ABSTRACT
Silane-functionalized graphene nanoplatelets (GNPs) were prepared using a newly developed approach based upon a simple two-step strategy. The effect of their dispersion and interfacial bonding on the mechanical properties and thermal conductivity of reinforced silicone rubber (SR) was investigated. It was found by Raman mapping that the silane-functionalized GNPs could be dispersed uniformly into the SR matrix, leading to an increase of up to 25% in Young's modulus at only 2 parts per hundred rubber (phr) loading and a considerable enhancement of up to 150% in the thermal conductivity at 5-phr loading. Both the Young's modulus and thermal conductivity experimental results were found to be in agreement with the values predicted using theoretical models.
Introduction

Silicone rubber (SR) is an extensively used industrial material that has received considerable interest owing to its outstanding properties. Its excellent physical properties and chemical inertness, wide working temperature range (-100 ~ 300°C) as well as better tolerance to UV, ozone and ageing compared to its organic counterparts make this material suitable for applications in extreme environments [1, 2]. Traditionally, SR finds applications in circumstances where good thermal stability, high dielectric strength and fire resistance are desired. Nowadays, novel silicone materials are expected to meet the increasing demands for highly thermally conductive rubbery materials with reasonably good mechanical properties applicable in extreme conditions raised by the development of modern technologies [3, 4].

Graphene, first isolated in 2004 [5], is a two-dimensional (2D) and one-atom-thick nanomaterial consisting of $sp^2$-hybridized carbon atoms. Its outstanding mechanical, thermal and electric properties make this nanomaterial have great potential as reinforcements in polymer composites [6]. The high cost and complicated production process may, however, limit its large-scale applications. Graphene nanoplatelets (GNPs), consisting of multiple layers of graphene, with thicknesses ranging from that of graphene to approximately 100 nm, have attracted attention as an economically viable alternative to graphene in large-scale applications [7]. Both graphene, usually in the form of graphene oxide (GO), and GNPs have been studied as reinforcing fillers to improve the mechanical properties and thermal conductivity of the silicone rubber composites [8–13]. The overall reinforcement of these graphene-based materials to the SR matrix depends significantly on its dispersion level as well as the interfacial adhesion between filler and matrix [12, 14, 15]. The later can be significantly improved by the surface modification of the fillers, particularly GO [12, 15–23]. Silane coupling agents, such as (3-aminopropyl)triethoxysilane (APTES) and vinyltrimethoxysilane (VTMS) [12, 15, 19–24], are typically used to react with GO or GNP fillers to improve the compatibility with the SR matrix. The similarities in chemical composition and structure of the functional groups with polysiloxanes allow the formation of a better interface between the functionalized fillers and the matrix, thus resulting in an enhancement of both the mechanical properties and the thermal conductivity of the SR composites.

This work aims at the study of the effect of silane-functionalized GNPs (f-GNP-Si) upon the mechanical properties and the thermal conductivity of SR composites. The covalent functionalization of GNPs with a silane coupling agent was performed using a simple two-step strategy. Typically, GO or rGO is used as a precursor for further reactions with silane coupling agents [17–20, 22]. In this work, a different
approach was used as first step involving the introduction of carboxyl functionalities to the surface of the GNP, through a solvent-free reaction, according our previous work [25, 26]. The second step comprised the reaction of those carboxyl functionalities with (3-aminopropyl)-trimethoxysilane (APTMS). The dispersion of the f-GNP-Si into the SR matrix was also analysed and compared with that of unmodified GNP/SR composites.

**Experimental**

**Materials**

Micronized graphite (grade Micrograf HC11) with a surface area of 27 m²/g and an equivalent diameter of about 10 μm was provided by Nacional de Grafite, Brazil. These micronized graphite particles typically have more than 10 layers; thus, they should be formally termed as “graphite” nanoflakes. Such materials are, however, often labelled “graphene” nanoflakes in the literature [27], and therefore, this terminology will also be adopted in this present study. Paraformaldehyde (PFA) reagent grade, crystalline, iminodiacetic acid (IDA) purum ≥ 98% and (3-Aminopropyl)-trimethoxysilane (APTMS) 97% were purchased from Sigma-Aldrich, ethanol absolute (EtOH) was purchased from VWR Chemicals, and acetone analytical reagent grade and chloroform, analytical reagent grade were purchased from Fisher Scientific. The two-component room-temperature vulcanizing SR (Xiameter RTV-4234-T4) was purchased from East Coast Fibreglass Supplies.

**Functionalization of the graphene nanoflakes**

The carboxyl-methyl-pyrrolidine-functionalized GNP (f-GNP, scheme 1) was functionalized according a procedure described in our previous work [25, 26]. The f-GNP-Si was prepared as follows: APTMS (2.0 ml) was added to a suspension of f-GNP (3.0 g) in chloroform (200 ml). The mixture was stirred under N₂, at room temperature, overnight. The resulting mixture was washed with chloroform and collected by vacuum filtration. The product, f-GNP-Si, was dried overnight in a vacuum oven.

**Preparation of the silicone rubber nanocomposites**

The silicone rubber (SR) nanocomposites were prepared as follows: a suspension of GNP or f-GNP-Si in chloroform (20 mg/ml) was sonicated for 1 h. Suspensions with the appropriate loadings of GNPs were hand-mixed into the silicone rubber base compound for the preparation of GNP or f-GNP-Si-reinforced SR with selected loadings: 0.5, 1.0, 2.0 and 5.0 phr, respectively. After complete solvent removal in a vacuum oven, the GNP or f-GNP-Si/silicone compounds were mixed five times in a three-roll-mill (Lab Model from Torrey Hills Technologies) to achieve a good dispersion. After the addition of the curing agent and further manual mixing, the mixtures were deposited into a Teflon mould, degassed under vacuum and cured at room temperature for 24 h.

**Characterization and testing methods**

Thermogravimetric analysis (TGA) was performed on a Modulated TGA Q500 from TA Instruments. The samples were heated at 10 °C/min under a constant flow of N₂. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra X-ray photoelectron spectrometer; curve fitting was accomplished using CasaXPS software. The Raman spectra acquisition and mapping were undertaken on a Horiba Labram HR Evolution confocal microscope, equipped with a motorized x–y stage, using an excitation laser of 633 nm and a 20 x objective lens. The maps were obtained from a 30 x 30 point array with a step size between each point of 4.0 μm (900 spectra). All data were analysed using the LabSpec 6 software. Scanning electron microscopy (SEM) analysis was performed using a FEI Quanta 250 FEG microscope equipped with energy-dispersive X-ray spectroscopy (EDS) system. Differential scanning calorimetry (DSC) was performed on a TA Q100 from TA Instruments under nitrogen atmosphere. The samples were heated from –80 °C to 150 °C, cooled to –80 °C and heated to 150 °C again. The heating/cooling rate was set at 10 °C min⁻¹.

The mechanical property measurements were taken with a universal testing machine (Instron 5960) at a crosshead speed of 100 mm/min according to ISO 37. The values reported were the average of 8 individual test results. Thermal conductivity of the
composites was measured using a LFA 457 MicroFlash® apparatus (NETZSCH, Germany). The samples were prepared according to ASTM E1461 and were tested over a temperature range from 25 to 150 °C.

Characterization of the functionalized nanoplatelets and nanocomposites

Silane-functionalized graphene

The functionalization of the GNPs was carried out using a two-step strategy, as depicted in scheme 1. The first step involves the functionalization of the GNP through 1, 3-dipolar cycloaddition reaction leading to the formation of carboxyl-methyl-pyrrolidine-functionalized GNPs (f-GNP, scheme 1). The detailed characterization of these functionalized GNP is described in references [25, 26]. The second step involves the reaction of the carboxylic acid functional groups of the f-GNP with a silane coupling agent APTMS to obtain the f-GNP-Si (scheme 1).

Figure 1 shows the TGA results (Fig. 1a) as well as the XPS wide scan spectra (Fig. 1b), the Si 2p (Fig. 1c) and C 1 s core-level spectra for the GNP, f-GNP and f-GNP-Si (Fig. 1d–f). The TGA curves of the GNP presented a thermally stable material with a weight loss of less than 2 wt% at 600 °C. In contrast, the f-GNP and f-GNP-Si showed higher values of weight loss at 600 °C (up to 18 wt%) that can be attributed to the thermal decomposition of the functional groups. The f-GNP showed a single degradation step that starts at around 250 °C and may be related to the decomposition of the carboxyl-methyl-pyrrolidine functional groups. On the other hand, in the f-GNP-Si two degradation steps were identified: one below 200 °C, which may result from the thermal degradation of the APTMS chains, and a second step at around 250 °C that can be related to the degradation of the remaining functional groups attached to the pyrrolidine groups.

The surface compositions of the GNP, f-GNP and f-GNP-Si were analysed by XPS. The wide scan spectra in Fig. 1b show peaks centred at around 284 eV, 399 eV, 531 eV and 102 eV corresponding to the binding energies of carbon, oxygen, nitrogen and silicon, respectively. The oxygen content in the GNPs was found to be very low (less than 2%). The nitrogen and oxygen atomic concentrations increased from f-GNP to f-GNP-Si (Table S1) as expected. The [N]/[O] ratio for both f-GNP and f-GNP-Si was found to be around 0.6, while the [Si]/[O] and [Si]/[N] ratios were found to be around 0.3 and 0.5, respectively, for the f-GNP-Si (Table S1, supporting information). These ratios are in agreement with the structures of the f-GNP and f-GNP-Si presented in Scheme 1.

The Si 2p core-level spectrum of the f-GNP-Si in Fig. 1c shows peaks at binding energy values of 101.6 and 102.4 eV corresponding to the contributions of Si–C and Si–O bonds, respectively [28]. The C 1 s core-level spectrum of GNP (Fig. 1d) shows a main peak at 284.5 eV that corresponds to the C=C (sp² bonded carbons). Very small contributions at 285.2 eV, 286.1 eV and 287.2 eV are also identified corresponding to the C–C (sp³ bonded carbons), C–OH (alkoxy) and C=O (carbonyl) moieties, respectively. These contributions may be related to the production method used for these commercial GNPs. The broad weak peak at 291.1 eV is related to the π–π* shake-up transition. The C 1 s core-level spectra of the f-GNP and f-GNP-Si become more asymmetric when compared to the GNP spectrum which is related to the increase in the contributions at 284.5 eV.

Scheme 1 Functionalization scheme of the GNP; (i) IDA and PFA, 200 °C, 5 h; (ii) APTMS, chloroform, room temperature, overnight.
285.2 eV, 286.1 eV and 287.2 eV, explained above. A new contribution is clearly identified at 288.9 eV for the f-GNP arising from the C(=O)O (carboxyl) moieties derived from the carboxylic acid functionalities. Interestingly, this contribution becomes less pronounced for the f-GNP-Si and a new contribution also appears at 283.3 eV, arising from the C–Si bonds [28–32], suggesting that the carboxyl moieties of f-GNP had reacted with the APTMS molecules.

Raman spectroscopy is an important tool for the characterization of graphene. Figure 2 presents the Raman spectra of the GNP, f-GNP and f-GNP-Si. The three main characteristic bands are identified in all spectra: The D band, at around 1330 cm\(^{-1}\), the G band at around 1580 cm\(^{-1}\) and the 2D band at around 2680 cm\(^{-1}\), typical for graphitic materials [33]. The f-GNP and f-GNP-Si showed a more prominent D band along with a shoulder in the G band at around 1620 cm\(^{-1}\) (D’ band) indicating the formation of sp\(^3\) bonds related to the covalently attached functional groups at the GNP surface [25, 34]. The \(I_D/I_G\) ratios of the GNP, f-GNP and f-GNP-Si are 0.09, 0.49 and 0.57, respectively.

The SEM images of the GNP and f-GNP-Si are presented in Fig. 3a, b, respectively. The images showed that the functionalization process resulted in an increased roughness of the surface of the GNP flakes. The EDS single spectra acquired on the GNP (blue spot) and on f-GNP-Si (red spot) are presented in Fig. 3c and clearly showed peaks related to the carbon and oxygen on both samples. Moreover, the
f-GNP-Si showed two additional peaks that are related to nitrogen and silicon. These results are in agreement with the XPS analysis. The EDS mapping of the f-GNP-Si (Fig. 3b) showing the distribution of the carbon, oxygen and silicon elements are presented in Fig. 3d–f, respectively. As depicted in these figures, the distribution of these elements is homogenous all over the sample.

**Thermal analysis**

The influence of GNP and f-GNP-Si on the thermal behaviour of SR was investigated by DSC analysis, and the results are shown in Fig. 4 and Table S2 (supporting information). The melting temperature ($T_m$) was obtained measuring the position of the peak maximum, and the endothermic melting enthalpies ($\Delta H_m$) were calculated measuring the area under the corresponding peaks. By considering the melting enthalpy of 100% crystalline PDMS ($\Delta H_0$) as 37.4 J/g [35, 36] the degree of crystallinity ($\chi_c$) of the neat silicone rubber as well as the GNP and f-GNP-Si SR composites was estimated by the equation:

$$\chi_c = \frac{\Delta H_m}{\Delta H_0 \times (1 - W_f)} \times 100$$

(1)

where $W_f$ is the weight fraction of the filler.

As depicted in Fig. 4, the DSC thermograms showed a slight increase in $T_m$ with the increase in
GNP and f-GNP-Si loading. These phenomena might be related to the limited mobility of the SR chains induced by the incorporation of rigid fillers [16]. Furthermore, the increase in $T_m$ is more prominent for the f-GNP-Si composites. The silane functional groups at the surface of the f-GNP-Si offer active sites for a more effective interaction with the silicone rubber chains which results in an increase in the melting temperature.

Moreover, the degree of crystallinity, $\chi_c$, of the silicone rubber composites was found to decrease with the increasing GNP and f-GNP-Si loading. The addition of GNP and f-GNP-Si might, again, hamper the rearrangement of the silicone rubber chains during the crystallization process. Similar results have been obtained for the incorporation of GNPs into silicone rubber [12] and polyurethane [37] matrices.

### Nanoparticle distributions

The distribution of the GNP and f-GNP-Si in the silicone rubber matrix was analysed by Raman spectroscopy, mapping the relative intensity of the GNP or f-GNP-Si G band to the silicone rubber 1410 cm$^{-1}$ band ($I_G/I_{1410}$) over a cross-section area of $120 \times 120 \mu m^2$ (Fig. 5).

The typical spectra in the region from 1350 cm$^{-1}$ to 1650 cm$^{-1}$ for the GNP and f-GNP-Si SR composites at 2 phr and GNP and f-GNP-Si SR composites at 5 phr are shown in Fig. 5a–d, respectively. Figure 5e–h shows the optical microscopy images of the analysed cross sections, and Fig. 5i–l shows the colour-coded Raman mapping of $I_G/I_{1410}$ for the same samples. To facilitate the comparison, the $I_G/I_{1410}$ values were normalized into the range of 0 to 5 in the colour-coded Raman maps.

It can be seen from the maps that there is less intensity variation for the f-GNP-Si SR composites when compared with GNP SR composites (at the same loadings) indicating that the distribution of the f-GNP-Si in the silicone rubber matrix is more uniform than that of GNP. These results can be related to the better compatibility of the f-GNP-Si with the SR matrix, as discussed above. The GNP and f-GNP-Si dispersions can be quantified by calculating the standard deviation for the $I_G/I_{1410}$ data set of the Raman mapping, as reported previously [38]. Higher standard deviation values correspond to a larger variation in $I_G/I_{1410}$, representing a less homogeneous dispersion. In our results, the standard deviation values of the $I_G/I_{1410}$ for the GNP SR and f-GNP-Si SR composites at 2phr are 0.9 and 0.6, respectively, and for the GNP SR and f-GNP-Si SR composites at 5 phr the standard deviation values are 2.4 and 1.3, respectively.

It is therefore clear that: (1) the dispersion becomes better for the f-GNP-Si, probably due to a better compatibility and interface with the SR matrix; (2) as the increasing loading (at 5phr) the dispersion become less homogeneous, possibly caused by the formation of larger agglomerates at the interface with the SR matrix. It is worth mentioning, although, that despite the 5-phr loading leading to the formation of larger agglomerates, the f-GNP-Si present at this loading has a better dispersion than that of GNP and there is still a positive effect in the mechanical properties when compared to the neat SR.

### Properties of the silicone rubber nanocomposites

#### Mechanical properties

The tensile properties of the GNP and f-GNP-Si silicone rubber composites at different GNP loadings are presented in Fig. 6. The representative stress–strain curves of the SR and SR composites at 2-phr filler loading are presented in Fig. 6a. The GNP SR composites showed a decrease in the Young’s modulus (Fig. 6b) with the increasing of the GNP loading, which is typically attributed to the presence of agglomerates as well as a poor interaction of the GNP at the interface [6]. In contrast, the Young’s modulus was found keep increasing with the increase in filler loading up to 2 phr for the f-GNP-Si SR composites corresponding to the maximum improvement of 25% compared with the neat SR. Hence, the positive effect of the f-GNP-Si incorporation into the SR matrix upon the Young’s modulus suggests that the functionalization of the GNP has an important role in the mechanical property performance enhancement of the SR composites probably due to its better compatibility with polysiloxanes, and consequently a better interface and dispersion, when mixed into the silicone rubber matrix. Moreover, the ultimate tensile strength (Fig. 6c) increased gradually with the increase in the loading for both the GNP and f-GNP-Si-reinforced SR composites up to 2 phr followed by a decrease at 5 phr. The maximum improvement (at 2
phr) was found to be 12% and 21% for the GNP SR and f-GNP-Si SR composites, respectively. The deterioration in the mechanical properties of f-GNP-Si SR composites at 5 phr may be related to the restacking and agglomeration of the fillers [6, 39].

The elongation at break (Fig. 6d), though, was not greatly affected by the incorporation of either the GNP or f-GNP-Si into the silicone rubber matrix.

The effect of the GNP reinforcement upon the SR matrix can be evaluated according to an equation derived by Young et al. [27]:

$$E_c \approx E_m \left[1 - \frac{s^2}{12(1 + v)} \frac{\eta_0}{\phi^2}\right]$$  (2)

where $E_c$ and $E_m$ are the Young’s modulus of the composite and matrix, respectively; $\phi$ is the volume fraction of the GNP, $s$ is its aspect ratio, $\eta_0$ is the Krenchel orientation factor of the GNP, and $v$ is the Poisson’s ratio of the matrix (typically $v \sim 0.35 – 0.5$) [27]. In this study, an effective aspect ratio $s \sim 715$ was used for the GNP based on their average lateral size of about 10 $\mu$m (given by the producer) and the thickness of 14 nm [40]. The volume fraction of the

Figure 5  a–d Typical Raman spectra, e–h optical microscopy images, i–l colour-coded Raman mapping of ($I_G/I_{1410}$) for the GNP and f-GNP-Si SR composites at 2 phr and for GNP and f-GNP-Si SR composites at 5 phr, respectively. The standard deviation (SD) in the values of ($I_G/I_{1410}$) in the colour-coded maps is also indicated.
GNPs was determined from the phr using a density of 2.3 g/cm$^3$ for the GNPs and of 1.1 g/cm$^3$ for the SR. The Krenchel factor for a fully oriented GNPs is equal to 1, while for randomly aligned GNPs, it is equal to 8/15 [6, 41, 42]. This equation demonstrates that for soft matrix materials $E_c$ is independent of the filler modulus being dependent only on the volume fraction, orientation and aspect ratio of the GNPs [27, 39].

Figure 7 presents the comparison between the experimental results and the predictions of the Young's modulus for both full and random orientation of up to 2 phr GNPs in the SR matrix. As depicted in Fig. 7, our experimental data show a close correlation with the prediction for random orientation of the GNPs. However, at higher filler loading (> 2 phr) the Young's modulus values tend to be lower than the predicted ones. This can be related to the restacking and agglomeration of the fillers which results in significant reduction of the effective aspect ratio values [6, 39].

Figure 7 Young's modulus of f-GNP-Si SR composites with up to 2-phr loading plotted against volume fraction (blue spots). The red and black lines represent the predictions based on Eq. 2 for composites with random and full orientation of the GNPs, respectively.
Interface and microstructure

To better understand the mechanisms of the tensile fracture of the GNP and f-GNP-Si silicone rubber composites, SEM images were obtained from the fractured cross sections of the neat SR as well as the GNP and f-GNP-Si SR composites at 2-phr loading, which was found to be the optimal loading. SEM images of 5-phr-loaded SR composites, where the tensile strength dropped significantly, were also acquired.

The neat silicone rubber in Fig. 8a displays a flat and smooth fracture surface. The white arrows in Fig. 8b indicate the weak interfacial bonding of the GNP (at 2 phr) with the silicone rubber matrix. In contrast, the fracture surface of f-GNP-Si-reinforced SR composite (Fig. 8c) showed an enhanced filler–matrix interaction: the f-GNP-Si flakes can barely be distinguished from the SR matrix. Representative f-GNP-Si flakes, as highlighted by white arrows, were found incorporated in the SR matrix without significant cleavage. Such morphological difference can be related to the improved compatibility of the silane functional groups of the f-GNP-Si with the siloxane chains of the SR matrix. These improved filler–matrix interactions should contribute to enhanced SR

Figure 8 SEM images of the cross sections of: a silicone rubber, b and c GNP and f-GNP-Si silicone rubber at 2 phr, respectively, d and e GNP and f-GNP-Si silicone rubber at 5 phr, respectively.
composite mechanical properties, in agreement with the experimental results for the f-GNP-Si SR composites discussed above. Figure 8d, f shows SEM images of the GNP and f-GNP-Si SR composites at 5 phr, respectively. Both images show the formation of larger agglomerates of GNPs as well as f-GNP-Si at the interface which can be closely related to the deterioration in the mechanical properties of these SR composites. These results are in agreement with the Raman mapping analysis (Fig. 5k, l) that correspond to the mapping analysis of the GNP and f-GNP-Si SR composites at 5 phr, respectively. These images, as discussed before, show the formation of larger agglomerates at this loading.

**Thermal conductivity**

Figure 9a shows the thermal conductivity of the GNP and f-GNP-Si silicone rubber composites. In both cases, the thermal conductivity increased with the increasing loading of GNP and f-GNP-Si. For loadings up to 2 phr ($\phi \approx 0.009$), the GNP SR composites showed better performance in the thermal conductivity. However, at 5 phr ($\phi \approx 0.02$) the opposite behaviour was observed and the f-GNP-Si SR exhibited a higher conductivity than that of GNP SR, showing an increase of 150% of the thermal conductivity when compared to the neat SR.

The effective thermal conductivity of the GNP SR composites ($k_e$) can be predicted according the Lewis–Nielsen model [43, 44]

$$k_e = k_m \frac{1 + AB\phi}{1 - B\psi\phi}$$  \hspace{1cm} (3)

where

$$B = \frac{k_f/k_m - 1}{k_f/k_m + A}$$  \hspace{1cm} (4)

$$\psi = 1 + \left( \frac{1 - \phi_m}{\phi_m^2} \right)\phi$$  \hspace{1cm} (5)

In Eqs. (3), (4), (5), $k_m$ is the thermal conductivity of the matrix, $k_f$ the thermal conductivity of the filler, $\phi$ is the filler volume fraction, and $\phi_m$ is the maximum filler volume fraction. The parameter $A$ is related to the generalized Einstein coefficient $k_E$ as $A = k_E - 1$, and it depends on the shape of the fillers, aspect ratio and their orientation with respect to the heat flow. The values of $A$ and $\phi_m$ are well tabulated for several different two-phase systems and can be found in the literature [44, 45]. Since the values of $A$ and $\phi_m$ are not known for graphene or other 2D fillers, in this work we therefore used $A$ and $k_f$ as the fitting parameters. The $\phi_m$ value was assumed to be 0.52, corresponding to the three-dimensional randomly packed fillers into the polymer matrix [44, 45].

As shown in Fig. 8a, the Lewis–Nielsen model follows the trend of our experimental results reasonably well. The deviation of the experimental result for the GNP SR at 5phr from the predicted values may be related to the restacking and agglomeration of the fillers which results in significant reduction of the aspect ratio of the GNP. It should be noted that parameter $A$ depends on the shape and the aspect ratio of the filler, and as the aspect ratio of the GNP decreases, the value of $A$ decreases as well, leading to a decrease in thermal conductivity. It is noteworthy that although the thermal conductivity of the f-GNP-Si SR composites at 5-phr loading is lower than the predicted value, it still represents an enhancement of 150% of the thermal conductivity when compared to the neat SR. There are, in fact, many factors that can

*Figure 9*  
(a) Thermal conductivity of the GNP and f-GNP SR composites at 25 °C;  
(b) comparison of our results with some reported in the literature for silicone rubber matrix reinforced with GNP and functionalized GNP and GO.
affect the thermal conductivity of graphene/polymer composites such as the intrinsic thermal conductivity of the filler, dispersion, interfacial adhesion and morphology of the heat transport pathways [9, 12, 14]. In general, the surface modification of graphene enhances the interface with the polymer matrix leading to a decrease in the interfacial thermal resistance [12, 14, 17–20]. However, it is also important that the filler loadings reach the percolation threshold, so they can connect to each other to form a thermal conduction pathway [14]. As discussed before (in the Raman mapping analysis and SEM images, Figs. 5 and 8, respectively), the f-GNP-Si showed a better dispersion as well as a better interface within the SR matrix. The larger agglomerates of f-GNP-Si at 5 phr (Fig. 8e) may be responsible for the deterioration in the mechanical properties. Agglomerations may, however, be beneficial for the thermal conductivity in allowing a thermal conduction pathway to be established that may be responsible for a larger increase in thermal conductivity and better performance.

Figure 9b shows a comparison of the relative enhancement of the thermal conductivity for the GNP and f-GNP-Si SR composites with some values reported in the literature for GNP [8–10], APTES- and VTMS-functionalized GNP [12], APTES-functionalized graphene oxide (APTES-GO) [20] and reduced graphene oxide (APTES-rGO) [22], VTMS-GO [19], acrylamide (AA)-functionalized rGO [18] and MQ silicone resin-rGO [17] silicone rubber composites at different loadings. In general, our silicone rubber composites exhibited a competitive performance in the thermal conductivity properties for both GNP and f-GNP-Si for similar filler loadings. Moreover, the f-GNP-Si SR composites at 5-phr loading showed a particularly high thermal conductivity enhancement at lower filler loading when compared with other GNP [8, 10] and functionalized GO and rGO [17–20] SR composites.

Conclusions

Silane-functionalized GNPs were successfully produced through a simple two-step strategy. The functionalized material showed better dispersion and interfacial adhesion into the silicone rubber matrix when compared with the as-received GNPs. The mechanical properties of the functionalized GNP silicone rubber composites enhanced with the increasing filler loading up to 2 phr and are in agreement with the theoretically predicted values. The thermal conductivity of the GNP and f-GNP-Si SR composites increased with the increasing loading showing a large enhancement (up to 150%) at 5 phr of the f-GNP-Si loading. The effective thermal conductivity of both GNP and f-GNP-Si SR composites was well predicted by the Lewis–Nielsen model.

Acknowledgements

The authors acknowledge funding from Beijing Institute of Aeronautical materials (BIAM) and from China Scholarship Council (CSC).

Declarations

Conflict of interest The authors declare no conflict of interest.

Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10853-021-06737-w.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

[1] Kim ES, Kim EJ, Shim JH, Yoon JS (2008) J Appl Polym Sci 110:1263. https://doi.org/10.1002/app.28633
[2] Lewis FM (1962) Rubber Chem Technol 35:1222. https://doi.org/10.5254/1.3539992
[44] Nielsen LE (1974) Ind Eng Chem Fund 13:17. https://doi.org/10.1021/I160049a004

[45] Pietrak K, Wisniewski TS (2015) J Power Technol 95:14

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.