THERMAL CONDUCTIVITY OF POLYMERS FILLED WITH NON-ISOMETRIC FILLERS: A PROCESS DEPENDENT, ANISOTROPIC PROPERTY

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Abstract

Non-isometric fillers, used to raise thermal conductivity of thermoplastics to up to 15 $Wm^{-1}K^{-1}$, become oriented during the injection molding process, bringing new opportunities for thermal management concepts for complete plastic housings. By changing the flow conditions, different filler orientation profiles and hence, distributions of conductivity values, are obtained. A 3-dimensional analytical approach for predicting the thermal conductivities of polymers filled with non-isometric fillers is presented.

Introduction

Thermal conductive plastics open up a vast range of options to set up novel concepts of polymer technological system solutions in the area of mechatronics. For instance, the three-dimensional structure of a mechatronic assembly's housing can be integrated entirely into thermal management /1, 2/. Furthermore, plastics materials modified with ceramic fillers may be employed for mechatronic components, such as inductance coil housings. It is therefore possible to achieve thermal, isolatory as well as mechanical functions in a single step by overmolding the electronic component /3/.

Metal or ceramic fillers such as aluminum /4/, graphite /5/ or aluminum nitride /6,7/ increase heat conductivities of plastics from approximately 0.15-0.5 $Wm^{-1}K^{-1}$ up to 20 $Wm^{-1}K^{-1}$ by using 60 vol.-% filler content /8/.

Higher heat conductivity incurs significant changes in the behaviors of cooling and thus processing by injection molding, as a whole. In case of non-isometric fillers, the property profile generated turned out to be extremely anisotropic /9/. Moreover, directional thermal conductivity was shown to be an important value to be entered into the material database for injection molding simulation /9/. Determining plastics' thermal conductivities as well as predicting them is therefore essential for the lay-out of process and component.

The properties of various highly filled plastics materials are subject to a large number of publications. Some of the values published for identical fillers, if used with different matrix materials, vary considerably /10/. Generating analytical models to predict properties has often shown to be difficult and imprecise, in particular for high degrees of fillers /11, 21/.

There is a large number of publications that develop and present a variety of analytical models /11/, as well as FEM models, to serve for calculation of thermal conductivity /12/. The present study shows the outstanding significance of the effect exerted by process conditions upon non-isometric fillers' orientations, and thus on orientation-related and process-dependent properties. This is true while analyzing characteristics as well as correspondingly describing thermal conductivity in a model.

Basics

Fiber orientation in the melt flow

Material properties of filled polymers are initially influenced by the compound mixture: matrix material and filler. Processing by injection molding leads to a characteristic filler orientation, directly linked to the velocity profile in the melt flow. Characteristic layer models can be observed, figure 5 /13/. The 3-layer model (a, b, a) assumes fillers oriented in flow direction in the boundary layers and fillers oriented perpendicular to flow direction in the core layer.

The flow velocities are mainly constant in the core layer, and because of transverse flow near the gate zone, fillers are oriented perpendicular to the flow direction /14/.

Due to shear velocity gradient from core to boundary layer different shear forces act on the fillers. This results in a rotation of the fillers around their transverse axis until the forces are in equilibrium, i. e. until the fillers are oriented in flow direction.

The correlation of anisotropic mechanical properties and filler orientation in the injection molding process is well investigated. Additionally it is shown if processing of thermal conductive polymers leads to a comparable filler orientation and layer distribution, and to what extent thermal properties in parts are influenced.

Orientation tensors are usually used for visualization of filler orientation in parts. Defining the angle between main filler axis and axis of the coordinate system, the tensor component can thus be determined, equations 1 to 3 /15/.

$$a_{11} = \sin^2\Theta \cos^2\phi \qquad (1)$$

$$a_{22} = \sin^2\Theta \sin^2\phi \qquad (2)$$

$$a_{33} = \sin^2\Theta \qquad (3)$$

The definition of the filler orientation angles is presented in Figure 1.

The value 1 stands for complete orientation in reference direction, here, while 0 means rectangular orientation.

Thermal conductivity models

To predict the thermal conductivity in multi-phase systems, a variety of analytical and empirical models were developed /11/. A common feature to all these models is the basic idea of filler and matrix arranged either in a parallel or serial order, in relation to heat flow /11/. Upper and lower limits of calculated thermal conductivity are thus obtained. The model developed by Halpin-Tsai /16/ is based exactly on this basic idea. Lewis and Nielsen extended the Halpin-Tsai model by also including the geometry of the filler particle, particle orientation and packing density into the calculations /17/:

$$k_c = k_m \left[\frac{1 + A_S B \phi}{1 - B\phi\psi} \right] \qquad (2)$$

k: thermal conductivity;
Indices: c: composite; m: matrix; f: filler; Ø: filler content; A_S: geometrical factor

with

$$B = \frac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A} \quad \text{and} \quad \psi = 1 + \left(\frac{1-\phi_m}{\phi_m^2} \right)\phi \qquad (3)$$

The values of the geometrical factor A_S and the packing density ϕ_m have already been determined for a variety of individual particle geometries, and can be found in the corresponding tables. For uniaxially oriented fibers, heat conductivity in fiber orientation may be determined by inserting the aspect ratio (2L/D) in A_S, corresponding to heat flow in fiber direction. To determine heat conductivity perpendicular to fiber orientation, A is given the value 0.5. The precise value of maximum packing density ϕ_m is unknown for the copper particles used. However, employing the value 0.8, which is the value usually applied for random uniaxial distribution of fillers, experimental values matched calculation results very well.

Experimental: Materials and Specimen

Compound preparation

On a ZSE 27 HP-40 twin-screw extruder by Leistritz various compounds were prepared. As a matrix material, PA6 (Ultramid B3 by BASF) was employed, and 20, 30 and 40 vol.-% of copper powder were integrated into the compound. The copper filler has a platelet-shaped, i.e. clearly non-isometric geometry, as shown in figure 2. The platelets' average diameter D50 is approx. 35 µm. Microscopic analyses revealed that the platelet particles are approx. 1 µm thick.

Production of the test specimens

On a Milacron K110S2-F standard injection molding machine by Ferromatik, the produced compounds were processed into 50 x 50 [mm²] plate specimens, as can be seen in figure 3. Plate thicknesses varied at 2, 3 and 4 mm.

Determination of thermal conductivity

Once the specimen were prepared, samples were taken out of the center of the injection molded plates. These samples were then submitted to nano flash measurements, thus determining orientation-related thermal conductivity. This was done by employing a LFA-447 measuring device by Netzsch GmbH to measure thermal diffusivity. So as to calculate heat conductivity from temperature conductivity, the values of specific heat capacity and material density must be known as well. The heat capacity was determined by a Q1000 DSC device made by TA Instruments. The test specimens' densities were measured on a Micromeritics AccuPyc 1330 gas pycnometer.

Microscopic investigation and analysis on filler orientation

Microscopic analyses were carried out on polished sections to find out the filler orientation over the test specimen's cross section. For this purpose, a longitudinal cut was made and the specimen polished right at the spot where the sample had been taken for the nano-flash measurements. Over the cross section, along the z-axis (Figure 3), the filler's angle of orientation, i.e. the angle between the platelets' main axis and flow direction x, was determined. The main axis sits in the platelets' plane and determines the orientation of the longest platelets. The determined angles therefore served to find out the tensor value a_{xx} for description of the filler orientation quantities. For each average tensor value of a coordinate on the z axis, at least 30 individual filler particles were measured regarding their positions. For the purpose of comparing relative laminar thicknesses, the plate thickness, i.e. the z-coordinate, was standardized.

Results and Discussion

From the following it can be seen that the findings from the investigations performed on orientation-related thermal conductivity reveal some systematic inter-relations. They are the direct results of the formation of a characteristic laminar structure, which is already known from short fiber filled plastics.

Microscopic analysis conducted on filler orientation may help explain the properties observed. Additionally, their quantitative evaluation may be used as input data for a modified Lewis/Nielsen model. Process- and component-related thermal conductivity may thus be calculated.

Material characteristics

Figure 4 shows the findings obtained from the measurements on thermal conductivities, for various filler contents. According to expectations, thermal conductivity increases as filler content is stepped up. The values reveal a pronounced systematic relation to measuring direction. Values in the y-direction are clearly the highest. Z-direction values, in contrast, are the lowest. If compared to y-direction values, they show a thermal conductivity that is 2 to 3 times lower. The values measured in flow direction, i.e. x-direction, are generally between those of the other two directions. At first glance, however, no pattern can be determined here. For instance, with 20 vol.-% filler content, values of x- and y-direction are similar, whereas with 40 vol.-% z- and x-values nearly match. However, using image analysis and model considerations, investigators were able to find an explanation for this.

Starting from the orientation of fiber-shaped fillers, an orientation model could be made up for plastics filled with plate-shaped particles /19/, which is well suited to explain the inter-relations presented (Figure 5). It starts from the assumption that the individual layers, in particle orientation, significantly contribute to a rise in thermal conductivity. In perpendicular direction, there is barely any such effect. This inter-relation is also directly complementary with existing analytical models such as the one by Lewis and Nielsen. In the z-direction, for instance, only the core orientation layer contributes to higher heat conductivity. In flow direction (x-coordinate) there are two well conductive layers, though, while in the y-direction, thanks to the platelets' three-dimensional structure, all layers have an increasing effect on good conductivity.

To analyze the effects exerted by influencing factors upon thermal conductivity, a variety of systematic investigations were carried out. They showed direction-related heat conductivity to be significantly determined by processing conditions and geometry. These investigations revealed a systematic inter-relation between flow-related filler orientation, corresponding characteristic layer formation and the level of thermal conductivity in the injection molded component. These inter-relations can be directly deducted from the known model descriptions available to describe filler orientations. Therefore, this paper will merely use the parameter of the component wall thickness d, to describe the effect on flow behavior, and thus on layer structure.

Figure 6 presents the values of thermal conductivity measured in z-direction, as a function of the specimens' wall thicknesses. The plot clearly reveals that, as the wall gets thinner, heat conductivity decreases considerably. For instance, a plate 4 mm thick shows a value three times as high as a plate 2 mm thick. In addition, it was found, that increased filler contents give rise to differences in absolute values above average.

Analysis of filler orientation

The presented effects found in analysis of properties can be directly related to process-dependant changes in layer structures during flow. Filler orientation analysis was conducted at the same measuring spots, where the samples for heat conductivity measurements had been taken before; model assumptions of the laminar model (Figure 5) were confirmed /19/.

For instance, figure 10 shows a plate 4 mm thick with a pronounced core layer B with fillers oriented perpendicular to flow direction. The 2 mm plate, though, reveals barely any core layer B; nearly all fillers are oriented in flow direction (Figure 11). The lack of core layer in this plate is the reason for the clearly reduced thermal conductivity in z-direction, if compared to the thick plates with pronounced core layers.

The angle between the oriented platelets and flow, i.e. x-direction, can be lumped by conversion into a tensor value a_{xx}, thus enabling comparison of process-related layer structures over the component cross section in terms of quantities, as can be seen in figure 12.

The plates 2 mm thick led to a value of 1 for tensor components, nearly over the entire cross-section. This corresponds to an angle of 0 degrees, related to the x-direction. The 4 mm plates, however, showed a broad core area with some of the tensor values ranging down to 0.2, which means an angle of approx. 80 degrees related to flow direction.

Analytical model of direction-oriented thermal conductivity

So as to enable calculation of the thermal conductivities of plastics filled with non-isometric particles, existing models must be adapted according to the shown relations between structure and properties. Available models such as the one from Lewis and Nielsen make it possible to calculate thermal conductivity in unidirectional direction of filler orientation. Subsequent investigations were aimed at using orientation analysis as a basis to link thermal conductivity to filler orientation and perpendicular to the main axis. To calculate the thermal conductivity that exists in a specific direction, the two model areas must be linked to each other, corresponding to the shares of the individual orientation layers. To determine thermal conductivity in z-direction, overall layer thickness in the area a (Figures 9 and 11) must be multiplied, perpendicular to filler orientation, with the value obtained in equation 2, and then added to the product of layer thickness b and thermal conductivity in filler direction. Equation 3 serves to show this:

$$k_c(\phi, A_S) = a \cdot k_{c,p}(\phi, A_S = 0.5) + ... \qquad (3)$$

$$... + b \cdot k_{c,s}(\phi, A_S = 2\frac{L}{D})$$

c: composite; p: perpendicular; s: flow direction; Ø: filler content; A_S: geometric shape factor/heat flow direction

Starting from the determination of filler orientation in x-direction, as shown in figure 12, the individual layer thicknesses a and b can be determined for the individual component thicknesses and filler contents. As the boundary value between the two layers, a tensor value is assumed, which corresponds to a 45 degrees-angle. At this angle, fillers contribute to the increase in thermal conductivity to the same extent in both directions. This is why this value is considered to define the boundaries between the two layers.

Based on the polishing made on the 4 mm plates, layer thicknesses for the filler contents of 20, 30 and 40 vol.-% were determined and entered into equation 3. Figure 7 shows the comparison of calculated values to results from thermal conductivity measurements (Figure 4). The properties discussed before are displayed very clearly here. X- and z-direction values show to be almost identical for the 40 vol.-% filler content, and this may be due to the fact that the overall thicknesses of the limiting layers a correspond to those of the core layer b.

The thicknesses of orientation layers were determined for the various plate thicknesses as well. After that, thermal conductivity was calculated by using equation 3. Figure 8 clearly shows a very good match of experiment and calculation. As filler content rises along with plate thickness, though, a slight deterioration reveals in the degree of accuracy. This may be contributed to the widely known fact that the Lewis/Nielsen model's accuracy deteriorates as filler contents are increased. In addition, microscopic images taken of the thick plates reveal that the individual layers of filler orientations need to be more strictly differentiated. It is not sufficient any more to make up a difference between orientation in flow direction and perpendicular to it. Many of the fillers rather show an orientation in between these two extremes. However, this problem might simply be solved by extension to a 5 or 7 layer model.

Another explanation for the difference between the theoretical mathematical model and the measured values are effects between the Cu/PA interfaces. Detailed research of the influence of coupling agents on thermal conductivity are in progress. It is already revealed that compatibilization increases thermal conductivity, although the effect is to be regarded as subordinate compared with the shown orientational effects. Based on actual research the aim is to extend this model with additional parameters, such as e. g. surface effects.

As was pointed out in the beginning of the paper, knowing direction-related thermal conductivity has turned out to be necessary for the process simulation for thermal conductive plastics /9/. In particular conductivity in heat discharge direction must be entered into the system. In the plate geometries shown, this corresponds to the value in z-direction. Even for high filler contents and thick plates, the presented calculated results would be sufficiently accurate to serve for simulation.

Conclusion

If non-isometric fillers are integrated into a plastics matrix, the properties obtained are highly anisotropic. This can be contributed directly to a characteristic layer structure of filler orientation generated. Subject to the individual conditions of flow, different types of layers may be obtained. In case parameters are altered, this does not only lead to change in the flow process, which is a known fact. It moreover alters the layer structure. Additionally, this is reflected in the thermal conductivity values of highly filled plastics. The thermal conductivity of highly filled plastics thus is a property significantly determined by the process, and component lay-out as well as process simulation have to pay account to this fact. Adapting available analytical calculation models, the engineer can carry out highly precise calculation of both orientation-relation, and, most of all, process-related thermal conductivity.

Current investigations are concerned with generating a filler orientation by means of injection molding simulation programs. This data may serve as input data for the layer model mentioned, thus enabling calculation of the global anisotropic thermal conductivity in injection molded components.

It is essential to provide for comparability of thermal conductivities of highly filled plastics in further investigations. In order to achieve this aim, test specimens, e.g. injection molded parts, need to be standardized their geometries and flow conditions during production. Certainly, this equally applies to model formation and evaluation.

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Key Words: Thermal conductive polymers (TCP), analytic model, direction dependent thermal conductivity

Figures:

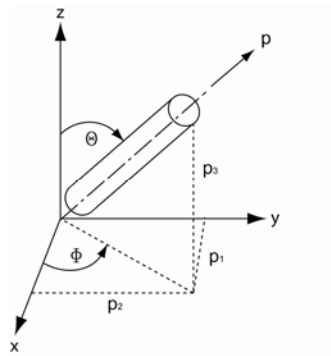

Figure 1: Definition of fibre orientation in a cartesian coordinate system with angles Θ und Φ

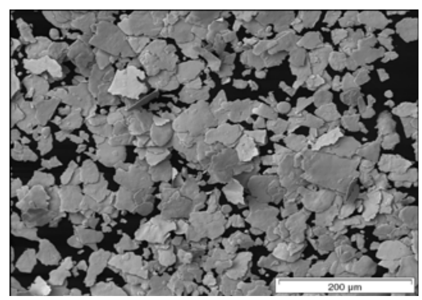

Figure 2: SEM-image of copper filler

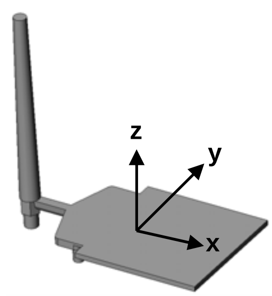

Figure 3: Specimen geometry

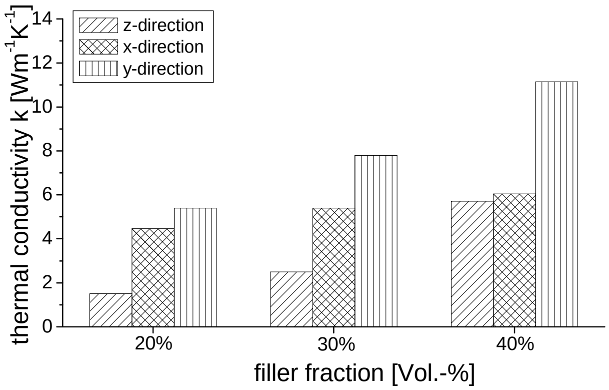

Figure 4: Direction dependent thermal conductivity of PA6+cu for a 4mm specimen

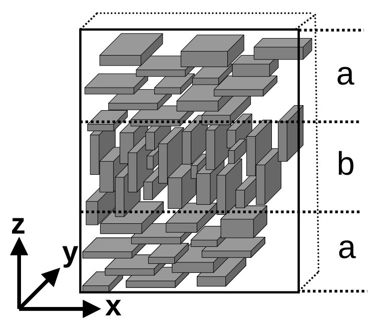

Figure 5: Layer-Model

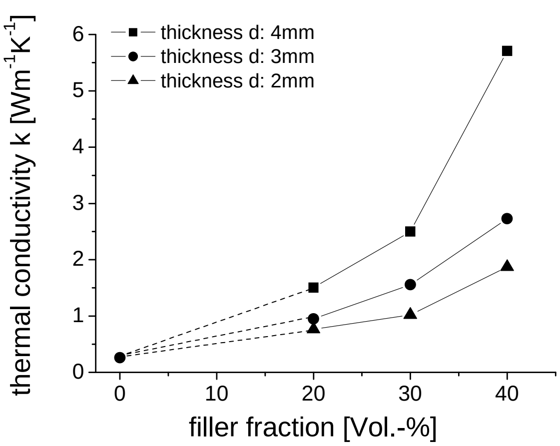

Figure 6: Thermal conductivity in z-direction of PA6 + cu for different specimen thickness

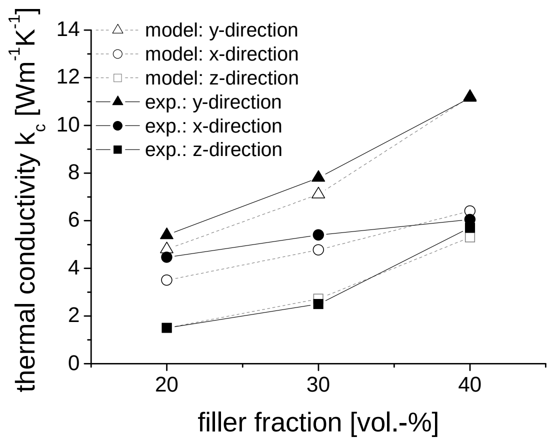

Figure 7: Comparison between calculated and measured therm. cond. of PA6 + cu for specimen with 4mm thickness

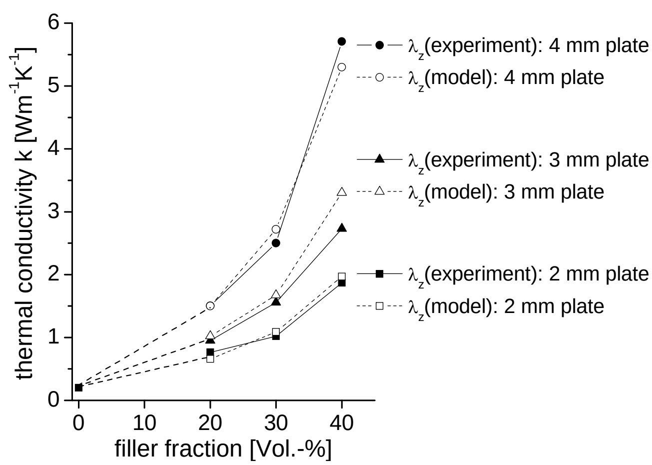

Figure 8: Comparison between calculated and measured therm. cond. in z-direction of PA6+cu for specimen with different thickness

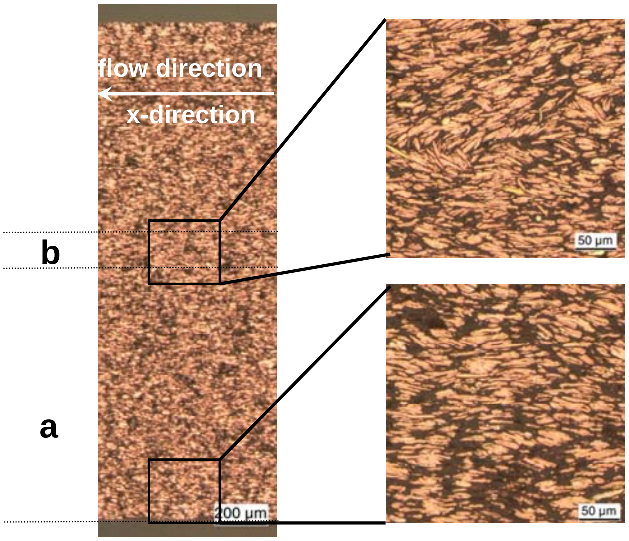

Figure 9: Filler orientation in flow direction on a 2 mm specimen

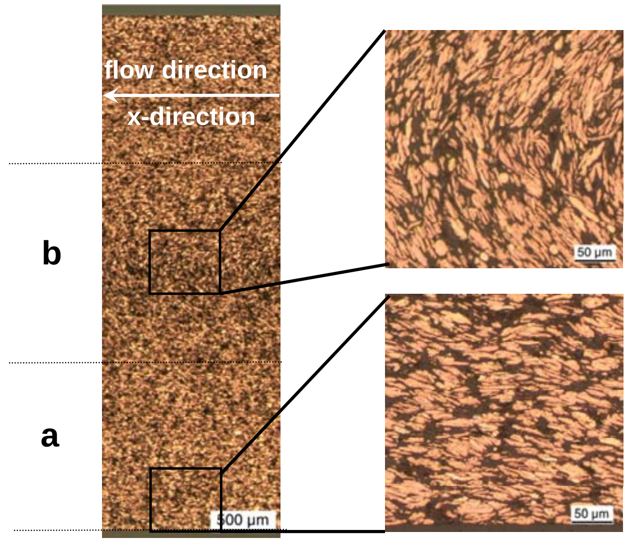

Figure 10: Filler orientation in flow direction on a 4 mm specimen

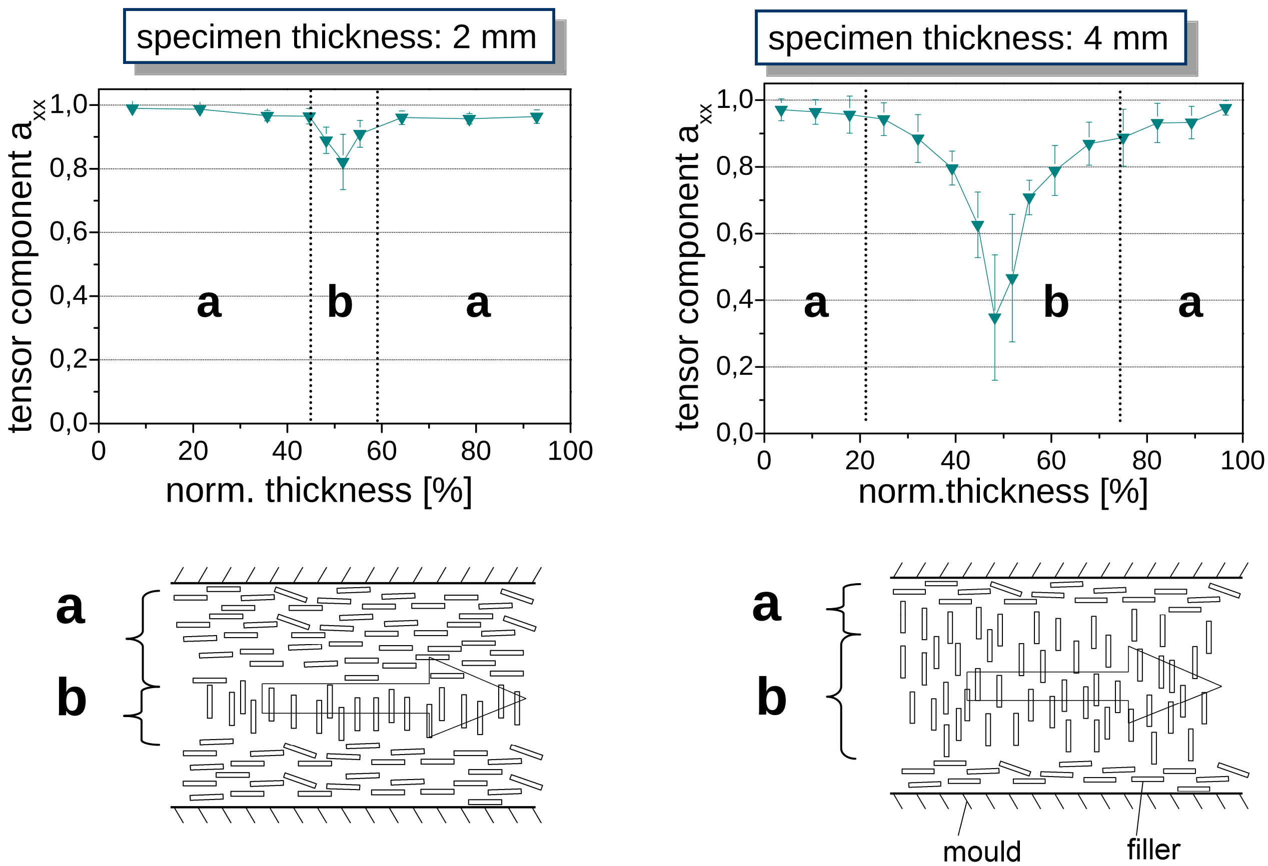

Figure 11: Values for tensor component a_{xx} for specimen of PA6+40 vol.-% cu with different thickness