Increased thermal conductivity of thermoplastic composites by manipulation of filler orientation

Tom Wieme[1], Berten Augustyns[1]; Dagmar D'Hooge[2,3]; Ludwig Cardon[1]
[1]Centre for Polymer and Material Technologies, Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 915, 9052 Zwijnaarde, Belgium

[2]Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 914, Zwijnaarde, Ghent B-9052, Belgium

3Centre for Textile Science and Engineering, Department of Materials, Textiles and Chemical Engineering, Ghent University, Technologiepark 907, Zwijnaarde, Ghent B-9052, Belgium

ABSTRACT: In order to make thermoplastics more attractive various heat management applications, the thermal conductivity has to be improved. For most heat exchanger applications, the through-plane thermal conductivity (TC) is of higher importance for increased efficiency. This study aims to improve the through-plane thermal conductivity of PA6-graphite based composites by injection molding them with chemical foaming agents (CFA's). The thermal conductivity in both the in-plane and through-plane direction was measured for virgin PA6, PA6 with 10, 20 and 30 wt% of graphite and the same composites with an added 3 wt% CFA. Both in- and through-plane TC was found to decrease by adding 3 wt% of foaming agents to a 0, 10 and 20 wt% graphite composite due to the insulating effect of trapped gas. The composite with 30 wt% of graphite with CFA showed an increased through-plane TC from 0.67 W/mK to 0.82 W/mK. This increase was caused by the adjusted orientation of the fibers by the expansion of the foaming agent. Tensile testing showed decreased yield strength with increasing amounts of fillers and foaming agents. With further optimization, a combination of fillers and foaming agents in thermoplastics could prove to be valuable in certain thermal management applications.

1 INTRODUCTION

Increased thermal conductivity of intrinsically thermally insulating polymer resins could open a variety of new markets in the polymers industry. The heat exchanger market, strongly dominated by heavy, expensive and corrosion vulnerable metals, could make valuable use of these new kinds of polymers. Electronics packing, like LED housing, could vastly improve the operation lifetime by dispersing waste heat. Research has shown that increased thermal conductivity can be achieved by adding thermal conductive fillers to the matrix[1–3]. Here, it is of utter importance to take into account the anisotropy after processing. The thermal conductivity in the direction of the polymer flow (in-plane thermal conductivity) will reveal a far higher thermal conductivity compared with the direction perpendicular to the flow (through-plane thermal conductivity)[4,5]. While certain designs of heat sinks could benefit more from a high in-plane thermal conductivity[6], the majority of applications require an increased through-plane thermal conductivity for improved efficiency (e.g. shell-tube heat exchangers). Though manifold of research has already been conducted on this topic, the best results can only be achieved by either adding stupendous amounts of fillers to the matrix or by compression molding the composites[7]. Humongous amounts of fillers can cause a severe decline in mechanical properties and hinder processing because of increased shear[8]. Compression molding, on the other hand, is a less favorable technique when it comes to production efficiency, notably for more complex shapes or continuous profiles, where respectively injection molding and extrusion are more common. Because of the lack of/low flow during compression molding (compared with injection or extrusion), fillers won't orientate much and thus won't show such anisotropic behavior. In order to achieve an enhanced thermal conductivity in the through-plane direction with low filler content and injection molding or extrusion, the filler orientation must be manipulated. Filler orientation by magnetic fields or electrostatic charges have proven to improve thermal conductivity of thermosetting composites[9,10]. However, the high viscosity of thermoplastics prevents these techniques from being used.

This research focuses on increasing the through-plane thermal conductivity of injection molded Polamide 6 (PA6)-graphite composites by using foaming agents to counter the alignment of the fillers caused by the polymer flow. Besides an increased through-plane thermal conductivity, the weight reduction caused by the foaming agents can be beneficial for several applications like automotive.

2 EXPERIMENTAL

2.1 *Materials*

Injection-grade Polyamide 6 (Technyl C 230 Natural, Solvay) was employed as matrix material. Graphite filler (Timrex KS500, Imerys) with and average size of 250 microns was used as thermal conductive filler. Endothermic carbon dioxide foaming agent (Cell Span CFA 897) was kindly provide by AxiPolymer.

2.2 *Sample preparation*

PA6 and graphite dried at 80°C overnight prior to compounding. Compounds of 10, 20 and 30 weightpercentage (wt%) graphite-PA6 were prepared by compounding in a twin-screw compounder (in-house build). The filament from the compounder was cooled in a water bath, chopped in pellets and dried overnight at 80°C. The dried pellets were dry mixed with 3 wt% foaming agents. An Engel e-victory 28T injection molding system (Engel Austria) was used to produce the test specimen. The mold temperature was kept at 75°C for all samples. The mold was of the cold-runner type, producing dogbones as described in ISO 527-2 specimen type 1A and impact bars with dimensions as described in ISO 179-1 type 1. No holding pressure was applied for the samples containing CFA's. The compositions of the different samples made are shown in table 1.

For thermal conductivity measurements, the wide part of the dogbones closest to the injection gate was cut off and sanded (grit 500) to assure good contact between the sensor and sample. The final dimensions of the samples for measuring thermal conductivity were 20mm*30mm*4mm. Samples of 10mm*10mm*4mm were cut out of the narrow part of the dogbone and sanded (grit 500) for measurement of the heat capacity. Prior to further measuring, all the samples were conditioned at 50% relative humidity at 23°C for at least one week.

Table 1: composition of different samples

Name	Graphite (wt%)	Foaming agent (wt%)
0-0	0	0
10-0	10	0
20-0	20	0
30-0	30	0
0-3	0	3
10-3	10	3
20-3	20	3
30-3	30	3

2.3 *Characterization*

The thermal conductivity of the samples were determined using the Transient Plain Source method with a Hot Disk TPS 2500S (Hot Disk Sweden).This allowed the measurement of in-plane and through-plane thermal conductivity of the samples. The nickel-kapton sensor used had a diameter of 3.189 mm. Double-sided measurements were conducted for improved accuracy. Measurement time and power output of the sensor varied from sample to sampe.

Heat capacity was measured using the Gold cell reference module on the Hot Disk TPS 2500S. A measurement time of 40 seconds was used during these measurements. Heat capacity values are required to calculate anisotropic thermal conductivity using the transient plane source method.

Density of the samples were determined by measuring weight in air and ethanol with a known density on a Precisa XR 205SM-DR (Precisa Switzerland). The density and mass are required to calculate the heat capacity using the gold cell reference module on the Hot Disk TPS 2500S.

Scanning Electron Microscopy images were taken on a Phenom G1 SEM (PhenomWorld, The Netherlands). The porous sample holder allowed images to be taken without requiring a gold coating.

Tensile tests were performend on an Instron 5565 tensile bench (Instron USA). An extension meter was employed to determine the Young modulus at a tensile speed of 1 mm/min. The extension meter was removed after an extension of 0.3% and the test continued at a speed of 50 mm/min. The modulus was calculated as the slope between 0.05 and 0.25% strain within the Bluehill 2 software (Instron USA).

3 RESULTS

3.1 *Heat capacity and density*

The results for the density and heat capacity are shown in table 2. A rather obvious trend of decreasing density when comparing samples with and without foaming agent can be noticed, while the density increases slightly with increasing amount of graphite.

Table 2: density and specific heat of the different compounds

Name	Density (g/cm^3)	Specific heat (MJ/m^3K)
0-0	1.110	1.6821
10-0	1.164	1.8108
20-0	1.230	1.8783
30-0	1.297	1.558
0-3	0.948	1.4658
10-3	1.007	1.5986
20-3	1.186	1.8264
30-3	1.211	1.7430

3.2 *Thermal conductivity*

The through-plane and in-plane thermal conductivity for the different compounds are displayed in figure 1.

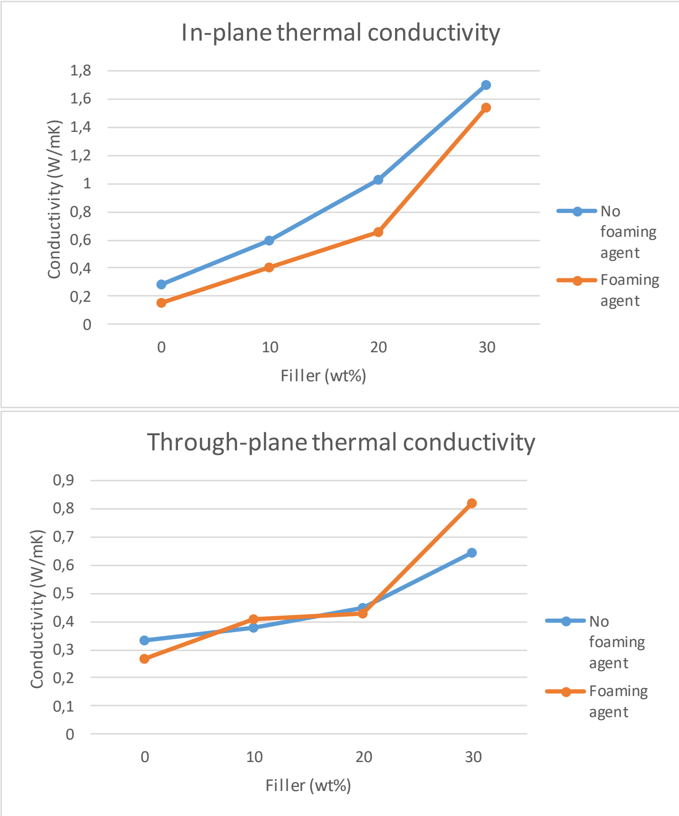

Figure 1. In-plane and through-plane thermal conductivity of the composites

Polyamide without filler shows an increasing thermal conductivity with increasing amount of graphite. The in-plane thermal conductivity increases more rapidly than the through-plane thermal conductivity. This phenome has two major causes, all related to alignment of the fillers due to the flow during processing. First of all, the graphite filler itself is anisotropic, with a higher thermal conductivity in the layer direction compared to the interlayer direction. Secondly, the in-layer free path is far longer than the through-layer path, meaning less matrix-filler interfaces and shorter distances through the non-conductive polymer, thus a better thermal conductivity in that direction. These effects are visualized in figure 2.

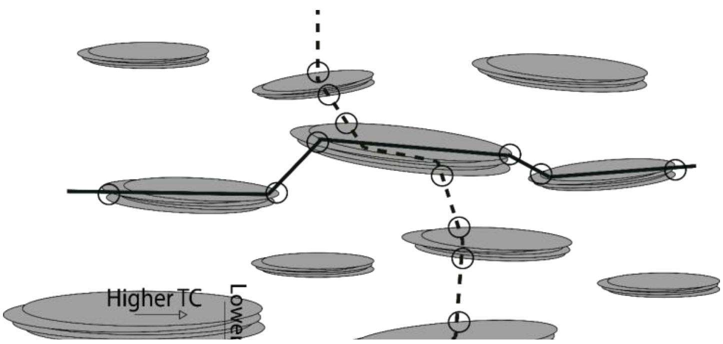

Figure 2. The orientation of the fillers after injection molding can easily explain the high in-plane and low through-plane thermal conductivity

The most efficient thermal paths for in-plane and through-plane conduction are drawn in straight line and dotted line respectively. Each transition from interface is drawn encircled.

Adding foaming agents causes a general decrease in thermal conductivity because of the insulating effect of (trapped) gas, which can clearly be seen in the virgin material with/without foaming agents. The through-plane thermal conductivity of 10 and 20 wt% of fillers remains more or less the same, despites the insulating effect of gas. For 30 wt% of graphite, a clear increase in thermal conductivity can be noticed for the compound with foaming agent. The in-plane thermal conductivity for the foaming agent compounds remain lower.

The increase in through-plane TC and decrease in in-plane TC can be explained as following: during the injection molding process, the gas formed by the foaming agents starts to expand. This expansion of gas causes the fillers to rotate, effectively declining the orientation in the in-plane direction and increasing alignment with the through-plane direction. This process is illustrated in figure 3.

3.3 *Tensile strength*

The modulus, tensile stress at yield and strain at break are shown in figure 4. The results are within the line

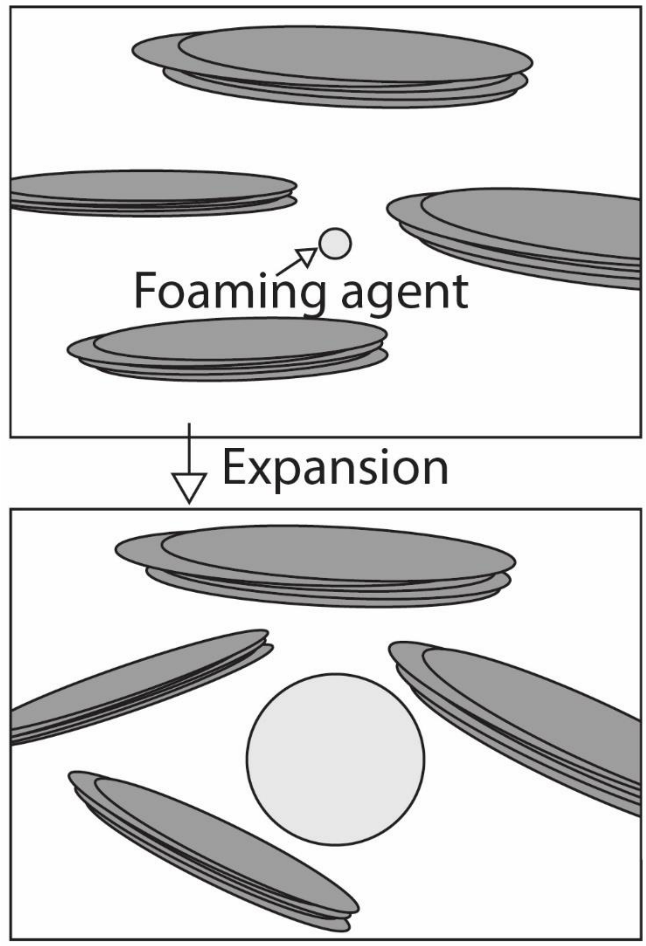

Figure 3. Expanding gas causes the fillers to re-orientate

of expectation: the modulus decreases with addition of foaming agents, but increases with increasing amount of graphite. The tensile stress at yield decreases with increasing amount of filler, which could be explained by the low tensile strength of graphite and perhaps relative weak interaction between the matrix and fillers that could ease the processes of cracking. These voids between filler and matrix also explain the significant decrease in strain at break. As SEM images show, the dispersion of graphite in the composite wasn’t optimal, as some graphite plates were still forming clusters in the composite. Extra voids introduced by the foaming agents further decrease the mechanical properties.

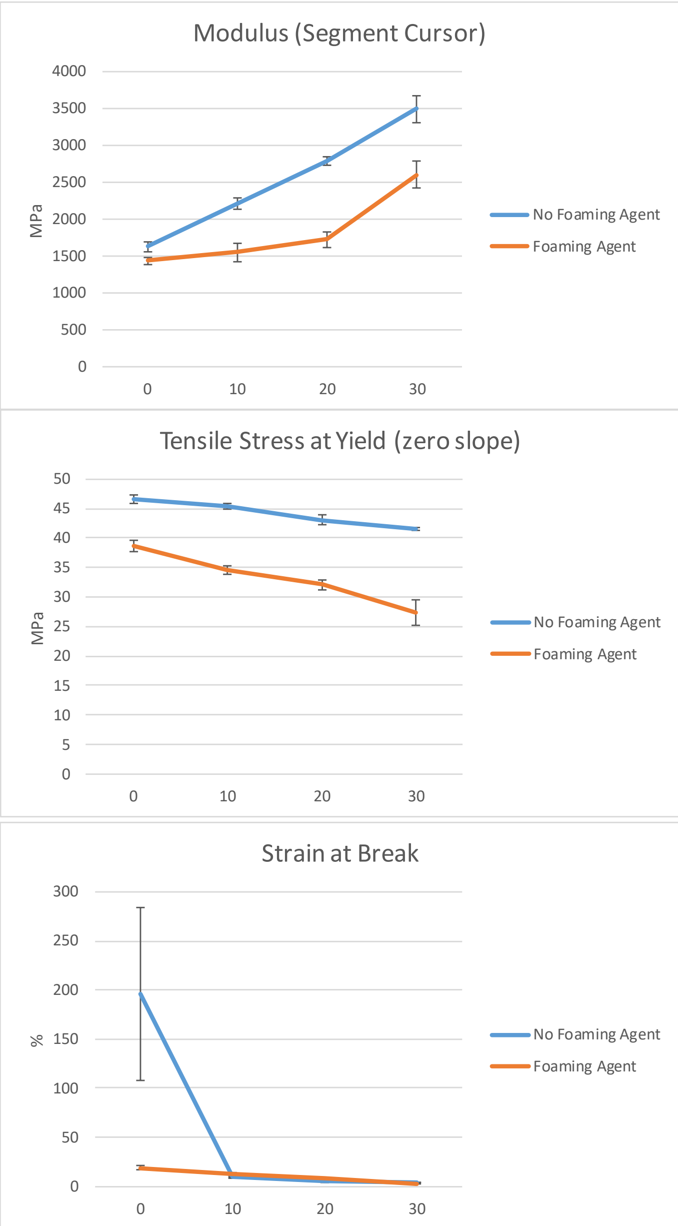

Figure 4. Modulus, tensile stress at yield and elongation at break of the different compounds. In general, CFA's and graphite have a negative impact on the porperties

3.4 *Scanning Electron Microscopy*

Figure 5 shows the composite of 30 wt% graphite without and with CFA. The pictures are taken from top view, the desired through-plane direction is from the top to the bottom of the image. Picture A clearly shows the graphite plates have a preferred orientation, that being the direction of flow during the injection process. This readily explains the high in-plane and lower through-plane thermal conductivity.

Picture B shows the graphite (1)being bend in a more through-plane direction by a bubble (2), most likely caused by the expansion of the CFA. This shows how the through-plane TC increases whilst decreasing the in-plane TC.

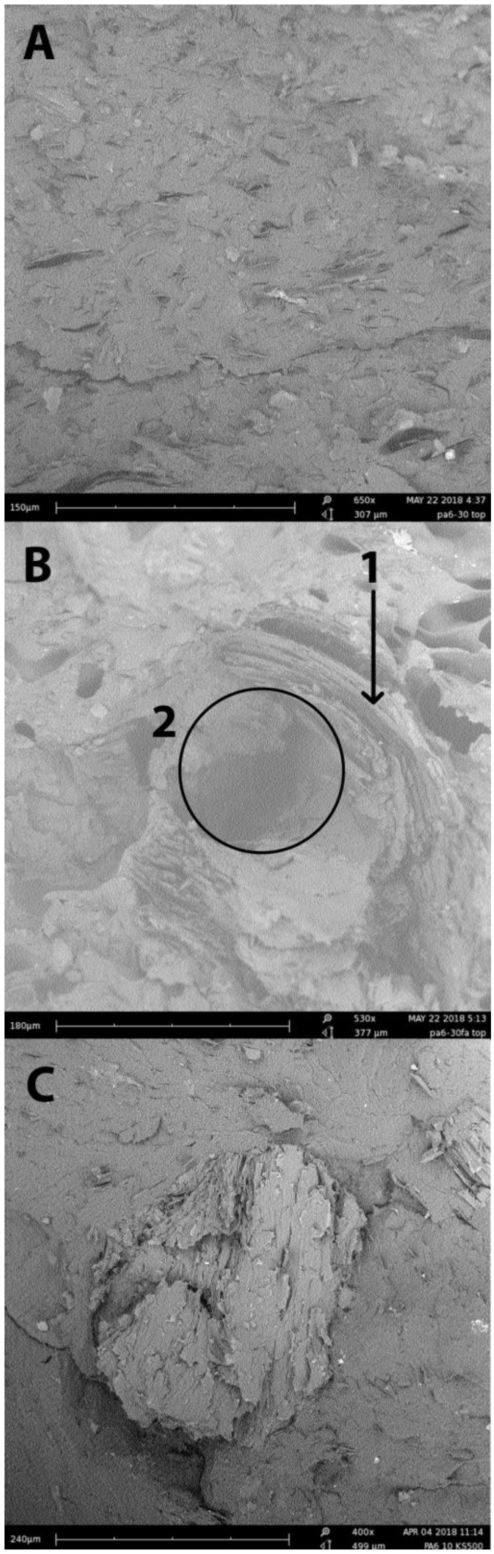

Figure 5. SEM images of (A) PA6 with 10 wt% of graphite (B) PA6 with 30 wt% graphite and CFA and (C) PA6 with 10 wt% graphite

Picture C shows a large cluster of poorly dispersed graphite. While this will likely improve both in- and though-plane TC (since a sphere won't orientate with the flow and a cluster reduces the amount of matrix-filler interfaces), it will most certainly decrease the physical properties of the material.

4 CONCLUSION

Despites the well-known insulating effect of foaming, the combination of CFA's and thermal conductive fillers can improve directional TC by changing the filler orientation caused by processing. This reduces of course the thermal conductivity in the opposite direction. Sufficient thermal conductive fillers have to be present in order to compensate for the insulating effect of trapped gas caused by CFA's. The through-plane TC of the composite with foaming agent and 30 wt% of graphite ended up as much as 0.82 W/mK, increasing the TC by 22% compared with the composite without foaming agent and as much 203% compared with the virgin polymer.

The yield strength of the samples decrease with increasing amount of fillers, due to the not-superb tensile properties of graphite in general and perhaps poor interaction between filler and matrix. Lumps of badly wetted graphite reduce the yield strength even more. Gas bubbles caused by the foaming agent reduce the strength even further. Because of the high Young modulus of the filler, the Young modulus of the composites increased as well.

Further optimization concerning the yield strength and fine-tuning the TC by controlling the size and amount of CO_2 bubbles could prove these materials useful for thermal applications that require through-plane TC rather than in-plane TC.

5 ACKNOWLEDGMENT

This research was supported by the VLAIO SBO-150013 project Composite Heat Exchangers www.compohex.ugent.be) funded by Flanders Innovation & Entrepreneurship (VLAIO). The authors would also like to thank Axipolymer for kindly supplying the foaming agent.

6 REFERENCES

1. Burger, N. *et al.* Review of thermal conductivity in composites: Mechanisms, parameters and theory. *Prog. Polym. Sci.* **61,** 1–28 (2016).
2. Chen, H. *et al.* Thermal conductivity of polymer-based composites: Fundamentals and applications. *Prog. Polym. Sci.* **59,** 41–85 (2015).
3. Han, Z. & Fina, A. Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review. *Prog. Polym. Sci.* **36,** 914–944 (2011).
4. Miller, M. G. *et al.* Measuring thermal conductivities of anisotropic synthetic graphite-liquid crystal polymer composites. *Polym. Compos.* **27,** 388–394 (2006).
5. Hussain, A. R. J. *et al.* Review of polymers for heat exchanger applications: Factors concerning thermal conductivity. *Appl. Therm. Eng.* **113,** 1118–1127 (2017).
6. Mazov, I. *et al.* Anisotropic thermal conductivity of polypropylene composites filled with carbon fibers and multiwall carbon nanotubes. *Polym. Compos.* **36,** 1951–1957 (2015).
7. Takahashi, S., Imai, Y., Kan, A., Hotta, Y. & Ogawa, H. Dielectric and thermal properties of isotactic polypropylene / hexagonal boron nitride composites for high-frequency applications. **615,** 141–145 (2014).
8. Enikolopyan, N. S. & Stalnova, I. O. Filled Polymers : Mechanical Properties and Processability. *Adv. Polym. Sci.* **96,** 1–67 (1990).
9. Lin, Z., Liu, Y., Raghavan, S., Moon, K. & Sitaraman, S. K. Magnetic Alignment of Hexagonal Boron Nitride Platelets in Polymer Matrix : Toward High Performance Anisotropic Polymer Composites for Electronic Encapsulation. *ASC Appl. Mater. Interfaces* **5,** 7633–7640 (2013).
10. Kim, K. & Kim, J. Vertical filler alignment of boron nitride/epoxy composite for thermal conductivity enhancement via external magnetic field. *Int. J. Therm. Sci.* **100,** 29–36 (2016).