

A REVIEW ON THERMAL CONDUCTIVITY OF EPOXY–CERAMIC NANOCOMPOSITE

Chhabi Ram Sahu¹, Dilbag Mondloe², Ajay Singh paikra³

¹M.Tech. Researcher, Dept. of Mechanical Engineering, GEC Jagdalpur, Chhattisgarh, India

^{2,3}Asst. professor, Dept. of Mechanical Engineering, GEC Jagdalpur, Chhattisgarh, India

ABSTRACT

Thermal management has become a serious problem with the development of electronics, where thermal interface material (TIM) is crucial for heat transfer from the device to heat sink. Addressing this challenge requires the development of new composite materials with enhanced thermal conductivity. Epoxy resin is one of that and it has been widely used in electrical and electronics industries due to its excellent adhesion and insulating properties. The past researches show that the internalization of filler materials of high thermal conductivity improves the thermal conductivity of epoxy composites, consequently improves the heat transfer in electronic devices. In this review paper the need of thermal interface material and epoxy as a thermal interface material are discussed.

Key Words: Thermal conductivity (TC), Thermal interface material (TIM), Thermally conductive fillers, Epoxy resin, Thermo-gravimetric analysis (TGA).

1. INTRODUCTION

Thermal management is critical to the performance, lifetime, and reliability of electronic devices. With the miniaturization, integration of electronics and the development of new filler materials lead to the emergence of new applications such as light emitting diodes, solar PV cells, electronic packaging and in various electronic devices thermal dissipation becomes a challenging problem. Addressing this challenge requires the development of novel polymer-based composite materials with enhanced thermal conductivity [1, 2].

For one-dimensional, steady state heat flow, the heat conduction rate is expressed by Fourier's equations (1) and (2)

$$q = \frac{\Delta T}{L} \quad (1)$$

Or

$$J = \frac{q}{A} \quad (2)$$

Where, q is rate of heat transfer (W); J is heat flux (W/m^2), k is isothermal conductivity $W/(m K)$; A is cross sectional transfer area (m^2); T is temperature difference ($^{\circ}C$); L is conduction path length (m). In solids, heat may be transported by charge carriers (such as electrons and holes) or by phonons (energy quanta of atomic lattice vibrations). For semiconductors and insulators the thermal conductivity is dominated by the contribution from phonons, while in metals the electronic contribution greatly outweighs the phonon contribution. For most polymers, the primary mechanism of heat conduction is through phonons [3].

The thermal conductivity (TC) of polymers (usually represented by Greek letter κ or Latin lowercase k), can be obtained from the Debye equation (3), i.e.

$$k = \frac{C_p v l}{3} \quad (3)$$

Where, C_p is the specific heat capacity per unit volume, v is the phonon velocity, and l is the phonon mean free path. For most polymers, l is extremely small due to scattering with other phonons, defects, and grain boundaries. Therefore, most polymers have a low TC in the range of 0.1–0.5 W/(m K), which is not sufficient for many applications that require high heat conduction [4]. However, polymers have the advantages of good processability, lightweight, high electrical resistivity, low water absorption, high voltage breakdown strength, corrosion resistance and most importantly, low cost. Polymer-based thermally conductive materials are therefore often desired in many applications.

Typically, heat conductive fillers, such as aluminum oxide, boron nitride, aluminum nitride, silicon nitride, diamond, graphite, metal particles, carbon nanotube, graphene etc., are introduced into polymers to increase TC. For applications that require both high TC and electrically insulating properties, electrically insulating fillers, such as aluminum oxide, boron nitride, aluminum nitride, etc. can be used, while graphite, metal particles, carbon nanotube, and graphene are often utilized in applications where electrical insulation is not required.

Packaging electronic devices is a growing challenge as device performance and power levels escalate. As device feature sizes decrease, ensuring reliable operation becomes a challenge. Ensuring effective heat transfer from an integrated circuit and its heat spreader to a heat sink is a vital step in meeting this challenge. For example, die size of the Pentium 2 was 25.4 mm square and the power dissipation was about 33 W. However, the Pentium 4 die is 12.5 mm square and will dissipate up to 80 W. It has been seen that the power dissipation from the CPU are in the range of 20 to 150W. [5]

It is well known that the reliability of an electronic device is exponentially dependent on the operating temperature of the junction, wherein a small increase of 10-15 °C can result in a two times decrease in the lifespan of the device [6,7]. And also the stability of an electronic device will be decreased 10% by per 2 °C rise in temperature when they are working for long time [8]. Thermal management in conventional electronics was difficult because the conducting path between heat sources and heat sinks were made of rigid materials that possess high thermal conductivity, such as metals. It is hard to make a perfect contact between heat sinks and electronics because of the differences in the flatness between the two surfaces because there are only three contact points between two rigid planes, which causes very poor thermal contact [9]. Therefore, there is need of a soft, deformable material capable of forming low-thermal-resistance contacts in the interface between the electronics and heat sinks. The general method to do this is to fill the air gap by using an elastomeric material with high thermal conductivity in the interface between the heat sink and the heated device. Such materials are called thermal interface materials (TIMs). TIMs conduct heat more effectively to the heat sink than air and thus they reduce the resistance to heat transfer caused by air voids in the device.

1.1 Theory of thermal interface material

Fig (1) shows the location of TIM in typical electronic packaging. Thermal interface resistance is a measure of how well heat is transferred across the interface of two mating rigid surfaces, such as a CPU and a heat sink base plate; for lower value of resistance the heat transfer will be higher.

Gwinn et al. [5] has explained more clearly the concept of TIMs. In the case of the CPU–heat sink interface, the interface resistance (per unit area) R_{int} is defined as (4)

$$R_{int} = \frac{T_{cpu} - T_{hs}}{Q} \quad (4)$$

Where T_{cpu} is the CPU (or electronic packaging) surface temperature, T_{hs} is the heat sink base plate temperature and Q is the power per unit area of heat emitting component.

The interface resistance is generally expressed in K cm²/W (or in K in.² /W). Fig. 2(b) and (c) shows that the CPU and heat sink surfaces being joined contain a combination of surface roughness and surface non-flatness. The micro roughness on a macroscopic non-planar is in the form of a concave, convex or wavy surface, resulting in as much as 99% of the interface area between the heat sink and CPU being separated by air filled gaps (Fig. 2a) unless a TIM is used. Theoretically, the mating surfaces will only contact each other at discrete points and remaining is filled with air. Because air is a very poor thermal conductor ($k_{air} = 0.026$ W/m K at room temperature), it acts as a thermal barrier preventing efficient heat transfer across the interface.

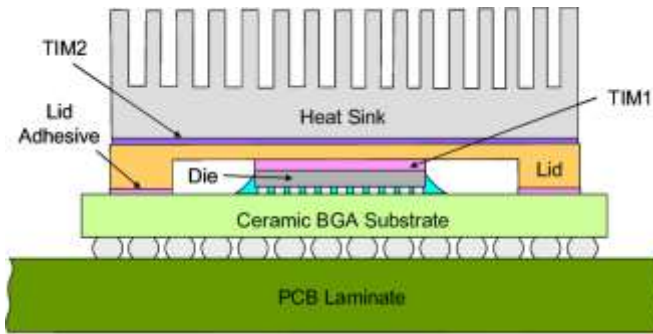


Figure 1: Typical Packaging Architecture for a High Performance Microprocessor, highlighting location of TIM1 and TIM2

If no TIM is used to enhance heat transfer across the interface, the total interface resistance, R_{int} is due to contact resistance. Contact resistance, $R_{contact}$, is composed of two parallel resistances: (1) conduction resistance at the points where the mating surfaces contact and (2) conduction and/or radiative resistance across the gaps of non-contacting area. The existence of TIM material adds a thermal conduction resistance across the material of thickness t .

$$R_{int} = R_{contact1} + R_{cond} + R_{contact2} \quad (5)$$

And

$$R_{cond} = \frac{t}{k_{TIM}A} \quad (6)$$

Where, $R_{contact1}$ the contact resistance between the TIM and the CPU surfaces is, $R_{contact2}$ is the contact resistance between the TIM and the heat sink base plate and R_{cond} is the conduction resistance across the thickness of the TIM. k_{TIM} is the TIM bulk thermal conductivity, t is the thickness of the TIM and A is the surface area of the electronic component across which heat transfer occurs.

1.2 Methods to reduce contact resistance

The trend in the electronics packaging industry is towards smaller, more powerful devices. With these small, high power components, however, there are also higher heat fluxes. As a result, engineers must find ways to minimize the thermal resistance from the electronic device junction to the ambient air.

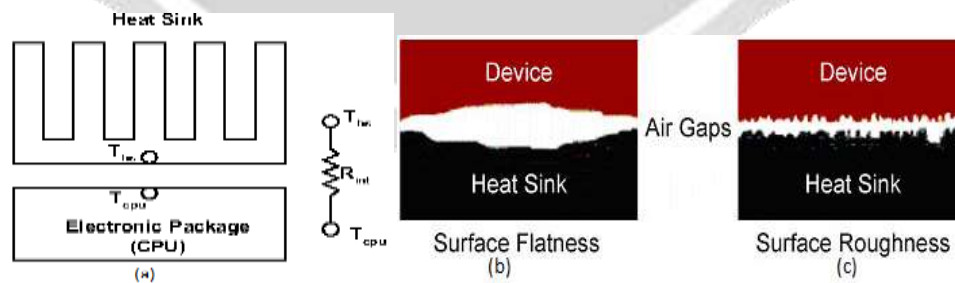


Figure-2: (a) definition of thermal interface resistance (R_{int}) (b) poor heat sink and CPU surface flatness, and (c) heat sink and CPU surface roughness.

Therefore, one way to reduce R_{int} is to reduce $R_{contact1}$, $R_{contact2}$ and R_{cond} . There are several factors that impact R_{int} , including surface flatness, surface roughness, contact force or clamping pressure, surface cleanliness, and interface materials.

a) Surface flatness and surface roughness

Surface flatness can be understood as widely spaced surface irregularities or "waviness" of a surface. Surface roughness is the submicron scale irregularities of a surface, usually as a result of machining, usage, and/or wear.

The contact between two imperfect surfaces will result in air gaps between them. (See Fig. 2(b) and (c).) Most contact areas consist of more than 90% air voids, which represent a significant resistance to heat transfer since air is not a very effective thermal conductor. So increasing surface flatness and by reducing surface roughness R_{int} is reduced at some extent but increasing surface flatness is costly.

b) Contact force

Another very important factor in minimizing contact thermal resistance is contact force, or the force with which the electronic device is pushed against the heat sink or cold plate. Electronic device and heat sink surfaces will never be perfectly flat. Consequently, there will always be air gaps in between. However, as the contact force pushing the two surfaces together increases so does the number of contact points between the two surfaces, resulting in a lower case to sink thermal resistance, R_{int} . Load constraints on electronic components and circuit boards make it difficult to use high contact pressure.

c) Surface cleanliness

Mounting surface cleanliness is also important in minimizing contact thermal resistance. Mounting surfaces should be kept free of all foreign material, such as dirt, oil, oxides, and films. Since most heat sinks and cold plates are stored after machining, a cleaning operation is recommended prior to mounting the device.

d) Thermal interface material

Finally, in order to further improve R_{int} , an appropriate Thermal Interface Material (TIM) should be used to fill the air gaps between the two surfaces. There are a number of technologies that can be used, including thermal greases and thermally conductive compounds, elastomers, adhesive tapes, etc., each with their own characteristics (operating temperatures, ease of application, curing time, pressure requirements, etc.) that can make them more or less desirable depending on the application.

Load constraints on electronic components and circuit boards make it difficult to use high contact pressure. Manufacturing highly finished surfaces to eliminate micro roughness is not practical due to cost constraints. Therefore, the practical alternative is to use a TIM with high thermal conductivity. Any interstitial substance that fills the gap between the mating surface and whose thermal conductivity is higher than air will reduce the contact resistance. Gwinn et al. [5] has mentioned the following characteristic that the ideal TIM (Fig. 3b) should have:

- a) High thermal conductivity with easily deformation by small contact pressure to fill the all uneven areas of both mating surfaces, including surface pores.
- b) Would not leak out of the interface.
- c) Would maintain performance indefinitely.
- d) Minimal thickness i.e. viscosity.
- e) Non-toxic and eco-friendly.
- f) Manufacturing friendly (easy to apply and remove) and low cost.

Ideal TIM has not yet been discovered, but there are several options available to provide reduced interface resistance. There are many types of TIM commercially available like thermal greases, elastomeric pads, solders, phase change materials (PCM), gels and adhesives [5, 9, 10, and 11]. Out of them Epoxy resin has extensively applied in electronics, insulators, printed circuit boards, semiconductor and packaging materials as adhesive due to superior properties such as low shrinkage, low thermal expansion coefficient (TEC), good adhesion and resistance to thermal, physical and chemical stability [12], heat resistance, high adhesive strength, good impact resistance, high strength and hardness, and high electrical insulation [13]. However, the thermal conductivity of epoxy resin is generally low (0.2 W/m k). Therefore, it is necessary to exploit effective method to improve the thermal conductivity of the epoxy resin. An attractive method is to add high thermal conductivity substances which are called fillers to the epoxy matrix.

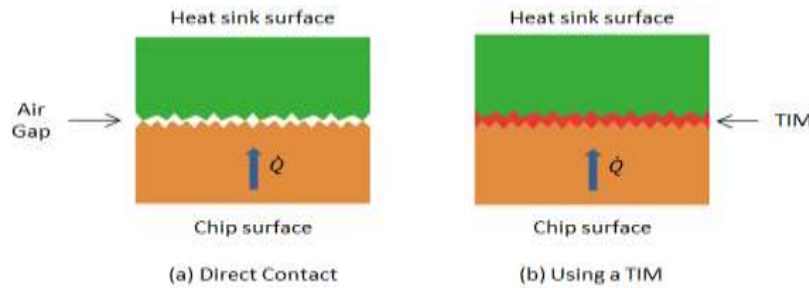
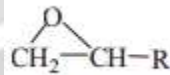


Figure 3: Exploded view of thermal interface when (a) no TIM is used, (b) when an ideal TIM is used.

Epoxy resins were discovered in 1909 by Prileschajew. Epoxy resins can be defined as low-molecular-weight pre-polymers containing more than one epoxide group of the form.



Epoxy resins are thermosetting polymers, which are cured by using wide variety of curing agents via curing chemical reaction. Generally the word 'epoxy resin' employs for both of resin and its curing agent. The properties of epoxy resins mainly depend on specific combinations of the type epoxy resins and curing agents used. Jin et al. [14] have studied various types of epoxy resins and curing agents and also discussed their synthesis and application area.

2. THERMALLY CONDUCTIVE FILLERS

Fillers given that polymers have low TC (generally less than 1.0 W/(mK)), making high-TC polymer-based materials requires introducing high-TC filler particles into polymer matrix [15–17]. Especially in the topic of the Nano fluids [18] and polymers [19]. Also, metal meshes and foams have been used in the thermal storage systems to improve the thermal conductivity of the systems. A few theories have been suggested on the heat transfer enhancement in Nano fluids or composite materials.

Fillers may be in the form of fibers or in the form of particles uniformly dispersed in the polymer matrix. The thermo-physical properties of fiber-filled composites are anisotropic, except for randomly dispersed fibers; while the thermo-physical properties of particle-filled polymers are isotropic [20]. The size of the fiber or particle may be of the order of Micro or Nano. Different types of fillers used in epoxy composite such as Metallic fillers, Carbon based materials, Ceramic fillers, and Hybrid fillers out of which ceramic fillers used extensively where high thermal conductivity and electrical insulation are required. Ceramic fillers have been widely studied for thermally conductive and electrically insulating composites due to their inherent properties. They lack free electrons, and the heat transfer is predominantly through phonons. There is only few work performed in nano range i.e. Thermally conductive composites and nanocomposites composed of epoxy resin as base matrix and aluminum nitride (AlN) as micro and nano filler have been studied at variable temperatures and loading of AlN[21],boron nitride[22] and nano-aluminum nitride-doped multi-walled carbon nanotubes[23]. A small amount of doping of nano material results in significantly increase in thermal conductivity.

2.1 Thermal properties of epoxy composites

The thermal conductivity measurement techniques can be divided into two groups. One is steady-state methods and another is transient methods. Steady-state methods are used when the system has achieved stability, while the transient methods are applied during the process of heating up or cooling down a material. Chen et al. [24] have investigated the different techniques associated with these two methods. Table 1 gives an overview of main thermal conductivity measurement methods [24] and Suganthi et al. [18] also described these two types of measurement methods.

Table-1: comparison of different thermal conductivity test methods

Methods		Temperature range	TC (W/mK)	Accuracy	Materials	Test standards
Steady state methods	Guarded hot plate method	80–800K	<0.8	2%	Glass, polymers and insulation materials	ASTM C177 ISO 8302 EN 12667
	Axial flow method	90–1300K	2-200	2%	Polymer, ceramics, metals	ASTM E1225
	Heat flow meter method	253–523K	<10	3%	Glass, polymers and insulation materials, ceramics	ASTM C 518 ASTM E1530 ISO 8301 EN 12667
	Pipe method	293–2770K	.02-200	2%	Metals, high conductivity inorganics, polymer composites	ISO 8497
Transient method	Laser flash method	373–3273K	>.01	3–5%	Glasses, polymers, ceramics, metals	ASTM E14 61 ISO 220074 ISO 18755
	Transient hot wire method	293–2273K	<25	1-10%	Glasses, polymers, ceramics, most of liquid, gas, powders	ASTM-C 1113 ISO 8894-1 ISO 8894-2
	Transient plane source method	20–1273K	.005-1800	5%	Insulation materials, powders, polymers, ceramics, metals, liquids	ISO 22007-2

2.2 Testing performed on epoxy-ceramic filler nanocomposites

Ceramic fillers cover all the metal and non-metal compounds including oxides, carbides, nitrides etc. Ceramic fillers are used when there is requirement of thermal conductivity in addition with electrical insulation. Many researchers have done investigation on thermal conductivity enhancement of epoxy resin using various types of nano ceramic fillers. Some of their analyses are discussed in table 2.

Table-2: TC testing performed on epoxy-ceramic filler nanocomposites

Filler	Method used	Filler loading	Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	k_c/k_m	References
Aluminium nitride	Transient plane source method	20 wt.%	0.280	-	Choudhury et al. [21]
Boron nitride	Transient plane source method	34.2 vol. %	2.78	-	Hutchinson et al. [22]
nano-aluminum nitride-doped multi-walled carbon nanotubes	Laser flash method	2 wt% nano-AlN-doped MWCNTs and 57.4 vol% micro-AlN	6.2	-	Choi et al. [23]

2.3 Thermal Gravimetric Analysis (TGA)

Thermo-gravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in chemical and physical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). TGA can give information about chemical phenomena, such as desolvation (especially dehydration), decomposition and solid-gas reactions (e.g. oxidation or reduction). Similarly TGA can give information about physical phenomena such as second order phase transition including vaporization, sublimation, absorption and desorption.

TGA can be used to evaluate the thermal stability of a material. It is generally used to investigate the thermal stability of polymers. In a desired temperature range, if material is thermally stable, there will be no observed mass change. Negligible mass loss corresponds to little or no slope in the TGA trace. TGA also gives the upper application temperature of a material. Beyond this temperature the material will begin to degrade.

CONCLUSIONS:

In this review, we discussed the research progress on thermally conductive polymer composites and their potential applications. Based on these studies, we can formulate several key messages:

1. Epoxy resins have better properties over other thermal interface materials. So it is better to use as thermal interface material than other polymers.
2. The thermal conductivity of an epoxy composite depends on filler loading. The thermal conductivity of epoxy composites increase with increase in filler loading into epoxy composite.

3. The thermal properties of epoxy composites vary with the type of epoxy resin and curing agent and also with the curing conditions.
4. High filler loading into epoxy composite causes poor processability, loss of mechanical integrity and inferior mechanical properties of epoxy composite. Also, High filler loading leads to high cost.
5. Size, shape and the orientation of the fillers into epoxy composites affect the thermal properties of epoxy composites.
6. The techniques employed for preparation of epoxy composites including mixing of epoxy and filler, curing conditions etc. also affect the thermal properties of epoxy composites.

ACKNOWLEDGEMENT

The author is grateful to the GEC Jagdalpur institute and Mr. Dilbag Singh Mondloe (Asst. Professor Mechanical Dept. GEC jagdalpur) for their support.

REFERENCES

- [1] Moore AL, Shi L. Emerging challenges and materials for thermal management of electronics. *Mater Today* 2014; 17:163–74.
- [2] Tong XC. *Advanced materials for thermal management of electronic packaging*. New York: Springer; 2011, 616 pp.
- [3] Han ZD, Fina A. Thermal conductivity of carbon nanotubes and their polymer nano composites: a review. *Prog Polym Sci* 2011; 36:914–44.
- [4] Huang XY, Jiang PK, Tanaka T. A review of dielectric polymer composites with high thermal conductivity. *IEEE Electr Insul Mag* 2011; 27:8–16.
- [5] J.P. Gwinn, R.L. Webb, Performance and testing of thermal interface materials. *Microelectronics Journal* 34 (2003) 215–222.
- [6] Kisang Ahn, Kiho Kim, Joohen Kim, Thermal conductivity and electric properties of epoxy composites filled with TiO₂-coated copper nanowire. *Polymer* 76 (2015) 313-320.
- [7] L.C. Sim, S.R. Ramanan, H. Ismail, K.N. Seetharamu, T.J. Goh, Thermal characterization of Al₂O₃ and ZnO reinforced silicone rubber as thermal pads for heat dissipation purposes, *Thermochim. Acta* 430 (2005) 155-165.
- [8] Wenhui Yuan, Qiangqiang Xiao, Li Li, Tao Xu, Thermal conductivity of epoxy adhesive enhanced by hybrid graphene oxide/AlN particles. *Applied Thermal Engineering* 106 (2016) 1067–1074.
- [9] Farhad Sarvar, David C. Whalley, Paul P. Conway, Thermal Interface Materials - A Review of the State of the Art, *Electronics System integration Technology, IEEE* (2006) 1292-1302.
- [10] D.D.L. Chung, Thermal interface materials, *JMEPEG* (2001) 10:56-59.
- [11] Ravi Prasher, Thermal Interface Materials: Historical Perspective, Status, and Future Directions, *Proceedings of the IEEE*, Vol. 94, No. 8, August 2006, 1571-1586.
- [12] L.Y. Yang, R. Niu, J.S. Xie, B. Qian, B.S. Song, Q.G. Rong, J. Bernstein, Design-for reliability implementation in microelectronics packaging development, *Microelectron. Int.* 28 (2011) 29–40.
- [13] Asif Abdul Azeez, Kyong Yop Rhe, Soo Jin Park, David Hui, Epoxy clay nanocomposites – processing, properties and applications: A review, *Composites: Part B* 45 (2013) 308–320.

- [14] Fan-Long Jin, Xiang Li, Soo-Jin Park, Synthesis and application of epoxy resins: A review, *Journal of Industrial and Engineering Chemistry* xxx (2015) xxx–xxx.
- [15] Xie BH, Huang X, Zhang GJ. High thermal conductive polyvinyl alcohol composites with hexagonal boron nitride micro platelets as fillers. *Compos Sci Technol* 2013; 85:98–103.
- [16] Liem H, Choy HS. Superior thermal conductivity of polymer nano composites by using graphene and boron nitride as fillers. *Solid State Commun* 2013; 163:41–5.
- [17] Zhou T, Wang X, Cheng P, Wang T, Xiong D, Wang X. Improving the thermal conductivity of epoxy resin by the addition of a mixture of graphite nano platelets and silicon carbide microparticles. *ExpressPolym Lett* 2013;7:585–94.
- [18] K.S. Suganthi, K.S. Rajan, Metal oxide nanofluids: Review of formulation, thermo-physical properties, mechanisms, and heat transfer performance, *Renewable and Sustainable Energy Reviews* 76 (2017) 226–255.
- [19] N. Burger, A. Laachachi, M. Ferriol, M. Lutz, V. Toniazzi, D. Rucha, Review of thermal conductivity in composites: Mechanisms, parameters and theory, *Progress in Polymer Science* 61 (2016) 1–28.
- [20] Sabyasachi Ganguli, Ajit K. Roy, David P. Anderson, Improved thermal conductivity for chemically functionalized exfoliated graphite/epoxy composites, *CARBON* 46 (2008) 806 – 817.
- [21] Mousam Choudhury, Smita Mohanty, Sanjay K. Nayak Effect of Surface Modification of Aluminum Nitride on Electrical and Thermal Characterizations of Thermosetting Polymeric Nanocomposites 2013.
- [22] John M. Hutchinson, Frida Román, Pilar Cortés, Yolanda Calventus Epoxy composites filled with boron nitride and aluminum nitride for improved thermal conductivity 2017, 62, nr 7–8.
- [23] Seran Choi, Hyungu Im and Jooheon Kim The thermal conductivity of embedded nano-aluminum nitride-doped multi-walled carbon nanotubes in epoxy composites containing micro-aluminum nitride particles (2012) 065303.
- [24] Hongyu Chen, Valeriy V. Ginzberg, Jian Yang, Yunfeng Yang, Wei Liu, Yan Huang, Libo Du, Bin Chen, Thermal conductivity of polymer-based composites: Fundamentals and applications. *Progress in Polymer Science* 59 (2016) 41–85.