INVESTIGATION OF THE THERMOVISCOELASTIC BEHAVIOR OF A CLOSED-CELL POLYMER STRUCTURAL FOAM UNDER PRESSURE FOR PROCESSING IN HYBRID LCM PROCESSES

Sarah Dietrich[1], Christina Dohmen[1], Felix Frölich[1], Alexander Jackstadt[1], Florian Wittemann[1], Luise Kärger[1]

[1]Karlsruhe Institute of Technology (KIT), Institute of Vehicle System Technology - Lightweight Engineering, Rintheimer Querallee 2, 76131 Karlsruhe, Germany.
Email: sarah.dietrich@kit.edu, Web Page: https://www.fast.kit.edu/english/lbt/

Keywords: Dynamic Mechanical Analysis (DMA), PET Foam, compression-mode

Abstract
In order to accurately capture foam core deformations during manufacturing of sandwich structures in Liquid Compression Molding (LCM), in this work, the thermoviscoelastic behavior of a closed-cell Polyethylene terephthalate (PET) structural foam is investigated in compression mode. Three different densities of a closed-cell PET foam by AIREX® are considered: T92.80 with a density of $\rho \approx 85\,\mathrm{kg/m^3}$, T92.100 with $\rho \approx 100\,\mathrm{kg/m^3}$ and T92.130 with $\rho \approx 135\,\mathrm{kg/m^3}$. The foam exhibits a transversely isotropic material behavior due to its manufacturing in strangextrusion process. Compression tests are carried out in the temperature range between 30 °C and 150 °C on a Dynamic Mechanical Analysis (DMA) 242 E Artemis machine from NETZSCH. A strong decrease in storage modulus above the glass transition temperature T_g is observed, as well as an unexpected increase in storage modulus with increasing temperature below T_g. Various influences of the foam structure such as surface effects, orientation effects due to extrusion or the expansion of blowing agent residues on the observed increase in stiffness are investigated as potential causes for the stiffness increase below T_g.

1. Introduction

Structural polymer foams are gaining importance for sandwich components due to their potential to reduce weight and CO_2 emissions while maintaining good flexural stiffness. For a targeted and accurate design of the structural behavior and the manufacturing process of composite sandwich structures, for example in liquid compression molding (LCM), it is necessary to understand and model the time- and temperature-dependent structural behavior of the foams.

Investigations on the influence of temperature on shear and compression behavior of PET and Polyurethane (PUR) structural foams have been performed by Garrido et al. [1] and Mazzuca et al. [2], observing a strong degradation of stiffness and toughness with increasing temperature. Rezaei et al. [3] and Seuffert [4] also show in quasi-static compression tests, that the mechanical properties decrease when the glass transition temperature is exceeded. In addition to the density of the structural foam, the temperature has the greatest influence on the material behavior.

The thermoviscoelastic behavior of thermoplastic closed-cell structural foams has been investigated by Garrido et al. [1] in bending mode, and by Santo et al. [5] and Denay et al. [6] in compression mode. While Garrido et al. [1] report a continuous decrease in storage modulus in the measured temperature

range in dual cantilever mode, similar to homogeneous materials, the DMA tests in compression mode by Santo et al. [5] on PET foam and by Denay et al. [6] on PUR foam show an increase in storage modulus with increasing temperature in the range below the glass transition temperature. Santo et al. [5] justify the measured increase in storage modulus with the collapse of foam cells and Denay et al. [6] argue that it is a structural effect of the foam due to a morphological change.

The cell morphology of the AIREX® T92 series under investigation has been analyzed by Fathi [7]. He shows in his work that the process-related cell morphology has a strong effect on the anisotropy and mechanical behavior of strand foams. The foams of the AIREX® T92 series have hexagonal strands of different sizes and differ in the wall thickness of the strand border zone. The T92.100 foam exhibits the highest strand bulk cell diameter and lowest strand border cell diameter amongst the three considered foam densities.

Static characterization test results are obtained by Seuffert [4] for the structural foam of the AIREX® T92 series, which provide material parameters for the behavior at individual temperatures. However, the stiffness of the foam core as a function of temperature is important for mapping the thermomechanical behavior during manufacturing in an LCM process. For this purpose, the viscoelastic behavior of the closed-cell AIREX® PET structural foam is investigated in this work, using DMA in compression mode.

2. Experimental setup

Three densities of a closed-cell PET structural foam by AIREX® are studied: T92.80 with $\rho \approx 85$ kg/m^3, T92.100 with $\rho \approx 100$ kg/m^3 and T92.130 with $\rho \approx 135$ kg/m^3. The foams have been manufactured in a strangextrusion process and thus, show a transversally isotropic behavior as they exhibit a hexagonal honeycomb structure with elongated cells and aligned monomer chains in extrusion direction.

The experiments are performed on a DMA 242 E Artemis machine by NETZSCH in compression mode in a parallel plate measurement system. A temperature range from 30 °C to 150 °C is tested with a heating rate of 1 K/min between the isothermal steps every 5 K and sample dimensions of 7.5 mm diameter and a height of 3 mm. The material behavior is determined in the frequency range between 0.1 Hz and 50 Hz. The setup of the compression DMA is represented in Figure 1 along with the acting forces. A constant static force is used to ensure that the sample is in contact with the load-introducing stamp at all times. The static force is superimposed by a dynamic force resulting from a fixed defined amplitude and an additional static force due to a proportionality factor $p > 1$ applied to the dynamic force. The load specifications are defined based on preliminary stress sweeps and cyclic tests.

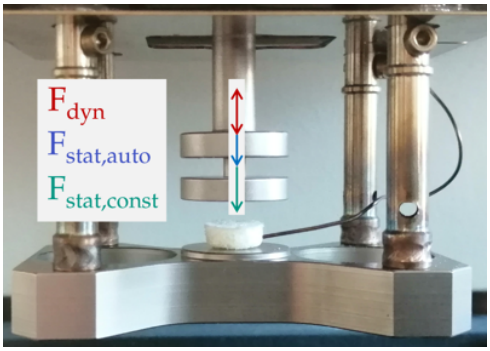


Figure 1: Sample holder of the NETZSCH 242 E Artemis DMA in pressure mode with representation of the force direction and superposition. An AIREX® T92.100 foam sample with a diameter of 7.5 mm and a height of 3 mm is placed on the sample holder.

The loads are summarized in Table 1 for the different foam density types. The amplitude is chosen

smaller for higher densities due to the maximum force of the used DMA machine. The dynamic load F_{dyn} is determined by the prescribed amplitude A and limited by the maximum dynamic load $F_{\mathrm{dyn,max}}$ due to machine specifications. The additional static load $F_{\mathrm{stat,auto}} = p\,F_{\mathrm{dyn}}$ is the dynamic load multiplied by the proportionality factor.

Table 1: Load specifications for the three investigated foam density types.

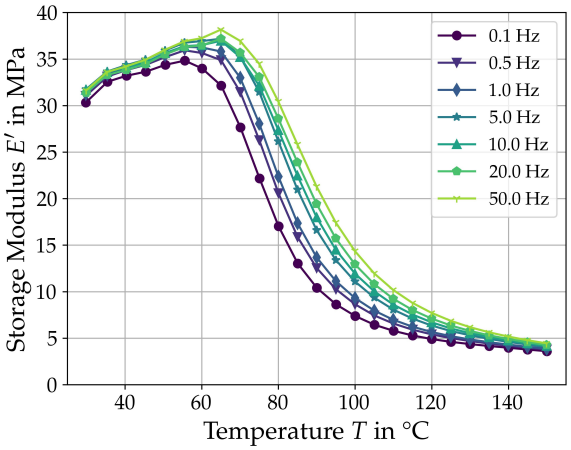
		T92.80	T92.100	T92.130
$F_{\mathrm{stat,const}}$	Static Force	1.5 N	2 N	3 N
A	Amplitude	19 µm	13 µm	10 µm
p	Proportionality Factor	1.3	1.3	1.3
$F_{\mathrm{dyn,max}}$	Maximum Dynamic Force	8 N	7.69 N	6.9 N

In order to investigate a possible expansion of blowing agent residues or water solved in the polymer with increasing temperature, a second campaign is performed, where the samples are tested cyclic. After the first test cycle, they are tempered for 10 hours at 150 °C, then cooled down with 2 K/min and tested a second time with the same test specifications. The second cycle is stopped when reaching a temperature of 110 °C because the range of interest is located between 30 °C and 80 °C. Another sample is tempered at 150 °C for 116 hours to ensure diffusion of blowing agent remains out of the polymer foam. In a next step, the open cells at the bottom and top of the samples are filled with fine filler to improve load introduction and investigate the influence of the open boundary cells due to cutting. The samples are tested in the extrusion direction by default. However, isolated tests are performed vertically to the extrusion direction to analyze the influence of the material orientation on the viscoelastic behavior.

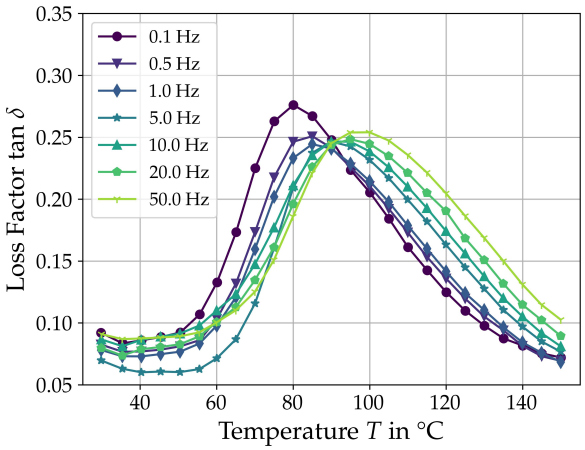
3. Results

The storage modulus and loss factor of the untreated samples, tested in extrusion direction, are represented in Figure 2 for the structural foams T92.130, T92.100 and T92.80, respectively. The loss factor shows a peak between 75 °C and 97 °C, depending on frequency and density, corresponding to the softening range of PET. For the storage modulus, an increase with increasing temperature is observed between 30 °C and $65-75$ °C and a strong decrease for temperatures above. The same increase of storage modulus with rising temperature below T_{g} was reported in literature [5, 6]. The increase in storage modulus is highest for T92.100, which was reported by Fathi [7] to have the highest cell diameters, which, in conjunction with a medium density, leads to higher thickness of the cell walls compared to cell size. The same behavior is observed for samples tested vertically to the extrusion direction.

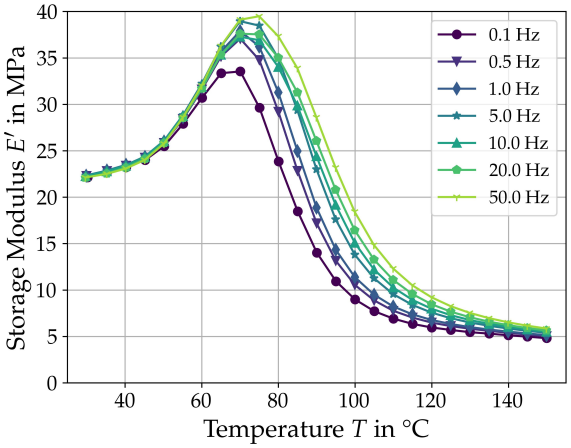
The results of the cyclic tests in the second campaign are shown in Figure 3. In the second cycle, after tempering fo 10 h at 150 °C a slight shift of the maximum of the loss factor towards higher temperatures can be observed, which is explainable by diffusion of water or blowing agent residues during tempering. However, the increase in storage modulus remains within the same order of magnitude. The observed increase in the second cycle is less pronounced for temperatures between 30 °C and 50 °C than in the first cycle and T_{g} is shifted towards higher temperatures. The same behavior is observed for samples, tempered for 116 hours at 150 °C and tested afterwards. The storage modulus is lower for the tempered samples, which can be explained by starting degradation of the polymer due to the heat treatment or different foam structures in the compared (tempered and untreated) samples (more or less strand bulk cells), but the increase below T_{g} remains unchanged. Moreover, the cyclic tests show, that the stiffness increase is a reversible phenomenon, because it occurs in a similar way in the second cycle. Thus, the storage modulus increase below T_{g} cannot be traced back to a collapsing cell structure as stated by Santo et al. [5].



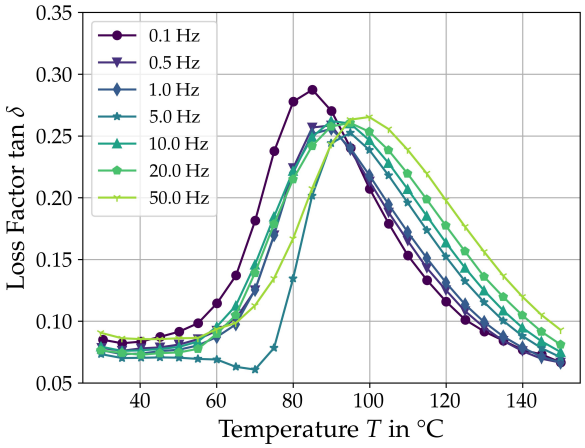
(a) Storage modulus E' of T92.130.



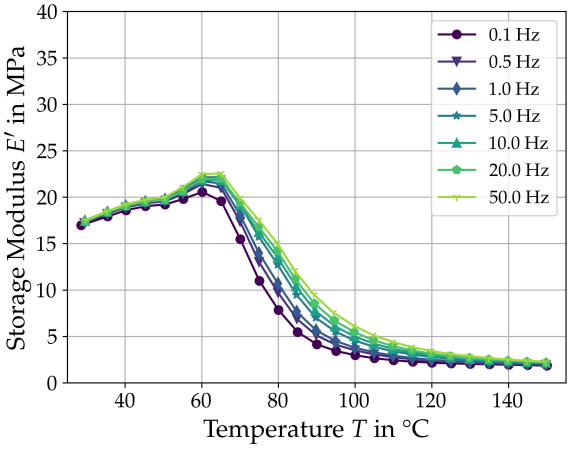
(b) Loss factor tan(δ) of T92.130.



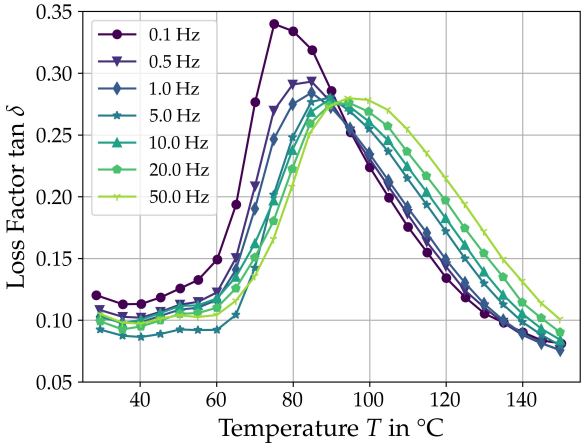
(c) Storage modulus E' of T92.100.



(d) Loss factor tan(δ) of T92.100.

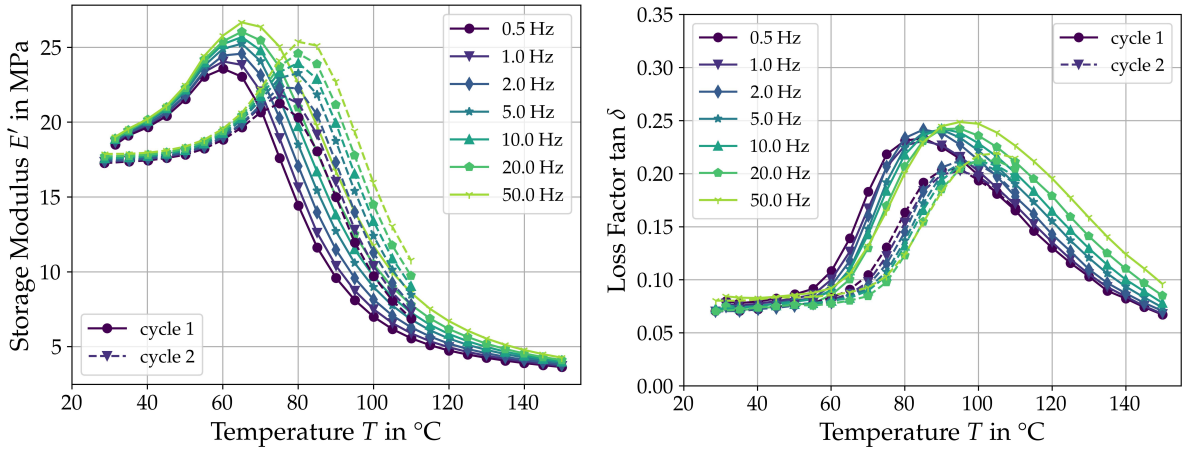


(e) Storage modulus E' of T92.80.



(f) Loss factor tan(δ) of T92.80.

Figure 2: Storage modulus (a, c, e) and loss factor (b, d, f) of the foams T92.130 (a, b), T92.100 (c, d) and T92.80 (e, f), at different frequencies tested in step-wise isothermal mode every 5 K, showing an increase of storage modulus between 30 °C and 65 °C before the softening range while the loss factor shows one peak between 75 °C and 97 °C, depending on frequency and density, corresponding to the softening range.



(a) Storage modulus E' of T92.130.

(b) Loss factor tan(δ) of T92.130.

Figure 3: Storage modulus (a) and loss factor (b) of one sample of T92.130 tested twice in step-wise isothermal mode in one clamping. After the first DMA cycle (cycle 1), the sample is held at 150 °C for 10 h without loading and then cooled down with 2 K/min. Afterwards, the test is run a second time with the same loads (cycle 2).

Another possible explanation for the observed effect is, that the force is not introduced homogeneously into the samples. As the specimen are cut from a closed-cell foam, in the boundary area lower stiffness is expected, because the cells are cut open there. A possible effect could be, that in the beginning, the tips of the open cell walls are tested, which soften with rising temperature and are compacted more and more, introducing part of the load into the closed-cell structure in the progress. Therefore, tests have been performed on specimens with filled cells on top and bottom as shown in Figure 4 in order to introduce the load more direct into the closed-cell part of the foam.

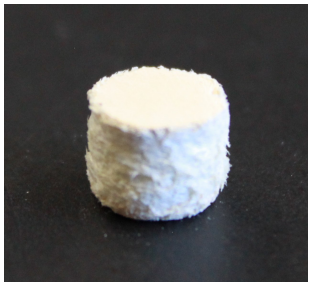
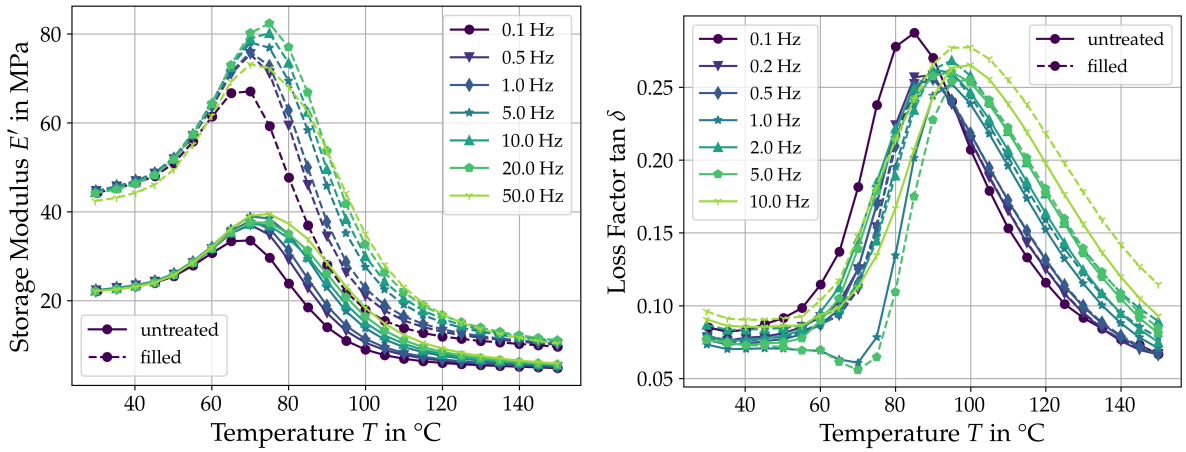


Figure 4: Foam sample filled at the top and bottom surface with fine filler for better load distribution and introduction into the closed-cell inner section of the foam.

However, Figure 5 shows, exemplary for foam T92.100, that the increase in storage modulus persists with filled boundary cells. The overall stiffness increases, but the relative change in storage modulus below T_g stays the same. Thus, the open boundary layer can be excluded as cause for the observed increase in storage modulus with increasing temperature.

In compression mode, thermal expansion of the polymer could be another possible explanation for measuring an increase in storage modulus with increasing temperature, as the thermal expansion imposes an additional pressure against the compression direction. However, an upwards estimation of thermal strain leads to results that are smaller than the measured phenomena and cannot be correlated to the results for the different foam densities. The T92.100 foam shows the highest increase in storage modulus, although



(a) Storage modulus E' of T92.100.

(b) Loss factor tan(δ) of T92.100.

Figure 5: Comparison of storage modulus (a) and loss factor (b) of T92.100 at different frequencies tested in step-wise isothermal mode every 5 K for an untreated and a surface-filled sample. The solid lines show the results for an untreated sample as in Figure 2 (c), (d) and the dashed lines for a sample with filled surface.

T92.130 has the highest density and thus, should have the highest thermal strain. Moreover, as the loss factor does not show unexpected behavior, the observed effect is likely to be due to the foam structure and not due to material effects of the PET.

Since in literature, the increase of storage modulus below T_g was only observed in compression and not in bending mode, a possible reason for the measured stiffness increase, is the static force, which is necessary in compression mode to ensure that the sample is in permanent contact with the stamp. As the static force is independent of the material stiffness, the softening of the polymer material due to higher temperatures might lead to a shift towards higher total strains, where the foam structure shows a non-linear stress-strain-relation due to the cell morphology and thus, a higher storage modulus is measured. However, this hypothesis has to be verified still.

4. Conclusion

In this work, different DMA campaigns in compression mode have been performed on a closed-cell PET foam by AIREX® in three different densities to analyze the thermoviscoelastic behavior. Specifically the observed increase in storage modulus below glass transition temperature has been investigated, which was also reported in literature for comparable foams tested in compression mode. Post-expansion of blowing agent residues as well as additional gas pressure in the cells due to temperature increase and evaporating water could be excluded as cause by cyclic tests and tempered samples. Moreover, surface effects were studied and did not show an effect on the observed increase in storage modulus, either. The effect was observed to be independent of material orientation.

However, the reason for the stiffness increase could not yet be clearly determined. Collapsing foam structure could also be excluded as cause for the observed effect, as the increase in storage modulus with rising temperature below T_g was shown to be reversible in cyclic tests. Morphological changes of the foam structure seem to be a more reasonable explanation. The static force was identified as possible cause for morphological changes leading to a nonlinear stress-strain-relation. As a next step, DMA tests are planned with varying static forces to further investigate this hypothesis.

Acknowledgments
The funding by the German Research Foundation (DFG) within the project "Modelling of the fluid-structure interaction in mold filling processes for an intrinsic manufacturing of fiber-reinforced composite sandwich components (FSI-Sandwich)" (project KA 4224/9-1 and HE 6154/8-1) is gratefully acknowledged. A special thank goes to the Institute for Pulsed Power and Microwave Technology (IHM) for providing the DMA machine.

References

[1] M. Garrido, J. R. Correia, and T. Keller. Effects of elevated temperature on the shear response of PET and PUR foams used in composite sandwich panels. *Construction and Building Materials*, 76: 150–157, 2015. ISSN 0950-0618. doi: 10.1016/j.conbuildmat.2014.11.053.

[2] P. Mazzuca, J. P. Firmo, J. R. Correia, and E. Castilho. Mechanical behaviour in shear and compression at elevated temperature of polyethylene terephthalate (PET) foam. *Journal of Building Engineering*, 42:102526, 2021. ISSN 2352-7102. doi: 10.1016/j.jobe.2021.102526.

[3] M. Rezaei, V. Karatzas, C. Berggreen, and L. A. Carlsson. The effect of elevated temperature on the mechanical properties and failure modes of GFRP face sheets and PET foam cored sandwich beams. *Journal of Sandwich Structures & Materials*, 22(4):1235–1255, 2020. ISSN 1099-6362. doi: 10.1177/1099636218781995.

[4] J. Seuffert. *Mold-filling Simulation of Resin Transfer Molding with Fluid-Structure Interaction*. Doctoral Thesis, Karlsruher Institut für Technologie (KIT), Karlsruhe, 2022. doi: 10.5445/IR/1000144393.

[5] L. Santo, D. Bellisario, and F. Quadrini. Shape Memory Behavior of PET Foams. *Polymers*, 10(2): 115, 2018. doi: 10.3390/polym10020115.

[6] A.-G. Denay, S. Castagnet, A. Roy, and G. Alise. Creep compression behaviour of a polyurethane foam from cryogenic temperatures: Size effect and long-term prediction. *EPJ Web of Conferences*, 6:25006, 2010. doi: 10.1051/epjconf/20100625006.

[7] A. Fathi. *Mechanical Properties of Strand PET Foams at Different Length Scales*. PhD thesis, Bayreuth, 2018.