Flexible Hematite (α -Fe₂O₃)-Graphene Nanoplatelet (GnP) Hybrids with High Thermal Conductivity

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Abstract. Hematite (α -Fe₂O₃) has several attractive properties such as corrosion resistance, catalytic activity, sensing properties, and magnetic features but also a room-temperature stable thermal conductivity of about 16 W/m K. Its use in polymer-matrix composites as a thermal performance enhancer is rather uncommon. In this study, hematite and graphene nanoplatelet (GnP) hybrids in a rubbery latex matrix were prepared and their thermal properties were characterized. The hybrids were mechanically stabilized into freestanding films by hot-pressing them into a porous cellulosic membrane. Optimization of total filler concentration and the α -Fe₂O₃/GnP ratio yielded thermal interface material (TIM) films with thermal conductivity of 8.0 W/mK. Infrared measurements showed that the TIMs significantly improved heat sink cooling and demonstrated rapid heat transfer in a system simulating stacked up electronic packing.

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Recent advances in nanotechnology have renewed interest in binary metal oxide materials (M_2O_3), where M is a trivalent metal that crystallizes in the corundum structure and occurs in n- or as p-type [1]. Both nanoscale and submicroscopic binary metal oxides have found a plethora of applications in supercapacitors [2], non-volatile resistance memories [3], ultrafiltration membranes [4], photocatalysis [5] and environmental toxic pollutant treatments [6,7] to name a few. Moreover, binary metal oxides have important applications in heat transfer. For instance, they can be used as thermochemical storage materials upon reversible redox reactions. At high temperatures, certain transition metals oxides (including iron oxide) undergo a reduction reaction and by that thermal energy is absorbed ($M_xO_{y+z} \rightarrow M_xO_y + z/2 O_2$). Below specific equilibrium temperatures, the reoxidation ($M_xO_{y+z} \rightarrow M_xO_y + z/2 O_2$) takes place and hence thermal energy will be delivered [8]. Additionally, metal oxide nanoparticle dispersed nanofluids have been reported to feature unusual enhancements in thermal conductivity (k) that even challenged the predictions by the classical effective medium theory [9, 10].

Among binary metal oxides, iron oxide nanoparticles have been extensively studied to exploit their magnetic, catalytic, thermal and optical properties for recording media, gas sensors, bioprocessing, magnetic refrigeration, ferrofluids, and so on. Hematite (α - Fe_2O_3) is the most stable form of iron oxide exhibiting unusual magnetic behavior (antiferromagnetism and weak ferromagnetism) with a relatively high thermal conductivity at room temperature (~ 16 W/mK) [11-13]. Its thermal conductivity declines at higher temperatures and after 600 K it stabilizes at around 5 W/mK. The thermal conductivity of magnetite (Fe_3O_4) also follows a similar trend [11]. Many complex electronic component networks feature several interfaces in which efficient thermal transport is indispensable to ensure long-term operation with no overheating and energy conservation [14-15]. Thermal interface materials (TIMs) play an important role in ensuring efficient interfacial heat transfer [16]. However, aside from solders/metal alloys, the actual thermal conductivity of thermal greases or gels and phase change materials (PCMs) are low ($2 > k > 0.5$ W/mK). Further issues such as stiffening in time, leaching, crack formation compromise the long-term reliability of many TIM materials. Special thermal interface coatings in the form of polymer nanocomposites have certain aptitudes that can overcome the abovementioned problems. However, the polymer matrices induce significant thermal transport barriers (resistance) among the fillers due to their low thermal conductivities ($0 \sim 0.1$ W/mK). This requires incorporation of a

large concentration of high- k fillers without significantly altering certain requirements such as conformity, ductility and adhesion [17].

In this work, we demonstrate that submicroscopic ($O \sim 100$ nm) hematite particles can be effectively used, together with GnPs, in the formulation of flexible high- k thermal nanocomposite coatings by using a distinct block copolymer with spherule-rubber morphology as the dispersive matrix medium [18]. For materials and methods, refer to the Supplementary Material. Block copolymers can be designed with varying hydrophilic and hydrophobic polymer segments with special functional groups like carboxyl, amine and hydroxyl and in solution, they form stable micellar morphology. As such, they have the ability to stabilize suspended nanoparticles based on effective hydrophilic-hydrophobic interactions or charged interactions such as Van der Waals, and hydrogen bonding [19-22]. As mentioned above, regardless of the thermal conductivity of the material, the polymer matrix has a significant limiting effect on the thermal conductivity of the composite known as the high thermal contrast effect [23]. There are two main approaches to enhance the thermal conductivity of the particle laden polymer composites. The first is the particle orientation and assembly within the polymer matrix (field structuring [23]) and the second is to use secondary additives with varying particle aspect ratios [24]. The scope of this work is the latter in which submicroscopic hematite particles and GnPs are co-dispersed in a rubbery matrix.

Rubbery acrylic copolymers have exceptional uniaxial tensile properties and strong adhesion to different surfaces including metals, ceramics and various plastics [25] Specifically, at room temperature, the polymer used herein has a Young's modulus of 31 MPa with a yield stress of 1.3 MPa; yield deformation of 3.5 %, tensile strength at break 5.7 MPa; deformation at break 420 % and storage modulus of 78 MPa [25,26]. Its morphology is in the form of aggregates of polymer spherules as shown in the TEM and AFM images of Fig. 1a and 1b. Typical spherule (particle) sizes range from 80 nm to 200 nm and the film or coating forms due to solvent evaporation causing closer particle packing [27]. Close particle packing results in severe deformation of the particles while fusing into one another forming a homogenous film structure [28]. Similarly, the average size of α -Fe₂O₃ particles were about 100 nm as seen in Figure 1c. The X-Ray powder spectroscopy profile of the particles are recorded in Fig. 1d.

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Figure 1. (a) TEM image of the acrylic copolymer latex particles. (b) AFM image of the same latex polymer particles. (c) TEM image of the aggregated as-received hematite particles. (d) XRD spectrum of the as-received hematite particles.

Inspection of the spectrum in Figure 1d essentially indicates rhombohedral hematite phase (α -Fe₂O₃) of iron oxide. The confirmation of the hematite phase was made by comparing peak positions with the International Diffraction Data Base (IDDC) file no. 33-0664. The peak positions were indexed in Figure 1d (hematite, PDF # 33-0664, the index *hkl* is based on ICSD no. 201096). Up to 60 wt.% hematite or 40 wt.% GnPs could be dispersed in the latex solution and upon drying they formed uniform crack-free coatings. As a substrate, we chose a porous cellulose membrane (see Fig. S1, Supplementary Material). Both sides of the membranes were rod-coated with the nanocomposite latex solutions and after drying, they were hot pressed into freestanding films as shown in Fig. 2a. The surface morphology of the 30 wt.% hematite-polymer composite coating before hot-press process is shown in Fig. S2 (Supplementary Material). The thickness of the produced films were about 150 μ m (Fig. S3, Supplementary Material), but they could be stacked

up on one another at 80°C with slight pressure (hot-press) to produce thicker versions. Additional TEM and SEM images of the Fe_2O_3 particles and selected polymer nanocomposites are shown in Fig. S4 (Supplementary Material). Detailed (Fourier Transform Infrared) FTIR, Raman and thermo-gravimetric properties of as-received $\alpha\text{-Fe}_2\text{O}_3$, GnPs and the $\alpha\text{-Fe}_2\text{O}_3/\text{GnP}$ (1:1) composites are given in Fig. S5 (Supplementary Material). The surface SEM micro-morphology of this conductor is shown in Fig. 2b. Various $\alpha\text{-Fe}_2\text{O}_3/\text{GnP}$ ratios were studied ranging from 0.3 to 30. The ratio along with the total high- k filler concentration determined both the electrical and thermal conductivity characteristics of the materials. Figure 2c demonstrates AC (alternating current) conductivity of the hematite-polymer composites with varying $\alpha\text{-Fe}_2\text{O}_3$ concentrations.

Figure 2. (a) Photograph of the GnP rich hybrid composite ($\alpha\text{-Fe}_2\text{O}_3/\text{GnP}$: 0.3). Inset: pure cellulose membrane, 35 wt.% hematite-polymer composite and 35 wt. % GnP-polymer composite. (b) SEM surface microstructure of the hybrid film shown in (a). (c) AC conductivity of hematite-polymer composites and (d) Direct current (DC) conductivity of GnP-polymer composite and the hybrids. Insets: Representative I-V curves of low and high conductivity hybrids.

Conductivity data displays frequency dependence, which appear to follow the universal power-law [29]. Composites with 10 and 35 wt. % hematite fillers display conductivity with nearly two slopes. The first slope (<100 Hz) has virtually no dependence on frequency, whereas the

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second slope (>100 Hz and 1 kHz for 25 wt.%) displays strong variation with frequency. This is known as crossover frequency. With increase in the concentrations of the hematite filler, conductivity increases, and the hopping (crossover) frequency for each curve shifts towards higher frequencies and eventually may become unnoticeable [30]. As shown in Fig. 2c, hematite has poor electrical conduction properties, however, electrical conductivity of hematite surface layers are known to be higher than its bulk. The near surface layers exhibit much stronger interaction between charge carriers than those occurring in the bulk due to deviations in stoichiometry and interaction with ambient oxygen [31, 32]. In fact, this is a well-studied and documented phenomenon in physics [31]. The near-surface layer of Fe_2O_3 exhibits much higher deviation from stoichiometry than the bulk phase resulting in strong interaction between charge carriers. This effect has been interpreted in terms of segregation of intrinsic lattice defects to the surface, and presumably also to grain boundaries, of Fe_2O_3 . This is the underlying reason for electrical conductivity at the surface. Moreover, according to Wang et al. [33] the surface of hematite particles are occupied with domains with distinct chemistry having unusual electronic structure due to the O_3 -terminated domains with a noticeable presence of states from the subsurface Fe layer. This causes both electronic and magnetic differences at the surface of hematite. Moreover, interaction of GnPs with polarized interfaces in polymer matrix composites is known to enhance thermal conductivity [32]. GnPs and hybrid filled latex polymer composites displayed DC (direct current) conductivity above 20 wt.% concentration levels as shown in Fig. 2d. In particular, the figure displays bulk resistance (ohm/square) data for graphene, GnP and hybrids with $\text{Fe}_2\text{O}_3/\text{GnP}$:1 and $\text{Fe}_2\text{O}_3/\text{GnP}$:2 ratios. In the case of filler concentration levels below 10 wt.%, I-V curves show hysteresis (see inset in Fig. 2d) resembling mixed ionic-electronic conduction [33]. No I-V curve crossing, typical for memristor behavior, was measured for low concentrations but rather a capacitive response was registered during the I-V sweeping [34, 35]. Above 25 wt.% concentration levels, the conductors displayed simple ohmic behavior due to the presence of GnPs (see inset Fig. 2d). Weidenfeller et al. [36] studied polymer composites with micronized (~ 10 μm) magnetite (Fe_3O_4) and showed that both DC electrical and thermal conductivity values improved significantly after 35wt. % concentration (resistivity 10 $\text{k}\Omega\text{ m}$) which they correlated with particle interconnectivity [36]. Finally, the mechanical properties of some selected composites are displayed in Fig. S6 (Supplementary Material) in which 50 wt.% $\alpha\text{-Fe}_2\text{O}_3/\text{GnP}$ (0.3:1) composite,

for instance, demonstrated about 120% elongation capability, rendering it reasonably foldable for certain applications (see Fig. 2a).

Thermal interface materials connect different thermal elements for efficient thermal management. The connections should minimize thermal contact resistance for active heat transfer. Thermal contact resistance occurs due to imperfect interface separation (local gaps) derived from mismatches in thermal expansion. The interfacial mismatch in thermal expansion also causes thermal stress, which can harm electronic components. The localized interfacial gaps will significantly increase the contact resistance, reduce the effective heat dissipation and accumulate heat within the devices. The minimization of interfacial contact resistance is correlated with the thermal expansion or the coefficients of thermal expansion (*cte*) of the thermal interface material [37, 38]. Measured thermal conductivity and the *cte* values of the hematite, GnP and hybrid filled composites are shown in Figure 3. The maximum filler ratio was 55 wt.%. Comparison of thermal conductivity of Fe₂O₃ and GnP filled composites (Fig. 3a) indicates that at after 5 wt.% concentration levels, on average, the thermal conductivity GnP filled composites is larger by sevenfold. At 50 wt.% GnP filled composite has 6.5 W/mK thermal conductivity compared to 0.87 W/mK of hematite filled composite. The hybrid system with Fe₂O₃/GnP of 0.3 however (Fig. 3b), features a higher thermal conductivity of 8.0 W/mK at the same 50 wt.% concentration. Note that the enhancement is achieved for the through-plane heat conduction mode because graphene is horizontally oriented within the polymer composite (see Fig. S4, Supplementary Material). This boost in thermal conductivity may be attributed to the synergetic effect known as the “bridge-link effect” of hybrid fillers [39]. Moreover, based on other detailed experimental works [40], enhanced thermal conductivity due to hybrid filling of polymers was explained by the better connectivity offered by structuring the filler with high aspect ratio (i.e. GnP) in the composite. Such conclusions were also drawn from mathematical modeling studies such that the presence of two dissimilar particulate fillers collectively contribute to the enhancement in the thermal conductivity value of such hybrid filler composites [41].

Figure 3. (a) Filler concentration dependent thermal conductivity of hematite and GnP-polymer composites. (b) Thermal conductivity of selected hybrids. Measurement uncertainty was recorded to be around 0.05 W/mK. (c) Room and elevated (75°C) temperature *cte* values of hematite and GnP polymer composites and (d) measured *cte* of hybrids at 75°C as a function of $\text{Fe}_2\text{O}_3/\text{GnP}$ ratio. Measurement uncertainty in *k* was within ± 0.3 W/mK and in *cte* $5 \times 10^{-5}/^\circ\text{C}$.

The *cte* values of polymer matrix composites depend strongly on temperature. In the case of electronic cooling, the *cte* values should not only be measured at room temperatures but at higher temperatures as well. Highly aligned carbon fiber filled epoxy composites for instance have *cte* values of about $2 \times 10^{-6}/^\circ\text{C}$ at concentration levels of 35 wt.% [42]. Carbon nanotubes (CNTs) are known to have negative *cte* values and are used to reduce the *cte* of polymers [43]. Effectively functionalized CNTs with 1 wt.% loading can reduce typical epoxy resin *cte* values down to $5 \times 10^{-5}/^\circ\text{C}$ below glass transition temperatures, T_g [38]. Note that compared to aligned carbon fiber or fiber mat reinforced polymer composites, the *cte* value is an order of magnitude higher. Similarly, functionalized graphene fillers also reduced the *cte* values of epoxy resins to levels of about $7 \times 10^{-5}/^\circ\text{C}$ below T_g and $25 \times 10^{-5}/^\circ\text{C}$ above T_g [44]. The T_g of the acrylic latex is 47°C that is lower than common epoxy resins ($\sim 135^\circ\text{C}$). Hence, it is expected to have higher *cte* values at temperatures corresponding electronic cooling applications. Figures 3c and 3d show the *cte* values for hematite and GnP filled composites at room temperature and at $75^\circ\text{C} > T_g$. GnP filled composites feature lower *cte* values compared to hematite filled composites and in both cases, the *cte* values were

increased by about $10 \times 10^{-5}/^{\circ}\text{C}$ when the temperature was increased to 75°C within the concentration range studied.

Figure 4. Photograph of the flat electrical heater and the heat sink. Inset: The schematic of the setup. (b) Series of infrared images of two metal blocks separated by the TIM films (manually placed). The bottom plate is heated by a hot plate. (c) Cooling curves of the metal plate inserted between the electrical heater and the heat sink in (a) without and with TIM films. (d) Cooling and heating curves of the bottom and top plates separated by the TIM films, respectively. Data extracted from the infrared images with $\pm 3^{\circ}\text{C}$ variation.

In the case of hybrid composites shown in Fig. 3d, as the $\text{Fe}_2\text{O}_3/\text{GnP}$ ratio decreases (increasing GnP concentration), the cte values decline again such that the difference between $\text{Fe}_2\text{O}_3/\text{GnP}:30$ and $\text{Fe}_2\text{O}_3/\text{GnP}:0.3$ reaches $10 \times 10^{-5}/^{\circ}\text{C}$. Measured cte values appear to be similar to nanoscale carbon filled thermosetting polymers such as silicones (PDMS) [45]. It has been demonstrated that microstructural features significantly influence the cte of graphene thermoset composites [41]. Changes in graphene dispersion, agglomeration, and alignment within the polymer matrix along

with the large differences between the elastic coefficients of graphene and the polymer, anisotropic *cte* values are reported for similar composites also supported by effective medium calculations using Green's function method [46].

In Figs. 4a and 4b, two distinct thermal experiments were presented in order to compare the performance of some of the selected TIM films. In the first experiment in Fig. 4a, an electrical resistive heater with bottom side insulation was used to heat a metal plate ($\sim 90^\circ\text{C}$) to simulate heating of a metallic component. The cooling of the metal plate was intended by placing a standard heat sink over the metal plate with or without the TIM films. Cooling profiles of the plate (measured by an embedded flat-head thermocouple) are plotted in Fig. 4c. A commercial thermal pad was also used for comparison purposes (TG-A1250 Ultra Soft Thermal Pad, $k \sim 12 \text{ W/mK}$; T-Global, Taiwan). Without any TIM film interfacing the heater and the metal plate, negligible amount of cooling was observed (a few degrees) and the metal plate started to heat up again after 400 seconds. However, the commercial thermal gap pad was very effective (Fig. 4c), within the first 75 seconds, the plate temperature reduced down to 53°C and started to heat again but stabilized at about 70°C . Similarly, the TIM films performed well, particularly, 50 wt.% GnP and the $\text{Fe}_2\text{O}_3/\text{GnP}$ (0.3:1) composites. The GnP-polymer composite underperformed slightly even though the initial rapid cooling periods were identical within the first 75 seconds. The hybrid with $\text{Fe}_2\text{O}_3/\text{GnP}$ (1:1) could not cool off the metal plate as effectively as the *high-k* counterparts and achieved only about 10°C cooling at steady state (after 600 s). In the second experiment depicted in Fig. 4b, the transient heating of the top metal block by the bottom one with different TIM films is shown in Fig. 4d. In an ideal case, due to efficient heat transfer, the top metal block should quickly heat up to the same temperature as the bottom plate [47]. Again, the 50 wt.% GnP-polymer composite and the hybrid $\text{Fe}_2\text{O}_3/\text{GnP}$ (0.3:1) demonstrated promising performance. In this case, however, compared to the cooling experiment, the hybrid performs much better and after 150 seconds, the temperatures of both metal blocks were equilibrated. The graphene composite, however, lacks behind considerably and after 300 seconds, the top block is still colder by about 4°C compared to the bottom block. This could be attributed to the establishment of different contact resistances between the TIM films and the surfaces. In the heat sink cooling experiment, the TIM film is in contact with an aluminum plate and a carbon coated heat sink (Fig. 4a) and the metal blocks in Fig. 4b are stainless steel. Lim et al. [48] argued that contact resistance between

nanocarbons and metals depend on the wettability of the metal surfaces and their work functions in a complex manner. Cola et al. [49] also indicated that thermal resistance across metal-nanocarbon interfaces is a complex phenomenon affected by local deformations, Van der Waals forces, roughness of the nanocarbon agglomerates, and the pressure. As seen in Fig. 2b, the TIM films do not have a very smooth surface texture and, most of the dispersed GnPs are coated with the polymer latex that introduces an extra contact resistance within the TIM film itself.

Even though single layer graphene has excellent thermal conductivity of about 5300 W/mK [45], outperforming other nanocarbon materials [50], the GnPs are more like graphite flakes with much lower thermal conductivity [51,52]. With proper dispersion, alignment and using specific polymer matrices that can tolerate large concentration of GnPs without compromising flexibility and workability, conformal TIM films or coatings can be produced with thermal conductivities approaching 10 W/mK [53-55]. Hybrid systems can help reduce bulk contact resistance between the polymer and a particular filler. In this study, since the near-surface layer of α -Fe₂O₃ exhibits much higher deviation from stoichiometry than the bulk phase resulting in strong interaction between the surrounding charge carriers, it can significantly enhance the thermal conductivity of GnP-polymer composites even by itself it is not an effective thermal filler. However, hematite filled rubbery latex matrix thermal conductivity can be improved at least by three times compared to the plain polymer enabling other effective filler like GnPs to function better. Extensive size and weight reductions associated with the latest developments in electronic technologies are accompanied by increased power consumption levels. Estimates indicate that in the near future, the heat flux at the die level will exceed 100 Wcm⁻². If such high levels of heat are not effectively dissipated or transmitted at the interfaces, the life, reliability, and performance of electronic components and devices will be jeopardized. This work intended to address this issue by developing cost-effective, paper-thin hybrid composites that can function as high-*k* thermal conductors at various interfaces.

Supplementary Material

See supplementary material for experimental methods and materials, SEM, TEM images of the composites, FTIR, Raman and thermo-gravimetric characterization of hematite and GnP powders and mechanical properties of some selected composites.

Data Availability

The data that supports the findings of this study are available within the article and its supplementary material.

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References

1. Wold A., Dwight K. (1993) Binary Oxides. In: Solid State Chemistry. Springer, Dordrecht. https://doi.org/10.1007/978-94-011-1476-9_8.
2. Zhang, Y., Li, L., Su, H., Huang, W., & Dong, X. (2015). Binary metal oxide: advanced energy storage materials in supercapacitors. *Journal of Materials Chemistry A*, 3(1), 43-59.
3. Tsai, Y. T., Chang, T. C., Lin, C. C., Chen, S. C., Chen, C. W., Sze, S. M., ... & Tseng, T. Y. (2010). Influence of nanocrystals on resistive switching characteristic in binary metal oxides memory devices. *Electrochemical and Solid State Letters*, 14(3), H135.
4. Sotro, A., Kim, J., Arsuaga, J. M., Del Rosario, G., Martínez, A., Nam, D., ... & Van der Bruggen, B. (2014). Binary metal oxides for composite ultrafiltration membranes. *Journal of Materials Chemistry A*, 2(19), 7054-7064.
5. Fu, X., Clark, L. A., Yang, Q., & Anderson, M. A. (1996). Enhanced photocatalytic performance of titania-based binary metal oxides: TiO₂/SiO₂ and TiO₂/ZrO₂. *Environmental science & technology*, 30(2), 647-653.
6. Magdalane, C. M., Kaviyarasu, K., Vijaya, J. J., Siddhardha, B., Jeyaraj, B., Kennedy, J., & Maaza, M. (2017). Evaluation on the heterostructured CeO₂/Y₂O₃ binary metal oxide nanocomposites for UV/Vis light induced photocatalytic degradation of Rhodamine-B dye for textile engineering application. *Journal of Alloys and Compounds*, 727, 1324-1337.
7. Gokul, P., Vinoth, R., Neppolian, B., & Anandhakumar, S. (2017). Binary metal oxide nanoparticle incorporated composite multilayer thin films for sono-photocatalytic degradation of organic pollutants. *Applied Surface Science*, 418, 119-127.
8. Block, T., & Schmücker, M. (2016). Metal oxides for thermochemical energy storage: A comparison of several metal oxide systems. *Solar Energy*, 126, 195-207.
9. Shima, P. D., Philip, J., & Raj, B. (2010). Synthesis of aqueous and nonaqueous iron oxide nanofluids and study of temperature dependence on thermal conductivity and viscosity. *The Journal of Physical Chemistry C*, 114(44), 18825-18833.

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0042404

10. Pastoriza-Gallego, M. J., Lugo, L., Legido, J. L., & Piñeiro, M. M. (2011). Enhancement of thermal conductivity and volumetric behavior of Fe x O y nanofluids. *Journal of Applied Physics*, 110(1), 014309.
11. T. Akiyama, H. Ohta, R. Takahashi, Y. Waseda and J. Yagi, 1SIJ Int.. 32 (1992) 829
12. Mo/lgaard, J., & Smeltzer, W. W. (1971). Thermal conductivity of magnetite and hematite. *Journal of applied physics*, 42(9), 3644-3647.
13. Tannhauser, D. S. (1962). Conductivity in iron oxides. *Journal of Physics and Chemistry of Solids*, 23(1-2), 25-34.
14. Xu, J., & Fisher, T. S. (2006). Enhanced thermal contact conductance using carbon nanotube array interfaces. *IEEE Transactions on Components and Packaging Technologies*, 29(2), 261-267.
15. Cola, B. A., Xu, X., & Fisher, T. S. (2007). Increased real contact in thermal interfaces: A carbon nanotube/foil material. *Applied physics letters*, 90(9), 093513.
16. Feng, B., Faruque, F., Bao, P., Chien, A. T., Kumar, S., & Peterson, G. P. (2013). Double-sided tin nanowire arrays for advanced thermal interface materials. *Applied Physics Letters*, 102(9), 093105.
17. Liu, C. H., & Fan, S. S. (2005). Effects of chemical modifications on the thermal conductivity of carbon nanotube composites. *Applied Physics Letters*, 86(12), 123106.
18. Zhang, L., & Eisenberg, A. (1995). Multiple morphologies of" crew-cut" aggregates of polystyrene-b-poly (acrylic acid) block copolymers. *Science*, 268(5218), 1728-1731.
19. Zhan, X., He, R., Zhang, Q., & Chen, F. (2014). Microstructure and mechanical properties of amphiphilic tetrablock copolymer elastomers via RAFT miniemulsion polymerization: influence of poly [styrene-alt-(maleic anhydride)] segments. *Rsc Advances*, 4(93), 51201-51207.
20. Chen, H., & Ruckenstein, E. (2014). Micellar structures in nanoparticle-multiblock copolymer complexes. *Langmuir*, 30(13), 3723-3728.
21. Chen, H., & Ruckenstein, E. (2016). Controlling nanorod oligomer aggregation in solutions. *The Journal of Physical Chemistry C*, 120(30), 16913-16918.
22. Chen, H., & Ruckenstein, E. (2009). Nanoparticle aggregation in the presence of a block copolymer. *The Journal of Chemical Physics*, 131(24), 244904.
23. Martin, J. E., & Gulley, G. (2009). Field-structured composites for efficient, directed heat transfer. *Journal of Applied Physics*, 106(8), 084301.
24. Zhou, Y., Wang, H., Xiang, F., Zhang, H., Yu, K., & Chen, L. (2011). A poly (vinylidene fluoride) composite with added self-passivated microaluminum and nanoaluminum particles for enhanced thermal conductivity. *Applied physics letters*, 98(18), 182906.
25. Wang, X., Yang, C., Jin, J., Li, X., Cheng, Q., & Wang, G. (2018). High-performance stretchable supercapacitors based on intrinsically stretchable acrylate rubber/MWCNTs@ conductive polymer composite electrodes. *Journal of Materials Chemistry A*, 6(10), 4432-4442
26. Taheri, S., Hassani, Y., Sadeghi, G. M. M., Moztarzadeh, F., & Li, M. C. (2016). Graft copolymerization of acrylic acid on to styrene butadiene rubber (SBR) to improve morphology and mechanical properties of SBR/polyurethane blend. *Journal of Applied Polymer Science*, 133(29).

This is the author's peer reviewed, accepted manuscript. However, the online version of record will be different from this version once it has been copyedited and typeset.

PLEASE CITE THIS ARTICLE AS DOI: 10.1063/5.0042404

27. Winnik, M. A. (1997). Latex film formation. *Current opinion in colloid & interface science*, 2(2), 192-199.
28. Gorce, J. P., Bovey, D., McDonald, P. J., Palasz, P., Taylor, D., & Keddie, J. L. (2002). Vertical water distribution during the drying of polymer films cast from aqueous emulsions. *The European Physical Journal E*, 8(4), 421-429.
29. Jonscher, A. K. (1999). Dielectric relaxation in solids. *Journal of Physics D: Applied Physics*, 32(14), R57.
30. Jonscher, A. K. (1977). The 'universal' dielectric response. *Nature*, 267(5613), 673-679.
31. Gleitzer, C., Nowotny, J., & Rekas, M. (1991). Surface and bulk electrical properties of the hematite phase Fe₂O₃. *Applied Physics A*, 53(4), 310-316.
32. Rufus, A., Sreeju, N., Vilas, V., & Philip, D. (2017). Biosynthesis of hematite (α -Fe₂O₃) nanostructures: size effects on applications in thermal conductivity, catalysis, and antibacterial activity. *Journal of Molecular Liquids*, 242, 537-549.
33. Wang, X. G., Weiss, W., Shaikhutdinov, S. K., Ritter, M., Petersen, M., Wagner, F., ... & Scheffler, M. (1998). The hematite (α -Fe₂O₃)(0001) surface: evidence for domains of distinct chemistry. *Physical Review Letters*, 81(5), 1038.
34. Hung, M. T., Choi, O., Ju, Y. S., & Hahn, H. T. (2006). Heat conduction in graphite-nanoplatelet-reinforced polymer nanocomposites. *Applied Physics Letters*, 89(2), 023117.
35. Kalaev, D., & Riess, I. (2014). Examining the crossing of I-V curves in devices based on mixed-ionic-electronic-conductors. *Solid State Ionics*, 262, 883-888.
36. Weidenfeller, B., Höfer, M., & Schilling, F. (2002). Thermal and electrical properties of magnetite filled polymers. *Composites Part A: Applied Science and Manufacturing*, 33(8), 1041-1053.
37. Wang, S., Tambraparni, M., Qiu, J., Tipton, J., & Dean, D. (2009). Thermal expansion of graphene composites. *Macromolecules*, 42(14), 5251-5255.
38. Yoo, Y., Lee, H. L., Ha, S. M., Jeon, B. K., Won, J. C., & Lee, S. G. (2014). Effect of graphite and carbon fiber contents on the morphology and properties of thermally conductive composites based on polyamide 6. *Polymer international*, 63(1), 151-157.
39. Pan, C., Kou, K., Zhang, Y., Li, Z., & Wu, G. (2018). Enhanced through-plane thermal conductivity of PTFE composites with hybrid fillers of hexagonal boron nitride platelets and aluminum nitride particles. *Composites Part B: Engineering*, 153, 1-8.
40. Lee, G. W., Park, M., Kim, J., Lee, J. I., & Yoon, H. G. (2006). Enhanced thermal conductivity of polymer composites filled with hybrid filler. *Composites Part A: Applied science and manufacturing*, 37(5), 727-734.
41. Agrawal, A., & Satapathy, A. (2015). Mathematical model for evaluating effective thermal conductivity of polymer composites with hybrid fillers. *International Journal of Thermal Sciences*, 89, 203-209.
42. Chen, Y. M., & Ting, J. M. (2002). Ultra high thermal conductivity polymer composites. *Carbon*, 40(3), 359-362.
43. Wang, S., Liang, Z., Gonnet, P., Liao, Y. H., Wang, B., & Zhang, C. (2007). Effect of nanotube functionalization on the coefficient of thermal expansion of nanocomposites. *Advanced functional materials*, 17(1), 87-92.

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44. Wang, S., Tambraparni, M., Qiu, J., Tipton, J., & Dean, D. (2009). Thermal expansion of graphene composites. *Macromolecules*, 42(14), 5251-5255.
45. Zhao, Y. H., Wu, Z. K., & Bai, S. L. (2015). Study on thermal properties of graphene foam/graphene sheets filled polymer composites. *Composites Part A: Applied Science and Manufacturing*, 72, 200-206.
46. Shi, Z., Li, X. F., Bai, H., Xu, W. W., Yang, S. Y., Lu, Y., ... & Li, W. B. (2016). Influence of microstructural features on thermal expansion coefficient in graphene/epoxy composites. *Heliyon*, 2(3), e00094.
47. Zahid, M., Masood, M. T., Athanassiou, A., & Bayer, I. S. (2018). Sustainable thermal interface materials from recycled cotton textiles and graphene nanoplatelets. *Applied Physics Letters*, 113(4), 044103.
48. Lim, S. C., Jang, J. H., Bae, D. J., Han, G. H., Lee, S., Yeo, I. S., & Lee, Y. H. (2009). Contact resistance between metal and carbon nanotube interconnects: Effect of work function and wettability. *Applied Physics Letters*, 95(26), 264103.
49. Cola, B. A., Xu, X., & Fisher, T. S. (2007). Increased real contact in thermal interfaces: A carbon nanotube/foil material. *Applied physics letters*, 90(9), 093513.
50. Balandin, A. A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan, D., Miao, F., & Lau, C. N. (2008). Superior thermal conductivity of single-layer graphene. *Nano letters*, 8(3), 902-907.
51. Shayganpour, A., Naderizadeh, S., Grasselli, S., Malchiodi, A., & Bayer, I. S. (2019). Stacked-Cup Carbon Nanotube Flexible Paper Based on Soy Lecithin and Natural Rubber. *Nanomaterials*, 9(6), 824.
52. Goyal, V., & Balandin, A. A. (2012). Thermal properties of the hybrid graphene-metal nano-micro-composites: Applications in thermal interface materials. *Applied Physics Letters*, 100(7), 073113.
53. Clausi, M., Grasselli, S., Malchiodi, A., & Bayer, I. S. (2020). Thermally conductive PVDF-graphene nanoplatelet (GnP) coatings. *Applied Surface Science*, 529, 147070.
54. Clausi M, Bayer IS (2021). In-situ graphene alignment in self-sealingstretchable films for efficient thermal interfacematerials. *Nano Select* 2; 433-446.
55. Lewis, J. S., Perrier, T., Barani, Z., Kargar, F., & Balandin, A. A. (2021). Thermal Interface Materials with Graphene Fillers: Review of the State of the Art and Outlook of Future Applications. *Nanotechnology*, 32, 142003.

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