THERMAL MAPPING AND FILLER SETTLING DETECTION IN POLYMER COMPOSITES WITH MTPS

Hakimian, A[1]*, and Clifford, J[2]
[1] Application Scientist, C-Therm Technologies, Fredericton, Canada
[2] Chemical Engineering Intern, C-Therm Technologies, Fredericton, Canada
* Arya Hakimian (arya.hakimian@ctherm.com)

Keywords: *polymer composites, thermal conductivity, thermal performance*

ABSTRACT

Uneven particle distribution within a polymer composite can introduce an unexpected and undesirable thermal performance. It is therefore crucial to have a reliable means of verification to assess filler uniformity. The Modified Transient Plane Source (MTPS) method was used to determine filler uniformity over the surface of a polymer composite. The one-sided nature of the sensor as well as the small active area allows for rapid, localized testing of thermal conductivity which can infer information on the filler concentration in the measured area. Likewise, the principles of operation relating to an assumption of a "semi-infinite" medium provides the ability to determine whether particle settling through the thickness of the sample has occurred. In both cases, the differences in measured thermal conductivity aligned with the visual inhomogeneities present in both samples, and therefore provides a simple method of determining composite uniformity for cases when no visual indications are present.

Introduction:

Creating composite materials can introduce new and beneficial performance properties. The introduction of thermally conductive fillers is a common way to increase thermal performance of a material. Amongst the many options available, common materials used include boron nitride, graphene, and highly conductive metals such as copper, gold and silver [1], [2]. The filler type selected may also have additional benefits such as chemical and/or mechanical stability improvements. It has also been shown that the shape (i.e., spherical, rod, platelet, etc.) of the selected filler can impact overall performance [1].

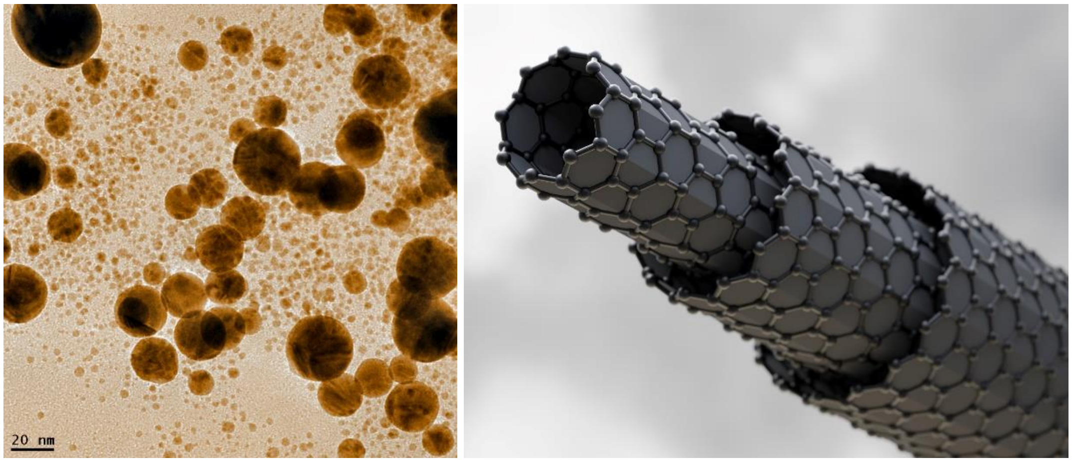

Figure 1. Example of filler shape differences (left spherical nanoparticle, right multiwalled carbon nanotube).

While many groups focus on increasing thermal conductivity, the incorporation of insulative fillers are also highly utilized in various applications such as packaging and storage. Common insulative fillers include materials such as aerogels and hollow glass microspheres [3], [4]. Whether the goal is to increase heat transfer properties through conductive fillers, or increase thermal resistance via insulative ones, the uniformity of filler dispersion will be crucial to overall performance. Localized agglomeration and inhomogeneous dispersion will adversely affect the performance of the material and can lead to thermal management issues. The ability to detect this is important to ensure materials are being manufactured and function as intended, whether injection molded, mechanically mixed or 3D printed.

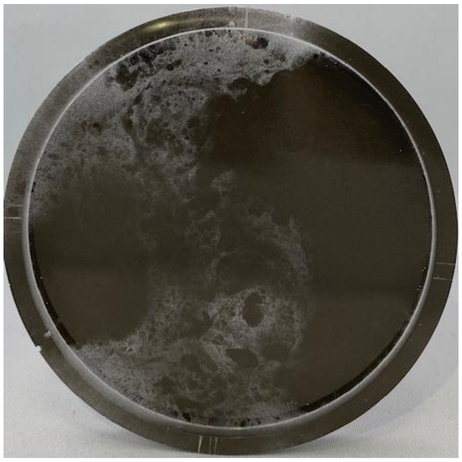

Figure 2. Example of a visibly non-uniform filler distribution in a polymer.

Thermal conductivity (k) is a critical performance attribute for such composites and can also be used to help detect potential issues surrounding filler dispersion via thermal mapping. Inhomogeneity of filler dispersion is unable to be specifically detected using traditional steady-state methods such as Heat Flow Meters (HFMs), since the heat flux measurement through the bulk reports an average across the entire sample [5]. Much research has been done on the principles and mathematical background of transient methods such as the Transient Plane Source (TPS) [6], and further developed into methods such as the MTPS [7] which was used in this study.

The MTPS (see Figure 3) is an enhancement of the TPS method that requires only a single-sided interface with the sample during the measurement. The sensor substrate is a glass coated ceramic, improving the heat flow into the sample [8]. It employs a one-sided interfacial heater/sensor surrounded by an integrated heated guard ring. A known current is applied to the spiral heating element contained in the sensor, providing a constant heat source to the sample being tested [6].

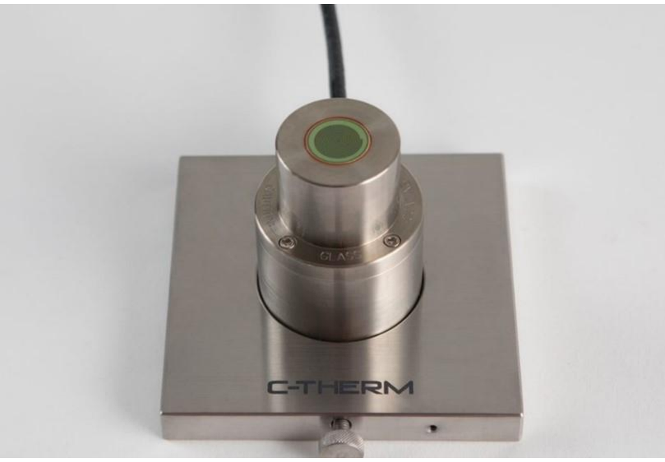

Figure 3. MTPS sensor used to measure the thermal conductivity of polymer composites in this experiment.

The heated guard ring provides a thermal barrier that surrounds the heater/sensor and eliminates lateral heat transfer at the sensor/sample interface [10]. Furthermore, the heater/sensor/guard ring assembly resides on a base of low thermal effusivity to ensure that nearly all the heat transferred in a measurement occurs between the heater/sensor/guard ring and the sample. The assumption of unidimensional heat flow is aided by the insulative backing material used in its construction [11]. The heat applied creates a change in the voltage drop across the sensor; the voltage is calibrated to temperature, meaning that the rate of voltage increase can be used to measure thermal properties of a sample [9]. The MTPS was selected for this study over other transient-based methods such as the TPS, since the sample type in question and setup requirements would violate key fundamental principles and assumptions of that method [12].

Sample Preparation:

Two different samples were prepared in order to test two different aspects of filler uniformity. For the first test conductive metal nanoparticles were mixed into a clear epoxy and cured until fully set. This was done in such a way as to induce visible non-uniform distribution across the surface (see Figure 1). The second sample was also produced by adding a conductive filler to the epoxy, but this sample was set in a much deeper mold to promote a more pronounced influence of settling. After curing the sample had visible differences in opacity from the top to the bottom (see Figure 4).

Figure 4. Filled polymer with a visible gradient (low concentration on top, high concentration on bottom)

Results:

Thermal mapping was performed across the surface the material. Measurements were performed at 9 different locations in order to build a thermal profile of the sample. These nine readings were taken in approximately a three-by-three square, as seen in Figure 4. This was done in order to maximize the number of readings that could be taken based on the available sampling area, and therefore produce the most comprehensive thermal profile of the sample.

The measured values for thermal conductivity were used to thermally map the material and correlate to the localized filler concentration.

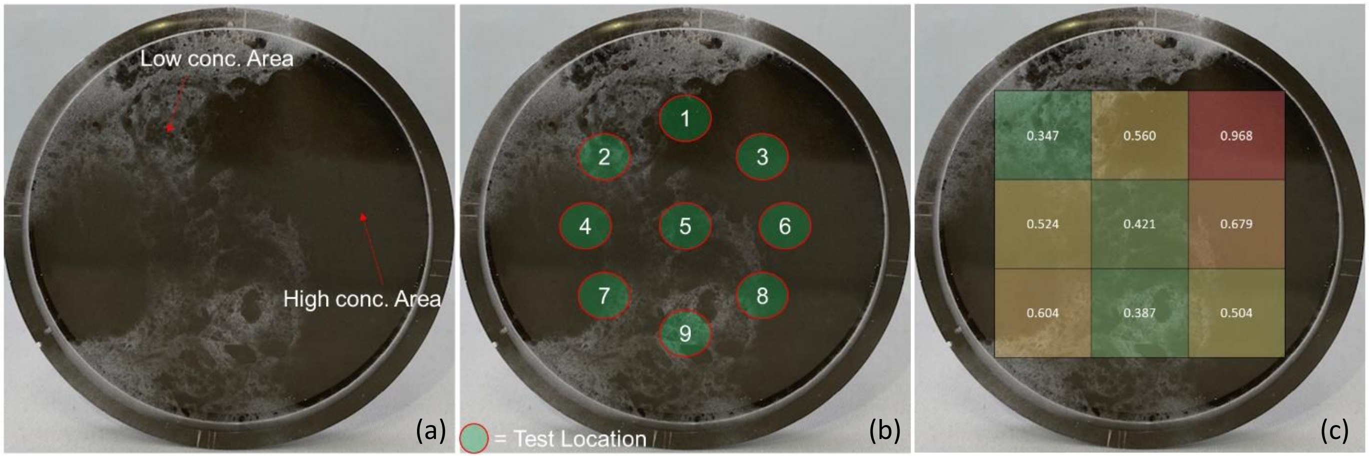

Figure 5. Non-uniformly filled polymer highlighting a) Areas with high and low filler concentration b) MTPS test locations and c) Resulting thermal values (W/mK) obtained from the measurements displayed as a thermal map.

Resulting measurements aligned with expected trends based on visible filler location. Test locations with high filler load (i.e., location 3 and 6) were amongst the highest in thermal conductivity. Locations with visibly low amounts of filler (i.e., location 2 and 9) were amongst the lowest. While for this sample the visual indications alone would be enough to infer poor filler distribution, the example highlights the ability to perform such testing on materials with an opaque polymer matrix or those that contain fillers that are not visibly discernible.

Settling detection was then performed on the second sample to give an indication of the uniformity of the particle distribution through the thickness. Settling effects in a material can cause uneven heat dissipation and result in the formation of a thermal gradient. Based on the MTPS principles of operation related to the probing depth of a "semi-infinite" medium, the MTPS can be used to detect if particle setting has occurred. This is accomplished by testing both the top and bottom side of a material in a specified zone. The reported thermal conductivity values can be used to infer if the additive is evenly distributed or settling towards one side.

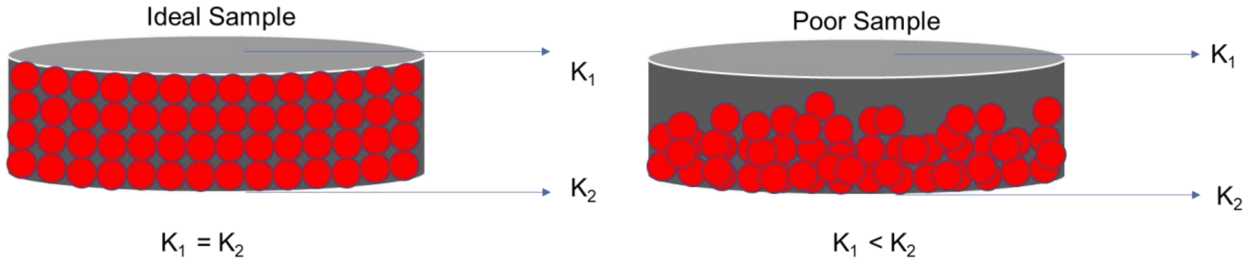

Figure 6. Example of a material with evenly distributed filler (left) and material with significant particle settling (right).

Results from the measurements can be seen in Figure 7. Reported values indicated a significantly higher thermal conductivity reading on the bottom side (1.48 W/mK) compared to the top (0.22 W/mK), which correlated to the visual difference in filler concentration. Again, as in the previous example the visual indications alone would be sufficient, however the example highlights the ability to perform such testing on materials where this would not be so easily detected based on visible information alone, including most opaque composites.

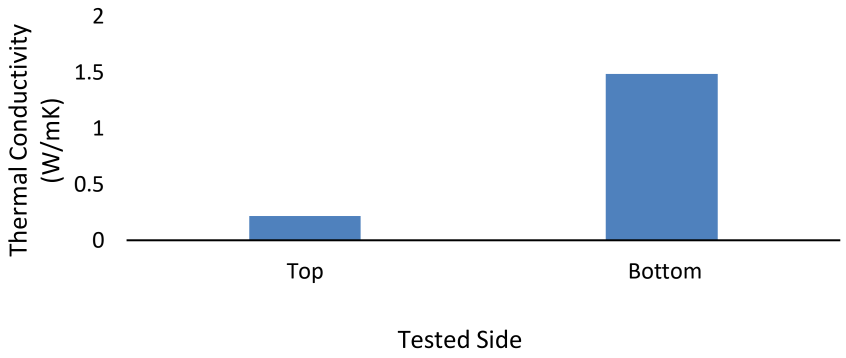

Figure 7. Thermal conductivity values for both the top and bottom surface of a filled polymer.

Conclusion:

The MTPS method can identify uneven filler dispersion using the measured thermal conductivity differences across a sample's surface, as well as the differences in particle distribution caused by settling. In both scenarios the thermal conductivity results aligned with what was expected based on the visual inspection of the samples. These results reinforce that thermal conductivity measured using the MTPS method can provide an indication of the uniformity in composite materials. This method of determining sample homogeneity can prove useful for opaque polymer composites where the uneven distribution is unable to be determined based on visible inspection alone.

References:

[1] H. Xie, D. Zhu, G. Huang, W. Yu, L. Zheng. “Enhanced thermal conductivity for nanofluids containing silver nanowires with different shapes”. *Journal of Nanomaterials* Vol. 2017, 2017.

[2] M. Clausi, M. Zahid, A. Shayganpour, I. Bayer. “Polyimide foam composites with nano-boron nitride (BN) and silicon carbide (SiC) for latent heat storage”. *Adv Compos Hybrid Mater*, 2022.

[3] S. Dalai, V. Savithri, P. Shrivastava, S. Sivam, P. Sharma. “Fabrication of zinc-loaded hollow glass microspheres (HGMs) for hydrogen storage”. *Int. J. Energy Res.*, Vol. 39, No. 5, pp 717-726, 2015.

[4] S. Cheney, C. Thellen, J. Ratto. “Investigation of expandable polymeric microspheres for packaging applications”. *Technical Report Natick/TR-12/020,* 2012.

[5] X. Meng, B. Yan, Y. Gao, J. Wang, W. Zhang and E. Long. "Factors affecting the in situ measurement accuracy of the wall heat transfer coefficient using the heat flow meter method". *Energy and Buildings*, Vol. 86, pp 754-765, 2014.

[6] International Standards Organization, Plastics - Determination of thermal conductivity and thermal diffusivity - Part 2 Transient plane heat source (hot disc) method, *Geneva: International Standards Organization*, 2008.

[7] N. Mathis and C. Chandler. "Direct thermal conductivity measurement technique". *United States of America Patent* 6,676,287 B1, 13 January 2004.

[8] M. Emanual, B. Brown, S. Ackermann and R. Bateman. "MTPS analytical temperature and heat flux solution with thermal contact resistance". *Journal of Heat Transfer*, Vol. 144, No. 7, 2022.

[9] V. Martinez-Ibanez, M. Garrido, C. Hidalgo Signes and R. Tomas. "Determination of thermal conductivity variation through modified transient plane source (MTPS), and its relationship with porosity variation on thermally treated Prada limestone". *IOP Conference Series: Earth and Environmental Science*, 2021.

[10] A. Harris, S. Kazanchenko, R. Bateman, J. Nickerson and M. Emanuel. "Measuring the thermal conductivity of heat transfer fluids via the modified transient plane source (MTPS)". *Journal of Thermal Analysis and Calorimetry*, Vol. 116, 2013.

[11] S. Jayachandran, R. Prithiviraajan and K. Reddy. "Characterization of various two-phase materials based on thermal conductivity using the modified transient plane source method". *AIP Conferene Proceedings,* Vol. 1859, No. 1, 2017.

[12] S. Al-Ajlan, "Measurements of thermal properties of insulation materials by using transient plane source technique". *Applied Thermal Engineering,* Vol. 26, No. 17, pp 2184-2191, 2006.