

EXPANDED GRAPHITE TO ENHANCE THE CONDUCTIVE AND MECHANICAL PROPERTIES OF GEOPOLYMER, PVA AND EPOXY

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Abstract

Expanded graphite is produced on commercial scale using various intercalating agents and physical expansion conditions. Little is known about the different effects these processing conditions may have on the electrical, thermal, and mechanical properties when used in composites since these may cause the materials to behave differently. The difference in physical processing conditions is known to cause a change in the degree of exfoliation of expanded graphite as this can be easily characterised; however, little is currently known of the effects which the various available intercalants have on the elemental composition as well potential residues in the final particles. The most common intercalants used are sulfuric- and nitric acid. Expanded graphite can be used to obtain graphene sheets by further exfoliation of the particles to enhance the conductive properties of the filler material. Expanded graphite is much cheaper than graphene and should exhibit greater conductive properties than graphite with increased or equal contribution to mechanical properties. It is the focus of this work to determine the effectiveness of expanded graphite as a better alternative to using graphite to enhance the conductive and mechanical properties of select composite materials and to characterise the differences attributed by two commercial expanded graphite filler particles.

Keywords: Expanded graphite, polyvinyl alcohol, geopolymer, epoxy, electrical conductivity

1. INTRODUCTION

Expanded graphite (EG) has been a topic of interest in recent years due to its unique conductive and sorptive properties. Graphite and specifically the graphene layers which it is comprised of is seen as one of the most conductive materials on earth. Its method of electrical and thermal conductivity occurs by electron delocalisation within the pi-orbitals of the graphene sheets. Graphite however is conductively anisotropic since it only conducts parallel to the graphene sheet layers and not perpendicular. To overcome this anisotropy EG has been seen as a method to obtain graphene to unlock the materials conductive potential. The common method of producing EG is by the chemical method where graphite is oxidised and intercalated using an intercalator which is typically sulfuric or nitric acid. This is then followed by a rapid expansion at temperatures of up to 900 °C [1]–[4]. A scanning electron microscope image of the expanded graphite samples used in this work is presented in **Figure 1**. There appears to be experimental differences in the use of expanded graphite and the reason for this has rarely been studied. It is suggested that during the intercalation other chemical reactions may take place causing non carbon atoms which are present in the oxidation and acids to bind to the graphene layers. This may reduce the conductive properties since functionalised graphene typically lacks free electron movement [5], [6]. Expanded graphite has been proven to enhance the conductive properties of various polymers including PVA and epoxy, however it is also the purpose of this work to compare the difference between available commercial EG materials.

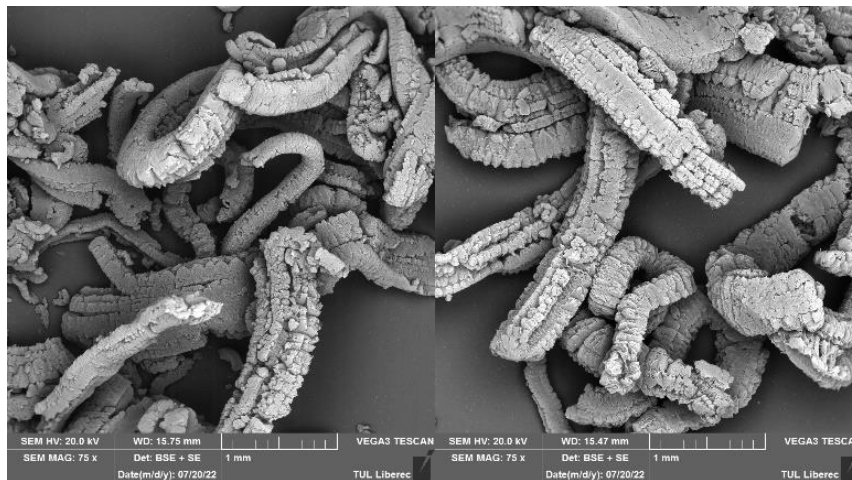


Figure 1 Samples EG1 (left) and EG2 (right)

2. EXPERIMENTAL

2.1. Materials

Graphite was obtained from (EPINIKON, Czech Republic). Expanded graphite type 1 and 2 was obtained from (Sorbetin s.r.o., Czech Republic). Geopolymer (BAUCIS LBNa+activator) was obtained from (Cesky Lupkove Zavody, Czech Republic). Fully hydrolysed PVA with an average molecular weight of 30000 grams per mol was used to make the 15% PVA solution for the PVA composites. For the epoxy samples a clear polyester resin was used and a suitable peroxide binder obtained from (Havel Composites sro., Czech Republic)

2.2. Sample preparation

For the geopolymer samples the filler was added to a 10 grams geopolymer and 8 grams activator and mixed with a mortar and pestle until the paste appeared uniform. This was then added to a glass fibre mat for reinforcement and wrapped in film. Curing was performed at 75 °C for 1 hour. A 15% solution of PVA and distilled water was prepared and used for the PVA composites. First 60 grams of the PVA solution was blended with 0.4 grams citric acid and stirred for 1 hour at 80 °C. the graphite filler was added to the PVA and citric acid mixture with mechanical stirring for 5 minutes. The paste was then poured into a mould and left for two days to dry. For the epoxy samples, 60 grams of polyester epoxy was used with graphite filler and mechanically stirred for 5 minutes. This was followed by the addition of 0.4 grams of binder with stirring. The paste was then transferred to a mould and cured at 60 °C for 1 hour.

2.3. Methods

Visual characterisation was performed using a Scanning Electron microscope (Vega 3 TScan). Tensile properties for the PVA and epoxy samples were tested using a tensile test instrument (Tiratest 2300) and the geocomposites were tested on the same machine for bending strength in the perpendicular sample direction. Electrical properties were measured using a two-probe technique with 1 cm spacing at a humidity of 68 % and a room temperature of 23.5 °C. Thermal properties were analysed using Differential Scanning Calorimetry (DSC) between 0 °C and 300 °C in an air atmosphere. This was not used to characterise the geopolymer due to the use of glass reinforcement. The particle grain size was determined using XRD over a 2 theta range from 4 – 60 degrees. This was performed only on the PVA composites since the particle exfoliation during mixing was most prominent for this sample as characterised by SEM.

The particle grain size of the expanded graphite was determined using the Scherrer equation as given in equation 1.

Equation 1 Sherrer equation

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is the crystallites size in nanometre and K is the Sherrer constant 0.9, lambda is the wavelength of the x-ray source at 0.15406nm, beta is the FWHM (full width at half maximum) in radians and theta is the peak angle. The peak position and FWHM was determined using peak integration software [7].

3. RESULTS AND DISCUSSION

3.1. SEM

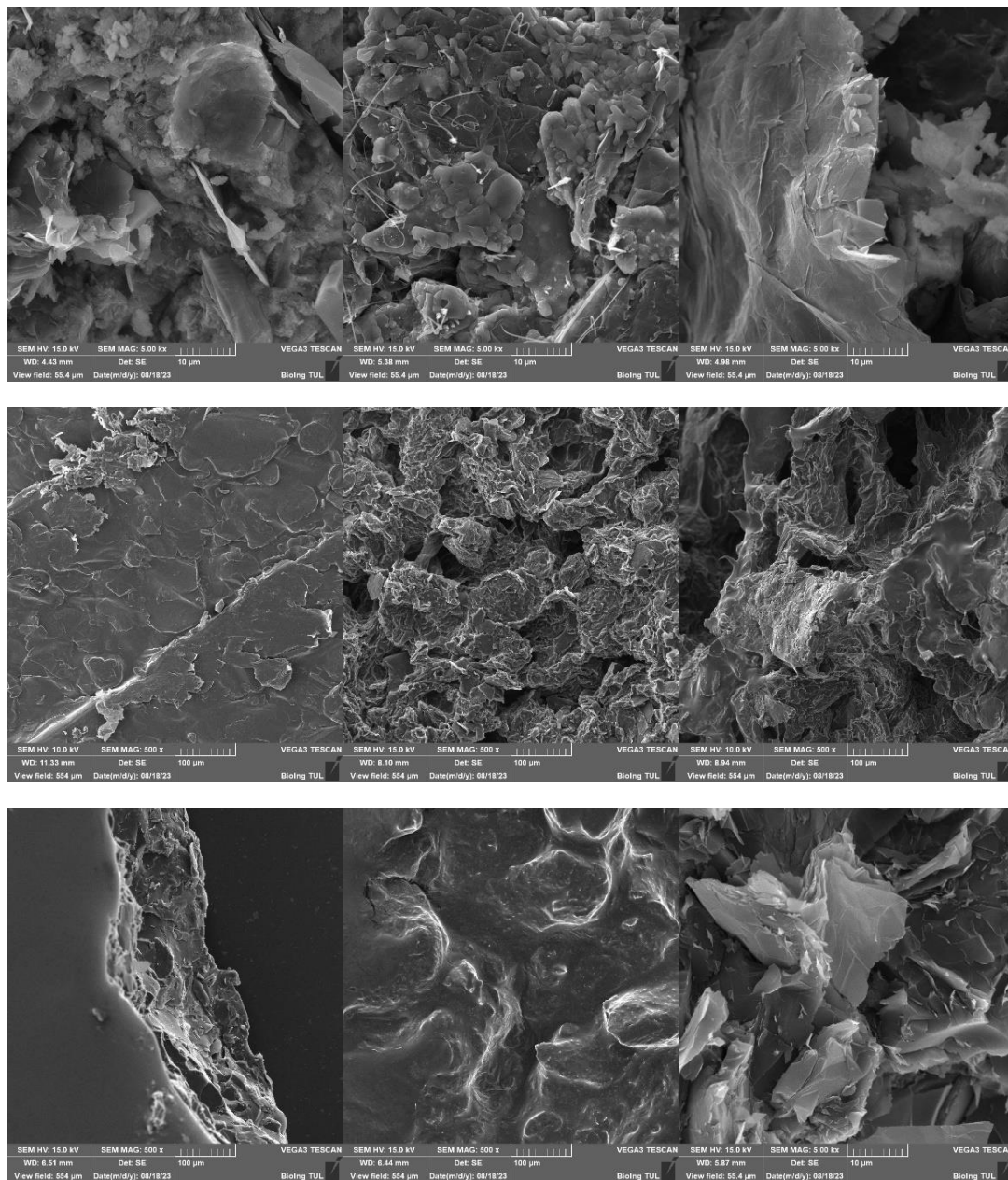


Figure 2 SEM of (Top left to right) Geocomposite with 10 % graphite, EG1 and EG2 respectively. (Middle left to right) PVA composite with 10 % graphite, EG1 and EG2 respectively. (Bottom left to right) Epoxy composite with 10 % graphite, EG1 and EG2 respectively.

As seen in the SEM images in **Figure 2** it was clear that at higher loading the expanded graphite particles were exfoliated to form very few layered structures resembling graphene whereas the graphite constantly had more layers although it was also partially exfoliated in the composites.

3.2. Tensile test

The composite tensile strength properties are depicted respectively in **Figure 3** as a function of strength vs displacement with the test method as described in the methodology.

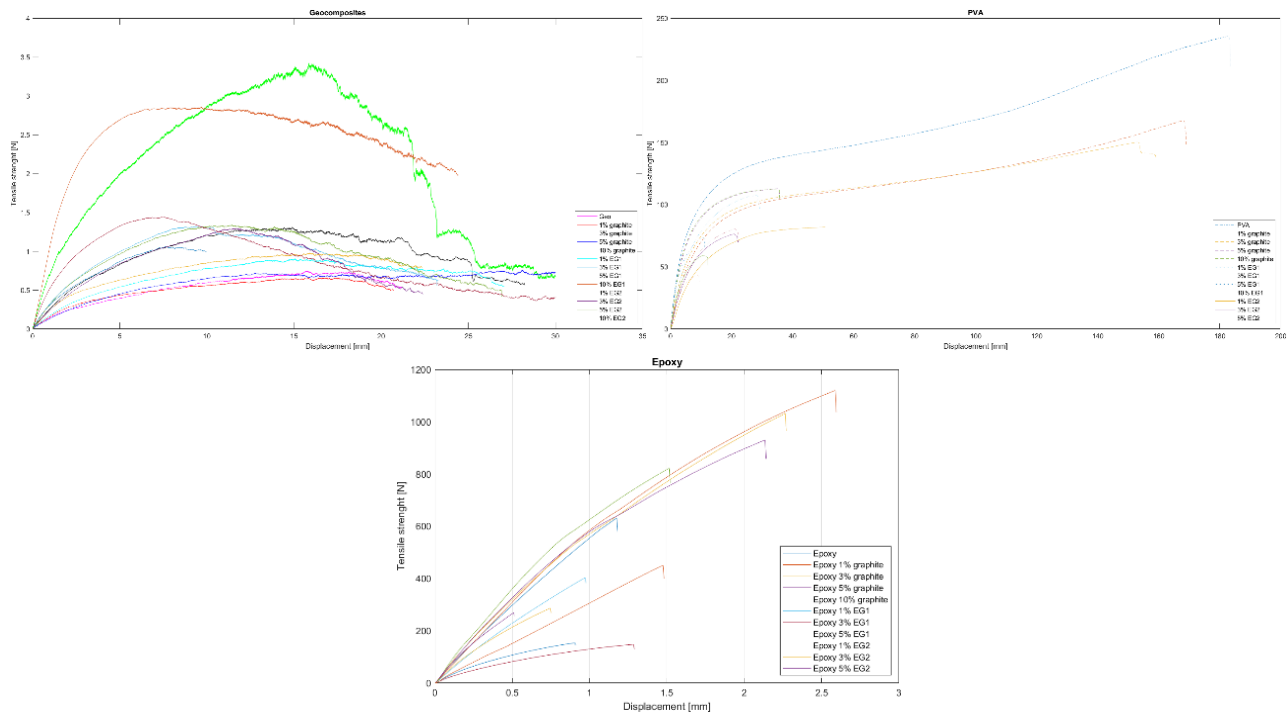


Figure 3 Tensile test curves of Geocomposite samples (Top left), PVA composite samples (Top right), Epoxy samples (Bottom)

It was noted from the tensile test graphs in **Figure 3** for both the geocomposite and epoxy samples that the addition of any graphite filler increased the initial modulus it was noted in most cases that the elongation at break was also improved, however some samples broke prematurely which was attributed to the presence of air bubbles in the structure. This was more prevalent in samples with higher filler loading and expanded graphite since this incorporated more air into the structure. For the epoxy samples the addition of graphite resulted in the greatest improvement in initial modulus and elongation at break. For the PVA composite samples, the addition of any graphite filler resulted in a modulus and elongation at break decrease. This effect occurred more with every consecutive increase in filler content, and it was less prominent with graphite compared to EG1 and EG2 which fared similarly.

3.3. Electrical properties

The electrical resistance of all the samples was plotted against the filler content as illustrated in **Figure 4**.

From the graphs in **Figure 4** it was determined that overall samples containing EG1 exhibited the greatest electrical conductivity and both expanded graphite samples fared remarkably better than samples containing graphite. There was one deviation from this observation where EG2 had a similar electrical resistance as graphite at 10% loading in the PVA composite, however at lower loading the electrical resistance was still lower than samples containing graphite. The largest differences in electrical conductivity were observed for the

geopolymer and epoxy composite samples where in the geopolymer samples there was a 3 orders of magnitude improvement in reducing electrical resistivity by using expanded graphite compared to graphite. The epoxy samples showed a 2 order of magnitude difference; however, the initial readings were different on both sides of the sample until the readings converged at higher loading. This is due to particle exfoliation during mixing where the particles are more evenly distributed and exfoliated at higher filler loading. This was confirmed by visual characterisation.

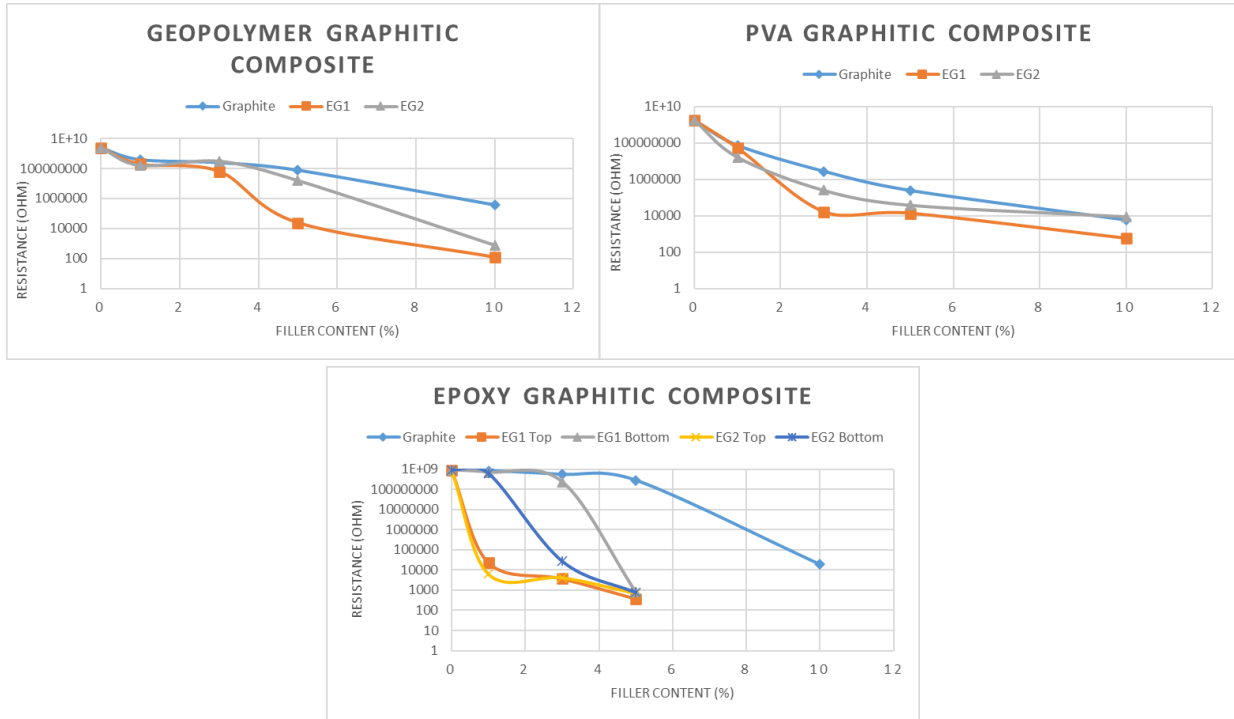


Figure 4 Electrical resistance measurements of Geocomposite samples (Top left), PVA composite samples (Top right), Epoxy samples (Bottom)

3.4. Thermal properties

The thermal properties of the PVA and epoxy samples are illustrated in **Figure 5** as a function of heat flow vs temperature.

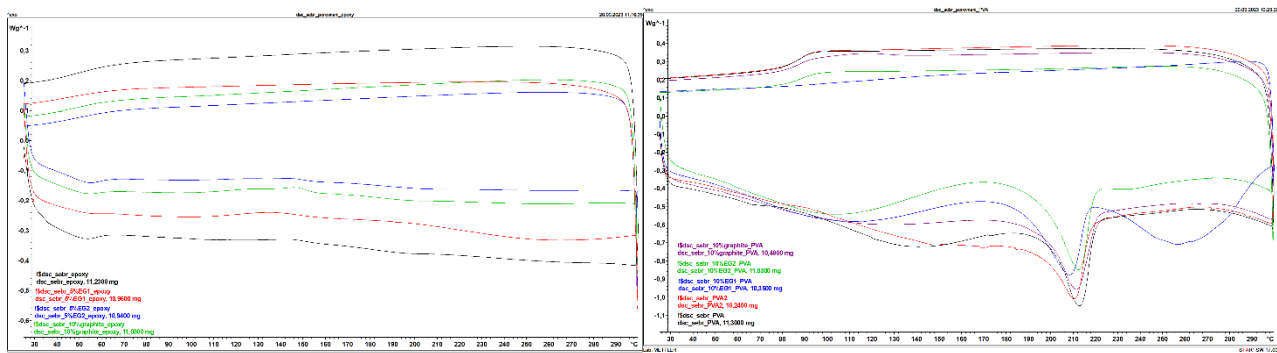


Figure 5 DSC curves of PVA composites (left) and Epoxy composites (Right)

As seen in **Figure 5** the heat flow through the sample was less for the samples containing filler compared to the pure PVA and epoxy. It appeared that the expanded graphite samples and specifically those containing EG2 exhibited the lowest heat flow even during melting in the PVA samples.

3.5. X-ray diffraction

XRD analysis was performed on the PVA composite materials to determine the grain size for the degree of exfoliation of the particles. The combined spectra are presented in **Figure 6**. The average crystallite size was calculated according to equation 1 and is presented in **Table 1**.

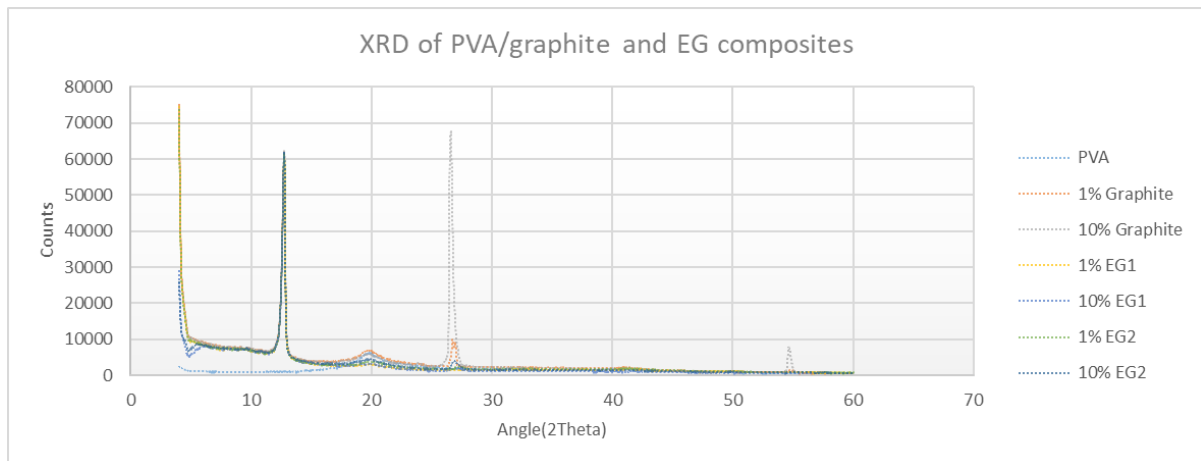


Figure 6 XRD of select PVA composites

Table 1 Average crystallite size

PVA Sample type	1 % Graphite	10 % Graphite	1 % EG1	10 % EG1	1 % EG2	10 % EG2
Average crystallite size	37.48	31.53	25.24	18.48	20.16	19.65

From the spectra in **Figure 6** it was noted that there are clear differences in the peaks between the materials analysed with the PVA peak consistently at around 20 degrees and the graphitic samples all sharing peaks at around 12.7 and 27 degrees respectively. The graphite samples have additional peaks around 54.75. The peak integration revealed that the average crystallite size (**Table 1**) was greater for the graphite samples due to less undamaged layers in the structure and more damaged graphene layers in the expanded graphite samples. Theoretically graphite should therefore exhibit a larger electrical conductivity, however it is due to its close layered anisotropic conductive properties that is hindering its overall electrical conductivity. EG 1 as a pure material does exhibit consistently greater electrical conductivity at lower particle loading compared to EG2 which can be attributed to its larger average crystallite size and the accessibility of its conductive graphene layers.

4. CONCLUSION

The electrical conductivity of the expanded graphite in the composites can be attributed to the accessibility of the graphene layers compared to the hinderance thereof in graphite due to its close layered structure. This is also enhanced by the exfoliation of the layers when mixing with polymers as confirmed by SEM and there does appear to be little degradation of the crystallite sites in the material as confirmed using XRD. It was proven that the addition of expanded graphite and graphite to PVA the modulus and elongation at break is reduced. For the epoxy and geocomposite samples the higher and more exfoliated loadings of filler attributed to an increase in modulus and elongation at break with the smaller graphite particles faring better as reinforcement. Even though both expanded graphite filler materials are sold without there being a difference indicated; this work has proven that there are distinctly different properties between the particles which can influence the final properties of composites in terms of conductivity and mechanical properties.

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