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Optically-regulated thermal energy storage in diverse organic phase-change materials†

Grace G. D. Han, a,b Joshua H. Deru,b Eugene N. Cho a,* and Jeffrey C. Grossman a,b

Thermal energy storage and release in aliphatic phase-change materials are actively controlled by adding azobenzene-based photo-switches. UV activation of the additives induces supercooling of the composites, allowing for longer thermal storage at lower temperatures. The mechanism of this process is studied by comparing phase change behavior across diverse materials.

Low-grade thermal energy storage in organic phase-change materials (PCMs) via solid–liquid phase transition shows potential efficacy in unique applications including thermo-regulating fabrics,1 temperature-adaptable buildings,2 and thermal protection of electronic devices,3 biomedical products,4 and food5 based materials such as carbon aerogels13 and graphene oxides,14 organic PCMs in diverse porous materials,12 particularly carbon-based materials such as carbon aerogels13 and graphene oxides,14 has been reported as a successful method which increases thermal conductivity of PCM composites and shifts crystallization points (Tc) of PCMs. However, the nano-confined PCMs still exhibit fixed Tc, determined by the composition of PCMs and nano-structured host materials, thus their phase passively responds to the changing ambient temperature.

Recently, we developed an active and dynamic method to prevent crystallization as the PCM cools to temperatures below the original phase transition temperature by incorporating photo-switching dopants.15 Although photo-switches were previously investigated as dopants in liquid crystals16–18 to optically change their phases, the application in thermal energy storage as integrated to traditional latent heat storage materials was newly discovered. In that proof-of-concept work, we demonstrated that the liquid phase of an organic PCM, tridecanoic acid, can be preserved at temperatures lower than its pure-phase crystallization point due to the increased inter-action with photo-switching azobenzene dopants upon UV activation. When cooled below TC, the new energy barrier for the liquid-to-solid transition introduced by the presence of switched azobenzene dopants19 can be overcome by simple visible light illumination, which switches the dopants back to their starting configuration and triggers the heat release from the liquid PCM composite. This hybrid photo-switch/PCM system demonstrated prolonged thermal storage well below the original Tc, enabled by the activated photo-switches, without compromising storage capacity due to the presence of metastable cis dopants that store additional thermal energy.15 The hybrid system show stability over 100 cycles (50 hours of fast cycling operation) and thermal storage time over 10 hours under a supercooled condition, while pristine PCMs crystallize within minutes when cooled below Tc.

Herein, we explore the optical regulation of thermal energy storage in diverse aliphatic PCMs and demonstrate the different degrees of lowering Tc of each PCM depending on their chain lengths and functional groups. The structures of the PCMs determine the degree of intermolecular interaction and the operation temperature of heat storage, and our results shed light on parameters and conditions that can be controlled to change the nucleation and crystallization of this class of thermal storage materials.

The strategy to make the Tc of organic PCMs optically triggerable is described in Fig. 1a. Upon heat absorption, the PCMs first melt (Tm ranging from 10 to 70 °C) while the azobenzene dopants with higher melting point of 73 °C remain aggregated and dispersed in the liquid PCM. UV illumination on the suspension activates trans-Azo dopants to isomerize into
Three groups of aliphatic PCMs including \(n\)-alkane,\(^{21}\) fatty acid,\(^{22}\) and fatty alcohol,\(^{23}\) were investigated in this study to expand the scope of PCMs and to compare the impact of relative polarity of PCMs on the efficiency of heat storage and on the intermolecular interactions that operate the heat storage cycle. We used one type of azobenzene dopant with a \(C_{13}\) chain, unlike the previous work\(^{15}\) that investigated the variation of dopant structures, in order to now focus on the role of PCM types and their interaction with the azobenzene unit upon isomerization. The expected heat storage capacities in the composites are listed next to the heat of fusion of pristine PCMs based on assuming complete \(cis\)-to-\(trans\) conversion of dopants and complete crystallization of composites (Supporting Note 1, ESI\(^+\)).

With the aim of maximizing the degree of supercooling (\(\Delta T_C\)), we first varied the ratio of dopants in the PCMs (Fig. 2a) which resulted in volcano-shaped plots (\(\Delta T_C\) vs. additive ratio) for two distinct PCMs with significantly different polarity, chain length, and melting point. Highly polar \(C_{13}\)-acid exhibits a max. \(\Delta T_C\) of 10.5 °C at 35 mol% additive ratio as a result of the maximized supercooling induced by the polar \(cis\)-\(Azo\) dopants with steric bulk. Upon further increasing the additive ratio, the incomplete UV charging of \(trans\)-\(Azo\) and the remaining nucleation seeds reduce the degree of supercooling.\(^{15}\) Non-polar \(C_{28}\) alkane shows a similar plot with max. \(\Delta T_C\) of 3.5 °C at higher (50–60 mol%) additive ratios.

These offset plots for two dissimilar PCM systems show overlapping features when \(\Delta T_C\) is plotted as a function of mass (as opposed to mol) % of dopants in the composite (Fig. 2b). For both composites, the max. \(\Delta T_C\) is found at around 50 wt%,
which infers that mass or volume ratio of dopants determines max. $\Delta T_C$ independent of the type of PCM. The molecular weight of C$_{28}$H$_{58}$ is identical to that of the azobenzene dopant, while the molecular mass of C$_{13}$-acid is about half (54%) that of the azobenzene dopant. Therefore, the degree of supercooling caused by each dopant isomerization in the C$_{13}$-acid is much higher than in the C$_{28}$H$_{58}$ as shown in Fig. 2a. Upon identifying the optimal additive ratio (50 wt%), we applied the identical condition to other PCM systems for further investigation and to achieve max. $\Delta T_C$. We also note that the C$_{13}$-acid composite with the highest additive ratio (80 wt%) has a small negative $\Delta T_C$ ($-1.7 ^\circ C$), which is caused by the presence of excess dopant that has a higher $T_C$ (61 $^\circ C$) than that of the PCM (38 $^\circ C$). As shown in Fig. S1 (ESI†), both C$_{13}$-acid and trans-Azo are significantly supercooled in the composite even before UV activation, displaying a significantly supercooled liquid PCM even before UV activation. For instance, the composite containing 50 wt% photo-switches solidify over a broader temperature range of 49–55 $^\circ C$ (Fig. S1, ESI†). In this particular case, $\Delta T_C$ is defined as the difference between $T_C$ of excess dopants, which leads to the abnormal and insignificant value.

Fig. 2c shows representative DSC plots taken on a composite (C$_{13}$-acid, 50 wt% dopant) before and after UV activation. For the uncharged composites, trans-Azo solidifies at $\sim 55 ^\circ C$, followed by crystallization of the PCM at around its intrinsic $T_C$ ($T_2$). A small exothermic peak $\sim 32 ^\circ C$ represents a minor polymorph of the C$_{13}$-acid. At any temperature between $T_1$ and $T_2$, the heat release from the supercooled liquid PCM can be controllably triggered by visible light illumination that isomerizes dopants and creates nucleation seeds of trans-Azo.

Fig. 3a shows the average $\Delta T_C$ measured for each composite containing 50 wt% photo-switches. Notably, $\Delta T_C$ generally decreases as the PCM possesses longer chains and higher melting points (Fig. 3b), except for C$_{15}$H$_{32}$ which showed a negligible $\Delta T_C$. $T_m$ of the PCM defines the heat storage temperature, and the lower $\Delta T_C$ measured at operation temperatures above 50 $^\circ C$ can be explained by the presence of an activation energy for azobenzene reverse isomerization (Fig. 3c). The activation energy for azobenzene derivatives that are mono-functionalized with ester or amide groups is known to be $\Delta H^\ddagger$ of 88–92 kJ mol$^{-1}$ and $\Delta S^\ddagger$ of $\sim$41 to 56 J mol$^{-1}$ $K^{-1}$ and the thermal triggering of cis-to-trans isomerization occurs at a temperature range of 70–120 $^\circ C$ (Fig. S2, ESI†) in the solid state, which effectively deactivates the photo-switch. Therefore, at higher temperatures, the ratio of cis isomer decreases, leaving the discharged trans-Azo acting as nucleation seeds in the composite, which in turn results in a lower value for $\Delta T_C$. Once the temperature is as high as 70 $^\circ C$, there is a very low number of cis-Azo molecules in the system, making the difference between the composite before and after UV activation negligible. C$_{15}$H$_{32}$, despite the low $T_m$ of $\sim 10 ^\circ C$, showed negligible supercooling, due to the poor miscibility of azobenzene in the short non-polar linear alkane.

Fig. 3 (a) $\Delta T_C$ measured for each composite and plotted against the chain length of each PCM. Composites with comparable charging levels (over 55%) were selected for plotting. (b) $\Delta T_C$ plotted against the melting point of each PCM. (c) Energy diagram of azobenzene isomerization highlighting the activation barrier for the triggered reversion process. (d) Charging amount of azobenzene in PCMs measured by $^1$H NMR and the corresponding $\Delta T_C$ value. The purple dotted line represents the max. charging amount of azobenzene dopant in dilute dichloromethane solution (ca. 5 x $10^{-4}$ M) at 25 $^\circ C$ which allows for unhindered and complete charging due to the low concentration and viscosity of environment, as opposed to that in PCM melt. Depending on the temperature of PCM and miscibility of azobenzene in PCM, the charging amount varies. (e) $\Delta T_C$ plotted against charging amount. The dotted line gives visual guidance, showing the correlation between the two terms. (f) Representative $^1$H-NMR plots of PCM composites before (bottom) and after (top) UV activation.

The ratio between cis and trans isomers after UV activation in each composite can be studied by analysing $^1$H NMR of the composite, following the UV charging for an identical time period (Fig. 3d). The percent charged indicates the yield of UV-activated trans-to-cis conversion. The max charging achieved in dilute solutions (e.g. dichloromethane) was 96%, shown for comparison in the figure (dotted line). The bar graphs illustrate the degree of dopant charging in selected composites of varying PCMs where the liquid PCM molecules solvate dopants. The charging amount ranges from 28% to 90% depending on the heat storage temperature as indicated under each graph. We observed that $\Delta T_C$ of each composite generally scales with the charging amount which is separately measured by $^1$H NMR. Fig. 3e confirms that charging amount is indeed one of the most significant factors that influence the degree of supercooling, $\Delta T_C$. In the case of C$_{18}$H$_{38}$, the charging was very efficient, achieving 80% conversion of azobenzene dopants from trans to cis, while $\Delta T_C$ is lower than the predicted value according to the general trend shown in Fig. 3e. We observed that non-polar PCMs are generally less
Among PCM molecules is strong relative to $E_b$ between PCM and cis-Azo, the crystallization of the PCM is likely to occur as the temperature drops. The selection of a PCM that interacts strongly with the cis-Azo can thus enhance stabilization of the liquid PCM composite at lower temperatures, increasing $\Delta T_C$. The operation temperature which is dependent on the PCM selection (Fig. 3b) also determines the charging amount of additives. Lastly, a PCM-independent factor is the critical composition (additive % in the composite), which should be considered when designing the heat storage systems.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1. N. Sarier and E. Onder, *Thermochim. Acta*, 2007, 452, 149–160.
2. A. M. Khudhair and M. F. Farid, *Energy Convers. Manage.*, 2004, 45, 263–275.
3. F. L. Tan and C. P. Tso, *Appl. Therm. Eng.*, 2004, 24, 159–169.
4. E. Oró, A. de Gracia, A. Castell, M. F. Farid and L. F. Cabeza, *Appl. Energy*, 2012, 99, 513–533.
5. R. K. Sharma, P. Ganesh, Y. V. Tyagi, H. S. C. Metselaar and S. C. Sandaran, *Energy Convers. Manage.*, 2015, 95, 193–228.
6. J. Pereira da Cunha and P. Eames, *Appl. Energy*, 2016, 177, 227–238.
7. S. A. Memon, *Renewable Sustainable Energy Rev.*, 2014, 31, 870–906.
8. Y.-J. Jin, B. Shin-Ill Kim, W.-E. Lee, C.-L. Lee, H. Kim, K.-H. Song, S.-Y. Jang and G. Kwak, *NPG Asia Mater.*, 2014, 6, e137.
9. T. Khadrian, M. Z. Hussein, Z. Zainal and R. Rusli, *Sol. Energy Mater. Sol. Cells*, 2015, 143, 78–98.
10. F. Agyenim, N. Hewitt, P. Eames and M. Smyth, *Renewable Sustainable Energy Rev.*, 2010, 14, 615–628.
11. K. Kant, A. Shukla, A. Sharma and P. H. Biwole, *J. Energy Storage*, 2018, 15, 274–282.
12. W. Aftab, X. Huang, W. Wu, Z. Liang, A. Mahmood and R. Zou, *Energy Environ. Sci.*, 2013, 6, 1392–1424.
13. X. Huang, W. Xia and R. Zou, *J. Mater. Chem. A*, 2014, 2, 19663–19668.
14. S. Zhang, Q. Tao, Z. Wang and Z. Zhang, *J. Mater. Chem.*, 2012, 22, 20166–20169.
15. G. G. D. Han, H. Li and J. C. Grossman, *Nat. Commun.*, 2017, 8, 1446.
16. C. Denekamp and B. L. Feringa, *Adv. Mater.*, 1998, 10, 1080–1082.
17. T. Ikeda and O. Tsutsumi, *Science*, 1995, 268, 1873–1875.
18. T. Ikeda, T. Sasaki and K. Ichimura, *Nature*, 1993, 361, 428–430.
19. A. M. Kolpak and J. C. Grossman, *Nanotechnology*, 2011, 22, 3156–3162.
20. M. Kenisarin and K. Mahkamov, *Renewable Sustainable Energy Rev.*, 2007, 11, 1913–1965.
21. T. Kouskou, A. Jamil, T. E. Rhafiki and Y. Zeraouli, *J. Energy Storage*, 2010, 94, 2158–2165.
22. Y. Yuan, N. Zhang, W. Tao, X. Cao and Y. He, *Renewable Sustainable Energy Rev.*, 2011, 29, 482–498.
23. S. Ali Memon, T. Yu Lo, X. Shi, S. Barbhuiya and H. Cui, *Appl. Therm. Eng.*, 2013, 59, 336–347.
24. A. D. Bond, *New J. Chem.*, 2004, 28, 104–114.
25. G. D. Han, S. S. Park, Y. Liu, D. Zhitomirsky, E. Cho, M. Dinca and J. C. Grossman, *J. Mater. Chem. A*, 2016, 4, 16157–16165.
26. T. J. Kucharski, N. Ferralis, A. M. Kolpak, J. O. Zheng, D. G. Nocera and J. C. Grossman, *Nat. Chem.*, 2014, 6, 441.