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Combination of micro-computed X-ray tomography and electronic microscopy to understand the influence of graphene nanoplatelets on the thermal conductivity of epoxy composites

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ABSTRACT

An innovative combination of micro-computed X-ray tomography (μCT) and electron microscopy (SEM) coupled to an image-processing software was used to study the thermal conductivity of graphene nanoplatelets(GNP)/epoxy composites. This approach afforded a precise and systematic analysis of the dispersion state of the fillers in the epoxy matrix. Here, the influence of GNP aspect ratio on thermal conductivity enhancement (TCE) and the relationship between dispersion state of the fillers and TCE is revealed. The aggregation level of GNP was finely tuned by varying the sonication power. An unexpected trend towards enhanced thermal conductivity upon aggregation of the fillers is demonstrated. Moreover, μCT analysis revealed the encapsulation of micro-voids, undetectable with conventional methods, by large fillers aggregates. This study demonstrates that aggregation of the fillers increases the thermal conductivity of epoxy composites as long as it does not lead to voids encapsulation.

1. Introduction

Polymer composites with high thermal conductivity are in strong demand for efficient thermal management in many modern applications such as electronics, batteries, aerospace devices, LED lightings, *etc*. [1–3]. However, neat epoxy resins, and bulk polymers in general, are poor conductors with thermal conductivities ~ 0.1 – 0.5 W/mK [4]. Improved thermal conductivity is achieved by incorporating high thermally conductive fillers in the polymers such as, traditionally, metallic particles [5].

Carbon fillers have attracted a lot of interest lately due to their extremely high intrinsic thermal conductivity (~ 3.000 W/mK for carbon nanotubes [6] and ~ 5.000 W/mK for single layer graphene [7]), light weight and high aspect ratio. Among these fillers, expanded graphite (EG) [8], carbon nanotubes (CNT) [9] and graphene/graphite nano-platelets (GNP) [10] are very promising for next-generation polymer-based composites. In recent years, several studies reported outstanding thermal conductivity enhancement (up to 3 – 5 W/mK) in nanocarbon/polymer composites [11–14]. However, this is usually achieved by densification of the carbon fillers in the polymer matrix, leading to a dramatic increase of the composite's viscosity and brittleness. Moreover, such viscosity increase cannot be tolerated in many applications due to processing requirements [15]. Therefore, optimization of the thermal conductivity at low fillers loading is crucial in order to improve the composite performances, while maintaining suitable viscosity and mechanical properties. To this end, in this study, we investigated the main parameters influencing the thermal conductivity at low loading fractions.

Thermal conductivity enhancement of nano-carbons/epoxy composites at low loading fractions is still underperforming compared to expectations and theoretical predictions. In recent years, several studies investigated the nano-carbons/epoxy composites thermal conductivity and spotted different parameters responsible of the poor enhancement of the thermal conductivity [16].

The dispersion state of the filler is usually given as the most crucial parameter to achieve optimal properties in nanocarbon/polymer composites. It is commonly reported that homogeneous dispersion is required to achieve optimal electrical [17], mechanical [18] or thermal

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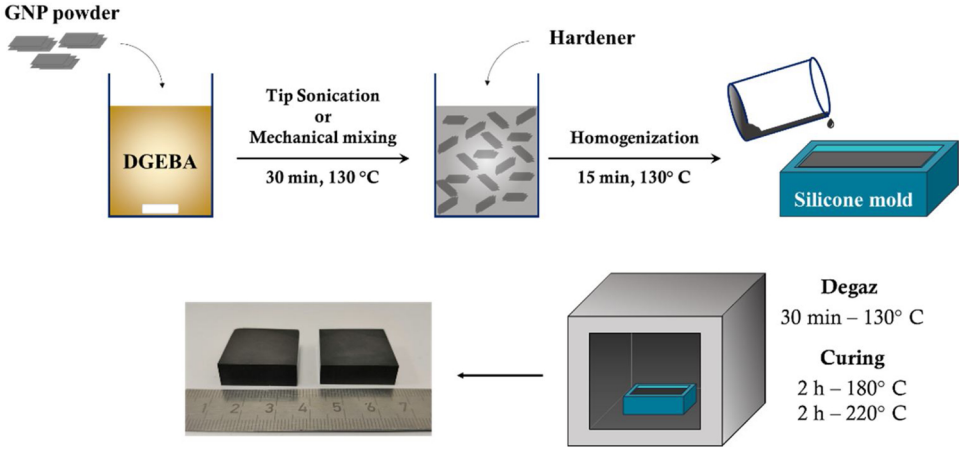

Fig. 1. Schematic of the epoxy composites production process.

[19] properties. However, several papers have contradictorily suggested fillers aggregation to enhance the composites properties compared to homogeneously dispersed fillers. For example, Song et al. [19] and Hoseini et al. [20] reported improved mechanical and electrical properties with aggregated fillers. Evans et al. [21] also supported theoretically that thermal conductivity of nanocomposites might be significantly enhanced as a result of particles aggregation. In the past decade, different papers have studied fillers functionalization to achieve improved dispersion and best interaction with epoxy matrix [22–25]. However, this approach does not allow understanding how the dispersion/aggregation level of the pristine fillers influences the thermal conductivity of epoxy nanocomposites.

Among the diverse dispersion techniques for the fillers, sonication is usually presented as a powerful method to achieve a homogeneous dispersion state. However, the benefit of sonication has been questioned by several reports. For example, Tarawneh et al. [26] demonstrated that extended exposure to ultrasound led to decreased mechanical performances. Chen et al. [27] also observed a detrimental influence of sonication on the tribological properties of CNT/epoxy composites. Thus, our understanding of the real influence of sonication on nanocarbon/polymer composites remains blurry and requires in depth investigation, especially for thermal conductivity enhancement. Indeed, electrical conductivity and mechanical properties have been far more studied than thermal conductivity effects.

Carbon fillers geometrical and morphological parameters are also under debate. It is commonly accepted that longer fillers have a positive influence on polymer composites thermal conductivity [3]. However, influence of the carbon fillers thickness and aspect ratio remains unclear. Shen et al. highlighted the good results obtained with thick GNP compared to few and mono-layer graphene particles in epoxy composites [28]. By opposition, Min et al. [17] suggested the highest aspect ratio, with thinnest fillers, to achieve the best thermal conductivity enhancement.

It appears that our understanding of the influence of the dispersion state and the geometrical parameters of nanocarbon fillers is still blurry. Moreover, the benefit of sonication on the composite performances is questioned by the contradictory results presented in the literature. Therefore, a critical work is required on the effective influence of these parameters on the thermal conductivity of epoxy composites at low loading fractions of carbon fillers. This is justified both by understanding and choosing the best parameters for thermal conductivity enhancement. In this study, we investigate and discuss the influence of sonication parameters, dispersion state and fillers geometrical parameters, in comparison with the advances in the field of thermal conductivity enhancement of carbon/epoxy composites. In particular, we investigate graphene nanoplatelets as very promising and economically-viable fillers. We used an innovative combination of SEM/ImageJ analysis coupled with micro-computed X-ray tomography (μCT) results to draw our conclusions. The data presented bring a novel and better understanding of the fundamental parameters influencing the thermal conductivity of epoxy composites.

2. Experimental and methods

2.1. Materials

Graphene Nano-Platelets (GNP) were purchased from Strem Chemicals with no further purification. Expanded Graphite (EG) from SGL group was used as received. The epoxy resin, D.E.R. 332 ™, liquid epoxy resin based on bisphenol A diglycidyl ether (DGEBA) (manufactured by DOW chemicals) with 4,4′-diaminodiphenyl sulfone (DDS, 97 %), as the hardener, were purchased from Sigma Aldrich. Both were used as received.

2.2. Preparation of GNP-EG/epoxy composites

GNP or EG powder (557 mg for 2 wt. %) was added to 20 g of DGEBA in a glass bottle. The mixture was placed in an oil bath at 130 °C and stirred, or probe sonicated for 30 min. After dispersion of the fillers, 7.3 g of (solid) hardener (DDS) was added to the mixture and homogenised for 15 min with continuous stirring (or sonication). Finally, the mixture was poured in a silicon mold and degassed in a vacuum oven. The epoxy composite was cured at 180 °C for 2 h followed by a post-curing step at 220 °C for another 2 h (Fig. 1).

The resin-to-curing agent weight ratio was 100:36.5. The probe ultrasonicator used is a Hielscher UP400S (400 W, 24 kHz) with power and phase regulation allowed. The sonotrode H3 was used for all composites with a 0.5 phase.

2.3. Characterization methods

The SEM micrographs were acquired on a Quanta FEG 200 (FEI) Spectrometer. For the coverage percentage of the fillers, all images were acquired with similar parameters (HV: 15.00 kV, Mag.: 100x, P: 100 Pa, WD ~ 9–10 mm Det.: LFD). For each sample, a minimum of six different images were randomly taken over the composite surface. All sample were previously polished with an automated procedure on a Struers Tegramin 25. SEM micrographs were post-treated with *ImageJ* to extract the surface coverage (in %) of the fillers on a section of the polymer composite. First, the pictures were duplicated without the parameter bar. FFT bandpass filter (100, 1 pixels, 5 % tolerance) was applied on the duplicates. The threshold was adjusted between ~

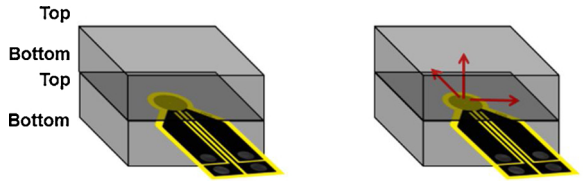

Fig. 2. The Hot Disk sensor was sandwiched with two composites pieces and the thermal conductivity was recorded (isotropic mode). Both sides (top and bottom) of the two sample pieces were tested.

70–90 to extract only the dark fillers over the greyish matrix background. Finally, the area limited to threshold (*i.e.* limited to the fillers) was divided over the total area to give the coverage percentage of the fillers.

The composites thermal conductivity was measured under normal temperature and pressure conditions with a Hot Disk TPS 2500S instrument according to the ISO 22007-2 standard. To avoid any error due to sedimentation or inhomogeneous dispersion of the fillers, the composite bar was debited into cubic pieces with a precision saw (Struers Accutom-50) and each faces ("top" and "bottom") were put in contact with the hot disk sensor (c5465, kapton coated). Hence, a minimum of 4 measurements were recorded (*i.e.* top-top, top-bottom, bottom-top and bottom-bottom) for all composites (Fig. 2).

The thickness of GNP fillers was recorded by mean of an AFM MFP3D Infinity from Asylum Research (Santa Barbara, USA). The tip used for the experiments is an AC160TS from Olympus (Japan) with resonant frequency of 300 KHz and 26 N/m stiffness. The topography was recorded in tapping mode by keeping the amplitude of the first tip resonance constant *via* the Z direction feedback loop electronic. Images of 512 pixels x 512 pixels were recorded between 0.5 Hz–1 Hz line speed.

The glass transition temperature (T_g) was recorded on a DSC NETZSCH 204F1 PHOENIX. Composites samples of ~ 10 mg were sealed in aluminium crucibles. The samples were heated from room temperature to 300 °C at 10 °C min^{-1}. The T_g values were taken at midpoint.

Raman spectra were acquired for GNP powders and epoxy composites using a Raman spectroscope (Renishaw inVia micro-Raman spectrometer) with a 532 nm laser. The Raman spectra were measured at a magnification of 100X in a wavenumber range of 900–2000 cm^{-1} for G and D peak analyses and 2000–2900 cm^{-1} for 2D peak analyses.

Wide-angle x-ray scattering (WAXS) testing was conducted using a Panalytical X'Pert Pro MPD diffractometer (Almelo, The Netherlands) in its transmission mode. Composite samples with dimensions of 1 cm (length) ×1 cm (width) ×0.2 cm (thickness) were characterized with the kα radiation of copper (wavelength λ = 1.54 Å) generated at 45 kV and 40 mA. The scattering signal was recorded between 2θ = 5° and 2θ = 40°, enabling to visualise the scattering of both DGEBA matrix and graphite-based fillers.

To characterize the 3D morphological features of the composites, micro-computed X-ray tomography (μCT) was employed. To this end, 4 mm × 1 mm × 1 mm rectangular samples were scanned by means of a μCT EasyTom 160 fabricated by RX solutions. The acquisition was conducted with an X-ray source voltage of 40 kV, current of 90 μA and power of 3.6 W, to ensure a good phase contrast between the epoxy matrix and graphene fillers. The frame rate was set to 2 frames per second and the number of average frames was 5. During the scan, the samples were rotated 360° in angular steps of 0.25°, providing 1440 projections. The source-object-distance was set at 3.5 mm while the source-detector-distance was 255 mm, enabling a voxel size of 1.75 μm. The detailed procedure of the 3D-reconstruction *via* software processing (Xact64, RX Solutions), and analysis of the reconstructed 3D volumes *via* Avizo software (ThermoFisher) can be found in the supporting information.

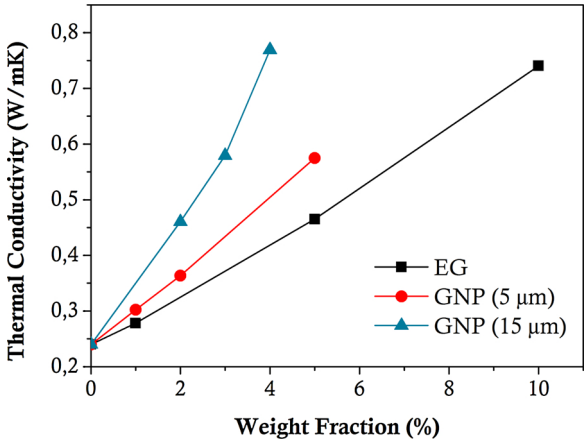

Fig. 3. Thermal conductivity of epoxy composites as a function of the weight fraction of different carbon fillers. Expanded Graphite (EG) depicted as black squares, 5 μm-long graphene nano-platelets (GNP) as red circles and 15 μm-long GNP as blue triangles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

All composite samples were prepared following the same procedure. Epoxy resin (Bisphenol A Diglycidyl Ether- DGEBA) was heated at ~ 130 °C to lower the viscosity and ease the fillers dispersion in the resin. It has been reported that low viscosity is a key parameter to achieve good dispersion [29]. Then, the hardener (4,4′-Diaminodiphenyl sulfone – DDS) was added and the composites were cured 2 h at 180 °C followed by a post-curing step at 220 °C for another 2 h. The thermal conductivity (TC) of all samples was measured using the transient plane source (TPS) method with a HOT DISK TPS 2500S.

3.1. Influence of fillers geometrical parameters

3.1.1. Particle size

Expanded Graphite (EG) and Graphene Nano-Platelets (GNP) are the most promising fillers for thermal conductivity enhancement in the polymer composites industry due to their commercial availability, low cost and excellent thermal conductivity. Hence, thermal conductivity enhancement of epoxy composites were compared with GNP and EG as a function of weight fraction (Fig. 3).

As expected, the general tendency shows an improvement in thermal conductivity for all composites as the weight fraction (wt. %) of highly conductive filler increases. It is clearly visible when comparing GNP and EG that fillers size plays a crucial role on the thermal conductivity. The thermal conductivity, ~ 0.77 W/mK (TCE – Thermal Conductivity Enhancement: 220 %), obtained with 4 wt. % of GNP (15 μm long) is much higher than ~ 0.45 W/mK (TCE: 88 %), obtained with 5 wt. % of EG. Our experimental data agreed well with previous reports. Shen et al. reported TCE values between ~ 96 and 240 with carbon fillers having different thicknesses [28]. Min et al. [17] also reported thermal conductivities around ~ 0.7 W/mK for epoxy composites with 2.703 vol. % GNP.

Thermal conductivity perpendicular to the surface of carbon platelets is much lower compared to the "in-plane" conductivity (~ 5 W/mK against ~ 3.000 W/mK for GNP) [7,30]. It is therefore beneficial to reduce the number of stacked sheets, with low inter-platelet conductivity, and rather promote an increase of platelets number for the same weight fraction in the composite. Switching from 3-D expanded graphite to quasi 2-D graphene nano-platelets allows a higher density of heat channels to be created in the polymer, with the multiplication of carbon fillers objects for the same weight fraction.

Nevertheless, reducing the fillers thickness does not always cause

thermal conductivity enhancement. It has been demonstrated that mono and few layers graphene can roll up into nano-scrolls and lose the benefit of low dimensionality [28,31]. Shen *et al.* demonstrated that monolayer and few-layer graphene were least efficient in enhancing the thermal conductivity of polymer composites compared to thicker GNP with a better rigidity [28]. Carbon nanotubes (CNT) have been extensively studied due to their low dimensionality (1D) in polymer composites. However, their low rigidity was also reported detrimental for thermal conductivity enhancement due to wall bending and reduced thermal conductance at the interfaces [32]. Low dimensionality is crucial as long as good rigidity is maintained. Therefore, GNP with quasi-2D aspect and high rigidity is probably the best compromise for TC improvement in polymer composites.

3.1.2. Aspect ratio

Thickness of the fillers plays a crucial role for maintaining the rigidity and avoid wrinkles/folding of the fillers. Fig. 3 also suggests that long GNP (average lateral size ~ 15 µm) are more efficient in enhancing the thermal conductivity compared to short GNP (average lateral size ~ 5 µm). Influence of filler's aspect ratio was studied using different GNP batches having the same thickness (*i.e.* number of stacked sheets) with different length/diameter ranging from ~ 1 µm to ~ 25 µm long. The aspect ratio of the different fillers was calculated by dividing the length/diameter of the fillers by their thickness. The lateral size announced by the supplier (*i.e.* ~ 1–2, 5, 15 and 25 µm) was consistent with our analyses: 1.7 ± 0.8 µm, 6 ± 3 µm; 14 ± 6 µm and 25 ± 10 µm (Fig. 4), however the few nanometres announced for the thickness (~ 6–8 nm) was actually observed to be around ~ 20 nm (AFM measurements, Fig. S.1) probably due to aggregation arising during processing of the fillers. It is noteworthy that the lateral size distribution in the batch "GNP-25" did not fit with the Lognormal function. Thus, the distribution was fitted with a simple Gaussian function. The broader distribution in this batch probably comes from the purification process employed by the supplier.

Thermal conductivity enhancement was plotted as a function of aspect ratio of the nanocarbon fillers (Fig. 5). It is usually reported that increasing the aspect ratio leads to a monotonically enhancement of the thermal conductivity in polymer composites [17]. However, we observed that thermal conductivity enhancement follows a trend towards saturation around an aspect ratio between ~ 500–700.

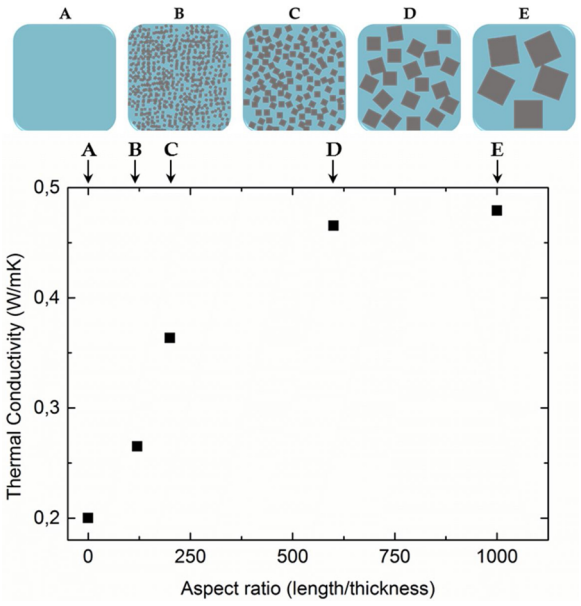

Fig. 5. Influence of GNP aspect ratio on the thermal conductivity of epoxy composites. Schematic representation of a) neat epoxy resin and epoxy composites with b) 1 – 2 µm GNP c) 5 µm d) 15 µm GNP and e) 25 µm GNP.

This trend is understood by considering two key aspects. First, the longer the fillers, the more likely a "heat channel" is created between the carbon fillers (the probability of contacts between fillers increases with aspect ratio). Second, as the fillers are getting longer, the number of interfaces between the polymer and the fillers reduces. Thus, the influence of interfacial thermal resistance (ITR) reduces when aspect ratio increases. Every time the heat wave has to face an interface between the filler and the epoxy matrix, the acoustic mismatch (phonon

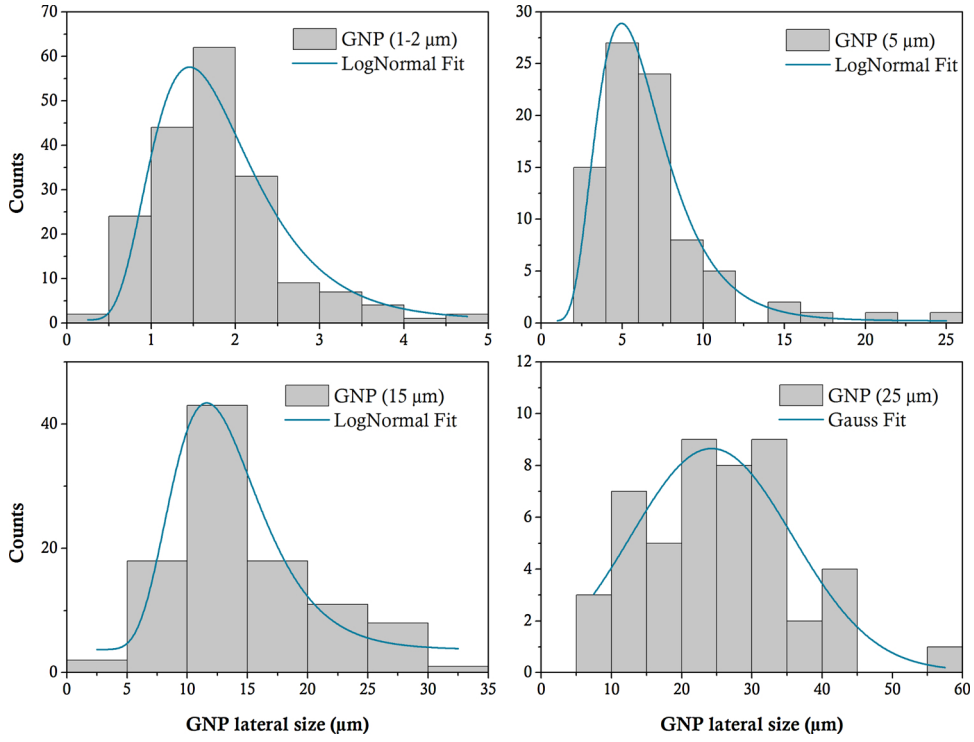

Fig. 4. Histograms of fillers size distributions based on SEM images for a) GNP (~ 1 – 2 µm) b) GNP (5 µm) c) GNP (15 µm) and d) GNP (25 µm).

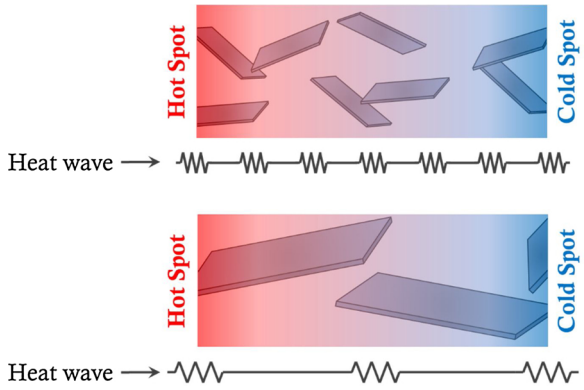

Fig. 6. Schematics of fillers aspect ratio influence. With smaller fillers, the heat wave faces more interfacial thermal boundaries (*i.e.* more thermal resistances), leading to a decrease in the overall thermal conductivity.

scattering) leads to a decrease in the overall thermal conductivity of the composite. Therefore, the longer the fillers, the less interfacial thermal resistance (sometimes referred as Kapitza resistance) is influencing the composites thermal conductivity (Fig. 6). This classic way of considering thermal conductivity in polymer composites explains why TC increases with aspect ratio. However, it does not predict a saturation at high aspect ratio values.

Experimental reports of saturation effects date back to 2007 with the work of Yu et al. [32] or more recently with the work of Wattanakul et al. [33] on BN fillers. However, the results were not discussed or interpreted with classical models [34]. Thus, in the literature, it is still generally accepted that a linear increase should be observed with aspect ratio. Nevertheless, recent theoretical works have offered new ways to apprehend these results. For instance, Ruminski et al. [35] investigated the geometrical parameters of nanocarbon fillers and predicted, based on a modified Bruggeman model, a plateau occurring in the same range as we obtained in Fig. 5. Zeng et al. [36] and Bonfoh et al. [37] both theoretically investigated the influence of the filler size on the effective thermal conductivity. They both demonstrated a saturation trend dependent on the size and aspect ratio of the fillers. The saturation trend was explained as a gradual diminution of the ITR influence until a negligible value. Luo and Lloyd [38] and Hu et al. [39] also supported a saturation trend by investigating the phonon frequencies excited as a function of fillers length/lateral size. They observed an increase until a limit where all possible phonon frequencies were activated.

These theoretical works suggest that influence of ITR reduces when increasing the filler size, either with a reduction of the number of

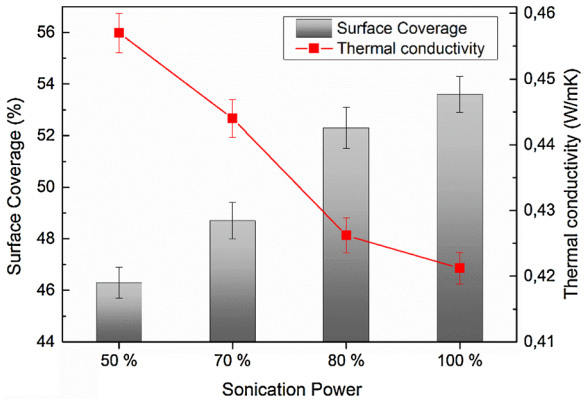

Fig. 8. Thermal conductivity and percentage of surface coverage by the fillers after 30 min sonication, with different sonicaton power (in percent of full power), for epoxy composites containing 2 wt. % of GNP (25 µm). (For interpretation of the references to colour in this figure text, the reader is referred to the web version of this article.)

Table 1
Glass transition and thermal conductivity for 2% wt. GNP (25 µm)/epoxy composites.

Sample	Sonication power (W)[a]	T_g (°C)[b]	Thermal Conductivity (W/mK)
GNP(25)-50	200 (50 %)	218	0.451 ± 3.10^{-3}
GNP(25)-70	280 (70 %)	222	0.444 ± 4.10^{-3}
GNP(25)-80	320 (80 %)	220	0.426 ± 3.10^{-3}
GNP(25)-100	400 (100 %)	220	0.421 ± 2.10^{-3}

[a] Power percentage in brackets.
[b] Midpoint (DSC).

resistances, as schematically depicted in Fig. 6, or by increasing the intrinsic thermal conductivity of the fillers, with a higher number of excited phonon frequencies. Thus, the influence of ITR reduces until a limit where it becomes negligible and where the effective thermal conductivity reaches a plateau as observed in Fig. 5. This consideration also led Shen et al. and Wang et al. to propose a critical size theory for functionalization [40,41]. Our results support experimentally the recent theoretical predictions and suggest that appropriate size selection of the fillers should be considered in order to optimize the thermal conductivity enhancement.

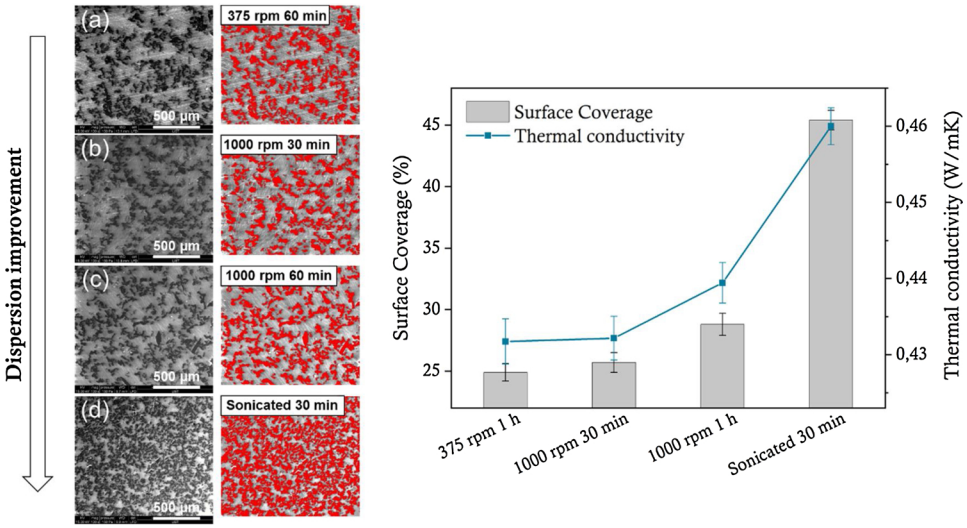

Fig. 7. Left (Top – down) SEM micrographs with the corresponding ImageJ-processed images of composites containing 2 % in wt. of GNP (25 µm) mechanically stirred for a) 60 min at 375 rpm, b) 30 min at 1000 rpm c) 60 min at 1000 rpm and d) sonicated for 30 min. Right, thermal conductivity (blue line) and fillers surface coverage (grey bars) of the composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

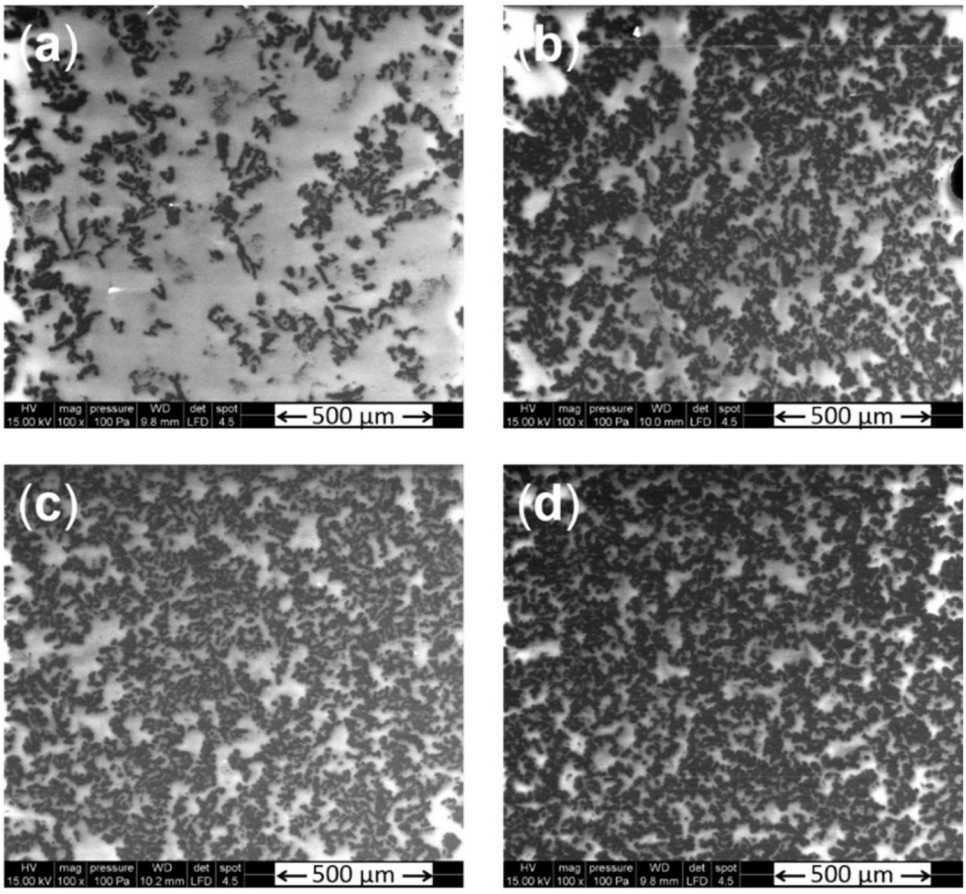

Fig. 9. SEM images of epoxy composites containing 2 % wt. of GNP (25 µm) a) mechanically stirred b) sonicated at 50 % of total power (*i.e.* 200 W) c) 70 % (280 W) and d) 100 % power (400 W).

3.2. Influence of dispersion process

3.2.1. Dispersion

Besides intrinsic fillers' characteristics (dimensionality and aspect ratio), the influence of dispersion state was investigated. Composites were produced by mechanical stirring and sonication. Duration and stirring rate were varied for mechanical mixing and compared with sonication. In order to evaluate numerically the dispersion state of fillers, SEM micrographs of the composites were analysed with *ImageJ*. The surface area covered by the fillers was extracted from a composite section of approximately ~ 1.9 mm^2. The software allows extracting the black fillers over the greyish matrix background (*i.e.* the epoxy resin) with a simple threshold differentiation (Fig. 7). Finally, the surface area covered by the fillers (highlighted in red) is divided by the total area to give a coverage percentage (*i.e.* numerical evaluation of the dispersion state).

Both the surface coverage and the thermal conductivity increase in a very similar trend when duration and/or stirring rate increase (Fig. 7). Moreover, thermal conductivity and surface coverage show the same abrupt increase when switching from mechanical mixing to sonication. The SEM micrographs clearly highlight that mechanical mixing and sonication have different impacts on the fillers dispersion. Increasing duration and/or stirring rate for mechanical mixing allows a better dispersion of the large GNPs aggregates. However, it does not allow these large aggregates to be broken up. Large aggregates (> 100 µm) are still visible on the SEM micrographs after mechanical mixing for 1 h at 1000 rpm. The abrupt increase in surface coverage observed with sonication suggests a disaggregation and/or delamination of the fillers under the power of ultrasounds. Moreover, the reduction in size of the aggregates is visible on the SEM micrographs.

It has been demonstrated for graphene oxide (GO) and CNTs that sonication is powerful enough to delaminate and reduce the fillers length/size. However, this has been observed for damaged (oxidized) fillers and the suspected mechanism of breakage was based on the already existing defects at the oxidized sites [42]. The same deterioration based on already existing defects and oxidized sites has been demonstrated for CNT while non-oxidized CNT remained intact [27]. In this work, a size reduction effect or delamination of the nanoplatelets by sonication was refuted by XRD (Fig. S.2) and Raman spectra (Figs. S.3 + S.4) analysis. Hence, we can conclude that the large increase in surface coverage is only due to disaggregation of the fillers (*i.e.* it only comes from the dispersion state and does not come from a modification of the fillers microstructure).

3.2.2. Sonication power

Sonication's influence was further investigated by comparing composites prepared with different sonication powers, for 30 min. It is noteworthy here that the graph (Fig. 8) shows a reverse trend for the thermal conductivity (red line) with respect to the area covered by the fillers (*i.e.* the dispersion state of the filler). The sample sonicated at 100 % power showed a thermal conductivity of ~ 0.42 W/mK (TCE: 75 %) at 2 wt. % compared to ~ 0.46 W/mK (TCE: 92 %) with a reduced sonication power (50 %).

The glass transition temperatures (T_g) of the different composite samples were measured by DSC (Table 1). The *Tg* value was found constant throughout the different samples. This point is crucial to assume that thermal conductivity enhancement is only due to the dispersion state of the filler. Prolonged sonication treatment have been demonstrated to cause an early polymerization and lead to a degradation of the mechanical properties in epoxy composites [43] or rubber

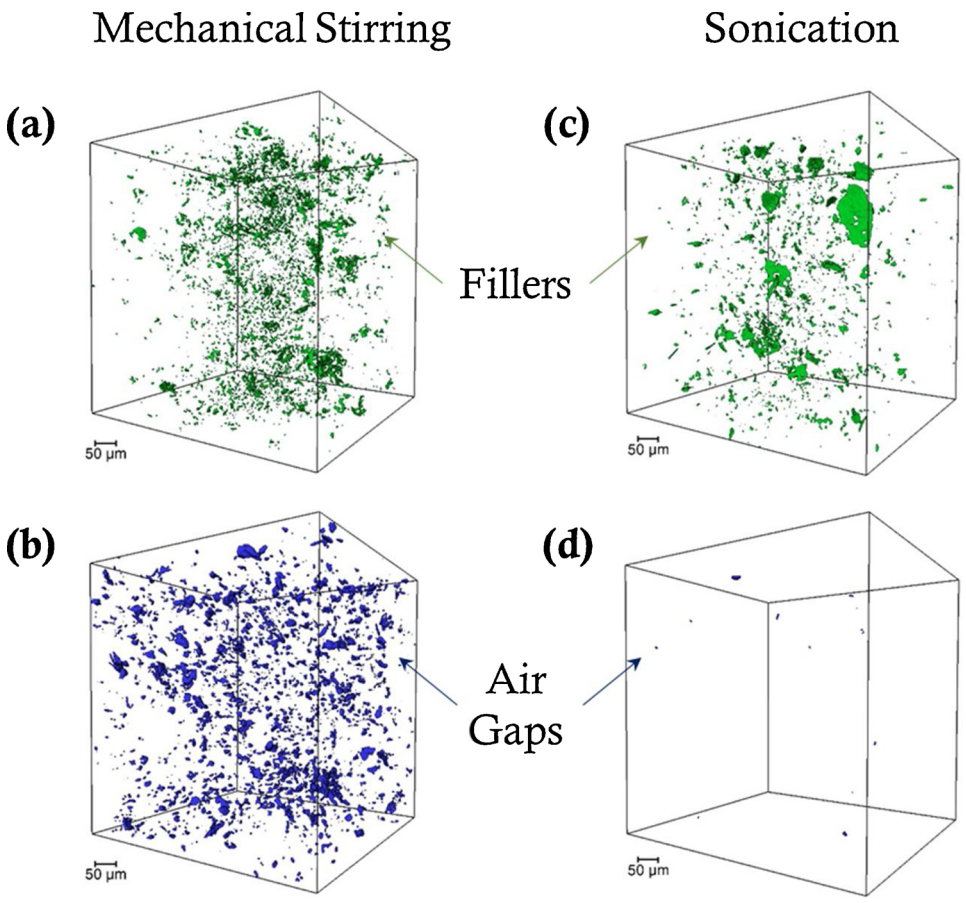

Fig. 10. µCT 3D-reconstruction of GNP/epoxy nanocomposites. The GNP fillers mechanically dispersed (a) or dispersed with sonication (c) are presented in green. The air voids observed in the same composite volume are presented in blue for (b) epoxy composite mechanically stirred and (d) epoxy composite sonicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

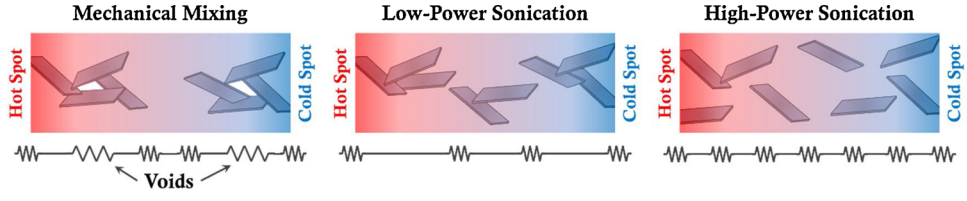

Fig. 11. Schematic representation of the different aggregation levels encountered in epoxy composites. The heat wave faces less interfacial thermal resistances when the fillers are aggregated (with low-power sonication or with mechanical mixing). However, large aggregates obtained with mechanical mixing causes micro-voids encapsulation, leading to a dramatic decrease of the thermal conductivity.

composites [26]. With the T_g values reported in Table 1, we assume that the thermal conductivity enhancement is due to a modification of the dispersion state.

In this study, we highlighted a clear trend towards lower thermal conductivities with higher sonication power (Fig. 8).The SEM micrographs (supported with *ImageJ* analysis) exhibit a quasi-full disaggregation at 100 % sonication power (Fig. 9d). On the contrary, mechanical stirring leads to much bigger aggregated structures (Fig. 9a). The samples obtained with 50 and 70 % power of sonication show a gradual disaggregation towards the homogeneous dispersion depicted in Fig. 9d. The sample at 50 % of sonication power depicts a mixture of small aggregates (size > 40 µm) and fully disaggregated fillers (size ~ 15–30 µm). Several other studies have reported a detrimental effect of harsh sonication conditions (time and power). Montazeri and Chitsazzadeh [44] reported that mild sonication power and time was best for mechanical properties improvement in MWCNT/epoxy composites. Suave et al. [45] also reported that lowest sonication power was best for the improvement of thermo-mechanical properties of carboxylated-SWCNT/epoxy composites.

From the analysis of the sonicated samples, aggregation of the fillers appears beneficial for thermal conductivity enhancement. By contrast, the most aggregated case obtained with mechanical mixing (Fig. 9a), shows the lowest thermal conductivity enhancement. For gaining deeper understanding of this phenomenon, the epoxy composites were further investigated by mean of micro-computed X-ray tomography (µCT). This non-destructive characterization technique allowed us to observe new features, invisible with conventional imaging techniques such as SEM analysis. Indeed, in Fig. 10, it clearly appears that a huge number of micro-scale voids are present in the epoxy composite, dispersed mechanically, when compared to the sonicated sample. Moreover, these voids are located in the same regions as the fillers. Therefore, we suggest that the micro-voids are related to and caused by the fillers aggregates. The large aggregates such as those observed after mechanical stirring are probably acting as encapsulating cages, leading to the formation of thermally insulating air pockets (micro-voids). These thermally insulating voids are obviously detrimental for the thermal conductivity enhancement of the composite.

It appears from the combination of SEM and µCT imaging that aggregation of nanocarbon fillers is beneficial to the thermal conductivity of the composite as long as this aggregation does not lead to the formation of micro-voids. Contrarily to the current view of ultrasounds effects, the present study suggests that sonication should not be considered as a conventional tool for improving the dispersion state of the fillers but rather as an effective tool for controlling the aggregation

level of the fillers in order to avoid the formation of micro-voids.

Finally, as mentioned in the introduction, several papers already suggested aggregation as a convenient way to improve electrical, and mechanical properties of polymer composites [16,19,20]. In this work, we demonstrated a clear trend towards enhanced thermal conductivity upon aggregation of the fillers. Moreover, in light of the combined analysis of the epoxy composites with SEM/imageJ and μCT, we are now able to propose a clear understanding of the process behind this phenomenon. Similarly to the results presented for the influence of the fillers geometrical parameters, aggregation can be viewed as a way to artificially increase the size of the fillers. At low loading fractions (below the percolation threshold), the fillers connected to each other allow the heat wave to go effectively from filler to filler without going through the polymer matrix. Thus, the heat wave faces less interfacial thermal resistances as if the fillers were disaggregated (Fig. 11).

Besides aggregation and dispersion state of the fillers, micro-computed X-ray tomography spotted micro-voids in nanocarbon aggregates. To our knowledge, this is the first time that such features are demonstrated in GNP/epoxy composites. Moreover, this observation allowed us to propose a clear vision of the process behind aggregation in polymer composites and its influence on the thermal conductivity enhancement.

4. Conclusion

The superior performance of GNP compared to EG is demonstrated for thermal conductivity enhancement in epoxy composites. This is directly related to the rigidity and quasi-2D characteristics of GNP. Further investigations on GNP dimensions showed that thermal conductivity increases along with GNP aspect ratio (length/thickness) until saturation.

The influence of the dispersion state of the fillers was precisely investigated with an innovative combination of μCT and SEM/imageJ analyses. An in-depth analysis of the sonication power demonstrated the ability of sonication to finely control the aggregation/dispersion state of the fillers. Surprisingly, a clear trend toward enhanced thermal conductivity upon aggregation was observed. However, the combination with μCT also demonstrated that large aggregates, obtained with mechanical mixing, can lead to micro-voids encapsulation. In this case, aggregation reduced dramatically the thermal conductivity. This explains the contradictory results reported in the literature about the influence of aggregation on the thermal conductivity. To the best of our knowledge, this is the first time that micro-voids encapsulation by nanocarbon aggregates is reported by μCT, while being undetectable with conventional techniques. This unprecedented precise study of the dispersion state of the fillers, along with the novel micro-features highlighted by μCT, highlights and provides a better understanding of the key parameters responsible of the thermal conductivity enhancement in epoxy composites.

CRediT authorship contribution statement

Sebastien Depaifve: Conceptualization, Methodology, Investigation, Writing - original draft, Visualization. **Sophie Hermans:** Conceptualization, Methodology, Writing - review & editing, Supervision. **David Ruch:** Supervision, Project administration. **Abdelghanni Laachachi:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2020.178712.

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