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# High technical applications (thermal and electrical resistivity aspects) of expanded graphite

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***Abstract:*** The expanded graphite (EG) powder was used as some kinds of materials in terms of application. Expanded graphite (EG) prepared from natural graphite by chemical treatment and thermal treatment. But, it keeps most excellent characteristics of natural graphite and overcame hard, fragile and some other defects of natural graphite. EG was usually used to improve the thermal conductivities with some high polymer materials. The thermal conductive networks, in which electrons could move freely, finally formed when the distant among conductive particles have been shorten because of the increment of EG content and the thermal properties of composites, meanwhile, could be adjusted by changing EG content in a wide percentage range. We described that the expanded graphite is also an excellent material for thermal conducting with some useful analytical data.

***Keywords:*** Expanded graphite, Thermal conductivity, Polymer

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## 1. Gerneal aspect for Expanded graphite

Mineral crystalline graphite flake is the starting material for the manufacture of expandable graphite. Mineral graphite is usually found either as inclusions in various metamorphic rocks, or concentrated in the silts and clays that result from their erosion. The graphite is recovered from the ore by crushing and flotation, and it is then treated to obtain flakes whose carbon content is up to 94-98%. Crystalline graphite consists of stacks of parallel planes of carbon atoms. Because no covalent bonding exists between the planes, other molecules can be inserted between them. This process, known as intercalation, is essential for the production of expandable graphite, where sulfuric acid is inserted into the graphite When the intercalated graphite is exposed to heat, the inserted molecules decompose to generate gas. The graphite layer planes are forced apart by the gas and the graphite expands. The expanded graphite is a low-density, non-burnable, highly conductive, physically inert, environmentally compatible and recyclable material. **Fig. 1.**

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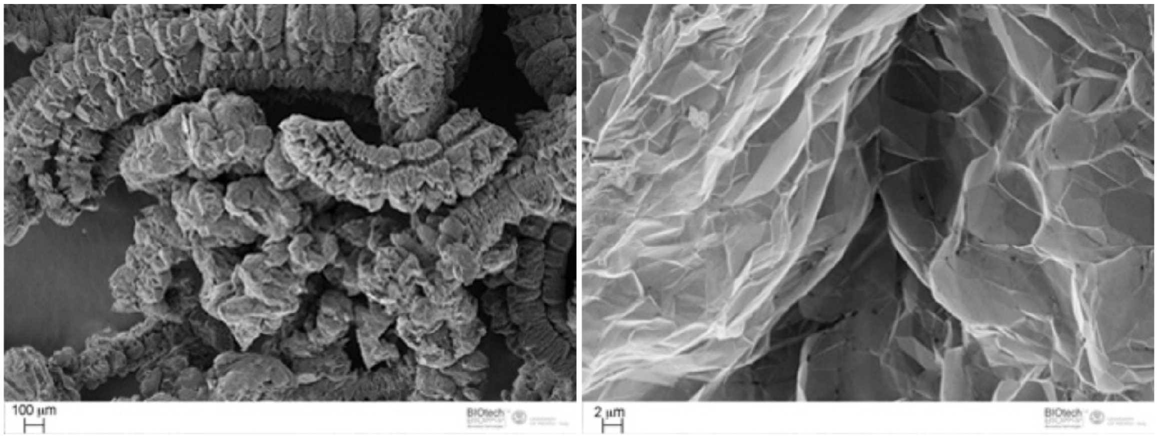


**Figure 1:** SEM images of expanded graphite [40]

Graphite is the most stable allotrope carbon in which the carbon bonding involves $sp^2$ (trigonal) hybridization. It consists of carbon layers with covalent and metallic bonding within each layer and are linked by a weak van der Walls interaction produced by a delocalized $\pi$-orbital [1]. Themorphology and pore structure of EG can be determined by altering preparation conditions, and there are many reports on preparation procedures, pore structure and application of EG [2–4]. EG is a highly porousworm-like and very light material with typical apparent densities of 0.002–0.01 $gcm^{-3}$, and is a material of growing importance because of numerous actual and potential applications in hydrogen storage [5], fuel cell [6], sensor [7], catalyst [8], biomedical materials [9], and adsorbent. The absorbing spaces of EG can be divided into two types. One is the wrapping absorption space (WAS) constructed by EG stacking on each other; the second is the pores in each EG worm-like segment [10].

The interlayer spacing of EG increases from 0.335 nm to approximately 0.8 nm and that of expanded graphite are several hundred times along the c-axis [11, 12]. It has been applied widely as a kind of functional carbon material used in sealing, catalyzing, space flight, military affairs, environmental protection, etc. [13, 14]. The expanded graphite keeps a layered structure similar to natural graphite flakes but with larger interlayer spacing [14]. The number of studies has been carried out on EG reinforced conductive polymer nanocomposites [15–19]. Due to its high electrical conductivity, EG is used as conductive filler with different thermoplastic materials such as polystyrene [15], PMMA [16–18], nylon-6 [19], etc. EG also possesses very high thermal conductivity, thus, it is used in improving the thermal conductivity of metal hydrides and heat transfer matrix in metal hydride composites [20–22]. Bipolar plate is one of the important components of polymer electrolyte membrane (PEM) fuel cell, which accounts as much as 60–80% of stack weight and 40–50% total cost of the fuel cell stack [23, 24].

Advantages

Excellent flame retardant effect with low material use

Halogen-free
Free of heavy metals
Non-polluting
Suitable for a wide range of applications
Reduces fume formation
Low cost

## 2. Thermal applications

### 2.1. *Expandable graphite as a flame retardant*

One of the principal applications of expandable graphite is as a flame retardant. As a result of the heat of a fire the graphite expands and creates an intumescent layer on the surface of the material. This retards the spread of fire and minimises one of the most harmful effects of combustion, the creation of toxic gases and fumes. **Fig. 2.**

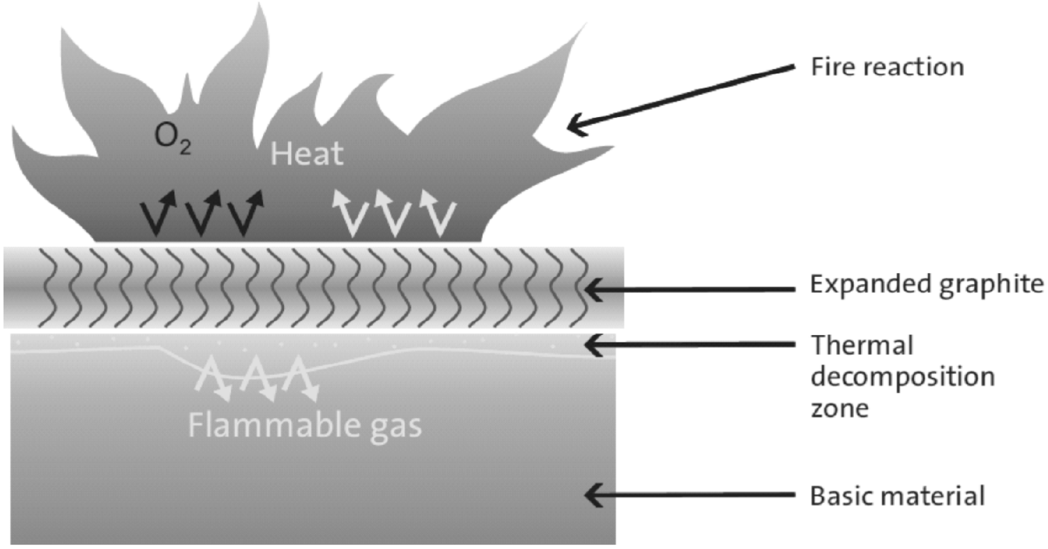


**Figure 2:** Schematic diagram of expandable graphite as a flame retardant [24-25]

### 2.2. *Thermal conductivity*

Nanofillers usually affect the ability to crystallize semi-crystalline polymers [25-29]. Distributed in the polymer matrix nanoparticles assisted by nucleation and growth of crystallites. In the case of characterized in this work nanocomposites, there was no significant effect of nanoparticles on the physical transitions in PET or they were very small. Only for the highest content of EG in investigated nanocomposites based on PET it can be stated repeatedly the increase of crystallization temperature (*Tc*) and melting temperature (*Tm*). EG content does not significantly affect the degree of crystallinity of PET, which is between 34,4÷36,1 (**Table 1**). This is probably due to the fact that the sizes of individual expanded graphite nanoplatelets were below the critical nucleation agents, as a result, may not constitute active centers of growth of crystallites. It also describes the lack of changes in the glass transition temperature (*Tg*) of semi-crystalline PET regardless of the EG content. In the literature [30-32], it was found that the addition of expanded graphite into the polymer matrix (PVC. PLA) improves the thermal stability both in oxidizing atmosphere and in an inert atmosphere. The studies of graphene influence on thermal properties of PET showed that 0.025% increase in graphene affects the thermo-oxidative resistance of nanocomposites. Of course, in an inert atmosphere in the process of degradation occurred at approximately 20°C higher than in an oxidizing atmosphere. The nanocomposite containing 0.1 wt% of graphene exhibits the highest temperature of 2% mass loss in an inert atmosphere. However, the differences between the temperatures corresponding to 2, 10 and 50% weight loss and the temperature of maximum rate of weight loss for obtained PET / EG nanocomposites and unmodified PET at 3 to 5! are within the measurement error. The value of activation energy (*Ea*) for the PET / EG nanocomposites increased with increasing content of expanded graphite. Both when the measurement was carried out in an oxidizing atmosphere and in argon. The values of *Ea* for the measurement carried out in air ranged between 247-268 kJ / mol. while for the measurement carried out in argon these values were in the range 304-318 kJ / mol. The results of research carried out in an oxidizing atmosphere and in argon are presented in **Table 2**.

**Table 1**
**Physical transition temperature and the degree of crystallinity of PET and PET/EG nanocomposites [38]**

| *Symbol* | $T_g$, °C | $T_m$, °C | $T_c$, °C | $X_c$, % |
|---|---|---|---|---|
| PET | 85 | 257 | 214 | 36.1 |
| PET/EG-0.025wt% | 83 | 251 | 207 | 35.3 |
| PET/EG-0.05wt% | 83 | 253 | 210 | 36.1 |
| PET/EG-0.1wt% | 83 | 252 | 214 | 36.0 |
| PET/EG-0.2wt% | 83 | 252 | 217 | 34.4 |
| PET/EG-0.4wt% | 83 | 253 | 217 | 35.8 |

**Table 2**
**Temperatures corresponding to 2, 10 and 50% weight loss activation energy and the maximum temperature of the mass loss rate for the nanocomposited obtained in an oxidizing atmosphere and in argon (Graphit Kropfmühl, Broacher) [38]**

| *Symbol* | $T_{2\%}$, °C | $T_{10\%}$, °C | $T_{50\%}$, °C | $E_a$, kJ/mol | $T_{DTG1}$, °C | $T_{DTG2}$, °C |
|---|---|---|---|---|---|---|
| | | | Measurement carried out in an oxidizing atmosphere | | | |
| PET | 366 | 402 | 438 | 257.07 | 440 | 539 |
| PET/EG 0.1 | 382 | 408 | 441 | 247.02 | 440 | 545 |
| PET/EG 0.2 | 381 | 407 | 441 | 255.25 | 441 | 549 |
| PET/EG 0.4 | 381 | 407 | 441 | 268.34 | 441 | 545 |
| | | | Measurement carried out in argon | | | |
| PET/EG | 387 | 413 | 442 | 313.53 | 441 | - |
| PET/EG 0.1 | 400 | 418 | 444 | 304.30 | 442 | - |
| PET/EG 0.2 | 395 | 415 | 443 | 316.36 | 441 | - |
| PET/EG 0.4 | 389 | 389 | 414 | 318.32 | 441 | - |

Pötschke *et al.* [33], investigated the comparison of carbon black (CB) as spherical particles multiwalled carbon nanotubes (MWNT) as fiber-like filler, and expanded graphite (EG) as platelet-like filler into polycarbonate matrix. Their results indicate that EG is a good candidate for cost-effective conductive filler materials for antistatic applications and its percolation concentration is significantly lower than that of CB. Zhao *et al.* [34], prepared nanocomposites based on poly (phenylene sulfide) (PPS) and expanded graphite (EG) or ultrasonicated EG (S-EG) by melt blending. They concluded that the PPS/S-EG nanocomposites exhibited higher conductivity, mechanical strength and thermal stability than the PPS/S-EG nanocomposites due to the small particle size of S-EG. Royal et al. [35] fabricated EG-filled poly(phenylene sulfide) (PPS) matrix composites by hot pressing and discussed their electrical conductivity properties. They obtained a percolation threshold at 1 wt.% (0.6 vol.%) EG and the electrical conductivity was improved to 14 orders of magnitude higher than the pure PPS. They concluded that PPS/EG nanocomposites may prove to be the futuristic high performance materials for antistatic/EMI shielding applications. Chen *et al.* [36] prepared polyurethane (PU)/expanded graphite powder (EGp) composite foams by filling mold curing reaction. They investigated the electrical properties of the prepared PU/EGp composite foams. They found the percolation threshold of PU/EGp composite foams about 5 wt.%, which is much lower than that of graphite nanosheets (GN) composite and carbon black (CB) composite. From the results they deduced that PU/EGp composite foams can be widely used for packing materials for the electron components. Mirzazadeh et al. [37], investigated the effect of interface and degree of interfacial interaction upon electrical conductivity threshold in polypropylene/ expanded graphite (PP/EG).

First of all thermal conductivity of pure HDPE was measured at three different temperatures using the method. The results are in good agreement with literature values; thermal conductivity decreases with increasing temperature. Then, thermal conductivity of HDPE nanocomposites containing 7 weight of EG5 and EG50 were measured using the same method. The measurements were done at 46°C and the results were given in **Table 3** [38]. It may be noticed that thermal conductivity value for nanocomposite filled with larger particle size graphite was much higher than the smaller particle size filled nanocomposite. The higher aspect ratio filler is the principal cause for higher thermal conductivity values.

### *2.4. Oxidation of expanded graphite in high temperature applications*

Critical to the performance of expanded graphite exposed to high temperatures is its resistance to oxidation. The factors which influence this are: a) The construction of the

**Table 3**
**Thermal conductivity of HDPE/EG5. HDPE/EG50 samples and pure HDPE [39]**

| *Particle weight concentration (%)* | *Particle volumetric concentration (%)* | *HDPE/EG5 sample* | *HDPE/EG50 sample* |
|---|---|---|---|
| | | *Thermal conductivity ($Wm^{-1}K^{-1}$)* | |
| 0 | 0 | 0.442 | 0.442 |
| 7.0 | 3.1 | 0.468 | 0.938 |

joint or housing in which the seal is being installed. b) The construction of the seal itself. These two factors determine the level of oxygen in contact with the seal. c) The media to which the seal is exposed both internally and externally, including their temperature and pressure. d) The physical nature of the expanded graphite itself. This can vary significantly depending on the geographical origin of graphite, differing technologies and substances used during the production of the expanded graphite, such as inhibitors. **Fig. 3.** and **Table 4.**

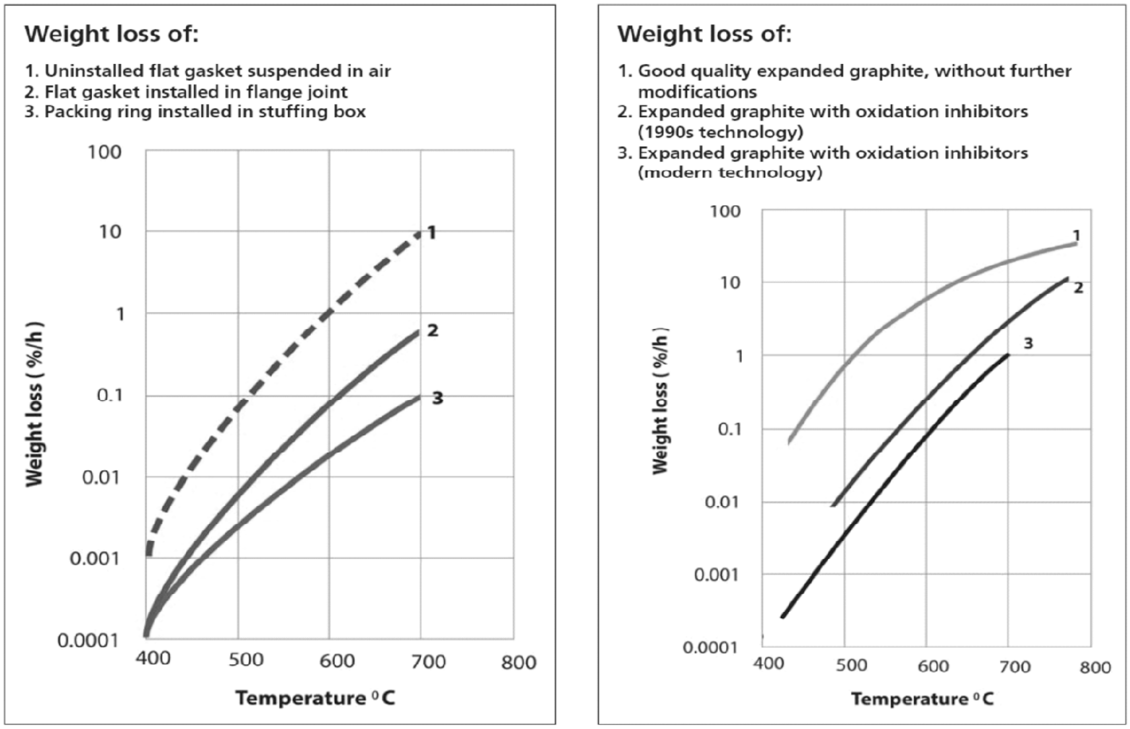


**Figure 3:** Weight loss of EG with some temperature condition [41]

**Table 4**
**Comparative properties of expanded graphite based bipolar plate [39]**

| *Properties* | *DOE-2010 target* | *Composites with 40% EG* | *Composites with 50% EG* |
|---|---|---|---|
| Bulk density (g/$cm^3$) | 1.90 | 1.47 | 1.50 |
| Flexural strength (MPa) | 25 | 49 | 54 |
| Modulus (GPa) | - | 4.3 | 5.6 |
| Electrical conductivity (S/cm) | 100 | 110 | 150 |
| Air permeability (MPa) | 0.5 MPa | No leak 0.78 MPa | No leak 0.78 MPa |
| Shore hardness | 50 | 55 | 50 |

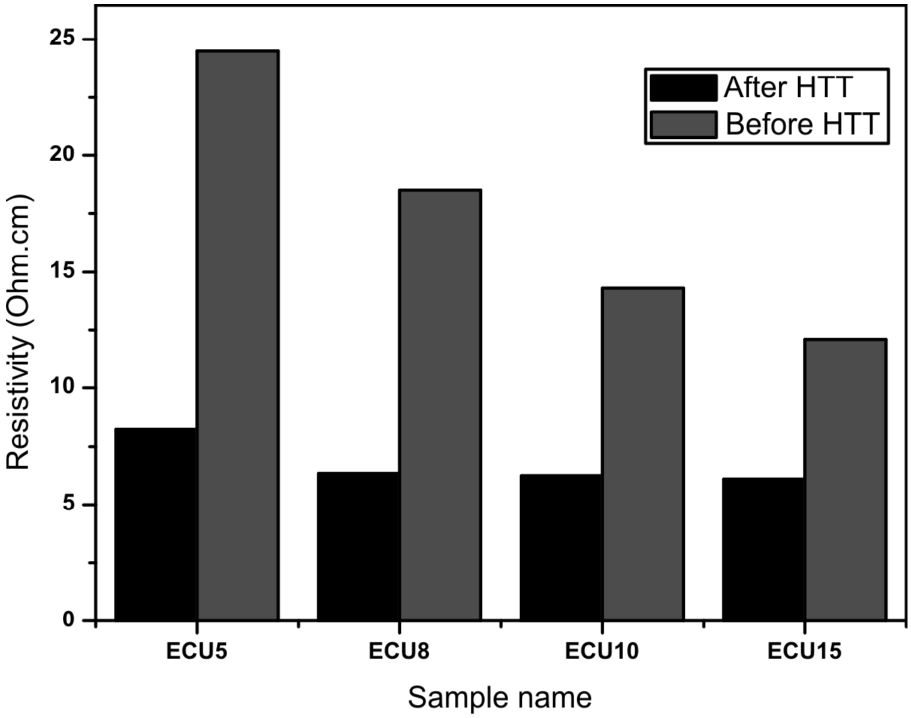
## 2.5. *Expanded Graphite packing*

The offered graphite product is made from high-grade materials and sourced from a reliable vendor base. It is durable and effective in providing insulation in oil refineries, nuclear power stations and thermal power stations. This product is resistant to high temperature and pressure. **Fig. 4.**

## 2.6. *Electrical Conductivity*

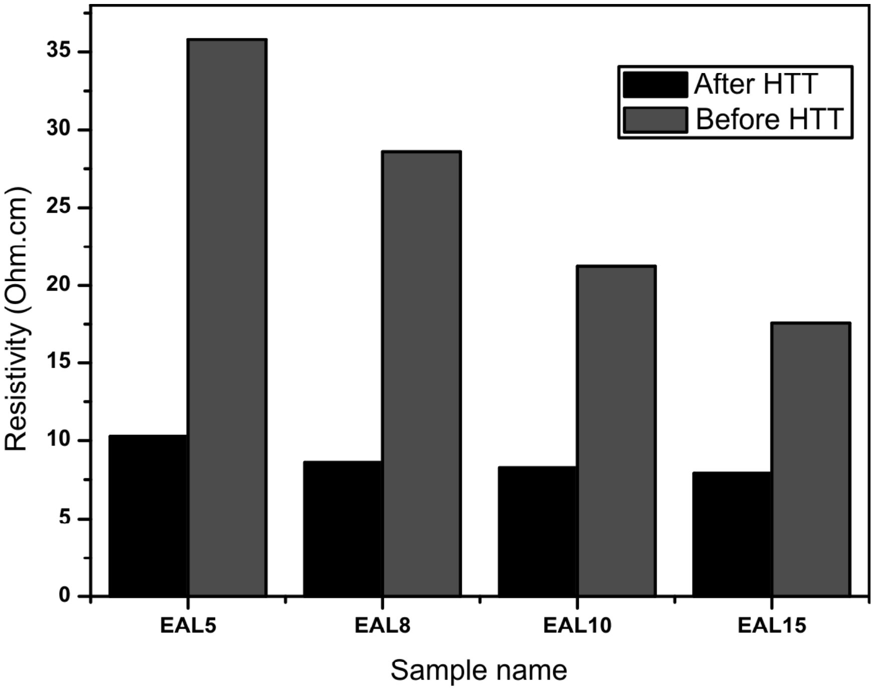
Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) is an intrinsic property that quantifies how strongly a given material opposes the flow of electric current. A low resistivity indicates a material that readily allows the flow of electric current. The electrical conductivity of cubic samples (monoliths) made of moderately compressed expanded graphite has been measured along two orthogonal directions, namely parallel and perpendicular to the pressing force. It is found that these highly porous materials exhibit a percolation behavior, with a transition from insulator to conductor occurring at a very low critical density. Besides, the monoliths are found to be quite isotropic as their porosity is high; conversely, increasing their apparent density makes them become more and more anisotropic thanks to the orientation of their constitutive graphite particles. Both percolation and effective media theories are shown to accurately fit the conductivity data as far as isotropic materials are concerned. Microstructural parameters derived from the fits are discussed and found to be in fair agreement with the expected description of compressed expanded graphite, i.e. insulating voids surrounded by thin conducting flakes. Electrical resistivity of heating plate using expanded graphite as additive material is shown in Fig. 5.

**Figure 4:** Expanded graphite packing materials [41-42]



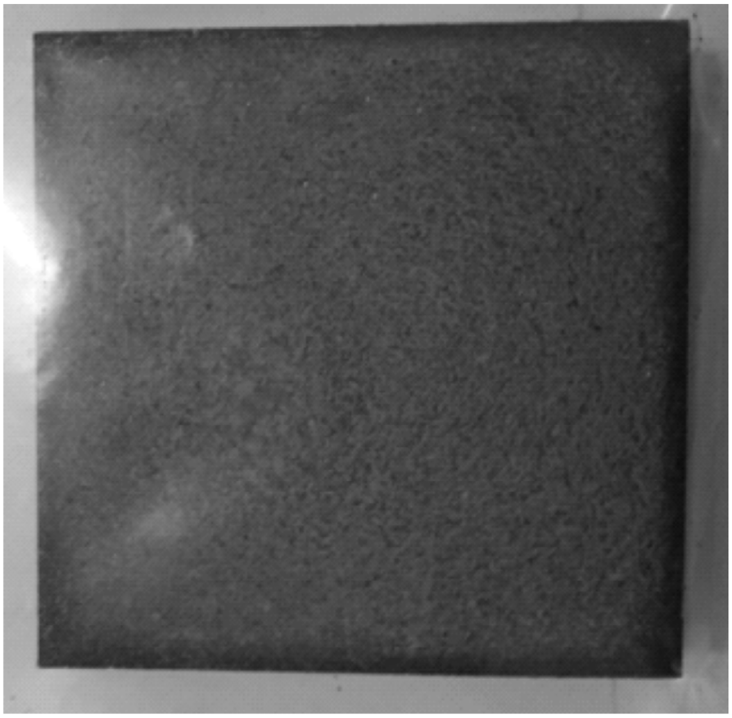
Resistivity (Ohm.cm)
0
5
10
15
20
25
After HTT
Before HTT
ECU5
ECU8
ECU10
ECU15
Sample name

(a)



Resistivity (Ohm.cm)
0
5
10
15
20
25
30
35
After HTT
Before HTT
EAL5
EAL8
EAL10
EAL15
Sample name

(b)



(c)

**Figure 5:** Electrical resistivity of heating plate using expanded graphite as additive material : (a) EG+Cu, (b) EG+Al and (c) example plate

## 3. Conclusions

In this investigation, we describe about expanded graphite with thermal properties. Each data reported in the figures are an average value base of literature results, which shows the repeatability in the properties of expanded graphite-based composite application. The expanded graphite (EG) powder was used as some kinds of materials in terms of application. EG was usually used to improve the thermal conductivities with some high polymer materials. The thermal conductive networks, in which electrons could move freely, finally formed when the distant among conductive particles have been shorten because of the increment of EG content and the thermaal properties of composites, meanwhile, could be adjusted by changing EG content in a wide percentage range. We described that the expanded graphite is also an excellent material for thermal conducting with some useful analytical data.

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