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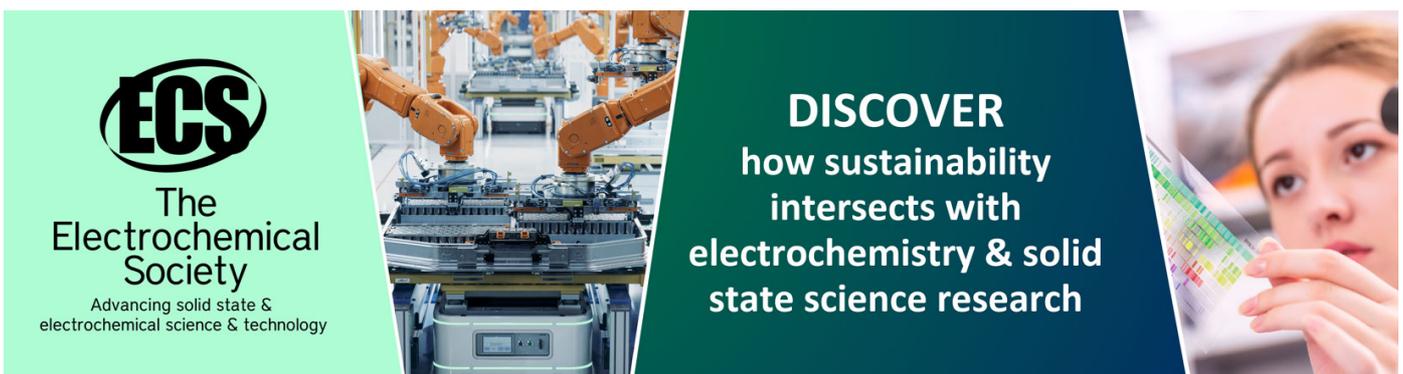
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Effect of carbon-based hybrid nano-fillers on the thermal conductivity of PCM composites

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Abstract. PCMs show great promise as thermal energy storage (TES) medium; however, their low thermal conductivity presents a major bottleneck for their potential application. Enhancement of the thermal conductivity of a paraffin based PCM material using GNP in combination with CNF, CNTs and TRG was investigated in this work. SEM was used to qualitatively assess the dispersion & distribution of the hybrid-nanofillers. DSC was used to determine the melting temperature, thermal capacity and latent heat, whereas thermal conductivity was measured using Hot Disk TPS Thermal Conductivity Instrument (TPS2500S). An overall increase by 143%, 158% and 174% in thermal conductivity and 179%, 193% and 214% in thermal diffusivity was observed for 2 wt.% hybrid loading of TRG, CNT and CNF respectively (pure PCM as ref.). Furthermore, the contribution of the CNF and CNT hybrid-fillers was evaluated to increase the composite PCM thermal conductivity by 122% & 110%, and diffusivity by 117% & 105% respectively (10%-GNP as ref.).

1. Introduction

Efficient energy storage and transfer has been perhaps the most challenging hurdle in the energy industry at the moment. The need to conserve energy and improve its utilization is increasing day by day with the increase in energy demand and growing notion of sustainability. The focus more recently, especially in Qatar, has been on sustainable alternates (i.e. Solar) to meet the local energy demand[1]. Phase change material (PCM) based latent heat storage systems have emerged as a very effective technique for thermal management systems[2] and have gathered significant interest in applications like solar energy systems, thermal energy storage (TES), active and passive cooling of PVs and electronic devices, etc.[3–5]. Thermal energy can be stored via two basic techniques: Sensible Heat Storage and Latent Heat Storage. In the former technique, the temperature of the storage material varies with stored energy, whereas in the latter, the storage material stores energy via phase change (i.e. steam-water, ice-water, etc.)[6–8].

The high latent heat of the PCMs and their relatively lower phase change temperature are the core properties which have interested researchers for the aforementioned applications[9]. Despite key desirable properties of PCMs (high energy-storage density and isothermal characteristics)[10], their low thermal conductivity[11,12] remains the major bottleneck for many applications. This paper investigates the effect of various carbon-based hybrid nano-fillers with different physical dimensions and features on the thermal conductivity and diffusivity of paraffin-based PCM nanocomposites.

2. Experimental

2.1. Materials



PCM used for the purpose of all experiments is Paraffin wax purchased from Rubitherm (RT42). Nanofillers used for the composite preparation included Graphene Nanoplatelets (Alfa Aesar 47132), Multi-Walled Carbon Nanotubes (MWCNTs) (Sigma Aldrich 724769), Carbon Nanofibers (CNFs) (Sigma Aldrich 719781), and TRG (Sixth Element SE1432). All materials were utilized as supplied without further treatment or purification.

2.2. Preparation of composite PCM

A pure GNP/PCM composite was first prepared by melt mixing aided with sonication using pure GNP as the nanofiller to observe the resultant thermal properties of the PCM and to serve as a control sample to observe the effect of hybrid-nanofillers. The hybrid composite samples were prepared using an overall carbon content of 10 wt.% while varying the composition of the hybrid filler (i.e. CNTs/CNFs/TRG) from 0-2 wt.%. Table Synthesis route used to prepare the hybrid PCM composites was melt mixing aided with sonication. A known mass of paraffin wax was melted in a vial and placed in a temperature controlled bath sonicator at 55 °C. Hybrid filler (0-2 wt.% CNT/CNF/TRG) was added to the vial containing the melted wax and sonicated for 30 minutes, followed by addition of the remaining GNP as the base nano-filler. The melted mix was again sonicated for 30 minutes while the bath sonicator's temperature was maintained well above 50C. The nanocomposite was then quenched in an ice bath and used as is for characterization.

Table 1. Summary of compositions of the hybrid nano-fillers in PCM composites.

Sample Code	PCM (wt.%)	GNP (wt.%)	Hybrid* (wt.%)
H-XXX-01	90	9.75	0.25
H-XXX-02	90	9.50	0.50
H-XXX-03	90	9.00	1.00
H-XXX-04	90	8.00	2.00

Where XXX is the filler code i.e. CNT for Carbon nanotubes, CNF for Carbon Nanofibers and TRG for Thermally Reduced Graphene

2.3. Characterization

2.3.1. Thermal storage properties.

Thermal properties, i.e. melting/solidification temperatures (T_m/T_f), latent heat capacity ($\Delta H_m/\Delta H_f$), and specific heat capacity (C_p), of the PCM composite were analyzed using DSC (Q2000, TA Instruments). DSC runs consisted of an initial melting/solidification cycle to remove the effect of uneven heating on the specimens, the second cycle was then used to record aforementioned thermal data. The DSC analysis was performed using a heating rate of 5 °C/min in a temperature bracket of 5 – 80 °C. Thermal cycling was also performed to observe the effects of repeated heating/cooling cycles on the PCM stability, a total of 40 cycles were run. TGA (TGA550, TA Instruments) was used to observe the effect of fillers on the stability of PCM. The thermal conductivity of the samples was measured by a Hot Disk thermal analyzer (Hot Disk 2500, Sweden) using the Transient Plane Source (TPS) method based on a transient technique. According to this method[13] a disk-shaped TPS sensor is placed between two circular sample pieces.

2.3.2. Morphology characterization.

Scanning electron microscopy (SEM) imaging was used to observe the morphology of the nano-fillers and qualitatively assess the dispersion and distribution of the nano-fillers within the composite materials. The high intensity of the SEM at higher magnifications resulted in the phase change of samples therefore a lower magnification was used qualitative assessment of the composite structure.

3. Results and discussion

3.1. Morphology and dispersion of Nano-fillers in composite PCMs

SEM images of the PCM composites revealed the dispersion and distribution of the nano-fillers within the composite. The images of nano-fillers after being dispersed in the PCM were taken with 2.00 wt% samples used as representative samples for a qualitative assessment of each nano-filler batch. SEM images of the GNP-CNF hybrid are presented in Figure 1 which shows the remarkable dispersion of the CNF in the composite with minimal agglomeration. CNT dispersion (see Figure 2) is similar to CNF; however, they appear to be more entangled unlike the CNFs which appear as separate individual strands.

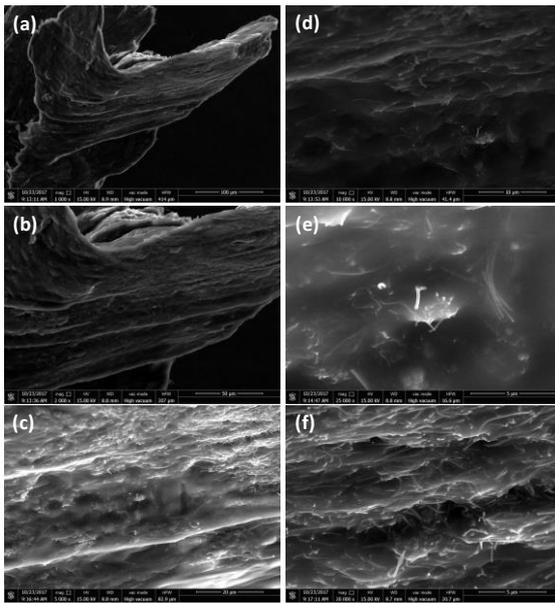


Figure 1. (a)-(f) SEM images of GNP-CNF hybrid nano-filler PCM composite.

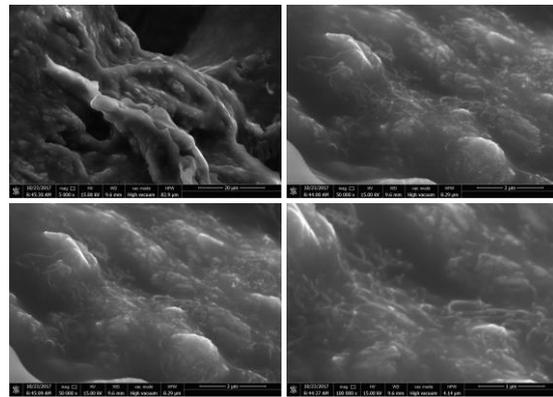


Figure 2. SEM images of GNP-CNT hybrid nano-filler PCM composite.

3.2. Thermal properties of composite PCMs

Thermal properties of the composite PCM were characterized using DSC. The melting/solidification onset temperature (T_m/T_f), latent heat of melting/solidification ($\Delta H_m/\Delta H_f$), and heat capacities for solid and liquid phases were extracted from the DSC heating and cooling curves obtained as per method described in experimental section and are provided in Table 3 (appendix).

The addition of nano-fillers serves an important role in increasing the thermal conductivity; however, it does so at the expense of the energy storage capacity as it does not add to the latent heat of fusion. Moreover, DSC analysis reveals the adverse effect of the addition of these hybrid nano-fillers on the phase change temperatures and enthalpies of the hybrid-nanocomposites. DSC heating/cooling curves of the pure and hybrid composites are presented in Figure 3 and Figure 4. The two characteristic paraffin peaks (solid-solid and solid-liquid phase change peaks) are visible and the addition of fillers contributes to a lowering of both the peaks. The peak temperatures during melting were around 18 °C and 43 °C whereas in the cooling cycle the peak temperatures were noted at 17 °C and 42 °C. As expected, melting temperatures and enthalpies are marginally lowered due to nanofiller addition; however, no obvious relationship can be established between the loading and the temperature. A qualitative assessment of the shrinking and lateral translation of DSC melting/cooling peaks also substantiates this observation. A quantitative comparison can be observed in Figure 5 and Figure 6 for the solid-liquid phase change onset temperatures and enthalpies. It was observed that the decrease in peak solid-liquid enthalpies for CNF, CNT and TRG were 16%, 14% and 12% respectively from a pure wax enthalpy of 135 J/g.

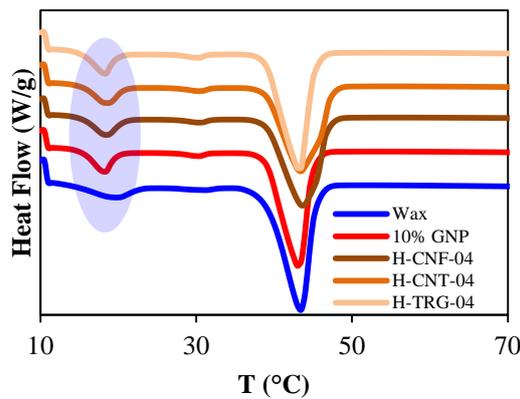


Figure 3. DSC Heating Curves for various filler types at maximum hybrid loading.

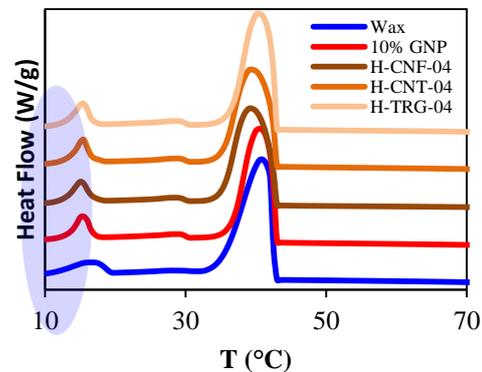


Figure 4. DSC Cooling curves for various filler types at maximum hybrid loading.

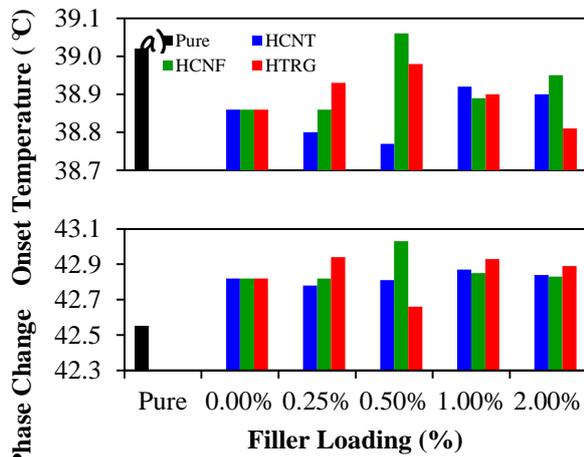


Figure 5. Variation of phase change onset temperature as a function of hybrid filler composition, a) melting and b) solidification process.

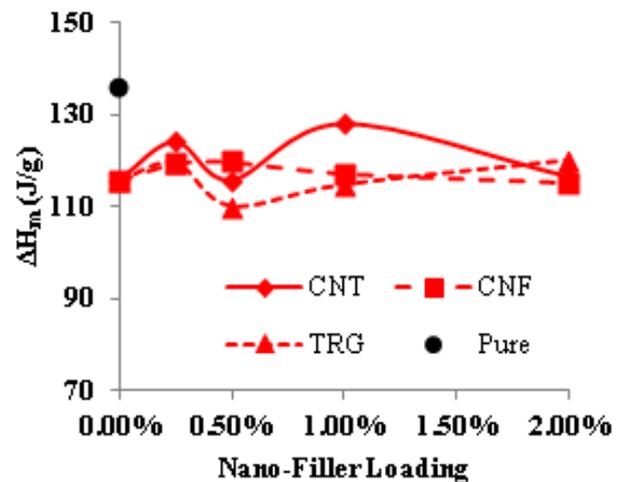


Figure 6. Latent heat of composite PCMs as a function of nano-filler loading during melting cycle.

3.3. Thermal conductivity of PCM

Solid phase thermal conductivity and diffusivity of the hybrid filler nanocomposites was measured as a function of the hybrid filler loading (0 – 2 wt.%). Measurements were performed as per procedure described in the experimental section and two readings were obtained for each sample point later averaged (average difference between values was 1%). Fig.7 summarizes the results, where inset a) presents the actual conductivity and diffusivity data, inset b) and c) presents the thermal conductivity and diffusivity enhancement (%) with the pure wax as the base on the left axis, and the enhancement with 10% GNP as the base on the right axis.

Results revealed that replacement of core GNP filler with CNF, CNT and TRG hybrids resulted in an overall increase in thermal conductivity. However, the enhancement in conductivity is less pronounced for TRG at 2 wt.% loading in comparison to CNT and CNF, whereas CNF dominates in promoting thermal enhancement. An overall increase by 143%, 158% and 174% in thermal conductivity and 179%, 193% and 214% in thermal diffusivity was observed at 2 wt.% hybrid loading of TRG, CNT and CNF respectively. There was an anomaly at 1 wt% loading which had slightly higher thermal conductivity increase for TRG resulting at 158%. This could be attributed to the TRG facilitating the

formation of a connected network of filler resulting in a more effective thermally conductive network within the composite.

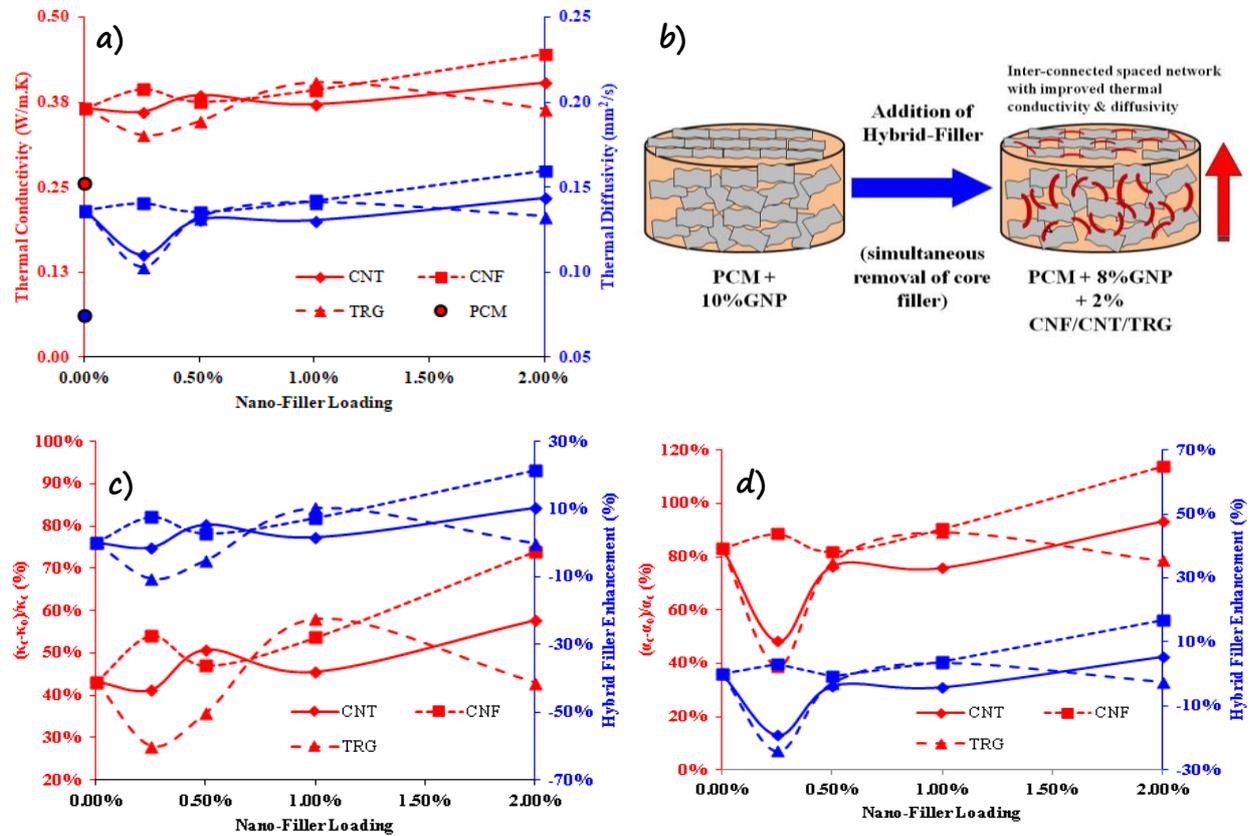


Figure 7. a) Results of measured thermal conductivity for various filler loadings, b) schematic of the proposed effect of the hybrid nanofiller on composite properties, c) & d) percentage enhancement in thermal conductivity (κ) and diffusivity (α) with reference to pure wax (left axis) and 10% GNP composite (right axis).

It is interesting to observe such a remarkable increase in the overall thermal conductivity despite the removal of 2 wt% of GNP which is known to have a planar structure and high contribution to thermal enhancement within composites. It is proposed that the increased thermal conductivity with the introduction of hybrid fillers allows for the spacing of the core GNP filler. This spacing and creation of a more porous and widespread network allows for a more thermally conductive network to be achieved, thus increasing the thermal conductivity and diffusivity (See Fig for schematic of the proposed process). This theory is further substantiated by the fact that though TRGs are inherently less thermally conductive than the GNPs, despite the introduction of 2 wt% TRG and simultaneous removal of the same amount of GNP maintained the net gain in thermal enhancement. CNFs' inherent structure (i.e. dimensions) and intrinsic thermal properties allow it to be a prime candidate for hybrid-filler for thermal conductivity enhancement, followed by CNTs.

To further observe the contribution of the hybrid-fillers, the thermal enhancement was compared to a control sample with 10% GNP only. The relative enhancement was evaluated using the formula $(\kappa_c - \kappa_0)/\kappa_0$, where κ_c is the bulk composite thermal conductivity and κ_0 the control sample (i.e. 10% GNP/pure PCM). Though at low loadings there was no significant thermal enhancement, however, at 2 wt.% loading CNTs and CNFs showed an increase of 122% and 110% respectively. No improvement was observed for TRG, however, it is still interesting as there was a reduction in the more conductive filler GNP and yet the overall conductivity was the same. It should be noted that the

introduction of highly-conductive hybrid-fillers is not alone responsible for the improved thermal conductivity, in fact, as demonstrated by Babaei et al.'s[14] molecular dynamic simulation results, the filler-induced alignment of matrix molecules i.e. PCM, is what results in the intrinsic thermal conductivity of the composite.

4. Conclusions

It can be concluded from the results of this work that the hybrid nano-fillers can have a significant contribution to the thermal enhancement of the overall nano-composites. As presented in the results, an overall increase by 143%, 158% and 174% in thermal conductivity and 179%, 193% and 214% in thermal diffusivity was observed at 2 wt.% hybrid loading of TRG, CNT and CNF respectively (pure PCM as ref.). Furthermore, the CNF and CNT hybrid-fillers contributed an increase of 122% and 110% in the thermal conductivity and 117% & 105% in thermal diffusivity of the composite PCM (10%-GNP as ref.). The improved thermal enhancement is attributed to the inter-connected spaced out filler network within the composite matrix. Future work should explore ways to make these composite form-stable without compromising the thermal conductivity of the final composite PCM.

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