

# The Relevance of Material and Processing Parameters on the Thermal Conductivity of Thermoplastic Composites

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**Thermoplastics composites show vast promise as an alternative for thermal management applications in the scope of the development of next-generation electronics and heat exchangers. Their low cost, reduced weight, and corrosion resistance make them an attractive replacer for traditionally used metals, in case their thermal conductivity (TC) can be sufficiently increased by designing the material (e.g., filler type and shape) and processing (e.g., dispersion quality, mixing, and shaping) parameters. In the present contribution, the relevance of both types of parameters is discussed, and guidelines are formulated for future research to increase the TC of thermoplastic polymer composites. POLYM. ENG. SCI., 58:466–474, 2018. © 2017 Society of Plastics Engineers**

## INTRODUCTION

As electronics are becoming faster and smaller, the efficient transfer of waste heat becomes an important aspect to ensure a good performance and a longer lifetime. Lightweight, cheap, thermal conductive, and electrical insulating polymer composites seem to be a promising material group for to resolve this challenge. In addition, manufacturers of, for example, heat exchangers for cars, heating, ventilation and air conditioning (HVAC), and desalination are interested in a better chemical resistance and fouling resistance [1] and have highlighted a higher degree of freedom for the design of polymeric composite materials compared to traditionally used metals. The wide variety of available polymers offers the opportunity to select the (co)polymer (blend) with chemical and physical properties suiting the intended application. However, these polymers require a far more improved thermal conductivity (TC) to truly compete with metals. Table 1 shows the TC of several metals used in current heat exchangers which are clearly lower than the TC values for popular commodity and engineering plastics. Fortunately, the TC of polymeric materials can be increased by adding fillers with a high intrinsic TC. It should be stressed that TC is an anisotropic property, meaning that the TC of a material can depend on the direction in which it is measured. Hexagonal boron nitride (hBN), for example, consists of stacked sheets, each sheet being built of covalently bonded boron and nitrogen atoms in a hexagonal shape, resembling the structure of graphite. The TC in the plane of a sheet possesses a value of 600

$W m^{-1} K^{-1}$ , while the through-plane value is 20 times lower [2]. Composites containing fillers with a high aspect ratio (AR), that is, the ratio of the length of the filler to its cross-sectional diameter, can also have anisotropic properties if these fillers are not efficiently distributed. Figure 1 represents a section of an injection molded sample containing fibrous fillers. Intuitively, it can be understood that these fillers will mainly show orientation in the direction of the flow during the processing step, that is, the in-plane direction. Perpendicular to the in-plane direction, through the thickness of the specimen, the through-plane or normal direction is defined. The direction perpendicular to both the in-plane and through-plane direction is known as the transverse direction [3].

Currently, main focus has been on the effect of the nature of the polymer matrix and the filler type, the filler shape, and filler quantity on the composite TC [1, 4–9]. Hence, the relevance of the material properties as such has been the key research angle. However, limited focus has been put on their interplay with the processing parameters, such as the differences induced by going from compression molding to injection molding processing. In the present work, a concise overview is first given on the TC measuring techniques and the state-of-the-art related to the relation between the material properties and the TC. Next it is elaborated in detail how the processing method allows to further regulate the TC of the composites.

## MEASURING AND PREDICTING THERMAL CONDUCTIVITY

It should be emphasized that care should be taken with respect to the method of TC measurement. Some measurement methods tend to produce unreliable results upon their use to characterize anisotropic materials. TC measurement methods such as the Heat Flow Meter [10] and the Hot Wire [11] are not designed to measure the TCs of anisotropic materials and can reproduce results that are not representative. While Laser Flash Apparatus [12] (LFA) and Guarded Heat Flow [13] measure the through-plane TC rather than average (mean value of different direction) TC, the ASTM standards allow to conclude that researchers should measure and interpret these results with care upon testing anisotropic materials. Recommended is the use of the Transient Plane Source [14] method, standardized by ISO [15] for plastics, homogenous, and anisotropic materials. The Transient Plane Source method is also able to measure the bulk, in-plane, and through-plane TC. Important is that samples are placed and measured correctly to avoid in-plane TC being confused with through-plane TC and vice versa.

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TABLE 1. TC of metals used in heat exchangers and TC of different polymers; room temperature.<sup>a</sup>

Metal	TC ( $\text{W m}^{-1} \text{K}^{-1}$ )	Plastic	TC ( $\text{W m}^{-1} \text{K}^{-1}$ )
Aluminum	247 [8]	High-density polyethylene (HDPE)	0.45–0.52 [9]
Copper	483 [8]	Polypropylene (PP)	0.14 [9]
Titanium	19 [74]	Polystyrene (PS)	0.14 [9]
Stainless steel 410	22 [74]	Polymethylmethacrylate (PMMA)	0.25 [9]
Alloy 600	15 [75]	Nylon-6.6 (PA6,6)	0.25 [9]
Alloy 800	12 [75]	Polyetheretherketone (PEEK)	0.25 [9]
Hastelloy C	13 [74]	Polyvinyl chloride (PVC)	0.17 [9]

<sup>a</sup>Polymers are considered to be homogenous.

There exist also numerous theoretical models for predicting the TC of a polymer-based composite material [16]. These theoretical models are yet not fully representative, as they assume for instance a continuous interface between the matrix and the filler, and a constant shape, size, and spatial distribution of the filler material or strongly depend on the orientation of the filler [16]. Higher filler loadings will result in a higher TC, but these loadings can pose a problem for processing [17] and the strength of the final composite [18, 19]. To better mathematically describe these aspects, an improved understanding of the relevance of the material and processing properties is thus needed, as covered in the next sections.

### RELEVANCE OF MATERIAL PROPERTIES

As polymer materials have no free electrons, the heat is transported as phonons which can be seen as thermal energy waves moving in a lattice configuration [20]. An elaborate and detailed explanation on the mechanism of thermal conductivity has been described in-depth by Burger et al. [7]. From a certain amount of filler onwards, an “endless” interconnected network of fillers is formed in the composite, which is called the percolation threshold. Unlike with electrical conductivity of polymer composites, the TC will not show a sharp increase at this point. From this point on, however, the TC of the composite will start increasing more rapidly, as all the extra fillers added will

thicken the existing network, easing the transport of heat waves [21]. But even upon blending in fillers, the resulting TC of the composite will still be low.

The main contributor to this behavior is the interfacial resistance within the composite. This results in a weak transfer of heat flow due to different phonon spectra of the matrix and filler, with additionally a weak contact at the interfaces causing the phonons to scatter back [22]. Even above the percolation threshold and thus high filler loadings, the TC of the composite will come nowhere near the value of the pure filler [23–25]. This is because the particles that do have direct contact with one another interact only with weak dispersion forces, that is, van der Waals forces and the small contact area between the filler particles also increases contact resistance [22]. For example, a single carbon nanotube is praised for its (theoretical) incredible TC of around  $5800 \text{ W m}^{-1} \text{K}^{-1}$  or even more, while a mat of several entangled nanotubes shows a TC of no more than  $35 \text{ W m}^{-1} \text{K}^{-1}$  [16, 17].

#### Filler Types

Popular fillers used for improving TC are the electrical conductive carbon nanotubes (CNTs), flake graphite, carbon fibers, and metal fillers such as copper, silver, gold, and others. As electrical conductivity is not allowed in electronic packaging, electrical insulating fillers with a high TC are applied. Boron nitride (BN), aluminum nitride (AlN), silicon carbide (SiC), and some oxidized metals that can be used as fillers for electronic packaging purposes. For industrial scale applications, cost is always an important parameter. For this reason, different forms of graphite seem the best candidates for applications that allow electrical conductivity as well. Besides the cost, other factors such as weight, corrosion resistance, and esthetics should also be considered when selecting the appropriate filler. BN could be considered as filler where the inherent black color of graphite-based composite would be less desirable. A more in-depth discussion on thermal conductive fillers can be found in other papers [1, 4, 8, 9].

#### Filler Shapes

It should be pointed out that the shape and size of fillers can have a more significant influence on the TC of the composite than the type of filler. While metals are sometimes described as bad fillers due to low TC of their composites compared with other fillers [26], it should be noted that in most of the reported experiments, the metals were powders, likely more or less spherical shaped, thus possessing a low AR. Nikhil et al. [27] showed that composites with gold nanofibers can display a TC of  $5 \text{ W m}^{-1} \text{K}^{-1}$ , even at filler amounts as low as 3 m%. Park et al. [28]

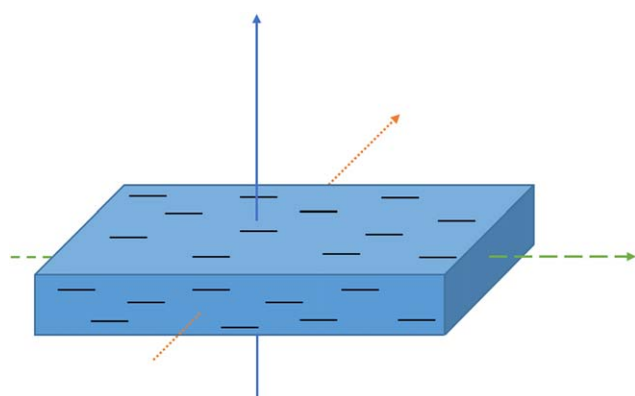


FIG. 1. Different directions of a composite with needle-like fillers. The green arrow represents the direction of polymer flow during processing and thus the main direction of filler orientation, which is also known as the in-plane direction. The blue full arrow represents the direction through the thickness of the specimen, better known as the through-plane direction. The orange dotted arrow represents the direction perpendicular on the in-plane and through-plane direction and is referred to as the transverse direction, represented by the green dashed arrow. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

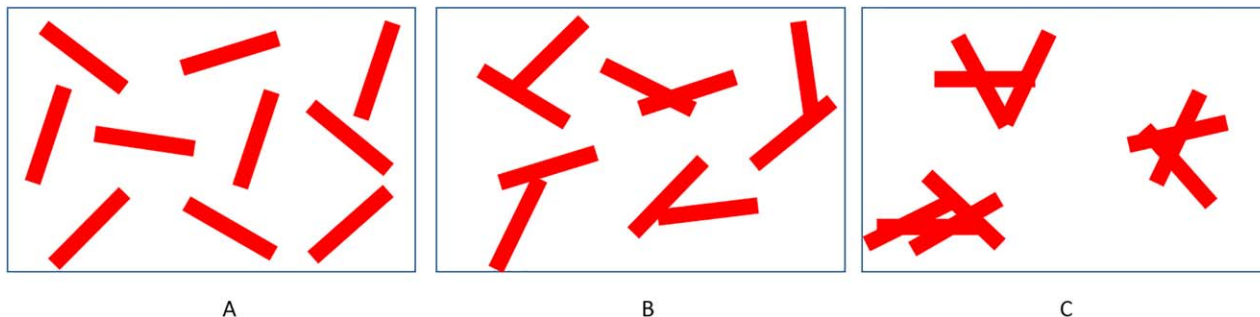


FIG. 2. A composite with high-AR fillers. Case A shows well-dispersed fillers; case B is less well dispersed; and case C has the worst dispersion and most agglomeration. Case B has the highest potential to achieve a high TC. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

indicated that by changing the shape of copper from sphere-like to flake-like an increase in TC can be noticed as well.

Bigg et al. [29] concluded in their study that spherical or isotropic irregular high TC fillers do not perform better once the TC of the filler reaches a value, which exceeds a factor 100 the TC of the matrix. For example, a spherical filler with a TC of  $50 \text{ W m}^{-1} \text{ K}^{-1}$  performs as well as a spherical filler with TC of  $100 \text{ W m}^{-1} \text{ K}^{-1}$  if the TC of the matrix is  $0.5 \text{ W m}^{-1} \text{ K}^{-1}$  or lower. This is however not the case for fillers with a higher aspect ratio, where the composite TC will increase with increasing TC of the filler material. In the same study, Bigg et al. [29] concluded that the increase in the composite TC with sphere-like fillers is limited to about 20 times the conductivity of the unfilled polymer. As that would put a low limit on the maximum TC of thermoplastic-based composites, it is recommended to use fillers with a higher AR.

A large AR also means that less filler will be needed to form an endlessly interconnected filler network, resulting in a higher TC at lower loading levels. As explained further, orientation of the filler due to processing can destroy this percolation network. It is generally accepted that larger particles result in better TC, since they have less matrix–filler interfaces thus less thermal interfacial resistance [30–33]. Some researchers found a higher TC for smaller particles, ascribing this to the ability of small particles being able to form better networks [20, 34]. On the other hand, Burger et al. [7] claim that this improved thermal conductive network does not make up for the extra thermal interfaces created by the many small filler particles. Besides that it is non-trivial to compare different results, as next to the filler size plenty of other factors also have their influence on TC. Even the making of smaller filler particles could change the AR, the general shape or the surface chemistry depending on the method. This makes it challenging even to compare some results from the same study.

More generally accepted is that soft filler particles perform better than rigid ones, as deformation of these particles allows a larger contact area between the particles [35]. This explains why talc, possessing a low intrinsic TC ( $10 \text{ W m}^{-1} \text{ K}^{-1}$  in-plane,  $1.8 \text{ W m}^{-1} \text{ K}^{-1}$  through-plane), still can achieve  $2 \text{ W m}^{-1} \text{ K}^{-1}$  in a polypropylene (PP)-talc 30 vol% blend [26].

## RELEVANCE OF PROCESSING PARAMETERS

The processing parameters for producing thermal conductive composites can have a huge effect on the TC which can be, as

previously mentioned, an anisotropic property. In this section, the effect of different mixing and shaping methods on the TC is discussed. The most important parameters for TC affected by mixing and further processing are the dispersion quality of the filler in the matrix, which is influenced by the presence of compatibilizers or coupling agents, and the final orientation of the filler after all processing steps. Special focus is also on the relevance of disruptive alignment.

### Dispersion Quality

Dispersion quality as defined on the scale of the filler is a difficult subject when it comes to TC. Figure 2 shows three different cases, all with the same “amount” of thermal conductive filler (red) in a nonthermal conductive matrix (white). Case A is characterized by a “perfect” dispersion, case B shows some dispersion characteristics but with a tendency to form agglomerates, while case C has a low dispersion quality with big clusters of filler and large gaps in between. In these examples, case B will most likely show the best TC in all directions. The semi-agglomeration creates a path for phonons to travel far distances in an unhindered manner. While the perfectly dispersed case might have a path with less distance to cover in the nonconductive matrix, it has far more interfaces to cross. This high number of interfaces might be a bigger obstacle for thermal transport than the little extra distance the phonons have to travel in an insulating matrix, making case B a better thermal conductor than A, despite being less dispersed. In case C, the gaps of nonconductive matrix between the filler agglomerations are too large to obtain a good TC. It should be kept in mind that this is a simplified explanation, since the intensity of the above trend can also depend on the thermal interfacial resistance, the contact resistance between fillers, the TC of the matrix itself and other factors. This reasoning is comparable with the reasoning why larger particles perform better than small particles at the same filler amount.

The orientation of fillers is more straightforward to explain. Flow in a molten polymer or polymer solution causes the filler to orientate. Figure 3 shows the filler distribution before and after such orientation. The TC will increase in the direction of the filler orientation, while the TC in the other directions will drop. It is clear that the thermal conductive path in the filler orientation direction has improved while the paths in the other

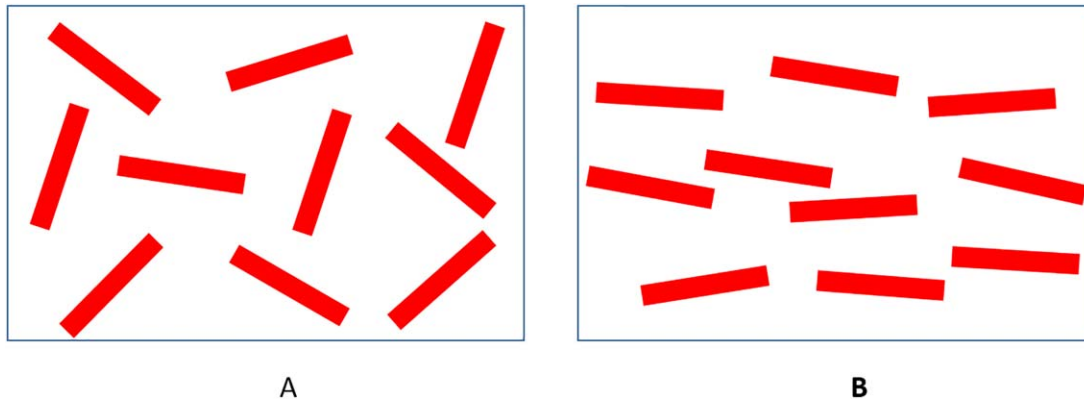


FIG. 3. Composite with high-AR filler. Case A shows the composite before processing; case B is after processing in which polymer flow has occurred. Fillers align in the flow direction, resulting in an anisotropic material and show improved TC in this flow direction. The sample before processing will have isotropic properties. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

directions have worsened, as it has more interfaces to cross and longer travel distances in the nonconductive matrix.

It is important to realize that compatibilizers or coupling agents can improve the interaction between the filler and the matrix and can increase the dispersion quality of the filler. As thermal interfacial resistance is a main cause for low TC, the use of compatibilizers and coupling agents seem to be a solution to improve the TC. The main advantage of coupling agents and compatibilizers is that the TC of the composite can be increased without increasing the filler volume. Several publications have confirmed that compatibilizers in combination with an epoxy [36] or a thermoplastic [31, 37–39] matrix increase the composite TC values. On the other hand, severe chemical reactions of filler materials, such as oxidation of CNTs, can damage the surface causing a lower TC of the filler [40]. This can result in a lower composite TC despite a better matrix–filler interaction.

Zhang et al. [38] tested the effect of compatibilizers on the TC of injection molded high-density polyethylene (HDPE) with  $\text{Al}_2\text{O}_3$  fibers as filler. The in-plane TC of the composites with compatibilizer was higher than the in-plane TC of the composite without compatibilizer. In contrast, the through-plane values of composites with compatibilizer were lower than the through-plane conductivity of the composite without compatibilizers. All the in-plane TC values were higher than the through-plane TC values. The general trend of higher in-plane values can be explained by the filler being orientated in the flow-direction, resulting in higher in-plane conductivity. Scanning electron microscopy (SEM) showed a better adhesion between matrix and filler upon using compatibilizers, which should normally improve TC. However, due to the strong matrix–filler adhesion with compatibilizers, the fillers showed even more orientation in the injection direction. The composite without coupling agent also showed alignment in the injection direction, but less explicit than the composite with compatibilizers. These phenomena can explain the increase in in-plane conductivity and decrease in through-plane conductivity with compatibilizers. Owing to the orientation phenomena of the filler, the effect of better interfacial contact between filler and matrix on TC cannot be exploited.

Ha et al. [39] pointed out that an improved dispersion quality can have a negative effect on TC in case additional interaction

processes are active. These authors combined graphene nanoplatelets (GNPs) with regular and carboxyl-CNT. The composite TC with surface-treated CNTs was lower than that of the composite with the regular CNTs. Regular CNTs form thermal conductive bridges between the different GNPs, increasing the TC of the composite. However, the functionalized CNTs show more attraction to the matrix and will be better dispersed, thus not forming a bridge between the other fillers. The damage to the nanotubes because of the functionalization process might also play part in the TC lowering. This bridge-formation effect is seen in many combinations of CNTs with the second filler [41–45] and shows great promise for improving the TC of polymer composites. The CNTs also seem to be severely less affected by polymer flow, thus show less orientation in the flow direction after processing [44].

#### Mixing

To obtain a uniformly dispersed composite compound, the matrix and filler material need to be well-mixed. The most commonly used mixing techniques in research laboratories are explained in this subsection. A differentiation can be made between melt, solution, and a powder mixing.

In a melt-mixing process, the polymer is heated above its melting temperature and mixed with the filler material due to shear in the mixing equipment [46]. Melt mixing is the preferred mixing method in industry because of its cost efficiency and low environmental impact [47]. Commonly used machines for melt mixing in industry are extruders and compounders, which are available in different shapes and sizes. The material can be extruded in filaments and granulated to use for further processing [48, 49]. Alternatively, the molten material can directly be extruded in tubes or plates [50]. Many researchers combine the use of “batch” melt mixers (instead of extrusion) followed by granulation for further processing [21, 48, 49]. This allows a longer mixing time, thus an increase of the dispersion quality of the filler. Melt mixing has some drawbacks despite being the most commonly used industrial mixing method. Because of the increase in dynamic viscosity, the amount of filler that can be blended in is limited. Fillers with high AR and irregular shapes

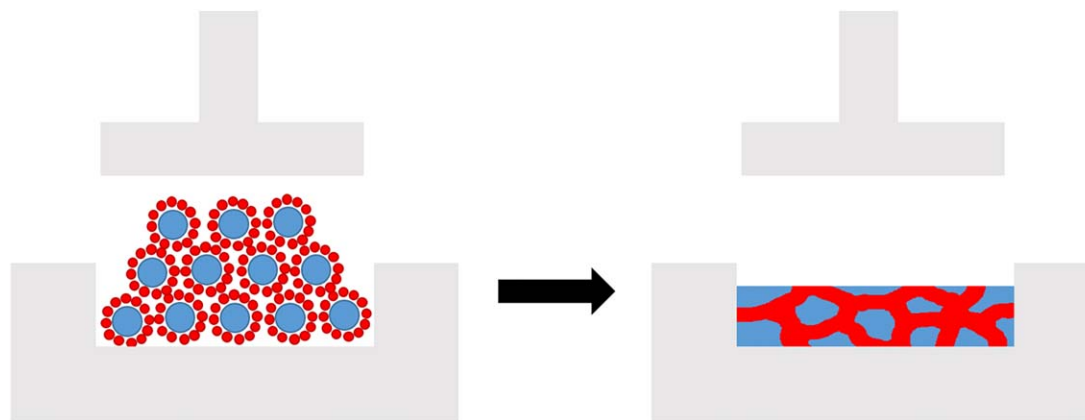


FIG. 4. By “coating” the surface or by using powder mixtures instead of well-dispersed fillers, thick thermal conductive paths can remain after thermoforming. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

cause more shear than sphere-shaped fillers, making it harder to blend in higher amounts of fillers with a high AR. Compared with other mixing techniques, melt mixing performs rather poor on the dispersion quality of filler; especially with nanofillers. After melt mixing, these nanoscaled fillers show strong agglomerated bundles rather than being well dispersed (cf. case C in Fig. 2). Large fillers will likely be damaged and shortened after the extrusion process due to the shear forces [51].

In contrast, in solution mixing, a solvent is added to the polymer to lower the dynamic viscosity and stirred until the polymer is completely dissolved. The filler material can be directly added in the polymer solution or dispersed separately in the solvent before being added to the polymer solution. Ultrasound treatment can be used to improve the dispersion quality by breaking agglomeration of small filler particles [46, 52]. The solution is then cast out on a surface and the solvent is evaporated mostly by increased temperature or reduced pressure, leaving behind a composite film. Alternatively, the composite can be precipitated by adding a nonsolvent to the polymer solution [44, 53]. As with melt mixing, the precipitated composite can be used in further processing steps. Composite films can be left intact, stacked for compression molding or granulated for extrusion, injection molding, or compression molding. Compared with melt mixing, solution compounding shows excellent dispersion quality and leaves the fillers undamaged as there are no excessive shear forces. Despite that this technique can drastically reduce agglomeration of fillers, it is overall less favorable in industry because of the environmental impact, higher costs, and health risks [21, 47].

Finally, powder mixing or dry mixing [20, 54] is the mixing of filler and polymer at temperatures lower than the melting point of the polymer. This results in extremely weak dispersions. Equipments such as a ball mill can improve contact between filler and polymer. Despite this inherent poor dispersion, creative use of these techniques can provide quite good results by changing the shape of the filler, which as explained above allows to alter the TC [28]. Too long mixing times result, however, in too small particles and a lower TC [28].

### Shaping

After the mixing step, the composite compound requires a finishing step to give it the desired shape. The processing

technique used in this step will mainly determine the final filler alignment, thus anisotropy of the material. Processing methods involving a high shear intensity, such as injection molding and extrusion, can although possibly damage (shorten) the filler [55, 56]. In what follows, the key characteristics of shaping via compression molding, solution casting, injection molding, pultrusion, extrusion, and 3D-printing are discussed.

In compression molding, a mold is filled with polymer-based materials, combined with other materials if desired. This model has commonly a disc or plate-shaped shape for property test samples. The mold is heated up above the melting point of the polymer matrix and closed under increased pressure for a few minutes to several hours. The mold can be filled with granules of a pre-mixed composite [2, 57], solution-cast films [58, 59] or even “sandwich” structures of alternately polymer layers and fibers or other materials [60, 61]. Fibers can be aligned in a controlled manner to improve the materials properties in the desired directions. Though compression molding is widely used by researchers, it is less seen on an industrial scale due to long processing times, nonconsistent quality, limited freedom in part design, and in some cases requirement of manual labor [62]. If a powder mixture is compression molded, the resulting product will remain heterogeneous, showing filler-rich and filler-poor regions. This can be useful for creating controlled thermal conductive pathways in the composite [54]. Large polymeric particles can be covered with a thin layer of thermal conductive filler, resulting in good conductive pathways after compression molding. This process is sketched in Fig. 4. However, the resulting material will likely show very low strength and will break easily around the filler-rich zones. When pellets of a premixed composite are used in compression molding, it will likely result in a sample with isotropic properties. This is because that during the compression molding process, there is little to no flow of the molten matrix, thus no significant orientation of fillers, resulting in an isotropic material.

Cast films obtained from solution mixing after solvent evaporation can be used to test material characteristics [34, 41]. Besides that the cast film will hardly have any practical applications without further processing. As explained above, the film casting process is too polluting and hard to scale-up for profitable industrial mass production. Film blowing or film extrusion

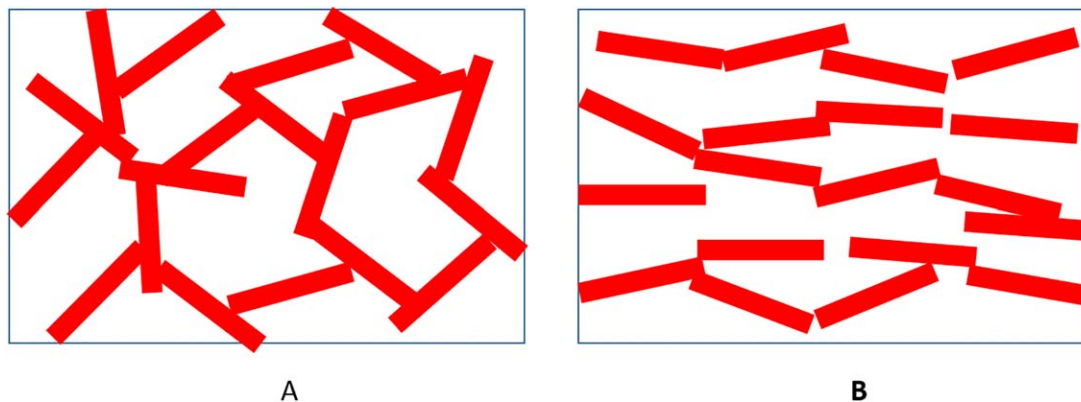


FIG. 5. Simplified version of filler orientation before and after injection molding. The through-plane conductivity will drop as the percolation network is broken. [Color figure can be viewed at wileyonlinelibrary.com]

is preferred for industrial scale film production. Note also that characteristics of the same composite can be significantly different when processed via another method. Fiber size, for instance, can be significantly reduced by processing via extrusion or injection [48, 63] while film casting leaves the fibers/filler untouched.

Injection molding is a widely used and popular method for shaping polymers and thus also for the production of composite materials. At the first approximation, it follows that the fillers align with the flow direction during the injection. Because of this, samples produced by injection molding will generally show a much higher through-plane TC than in-plane conductivity [25, 38, 44]. Changing parameters of the injection molding process can however influence the filler orientation [64], likely also changing the TC of the composite. Note that because of the increased TC, cycle times can be reduced as the parts will cool faster. On the other hand, this might have a negative impact on other factors such as crystallinity [65]. Injection molding of a composite can “break” an existing thermal conductive network achieved by blending filler and matrix, as shown in Fig. 5 (still assuming the alignment hypothesis). The random orientated fillers before injection molding (A) form a percolation network throughout the whole sample. After processing, fillers align in the flow direction and break the through-plane percolation network (B), though the in-plane network might end up better. This mostly results in a better in-plane TC and a worse through-plane TC. The reality, however, is more complicated. Depending on the type of polymer used, design of the part, amount of fillers and processing parameters, filler alignment cannot be complete. The “skin-core model”, that is, a model developed for specific fiber-reinforced polymers, shows that fibers close to the wall will have orientation in the flow direction, while the core has fibers orientated perpendicular with the flow direction (transverse direction) or a more random orientation [64, 66, 67]. Manipulating the orientation of these fibers will likely change the TC as well, though it is yet to be investigated how significant the impact will be.

To further highlight the difference between the above discussed processing methods specific focus is put on the work of Takahashi et al. [68] who clearly demonstrated that the mixing and processing methods have a severe impact on the TC. These authors made composites of BN (plate-like shape) and PP. One

sample was prepared by melt mixing followed by injection molding, the second sample was prepared by solution mixing followed by compression molding. As seen in Fig. 6, the sample prepared by melt mixing and compression molding showed overall a higher TC. This is mainly because of the filler orientation caused by the injection molding process.

Furthermore, extrusion is widely used in industry for the production of polymer sheets, pipes, films, and other continuous profiles. Because of the flow and shear, fillers will align in the direction of the extrusion, resulting in a high in-plane TC and lower through-plane conductivity [22]. Owing to shear in the melting step, large fillers particles could however break. Much similar to extrusion, pultrusion also allows the production of continuous profiles, but reinforced with continuous fibers. Although as almost no experiments have been performed with this technique for thermal conductive composites, it can be expected that using thermal conductive continue reinforced

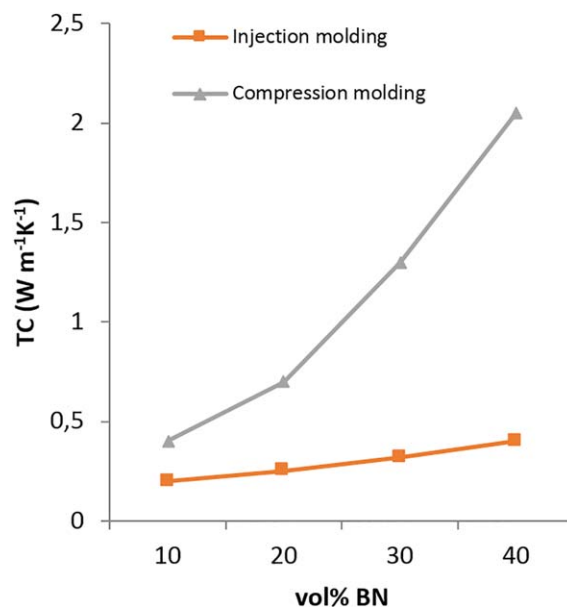


FIG. 6. TC of BN-filled PP by melt mixing/compression molding and by solution/mixing injection molding [68]. [Color figure can be viewed at wileyonlinelibrary.com]

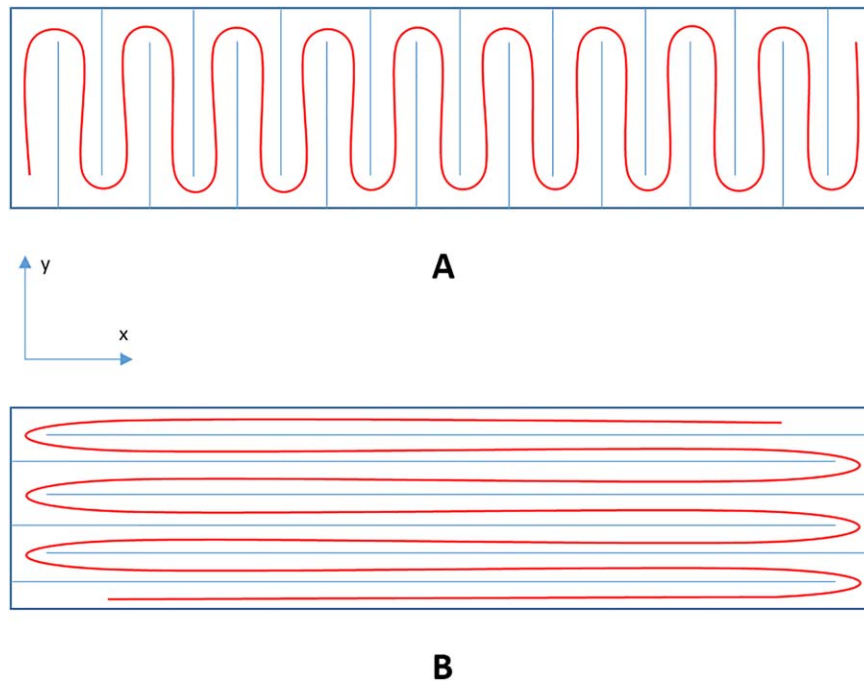


FIG. 7. How the printing pattern of 3D printed parts can influence the direction of high thermal conductivity. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

fibers—such as carbon fibers—will result in a profile with excellent in-plane thermal performances but a rather low through-plane TC. Note that the combination of thermal conductive fibers with thermal conductive composite matrices could be interesting to investigate.

Related to conventional extrusion is also extrusion-based 3D-printing. Despite that there has been few to no research activities on the improved thermal conductivity of 3D printed parts, this recent emerged technique could be of value for producing subcomponents for, for example, heat exchangers. A thermal conductive polymeric composite with a continuous carbon fiber reinforcement could be printed to achieve a good TC. Besides the possibility of making complex shapes without requiring an expensive mold, printing patterns could be adjusted to improve the conductivity in a certain direction. Figure 7 shows two different theoretical printing patterns. The curved red line is a continuous fiber reinforcement and shows the path of the print head. It is clear that, on the condition that the fiber is a thermal conductive material such as a carbon fiber, the printing pattern can adjust the direction of high TC. Example A will have an improved TC in the  $y$ -direction while example B will show a higher TC in the  $x$  direction. It is worthwhile in the future to investigate the actual TC improvement, the strength, and other properties of 3-D printed materials and whether this production method could be industrial applicable.

It should be further reminded that industry prefers the use of melt-mixing equipment and injection-molding or extrusion for processing polymeric materials. Researchers focusing on lab-scale production typically prefer solution mixing and/or compression molding with long residence times, generally resulting in higher TC values. These long processing times are not economically feasible, thus results should be interpreted with care when planning on upscaling or applying on industrial processes.

#### Disrupting Alignment

Some applications require a high through-plane TC rather than a high in-plane TC. As fillers are mostly oriented in the in-plane direction after injection molding or extrusion, disrupting this alignment can increase the through-plane TC at a cost of the in-plane TC. For example, Tian et al. [69] suggest the combination of sphere-like aluminum (Al) fillers to disrupt the in-plane alignment of the graphite nanoplatelets (GNP) for the use in thin thermal interface materials. Combining 4.5 m% GNP with 44.5 m% Al resulted in a TC of  $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ , while only 4.5 m% GNP or 44.5 m% Al resulted in a TC of, respectively, 0.6 and  $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ . Furthermore, Yuan et al. [70] and Lin et al. [71] tried to change the alignment of hBN in an epoxy matrix by coating the BN with ferromagnetic nanoparticles and applying a magnetic field. Despite the increase of the through-plane TC of this technique, it is doubtful whether this would work for thermoplastic matrices. The high dynamic viscosity of the matrix would likely prevent the fillers from aligning with the magnetic field, considering the dynamic viscosity of the uncured epoxy system with 20 m% BN filler was already too high to align the platelets [71].

In addition, Xu et al. [72] successfully increased the through-plane TC of injection-molded flake-graphite-filled polyamide 6 (PA6) in combination with PP. As PP and PA6 are immiscible, the PP formed droplets in the PA6 matrix. These droplets slightly changed the orientation of the flake-shaped filler in the matrix. Too large droplets will separate the flakes, preventing a dense thermal conductive network. Too small droplets on the other hand will have no effect on the filler orientation. The size of the droplets could be controlled by the compatibilizer concentration. The optimal result was gained by adding 1 m% compatibilizer to a 50 mt% PA6 matrix with 20 m% PP and 30 m% flake graphite composite, resulting in a through-plane TC of

2.703 W m<sup>-1</sup> K<sup>-1</sup>. The TC of only PA6 with 30 m% flake graphite was 2.03 W m<sup>-1</sup> K<sup>-1</sup> and the TC of PA6, PP, and flake graphite without compatibilizer was 2.23 W m<sup>-1</sup> K<sup>-1</sup>.

It can be concluded that any further advancement in filler orientation techniques could imply a great step forward in producing high through-plane thermal conductive composites [70]. A few techniques have been tested on experimental scale, such as magnetic alignment in thermosets and the use of foaming agents, but their industrial applicability for thermoplastics remains questionable [51, 70] or is yet to be tested on TC [73].

## CONCLUSIONS

This contribution thoroughly reviews the current state-of-the-art in the field of thermal conductivity of thermoplastic composites. Particular emphasis was placed on the material design (e.g., filler type and shape), the material anisotropy, and its relation to conventional processing (e.g., dispersion quality, mixing, and shaping).

Related to measuring the thermal conductivity of composites, it should be stressed that not all techniques are recommended for anisotropic materials. Besides that, it is important to notice that the bulk thermal conductivity of an anisotropic material has no relevance. In-plane and through-plane values should rather be measured and it should be clearly indicated whether the value given is an in-plane or through-plane value.

As spherical fillers show little to no promise in significantly increasing the TC of thermoplastics, sufficiently large fillers with a high aspect ratio (AR) are recommended. Besides that fillers with a high AR require a lower loading level to achieve at least the percolation threshold.

The mixing during the processing step can also have a significant influence on the composite TC, as it determines the dispersion quality and the (an)isotropic behavior. A perfect dispersion is not always desirable because of the increased number of matrix–filler interfaces which can cause a drop in TC. Close and dense packs of fillers are also not recommended because of the large distance in the nonconductive matrix that has to be crossed. Ideally, a relatively unhindered network of thermal conductive filler should thus be formed throughout the matrix. Further processing or shaping can cause anisotropy, where the composite will show a higher TC in the direction of the flow because of the filler orientation within the limit even a destruction of the percolation network.

In many cases, heat sinks for electronics and others can be designed in such a manner that the heat flow has the same direction as the orientation of the fibers, thus leading to a high in-plane TC. On the other hand, subcomponents for tube or plate-based heat exchangers require a high through-plane TC. Higher through-plane conductivity with extrusion or injection molding can be achieved by disrupting the alignment of fillers. Adding spherical fillers or adding an immiscible second polymer aids this process. Other techniques have been being tested but currently show little potential for being adapted on an industrial scale. It is clear that more research activities are required to achieve high through-plane TC values for injection molding and extrusion applications. On the other hand, the combination of the regular thermal conductive fillers such as graphite or BN with CNTs seems already promising as CNTs are less affected by the flow orientation. Furthermore, compression molding shows a high through-plane TC as fillers do

not display orientation but this technique is unfortunately less industrially attractive.

Coupling agents and compatibilizers can increase the TC by reducing the thermal interfacial resistance and by increasing the dispersion quality of the filler. On the other hand, very pronounced dispersions can decrease the overall TC by breaking thermal conductive bridges and the chemical bonding process of the coupling agent can reduce the TC of the filler itself. For injection and extrusion applications, the in-plane TC can increase due to a better filler orientation, while the through-plane TC is expected to decrease.

Overall it can be concluded that there are still uncertainties when it comes to unambiguously quantifying the TC of composites. This is because of the numerous factors influencing the TC, often depending on one another. This makes it very tedious to study one aspect without unintentionally changing another parameter. While high in-plane values are already achievable, the improvement of through-plane TC after injection molding or extrusion needs more attention in future research.

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