to a direct dependence of the degree of orientation \( \delta \) as shown in (5):

\[
\delta = \cos \alpha
\]

This correlation is shown in Figure 9. Angles larger than 90° are not possible because the magnetic direction of the particles is dictated during the magnetization prior to the magnetic measurement or during injection molding by the aligning magnetic field. Therefore an orientation angle of 135° will end as an angle of 45° because of the pole reversal during the processing or measurement.

![Figure 9. Relationship between calculated degree of orientation and real filler orientation.](image)

Pointed out by the different dotted lines in Figure 9 a measured magnetic degree of orientation of 90% means, that the average orientation angle of the particles is around 26°. If the average particle orientation of the fillers is 45°, which means a statistical distribution of the particle orientation, the resulting magnetic orientation will still be at around 71%.
For the results from Figure 9 the orientation angle in case of the MQA-compounds for 1, 2 and 4 mm will be 48°, 59° and 61°. For the HDDR-compound 49°, 52° and 55° respectively. As expected, the HDDR-compound shows no significant influence of the plate thickness on the filler orientation due to its near-isotropic particle shape. In contrast, the MQA fillers show a statistical distribution in the 1 mm plate, whereas for the 2 and 4 mm plate more particles have to be aligned in z direction than in x direction. Again this observation is in good accordance with the heat conductivity for the compounds with plate-like fillers shown in Figure 4 and 5. A sketch for the filler orientation of plate-like fillers in thermoset molding compounds for different specimen thicknesses is shown in Figure 10.

![Figure 10. Sketch for the filler orientation in thermoset molding compounds for different specimen thicknesses.](image)

The filler orientation in Figure 10 represents the average orientation angle shown in Figure 9. For the 1 mm plate there is almost a statistical distribution in the filler angles, whereas in the 4 mm plate the average filler angle in relation to the flow direction is 60°, which means more fillers are oriented in z direction (heat conductivity will rise) than in x direction (remanence would increase). While the thermoset becomes very low-viscous near the mold wall (higher temperature) the material in the middle remains rather high-viscous. Therefore, the high-viscous material is sliding on the low-viscous material into the cavity. The velocity gradient leads to high shear rates near the cavity wall which are responsible for the filler orientation in flow direction. The average filler orientation in the middle should be around 60 to 70° with respect to the flow direction.

**Conclusions**

Functionalized thermoset molding compounds show miscellaneous advantages compared to thermoplastic compounds. Beside their excellent thermo-mechanical properties and media resistance, improved heat conductivity can be reported. High heat conductivities in z direction, which are a main research focus for thermoplastics, can easily be realized by using thermoset materials as matrix material.

For the magnetic properties thermoset matrix material does not seem to be the first choice. As shown in earlier work, the properties measured on injection-molded specimens are minor compared to thermoplastic compounds [20]. Nevertheless, this apparent disadvantage is due to the flow-induced orientation in the specimen geometries used. Further work of the authors shall clarify, if this disadvantage remains for other geometries and for a free magnetic circuit design.

**Acknowledgement**

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