UNIVERSITY OF PARDUBICE

Faculty of Chemical Technology

Department of Graphic Arts and Photophysics

# COMPOSITE MATERIALS WITH HIGH THERMAL CONDUCTIVITY FOR PRINTING 3D STRUCTURES

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**2024** **Ing. Petr Roudný**

**Author**

Ing. Petr Roudný

**Programme of study**

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2808V027 Surface Engineering

**Supervisor**

doc. Ing. Tomáš Syrový, Ph.D.

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Department of Graphic Arts and Photophysics;
Faculty of Chemical Technology

# Abstract

The dissertation is focused on researching composite materials with high thermal conductivity for printing 3D structures using additive manufacturing. The work describes both possible approaches to the fabrication of such composites, which are commonly used, as well as new, theoretical possibilities for the preparation of segregated conductive structures. The influence of modifying polymer matrix by fillers on the mechanical properties is also summarized in detail. The hybrid filling method of randomly distributed thermally conductive fillers in different thermoplastic matrices was chosen for the experimental part. For fabricated composite materials, crystallinity, orientation of macromolecules, and orientation of fillers were observed, and the influence of individual fillers and polymers was evaluated. The printed samples or extruded filaments were further analyzed using laser flash analysis, SEM analysis, X-ray diffractometry, tensile tests, and hardness measurements.

Keywords: thermal conductivity, additive manufacturing, FFF 3D printing, composites, fillers

# Abstrakt

Disertační práce je zaměřena na výzkum kompozitních materiálů s vysokou tepelnou vodivostí pro tisk 3D struktur pomocí aditivní výroby. V práci jsou popsány jak možné přístupy k tvorbě takových kompozitů, které jsou běžně využívány, tak jsou popsány nové, teoretické možnosti přípravy oddělených vodivých struktur. Podrobně je také shrnut vliv modifikací polymerní matrice plnivy na mechanické vlastnosti. Pro experimentální část byla vybrána metoda hybridního plnění náhodně rozmístěných tepelně vodivých plniv v různých termoplastických matricích. U vytvořených kompozitních materiálů byla sledována krystalinita, orientace makromolekul, orientace plniv a byl vyhodnocován vliv jednotlivých plniv a polymerů. Tištěné vzorky nebo extrudované filamenty byly dále analyzovány pomocí metody laserového paprsku, SEM analýzy, rentgenové difraktometrie, tahových zkoušek a měřením tvrdosti.

Klíčová slova: tepelná vodivost, aditivní výroba, FFF 3D tisk, kompozity, plniva

# Content

# 1. Introduction

Plastics have many advantages over other materials, including low weight and density, cost, easier processing, and other properties [1]. However, polymers are generally thermal insulators [1] and bulk polymers usually have a very low thermal conductivity (denoted by TC or k) in the range of 0.1–0.5 W $m^{-1}$ $K^{-1}$ [2]. However, such TC is insufficient to meet the requirements for heat dissipation [3]. On the other hand, there are many applications where some advanced properties such as thermal conductivity should be beneficial. Thus, the modification of polymeric materials, which generally serve as thermal insulators to thermal conductors, makes sense for various reasons. Plastics have the potential to be used in various heat-intensive applications, such as a material for heat sinks, heat exchangers, some types of dies, or mold tooling (generally wherever heat exchange between systems is required), with the advantage of lower weight and simpler processing compared to, for example, metal equivalents. Many types of electronic devices are currently being developed that are packaged in plastic cases. Since in many cases, they contain elements such as processors, memories, or just conventional passive elements, they are subject to heating during operation. In order to ensure their functionality or efficiency, it is therefore advisable to dissipate this heat, e.g., by means of a housing or heat sink, which has a significantly higher TC than a conventional plastic housing. This leads to requirements ensuring the efficiency of heat dissipation in such electronic parts [3]. Significantly improved properties such as TC will significantly expand the potential development range and satisfy industrial applications.

In addition to improving these physical properties, a crucial aspect is the possibility of rapid prototyping of the mentioned structures using AM (Additive Manufacturing). Regarding AM, i.e., 3D printing, FFF (Fused Filament Fabrication) or FDM (Fused Deposition Modeling) technology enables the creation of advanced object geometries that may be unattainable by conventional thermoplastic processing methods such as injection molding, blow molding, etc. AM, including FFF technology, can offer the possibility of manufacturing even complex structures [3].

Do-it-yourself production without a mold opens opportunities as well. It is only needed to own an FFF 3D printer, which can rapidly reduce the processing time of a small order or offer simple and fast prototyping. A number of new types of applications are currently being developed using AM, where polymers, in this case, thermoplastics extruded using a material extrusion-based AM machine, have many advantages compared to conventional technologies of prototyping. As for material extrusion-based AM, the main advantages are presented by process flexibility and the possibility of rapid prototyping or fabrication of a small load of final parts. The next advantages cover the low cost, low weight, availability of material extrusion-based AM technology, etc.

In some recent scientific papers concerning TC polymers or composite materials, AM is increasingly appearing alongside conventional thermoplastic processing methods [4-9]. Year by year (calculated from 2000 to 2022), especially in recent years, more and more scientific papers concerning thermally conductive composites for AM are published (Figure 1) [3], probably for the reasons mentioned.

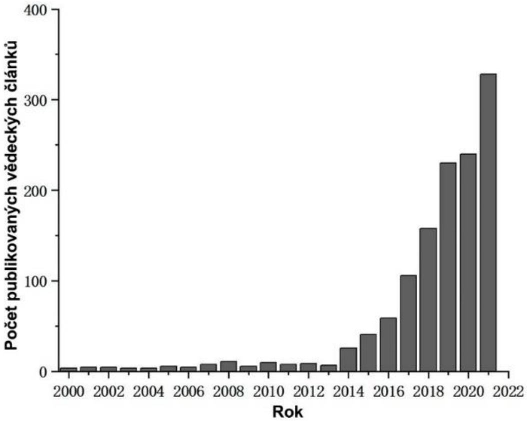

**Fig. 1:** Number of published scientific articles using AM technology for TC studies from 2000 to 2021 [3].

# 2. Brief analysis of the present status in the field of the dissertation topic

Many authors have tried to increase the TC of a polymer by randomly distributing a thermally conductive filler [10-14]. Various types of fillers can be used, It is possible to use metallic fillers, where $k_e$ (contribution of electrons) mainly contributes to heat transfer, or carbon or ceramic fillers (non-metallic solids), where $k_{ph}$ (contribution of phonon) mainly contributes to heat transfer [15]. Some authors have focused on the TC without the use of a filler, focusing on the crystallinity and orientation of the molecules in polymers [16, 17].

### Influence of crystallinity and molecular orientation to thermal conductivity of polymers

The crystallinity of semi-crystalline polymers and the molecular orientation of a polymer are considered to be important factors influencing the TC of polymeric materials [16]. Generally, crystalline materials have a higher TC than amorphous materials because the regularity of the lattice arrangement has an important effect on $k_{ph}$ [15]. The random conformation of the chains (including various imperfections in real crystals) causes the scattering of phonons, therefore in an ideal crystal lattice the mean free path would be infinite [18]. In terms of molecular orientation, parallel to the direction of orientation $k_{\parallel}$ increases significantly with an increasing degree of uniaxial stress or stretching orientation, while perpendicular to the direction of orientation $k_{\perp}$ decreases slightly [16]. These findings are summarized in detail by Choy [19]. As the authors describe in this study, a more significant increase in TC is achieved for semi-crystalline polymers, the structure of which leads to more significant changes. In this early study, the authors present data for PE (up to around 1 W m$^{-1}$ K$^{-1}$); however, they assume that the main features will be similar for other semi-crystalline polymers. In a later study [20], the authors report an increase in $k_{\parallel}$ for PEEK, but the change was not as significant as $k_{\parallel}$ was in the range of approximately 0.19–0.65 W m$^{-1}$ K$^{-1}$, depending on temperature, crystallinity of PEEK and molecular orientation.

The fundamental concepts of molecular orientation during extrusion including its impact are explained in [21]. If the filament cools rapidly, this orientation is largely maintained.

The orientation of macromolecules can also be achieved via FFF 3D printing, although very few authors have focused on this topic (where the filament is being stretched during 3D printing), and further research is needed. During the manufacture of 3D-printed plastic parts, the polymer chains are in most cases not oriented because the temperature range in which the orientation can be carried out effectively is relatively narrow, and achieving molecular orientation is, therefore, relatively difficult [22]. Unlike the initial molecular orientation present in the filament, the shear effects in an FFF 3D printer can induce a certain molecular orientation that depends entirely on the available time and temperature [23] At temperatures below the $T_m$ (melting temperature) or $T_f$ (flowing temperature) of the polymer, the force required for mechanical deformation is too high, and at temperatures close to the melting temperature (or flowing temperature) the polymer macromolecules can quickly relax to a random state, so it is difficult to achieve molecular orientation via 3D printing [22]. Thus, for successful molecular orientation, there must be a particular time interval [24].

Only a few studies have focused on molecular orientation in FFF 3D printing. Among these, Ghodbane et al. [22] aimed to increase the mechanical properties of Poly(Desaminotyrosyl-Tyrosine Dodecyl Dodecanedioate), but one may assume that this procedure will also increase $k_{\parallel}$. As the authors state, a high degree of molecular orientation comparable to drawn fibers can be achieved in 3D printing by moving the print head at sufficiently high speeds. By optimally combining printing condition parameters such as the print speed, nozzle diameter, filament extrusion pressure, and temperature, it is possible to keep the polymer in a semi-solid state at the nozzle tip, allowing the polymer to be stretched before cooling to a solid. Verbeeten et al. [23] also focused on the mechanical properties of the polymer. The authors found that the highest degree of orientation for ABS (Acrylonitrile Butadiene Styrene) printed at speeds of 5 mm $s^{-1}$, 20 mm $s^{-1}$, and 35 mm $s^{-1}$ was achieved at the highest speed. The authors evaluated it according to the dimensional changes after a thermal treatment as well. They found that the orientation of the printed part is slightly less noticeable than the orientation of the filament itself. At other speeds, the sample contraction was slightly less, and at the lowest speed, contraction was least significant. Higher orientation with higher print speed (9 mm $s^{-1}$ and 35 mm $s^{-1}$, respectively) was also reported by Verbeeten et al. in the study [25], when PLA was evaluated.

## Influence of thermally conductive fillers incorporated to the thermoplastic polymers

The following section describes the possibilities of incorporating a thermally conductive filler into a thermoplastic matrix, while the limits and effects of individual solutions on the final properties of the composite material are discussed as well.

Thermal conductivity can be increased by adding a nano-filler or micro-filler. Liu et al. summarized the possible ways of increasing the TC of a composite using nano-fillers in the study [26]. To some extent, the information summarized in this article can also be applied to micro-fillers. Nano-fillers will behave similarly to micro-fillers concerning thermal properties, but some differences can be noticed.

### *Influence of particle size*

Regarding the influence of thermally conductive particle sizes, inconsistent conclusions can be found across several studies, as confirmed in study [26], and it is not certain whether microfillers or nanofillers are more effective. There are more inconsistent conclusions from various studies on this topic and are summarized in the study [26]. Due to these inconsistent conclusions, the authors in [26] suggested an explanation that the structure of the formed conductive network is more important than the particle size, and it is good to focus on the morphology of the given composites. The TC increases synergistically with the created efficient three-dimensional thermally conductive network. Furthermore, the authors in [26] explain that larger particles show high intrinsic TC and low interfacial thermal resistance, while smaller particles allow good and high dispersion and a strong coupling effect between particles and the matrix, which allow for easier formation of a thermally conductive network. It may be the reason for the various observed trends in the effect of particle size used in the preparation of composite materials.

### *Combination of different shapes of fillers – focus on morphology*

The shape of the particles is a key property to forming a thermally conductive network and it is appropriate to focus on it. Some shapes provide higher TC, and spherical shapes increase TC less (when it is the same material with only a different morphology) [26].

The authors in [27-29] proposed information about the synergistic effect in creating an efficient three-dimensional conductive network to facilitate heat transfer. As stated by the authors in [26], certain combinations can increase TC. These are, for example, a combination of spherical fillers (0D for nano-particles) with tubular or wire-shaped particles (1D for nano-particles), a combination of sheet-shaped particles (2D for nano-particles) with spherical particles (0D for nano-particles), or a combination of sheet-shaped particles (2D for nano-particles) with tubular or wire-shaped particles (1D for nano-particles), where these particles can form a thermal bridge for the sheet-shaped particles (2D for nano-particles). However, possibilities can be combined, for example, using different particle distributions and different particle shapes [30].

### *Influence of volume fraction of particles to thermal conductivity*

As early as 1974, Nielsen [31] published the maximum possible filler content $\Phi_m$, which can be used in the polymer matrix for various shapes of fillers. For example, for spherical shapes, $\Phi_m$ is 0.60–0.7405, and for fibers and rods, $\Phi_m$ is 0.52–0.907, based on the type of packing. As Nielsen [31] further presents, the actual maximum possible filler content is lower than in theory. The maximum filler content increases with increasing polydispersity [32]. Smaller particles get into the gaps between the larger ones, but non-spherical particles cannot fill the gaps so effectively, and $\Phi_m$ tends to be lower [32]. The maximum possible filling of the polymer in bimodal mixtures is complicated to determine, and the situation is even more complicated if more than two types of filler with different particle distributions are used [33]. Josef Jancar [34] described the dependence of the specific surface on the maximum possible filling with $CaCO_3$ filler in a PP matrix. The data show an exponential decrease in the maximum $\Phi_m$ with increasing specific surface area.

However, the limitations for the maximum volume fraction of filler in the filament are also in the additive production itself (i.e. FFF 3D printing), which is summarized in [35], where authors state that a maximum filler volume fraction of about 45 % can be used for extrusion. There are many limitations to further increasing the filler volume fraction, such as increased viscosity, which requires higher processing pressure that can even clog the nozzle. Tekinalp et al. [36], however, observed nozzle clogging failure during printing with as little as 40 wt. % carbon fibers in ABS. According to [35], the nozzle may become clogged due to physical blockage caused by accumulated filler in the area of the nozzle orifice or due to excessive flow resistance caused by high viscosity. As the filler volume fraction increases, the potential for both types of clogging failure increases as well [35].

Fallon et al. [35] show that for monodisperse micro-fiber fillers, the theoretical maximum possible filling depends on the diameter of the nozzle and the diameter of the micro-fiber fillers (based on the most efficient packing). For a 0.4 mm diameter nozzle, the maximum possible filling decreases by about 10 vol. %. The maximum possible filling is in the range of ~90–86 vol. % for fibers with a diameter of ~2–10 µm. With increasing fiber diameter, the maximum possible filling decreases to ~80 vol. % for fibers with a diameter of around 40 µm. To increase $\Phi_m$, the authors in [35] recommend increasing the nozzle size or decreasing the filler diameter.

Many authors have influenced the TC of a polymer by increasing the volume fraction of the particles [10-14, 28, 37, 38]. It is a known fact that the TC increases with the volume fraction of the thermally conductive filler; for example, various models for estimating the resulting TC in a composite material commonly count the volume fraction of the filler [39]. The effect of high filler volume fraction for high TC using micro-fillers is stressed by Olifirov et al. [40]. As stated in this study, the main difference between a low, medium, and high filled system (more than 50 % by volume) lies in the heat transfer mechanism. In low or medium-filled systems, micron-sized fillers do not create continuous pathways. Thus, the heat transfer in such composite materials is driven by the polymer matrix, and the TC is lower. In highly filled systems, the filler particles are interconnected and create a continuous network. Then, heat transfer is driven by the structure of the filler network.

A problem with the formation of the composite material by random distribution of a thermally conductive filler in a polymer matrix is that a high volume fraction of a filler (higher than 50 vol. %) is required to obtain a TC of 1−5 W $m^{-1}$ $K^{-1}$ [41]. It may be difficult to achieve when the composite is intended to be used as filament for FFF 3D printing [35]. The difficulty with FFF 3D printing is that the resulting filament must have good flow/viscosity parameters in melt state and the final product must have good mechanical properties.

According to [42], as the volume fraction of a filler in the matrix increases, the viscosity of the mixture increases, which is suitable for polymers for extrusion, as confirmed by Kishore et al. [43]. However, care must be taken to not create rough and rigid filaments [43]. The author in [42] also states that there is always a certain range of shear stress in a given composite system in which the viscosity does not increase so rapidly, so this is an area that is ideal for processing, in this case, extrusion. However, the change in viscosity by adding a filler to the polymer depends on the properties of the filler (chemical composition of filler, size, shape, the roughness of the surface, specific surface, etc.). Generally, as the volume fraction increases, the viscosity increases, but the increase is dependent on the mentioned parameters of fillers, so the maximum volume fraction is different for each filler.

The effect of the filler on the processability of the composite material by extrusion can be also observed using MFI (Melt Flow Index) values [12], and a high reduction in MFI values could be problematic. However, the maximum volume fraction of filler will be different for different types of fillers, which was confirmed based on MFI in the study [12].

*Influence of thermal conductivity improvements to mechanical properties*

Since the mechanical properties change during the listed modifications, irrespective of whether they improve or worsen, it is necessary to understand the changes.

By orientation of the polymer chains, the mechanical properties can be significantly improved [22]. For semicrystalline polymers, it is stressed by Bigg [44]. However, Bigg [44] also states that, for example, highly oriented POM (Polyoxymethylene) has better mechanical properties than highly oriented PP (Polypropylene), but does not have the same mechanical properties as highly oriented HDPE (High-Density Polyethylene). Therefore, it is important to keep in mind that the mechanical properties can be improved differently for different polymers.

However, Verbeteen et al. [23] show that higher orientation at a higher print speed does not mean better mechanical properties. In their study, printed parts printed at a speed of 20 mm $s^{-1}$ had slightly better mechanical properties, such as modulus (from 2 168 ± 47 to 2 208 ± 5 MPa) or tensile yield stress (from 33.04 ± 0,47 to 49.71 ± 2.86 MPa) than when printing at a speed of 35 mm $s^{-1}$ (modulus from 2 018 ± 12 to 2 109 ± 44 MPa and tensile yield stress from 31.24 ± 0,37 to 47.44 ± 0.90 MPa), where better orientation was achieved. However, it needs to be pointed out that in FFF 3D printing, the mechanical properties are affected by the selected printing parameters [45-47]. In addition, the mechanical properties of parts made by FFF printing are highly anisotropic due to the weak point at the interface of the individual layers [48].

For filled systems, when the thermally conductive filler is distributed randomly in a polymer matrix, the changes in mechanical properties are no longer so uniform. Gao et al. [49] state that the mechanical properties of a filled polymer depend primarily on three factors. These are the strength and modulus of the filler, strength and chemical stability of the polymer matrix, and the effectiveness of adhesion between matrix and filler. However, Nurul et al. [12] also emphasize particle size. However, the volume fraction of the filler in the polymer matrix is also important. At higher filling, strong interactions between particles can occur, and mechanical properties such as tensile strength can decrease [12].

Some results found across papers are even contradictory due to the dependence of composites' mechanical properties on various factors. For example, Altay et al. [50] found that the tensile strength of the thermally conductive composite materials formed decreased from approximately 70 MPa to less than 60 MPa, using 50 wt. % h-BN (Hexagonal Boron Nitride) and SG (Synthetic Graphite), but most when using AlN, to above 40 MPa. According to the authors, this can be caused by poor dispersion of particles, resulting in poor adhesion between the matrix and the filler, which decreases the overall strength of the composite material. However, Cho et al. [11] found that the tensile strength increased almost linearly with the increasing volume fraction of carbon fibers with a length of 6 mm and a diameter of 7 μm (5–30 vol. %) in the polyketone (POKETONE™) matrix, from approximately 80 MPa to 150 MPa.

# 3. The goals of the dissertation

- Fabrication of thermoplastic composites with high thermal conductivity in the printing direction and also perpendicular to the printing direction while maintaining good mechanical properties for printing 3D structures. Characterization using the laser flash analysis, tensile test, hardness measurement, etc.
- Comparison of the behavior of different types of fillers in various polymers and determining the best combinations.
- Subjective and objective determination of printability using FFF 3D printing for created composites, ensuring the best possible printability.
- Chemical and physical modifications of selected composites and fillers (e.g., tempering samples to increase crystallinity, hydroxylation of h-BN) and discussion of their effect on the resulting thermal conductivity.
- Characterization of the fillers and the behavior of the fillers in the matrix using SEM.
- Ensuring sufficient adhesion of the composite to the platform during FFF AM.

# 4. Presentation of the elaboration methods

In order to fulfill the defined objectives and requirements of the dissertation thesis, the available equipment and technologies of the Department of Graphic Arts and Photophysics, Institute of Chemistry and Technology of Macromolecular Materials, and Institute of Applied Physics and Mathematics in the Faculty of Chemical Technology were mainly used. However, some tests were carried out at the Institute of Printing Science and Technology, Technischen Universität Darmstadt. The main equipment and technologies used are briefly described below.

**Filament Extrusion** – Filaments with a diameter of ~1.75 mm were wound onto a spool by means of a Felfil Spooler. RPM (Revolutions Per Minute) of the screw was adjusted operatively as needed but was kept mainly between 7 and 9. The pull speed was also adjusted operatively as needed but mostly kept between 0.5 and 0.7 m per minute.

**FFF 3D Printing –** The samples were printed on an Original Prusa i3 MK3S+ material extrusion-based AM machine. To improve the adhesion of the composites to the build platform, the smooth PEI (polyetherimide) build platform was covered with Kapton tape. In the first instance, the Kapton tape on the build platform was sprayed with 3DLAC (glue for improving part adhesion to the build platform). However, 3DLAC loses its properties at build platform temperatures set for printing from the fabricated composites. Therefore, the Kapton tape was coated with Nano Polymer Adhesive from Vision Miner, which works even at higher temperatures.

BROZZL hardened steel nozzle with a diameter of 0.4 mm was used to print all samples. The model for measuring $k_{\perp}$ was prepared for printing in PrusaSlicer 2.5.0. Here, the rectilinear fill pattern with a cross-hatching was used. The print speed was set to 10 mm/s. Standing cylinders with a diameter of 12.5 mm and a height of 6 mm were printed from the individual filaments. The model for measuring $k_{\parallel}$ was prepared for printing in Simplify3D 4.1.2. Here, the rectilinear fill pattern was used without cross-hatching, just parallel lines with angles of 180 and $-$ 180. The print speed was set to 12 mm/s. In both cases, the layer height was set to 0.1 mm, the fill density to 100 %, and the fill pattern was rectilinear. Samples with a thickness of 1 mm for measurement were cut on a saw Well model 3500 basic with a diamond string.

**Laser Flash Analysis** – The thermal diffusivity and thermal capacity of the composites and neat polymers were measured by the non-stationary laser flash method on the LFA-457 Netzsch instrument. The apparent density of all samples was obtained geometrically. The method involves heating the front side of the sample with a short-energy laser pulse. The temperature rise on the rear surface is measured against time using an infrared detector. At each temperature, the measurement was carried out 3 times, and then, the average value was reckoned up. The TC could be determined from the equation 1 [51]:

$$k\ (T) = \alpha(T)\ c_p(T)\ \rho(T), (\mathrm{W\ m^{-1}\ K^{-1}}) \tag{1}$$

where $k$ is the thermal conductivity, $T$ is the temperature, $\alpha$ is the thermal diffusivity, $\rho$ is the density, and $c_p$ is the specific heat capacity.

**Tensile tests** – Tensile tests are carried out according to ČSN EN ISO 527-1,2 [52, 53] standards. As described in the technical standard ČSN EN ISO 527-1 [52], the test specimen is subjected to uniaxial tensile stress, is stretched at a constant speed, and the deformation (elongation) depending on the load is monitored using a deformation curve.

The Zwick Z050 and Instron 5500R testing machines were used to measure the tensile properties of all filaments, and stress-strain diagrams were created from the measured data. Unfortunately, unifying the speeds was impossible, which must be considered when comparing the results. Three measured samples were selected for each filament, and curves with the dependence of stress on strain were created from the average values. Filaments cut to 5–8 centimeters were clamped separately in the jaws. Testing was performed at room temperature with a moving jaw speed of 0.1 mm/s on a Zwick Z050 tester (used for testing primary composites and neat PC i.e., Polycarbonate) and 2 mm/min on an Instron 5500R tester (used for testing selected composites and neat PC and PET i.e., Polyethylentereftalate). The results are not affected by slight differences in filament diameters, as the stress is calculated as a quotient from the standard force and area intersection, in which the filament diameter is taken into account.

**Hardness Measurement –** Samples for Shore D hardness measurements of the primary composites were prepared for printing in Simplify3D 4.1.2 (measured on a Sauter HDD 100-1 Shore Hardness Tester with a compressive force of 50 N). The dimensions of the samples were 2 × 1 × 1 cm. In the next step, the hardness of selected composites and unfilled polymers was measured using the Shore D method (Deadweight Durometer Test Stand Model 473 with a pressure force of 50 N) and the ball indentation method (HB5/62.5, measured on a Nemesis 9000 universal hardness tester). The mentioned method was used to verify the accuracy, as a ball with a diameter of 5 ± 0.05 mm can show more accurate values than hardness tester with a cone-shaped tip with a round canopy, where the data can be more affected by the hardness of the filler used. The dimensions of the samples for hardness measured by the ball indentation method were 4 × 4 × 0.4 cm with 100 % fill density, rectilinear pattern with hatching, layer height 0.1 mm, and nozzle with a diameter of 0.4 mm was changed for the nozzle with a diameter of 0.8 mm. The print speed was left at default in PrusaSlicer 2.5.0, however, the speed was reduced to 70 % during printing.

**SEM Analysis** – Tescan VEGA 1530 SB and TESCAN VEGA 3 EasyProbe scanning electron microscopes were used to check all printouts, understand the behavior, and further outline the research. First, the filler itself was characterized. Furthermore, polished remains of samples were observed after cutting the samples for the TC measurement. Three types of printed and cut samples were observed (Figure 2). They were ground on a polishing device, first on a coarse disc with a diamond paste of 5/3 µm and then on a fine disc with a diamond paste of 1/0 µm.

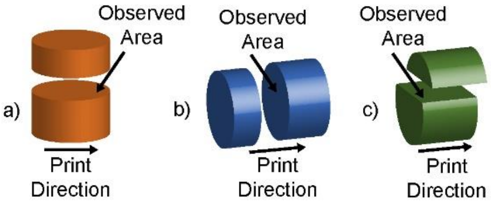

**Fig. 2**: Samples for SEM analysis after cutting samples a) for measuring $k_{\perp}$, b) for measuring $k_{\parallel}$, c) for measuring $k_{\parallel}$ with horizontal cut with the printing direction.

**X-ray diffraction analysis** – The crystallinity of polymers and composites and the orientation of the fillers were verified using X-ray diffraction analysis on a D8 Advance, Bruker, VB. Tempered samples above $T_g$ of PA11, PET, and PETG for measuring $k_{\parallel}$, and cube-shaped samples of size 15 × 15 × 3 mm for composites based on PETG were analyzed.

**Dynamic mechanical analysis** – The result of $T_g$ (Glass Transition Temperature) measurement by the DMA method at frequency includes storage modulus $E'$, loss modulus $E''$, complex modulus $E$, and loss factor $tan\ \delta$ [54]. One of the obtained temperatures is then considered to be $T_g$. The $T_g$ of selected composites and polymers was measured using DMA on the NETZSCH DMA 303 Eplexor device. For the measurement, samples with dimensions of 3 × 0.5 × 0.2 cm (100 % filling density, rectilinear pattern without hatching, layer height 0.1 mm) were prepared, clamped in a single cantilever clamp. For sample preparation, the nozzle with a diameter of 0.4 mm was replaced by a nozzle with a diameter of 0.8 mm. The heating rate was set to 3 K/min and the frequency to 1 Hz.

**Printability** – A filament testing machine is an in-house developed device by Nienhaus [55] at the Institute of Printing Science and Technology, Technical University

Darmstadt, which measures the necessary force needed to extrude filament through the hotend over the extrusion velocity and temperature. It enables a quick overview of achievable print speeds and recommended extrusion temperatures. The behavior of primary filaments at a temperature of 250 °C was observed.

# 5. Main results

**Primary composites** – In the first phase, a set of composites was created, which were tested in detail and served primarily as initial experiments for the design of other composites. The composition of individual composites is described in [56]. PC (Makrolon® 2407) was used as a matrix. Four types of fillers were used for these tests. The fillers used was h-BN (HeBoFill® CL-ADM 020) with a $D_{50}$ of 20 µm, EG (Expanded Graphite) (SIGRATHERM® GFG5) with a D50 of 5 µm, milled PCFs (Pitch-based Carbon Fibers) (Dialead K223HM) with a length of 50 µm and a diameter of 11 µm and Al (Aluminum Powder) (AlPRA) with a $D_{50}$ of 51.47 µm. In addition to different sizes, these fillers have various shapes, i.e., h-BN and EG flakes, PCFs fibers, and spherical Al particles, in order to create a continuous, thermally conductive network even at lower filling volumes. The individual ratios for the composites were designed taking into account the initial set of experiments, the properties of all fillers, and the general workability. These composites are based on a MIX of the aforementioned fillers and on h-BN itself. In this thesis, the composites are marked first by the matrix type and then by the filler or by a number indicating the mass percentage of the fillers, respectively the sum of the mass percentages of the fillers.

The composite with PC 20 BN_10 Al has the highest $k_{\perp}$, of up to 0.38 W m$^{-1}$ K$^{-1}$. It is likely due to the spherical Al particles, which retain high TC in all directions. For this reason, it is a composite that served as a default to increase k⊥ in other composites.

An almost 2-fold jump in TC from 20 MIX means that TC does not increase linearly with the addition of filler. The increase between 10 and 20 wt% of fillers is approximately half smaller and the increase between neat PC and 10 wt% of fillers is again approximately half smaller as well. From this point of view, it would be interesting to try whether it is also possible to create a composite with an even larger amount of fillers, e.g., 40 wt. %. We even tried to extrapolate the TC values and it turns out that the TC of the composite with 40 wt. % of the mixture of fillers could be somewhere around 2.35–2.55 W m$^{-1}$ K$^{-1}$ depending on the temperature. The dependence does indeed appear to be exponential.

The PC 40 MIX composite was fabricated so that the prediction could have been confirmed or refuted. The filler ratios were kept as for the PC 30 MIX composite. The real TC almost correlates with the extrapolated data but is ~14 % lower. It is also the maximum concentration of fillers in the polymer at which the composite is noticeably less printable. However, the character of exponential growth is distinct.

When h-BN-based filaments are compared at filament testing machine, relatively large standard deviations occur. It may be caused by agglomerates of h-BN, which are more difficult to push through and can temporarily or partially clog the nozzle. On the other hand, h-BN-based filaments need less extrusion force compared to neat PC and MIX-based composites, probably due to the lubricating properties of h-BN. However, there is no statistically significant difference between individual h-BN-based filaments, except for filament PC 20 BN_10 Al, which requires a higher extrusion force due to the incorporated Al. As for the filaments with a mixture of fillers, there are no such deviations. Basically, except for initial speeds, the more filler concentration is in the composite, the higher the extrusion force is required. However, this cannot be said for h-BN-based filaments. It can be confirmed, for example, by the fact that the material does not spontaneously flow out of the nozzle before printing. However, this phenomenon sometimes occurs with h-BN-based filaments, due to the lubricating properties of h-BN. Interestingly, these filaments have a similar required extrusion force as neat PC.

**Exchange of thermoplastic matrix** – In the next step, the same composition and filler ratios, but different polymers, were used for the 30 MIX composite. PA11 (Polyamide, unlabeled sample), PET (BASF, Ultrafuse®) and PETG (Poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate)) (Polymaker, PolyLite™) were tested. During the tests, $k_{\parallel}$ was measured and interestingly, the best TC was achieved using PET, TC is almost 1 W m$^{-1}$ K$^{-1}$ higher than for PC composite, depending on temperature, and the maximum TC measured is 2.408 W m$^{-1}$ K$^{-1}$ at 22.9 °C.

**Effect of filler used on TC** – Another set of experiments involved removing one filler used and observing the effect on the resulting TC. The PC 30 MIX composite served as the starting material, and $k_{\parallel}$ was measured. h-BN, PCFs, EG, and Al were successively removed (the composition of the composites is available in the dissertation [57]).

The most interesting finding is that after removing Al, $k_{\parallel}$ increases sharply, by almost 1 W m$^{-1}$ K$^{-1}$. The highest measured value was 2.477 W m$^{-1}$ K$^{-1}$ at 80 .7 °C. It can be caused by several reasons. Al is quickly covered in air with a thin layer of $Al_2O_3$ oxide, which is several times less thermally conductive than Al. The $Al_2O_3$ layer can thus serve as a barrier. Another reason may be that Al conducts heat mainly by electrons, while the rest of the fillers conduct heat by phonons, which may lead to heat loss at the interface. However, it is most likely that Al is not wetted by the PC matrix and separates nanometrically from it. EG behaves neutrally but helps workability. PCFs and h-BN have a positive overall effect. Therefore, this experiment disproves the theory that only the amount of filler affects the resulting TC, not the filler itself.

**Removal of Al from PET composites** – Since the PC-based composite without Al showed interesting properties, this approach was also tested in PET, where the PET 30 MIX composite is the best thermal conductor compared to the other polymers used. Other concentrations were also tested as part of the experiment; PET 35 MIX without Al and PET 40 MIX without Al. When using a PET matrix, composites are much easier to print than in the case of PC, probably due to the lower viscosity of the melt.

An interesting phenomenon is that although the filler mixture 30 MIX is the best thermal conductor in the PET matrix, when Al is removed, the PC composite conducts heat slightly better, but PET composites have subjectively better printability. However, the PET 40 MIX without Al composite is the best conductive composite in this research with a maximum $k_{\parallel}$ value of 2.941 W m$^{-1}$ K$^{-1}$ at 27.1 °C, which is approximately 12-fold higher TC value than neat PET. Since the values of $\alpha$ and $c_p$ are similar to those of PC composites, the density of the polymer also plays an important role here (PET has a higher density than PC).

Since the PET 35 MIX without Al composite is very well printable and, at the same time well thermally conductive (up to 2.454 W m$^{-1}$ K$^{-1}$), the synthesis of h-BN to OH-BN was carried out (described in detail in the dissertation [57]), and the same composite with OH-BN instead of h-BN was fabricated. As some research suggests, the OH-BN should wet the matrix better and conduct heat better. In this case, however, there was no increase in TC. The maximum values here are 2.031 W $m^{-1}$ $K^{-1}$. The degraded properties may probably be related to the unknown catalytic effect of OH-BN. However, this cannot be said definitively at the moment, and the chemical modification of h-BN will have to be further investigated in the future.

**Composites thermally conductive perpendicular to the printing direction** – In this section, composites, which are supposed to conduct heat more efficiently perpendicular to the printing direction, which is generally much more problematic, as small cavities occur between the individual lines layered on top of each other, which are filled with air, which is a thermal insulator are described here. To reduce the formation of voids, it can help to increase the extrusion multiplier to 1.2 so that 1.2 times as much material is extruded and the resulting voids are filled. Also, most fillers are subject to orientation during printing, and some thermally conductive fillers, e.g., graphite, conduct heat well only in the *a*-axis and are thermal insulators, or they are many times less thermally conductive in the *c*-axis [58]. It is also advisable to use an amorphous polymer here because when the crystals are oriented, as can occur in FFF 3D printing, the TC decreases perpendicular to the direction of orientation [16, 19] .

The best results from all tests were achieved at the composite PC 10 Al MIX_10 BN_10 Si_N, with an Al mix (3.33 wt. % Al with $D_{50}$ 51.47 μm; 3.33 wt. % Al with $D_{50}$ 9–11 μm from Nanografi; 3 .33 wt. % of flaky Al), further with 10 wt. % h-BN and 10 wt. % Si_N (fabricated filler based on highly doped silicon). Since the $k_{\perp}$ results of this composite were the highest, setting the extrusion multiplier to 1.2 was tried here. This setting led to a noticeable increase in $k_{\perp}$, by an average of 37.6 %, up to a value of 0.581 W $m^{-1}$ $K^{-1}$ at 140.9 °C. Although this is still a relatively low value, it is a significant shift compared to previous results published across the literature.

**Dynamic Mechanical Analysis** – DMA results show that the $T_g$ of most samples does not change (or changes only negligibly) due to the influence of fillers. Only for the sample

PC 10 Al MIX_10 BN_10 Si_N, Tg decreases by 3.7–8.8 °C, depending on which parameter Tg is derived from.

**Hardness** ***a) Shore D of primary composites*** – h-BN-based composites are generally less hard, and the hardness decreases significantly with the addition of more h-BN. The addition of Al to h-BN-based filaments increases the hardness significantly. Composites with a mixture of fillers are generally harder, and it cannot be stated that the hardness decreases with the addition of more fillers, but it is rather similar. Removal of PCFs results in slight hardness losses. Interestingly, some of these composites are even harder than neat PC. It can be attributed to some types of fillers, Al and PCFs are probably influential to higher hardness of final composite.

***b) Shore D of selected other composites*** – It is interesting that in the case of the PET matrix, the hardness decreases more significantly with the addition of fillers than in the case of the PC matrix. As can be expected, the removal of Al leads to a decrease in hardness. For PET, filler concentration also seems to be more important.

***c) ball indentation hardness of other composites*** – In some cases, less noticeable and more significant differences can be seen. However, this method can be considered more accurate even according to a subjective assessment because, for example, PET 35 MIX without Al with OH-BN composite is, at first glance, softer than the identical composite with non-hydroxylated h-BN. Furthermore, it makes sense that a composite with a higher filler concentration would be less hard than one with a lower concentration, which was confirmed by measurement here. On the other hand, it is curious that although neat PC is harder than neat PET here, the 30 MIX composite is harder in PET than in PC, which was the opposite for the Shore D method. It is, therefore, ideal to look at hardness comprehensively and draw conclusions about individual composites from both types of measurements.

**Tensile properties of** ***a) primary composites*** – As expected, filaments with a mixture of fillers generally have higher tensile strength than h-BN-based filaments. For h-BN-based filaments, the trend is that the more filler in the composite, the lower the tensile strength of the filaments, and the smaller the elongation of the filament before breaking. For these composites, the decrease is more significant, and the composite 30 BN has an ultimate tensile strength of only about 12.3 MPa. It is almost 5-fold less than a neat PC. The most likely reason is that the adhesion of h-BN to h-BN is less than that of PC to h-BN. This means the h-BN will delaminate and separate from the matrix even at slight stress. The addition of Al makes the filament tougher. MIX-based filaments are generally slightly more brittle than h-BN-based filaments but also have higher tensile strength. As expected, removing the PCFs reduces the ultimate tensile strength, but the composite becomes tougher. Overall, it could be concluded that PCFs are therefore a good choice for increasing the ultimate tensile strength of thermally conductive composites. The filament from neat PC is, with some exceptions tougher than the other filaments. It also has the highest ultimate tensile strength, so adding fillers reduces the tensile strength in all cases.

***b) other composites*** – The ultimate tensile strength decreases in the case of composites PC MIX without Al, PC 30 MIX, and PC 6 Al 1_6 Al 2_10 BN_10 Si_N by approximately half. For the PC 10 Al MIX_10 BN_10 Si_N composite, it decreases approximately by ¾, which can be attributed to the large amount of incorporated Al filler in the composite. All composites are also more brittle than unfilled PC. An interesting point is that removing Al from the 30 MIX composite leads to a slight increase in the brittleness of the composite.

When comparing the values of the PC 30 MIX composite and neat PC with the values measured on the Zwick Z050 instrument, the PC 30 MIX composite is more brittle than the neat PC and has slightly less than half the ultimate tensile strength. In the case of this measurement, it is little more than half. However, with a few percent deviations, the data can be considered comparable. However, the ultimate tensile strengths are more difficult to compare. While the PC 30 MIX composite tested on the Zwick Z050 instrument shows a tensile strength above 30 MPa, the same composite tested on the Instron 5500R shows an ultimate tensile strength of approximately 10 MPa lower. Likewise, the neat PC tested on the Zwick Z050 shows an ultimate tensile strength of less than 60 MPa, while the neat PC tested on the Instron 5500R whiless than 50 MPa. It can, therefore, be stated that the Instron 5500R gives slightly lower values than the Zwick Z050. The given values of the ultimate strength of unfilled PC in the material sheet are 66 MPa at a moving jaw speed of 50 mm/s [59], so it can be assumed that the values obtained from the Zwick Z050 device are closer to the actual values. Incorporating the filler into the PET matrix reduces the strength limit more significantly than in the case of the PC matrix. However, what is interesting is the fact that the fabricated composites are tougher than the neat polymer (but still brittle compared to PC composites). The only exception is the composite with OH-BN, where polymer degradation probably occurred, and the composite is more brittle. An interesting point is that the PC 30 MIX composite behaves oppositely to the PET 30 MIX composite, i.e., it becomes more brittle, while PET becomes tougher. In general, however, the ultimate tensile strength of these composites is relatively low, as the elongation of the filament compared to PC composites.

**SEM Analysis** – After 3D printing, in some samples for measuring $k_{\parallel}$, poor affinity between PC and h-BN was observed. It may result from the different surface free energy and, thus, the poor affinity between PC and h-BN. In addition, it was observed that in samples for measuring $k_{\parallel}$, voids between individually printed lines arise randomly and differently for each composite. The reason may be that h-BN migrates into the voids, and repulsive forces driven by the difference of surface free energy components push the polymer to the sides during printing, thereby increasing the voids, or it may cover the surface of PC and prevent fiber (lines) sintering, thereby enlarging the voids. A certain combination of fillers will likely support the adhesion of the layers, while others will suppress it.

For sample 30 MIX for measuring $k_{\parallel}$ with horizontal cut with the printing direction, it was observed whether there was a conductive connection between the individual fillers, i.e., if the fillers were touching (Figure 3). Smaller particles of EG with $D_{50}$ of 5 μm form a highly uniform distribution across the PC matrix. PCFs are, in most cases, oriented in the print direction, which was expected. Used Al particles are relatively large. Although such particles should have, according to Liu et al. [26], high intrinsic TC and low interfacial thermal resistance compared to smaller particles, there are still, even at 30 wt. % filler, not connected places where heat cannot be satisfactorily conducted. This is also contributed by h-BN, which is not visible at all on the cut surface. It is probably caused by the migration and h-BN does not participate in the conductive structure but has its heat transfer mechanism. Since dark spots can also be seen in the matrix prepared for measuring k‖ with a horizontal cut, it is also possible that the h-BN particles were removed from the surface by polishing. These spots would be tiny depressions after the h-BN since h-BN particles do not adhere well to the surface.

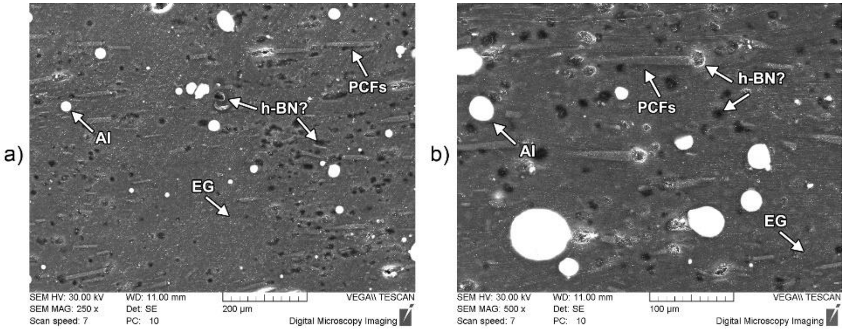

**Fig. 3:** Close-up thermally conductive network of PC 30 MIX for measuring $k_{\parallel}$ with horizontal cut with the printing direction when zoomed in a) 250×, b) 500×

A sample of PC 30 MIX without Al composite with a horizontal cut in the printing direction was observed in the next step. As can be seen from Figure 4a, the fillers are far less visible in the PC matrix here than in the case of the PC 30 MIX sample. In addition to the adhesion of the layers, the Al filler can also affect the overall spread of the composite melt. As with the PC 30 MIX composite, there are unconnected areas where heat cannot be conducted satisfactorily. Furthermore, h-BN is not visible. The initial theory for the PC 30 MIX composite was that the h-BN migrated into the voids between individual printed lines. However, such a phenomenon is unlikely here. Most likely, it is a aforementioned combination of migration into the cavities and poor adhesion of h-BN to PC; therefore, h-BN does not hold well on the surface and falls off during polishing.

In the next step, a sample PET 30 MIX composite with a horizontal cut in the printing direction was observed. As shown in Figure 4b, the fillers are far less visible in the PET matrix than in the case of the PC 30 MIX sample, and it appears that the fillers are covered by a thin layer of polymer. This could be due to an overall better wetting of the fillers by the PET matrix, which also explains the better TC of this composite. However, the consideration of better wetting can be refuted with the help of the literature, which reports a PET surface free energy of 42–44 mN/m [60-62], i.e., higher than for PC, and at the same time, PET has a smaller proportion of the polar component than PC [60]. Another explanation could be that molten PET has visibly lower viscosity at printing temperatures than molten PC, making the PET more spreadable and thus better encapsulating the fillers. It can also be explained from the point of view that PC has a bulky structural unit; terephthalate in PET is smaller than bisphenol in PC and will interfere less sterically. The sample processing may also have some effect, e.g., randomly varying polishing time and pressure; however, if it were to be the effect of this phenomenon alone, the result would probably not be so visibly different.

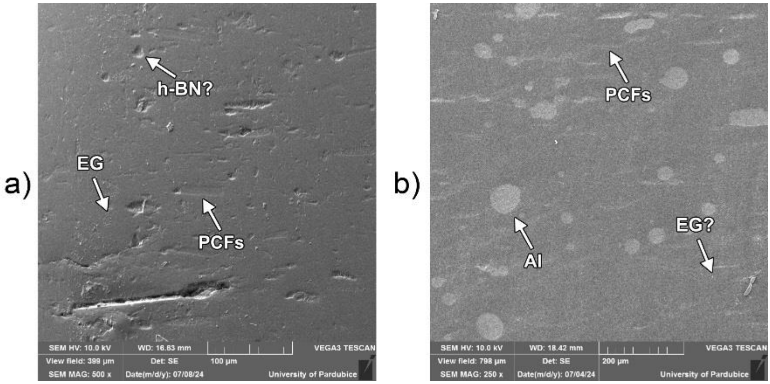

**Fig. 4:** Close-up thermally conductive network for measuring $k_{\parallel}$ with horizontal cut with the printing direction of a) PC 30 MIX without Al, b) PET 30 MIX

Even the PET 35 MIX without Al with OH-BN composite was subjected to SEM analysis in order to determine the differences between the composite with unmodified h-BN and with OH-BN. Here, there are already particles on the surface, and based on the shape of the particles, it can be assumed that these are OH-BN particles and that these particles are held on the surface of the polymer after chemical modification, probably by means of hydroxyl groups, because the modification should improve the affinity to the polymer. So, the original intention probably works; it is only necessary to clarify why the modification worsens the resulting properties (thermal-technical but also mechanical)

**X-ray Diffraction Analysis and Crystallinity and Orientation Analysis –** Most samples show no significant changes in structure, or the results are ambiguous. However, in the case of PETG samples, it was found that in all samples, the filler crystals are not oriented randomly, but certain crystal planes are preferred, which is most evident in h-BN. Thus, it confirms that filler orientation occurs in FFF 3D printing. Furthermore, it is visible that for PETG at a temperature of 125 °C, changes in the polymer itself occur on its wide band. Weak (but distinct) diffraction lines appear. The polymer begins to crystallize, and $\beta_X$ is 8–11 %. However, only the sample with fillers behaves this way; the control sample of neat polymer did not show any changes, so the filler behaves here as a nucleating agent.

# 6. Conclusion

The dissertation deals with preparing and evaluating composite materials with high thermal conductivity for printing 3D structures using additive manufacturing. The work summarizes the knowledge and results of research in this area and focuses primarily on the method of randomly distributed thermally conductive fillers in a thermoplastic matrix. However, related issues are also described, i.e., adhesion to the printing platform, thermal and technical properties of materials, division of polymers and composites, mechanical properties and characteristics, etc.

Based on the research and initial preparation of the composites, a hybrid filling method of randomly distributed thermally conductive fillers in a thermoplastic matrix was chosen for the experimental part, where a wide range of fillers and polymers such as PC, PET, PETG, and PA11 was used. Many different options have been tested and an interesting finding is how differently specific polymers behave with the same fillers. E.g., in the hybrid filling of h-BN, PCFs, EG, and Al, PC is more thermally conductive without Al, while in PET, Al has a rather positive effect.

When it comes to composites with increased $k_\parallel$, the best thermally conductive PC composites are PC 30 MIX without Al and PC 35 MIX without Al, which, however, is poorly printable, and the composite PC 40 MIX, which also has a problem with poor printability of FFF technology. Also interesting is the composite PC 30 MIX Cu instead of Al, where the Cu filler could find application in the future, especially in PET composites. Among the PET composites, the PET 30 MIX composite, the PET 35 MIX composites without Al, and PET 40 MIX without Al are very thermally conductive. Composite

PET 40 MIX without Al, is the most conductive composite created with $k_\parallel$ 2.941 W m$^{-1}$ K$^{-1}$ at 27.1 °C, which is approximately 12× higher $k_\parallel$ than in the case of neat PET. However, it is necessary to consider that PET-based composites have generally poorer mechanical properties and, with some exceptions, even more proportionally impaired to neat polymer than PC composites. The glass transition temperature was measured by DMA, and with one exception, composite PC 10 Al MIX_10 BN_10 Si_N, it does not change with the addition of filler. Similar behavior is expected for composites based on PETG; they only have a slightly worse $k_\parallel$ (compared to sample 30 MIX), and composites based on PA11 conduct heat the worst. It can be caused by many reasons, including, for example, the lowest density of the polymers used.

For composites with increased $k_\perp$, the thermally conductive composite is the best PC 10 Al MIX_10 BN_10 Si_N with the extrusion multiplier set to 1.2, where a $k_\perp$ of 0.581 W m$^{-1}$ K$^{-1}$ at 140.9 °C was achieved.

In further research, it is possible to follow up on the chemical modification of the fillers; in this work, the hydroxylation of h-BN led to unsuccessful results. In order to remove the top layer of $Al_2O_3$, chemical modification of the surface of Al particles could also be interesting from the TC point of view.

For coolers and heat exchangers operating on the principle of a radiator, it is important to mention that the printed element needs to get rid of heat and radiate it. The radiation ability of the material also plays a role here. On the one hand, an absolute black body is an ideal emitter. On the other hand, Wien's displacement law states that when a black body radiates, the maximum energy is emitted at a wavelength that decreases with increasing temperature. A warmer body thus emits radiation at shorter wavelengths. So, the material cools as it radiates. However, TC measurements across samples show that different composites perform best at different temperatures. An interesting solution could be to try, for specific applications with a known working temperature, using black paint as an emitter and creating a checkerboard where the “emitter/non-emitter” locations would be determined proportionally, e.g., using a bolometer.

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