Nanostructured Phase Change Materials for Green Building Applications

Lai Yiting, Gan Ming Yi

Hwa Chong Institution

In collaboration with Institute of Materials Research and Engineering

Phase change materials (PCM) have proven to be excellent in storing thermal energy and have garnered interest in recent decades due to this property. With the recent global trend of energy reduction in buildings using novel technology, including in Singapore, PCM has become a suitable candidate to be incorporated into conventional building materials. In this study, the limitations of direct incorporation of PCM into concrete were investigated by analyzing one-dimensional heat conduction in a cylinder filled with paraffin wax. The results of this study showed that microencapsulation was essential for application of PCM in concrete. Subsequently, the thermal reduction effects of incorporating varying concentrations of Octadecane microencapsulated with Copper nanowires in я PMMA/polystyrene shell were explored using hotbox testing. Temperature reduction of as high as 12.5°C was achieved by the composites. Thermal stability was also demonstrated using TGA (thermos gravimetric analysis).

Keywords; Phase Change Materials; Microencapsultion; concrete

Introduction

Phase change materials (PCM) have garnered great interest in recent years due to their potential to be an excellent form of thermal energy storage when integrated into building materials. They can store heat energy in a latent form, resulting in higher heat storage capacity per unit volume than conventional building materials. By absorbing heat as the ambient temperature rises, and changing from solid to liquid phase, then returning to its solid state by releasing absorbed heat back into its surroundings when the ambient temperature drops, PCM can stabilise the interior temperature and provide thermal comfort by influencing building surface temperatures [1].

Since Singapore has pledged its commitment to reduce its Emissions Intensity by 36% from 2005 levels by 2030 under the UNFCCC-United Nations Framework Convention on Climatic Change, there will be a stronger impetus for businesses to harness energy efficiency innovations and develop sustainably. Several initiatives have been introduced by The Government so far, such as the Energy Conservation Act that mandates energy reduction practices for large energy users and the BCA Green Mark certification for buildings to encourage companies to invest in and use energy efficient technology [2]. Currently, air conditioning systems comprise up to 50% of total energy consumption in a building in Singapore which has hot and humid conditions [3]. Hence, it has become clear that reducing total energy consumption of buildings by cutting down on air conditioning usage can have a major impact on the total greenhouse gas emissions in Singapore. The idea of incorporating PCM into building materials to absorb heat in the day and lower interior temperatures of buildings without air conditioning can hence bring about great possibilities.

In addition, the demand for concrete has been on the rise in Singapore. According to the Economic Survey of Singapore 2010, there was a reported rise of 5.2% on ready mixed concrete due to the increased infrastructure projects aimed at meeting needs of our increasing population [4]. For sustainable construction, the Singapore government has set a national target to make 80% of Singapore buildings 'green' by 2030, by using materials with energy efficient features [5]. The term "Green Concrete" had also been greatly promoted by the Building and Construction Authority of Singapore [6]. This research hence offers an alternative form of "Green Concrete" amidst other smart concrete innovations.

Microencapsulated PCM are known to display improved thermal conductivity via increasing heat transfer area [7], have enhanced stability, and can better maintain storage material volume during phase change. We utilised this method in this research due to the limitations of applying PCM directly onto concrete walls due to their low thermal conductivity, potential leakage, and fluctuating storage material volume [8]. Direct incorporation of powdered microencapsulated PCM into concrete was also conducted as it was the simplest and most cost-effective method that can easily be done in large scale production, compared to other methods of incorporation like immersion [9, 10]. In order to achieve efficient heat absorption upon phase change, copper nanowires are incorporated to enhance the thermal conductivity of phase change materials.

This project first seeks to investigate the limitations of incorporating PCM directly in concrete without microencapsulation using Paraffin wax in a theoretical study. It then subsequently aims to study the thermal performances of concentrations different of PCM (Octadecane) microencapsulated with copper nanowires in PCM-cement composites. Octadecane (melting point: 28°C) is used as PCM because this corresponds to the temperature change in Singapore, which can greatly fulfill the performance of PCM. The thermal performance will then reveal the energy saving potential (lowering of indoor surface temperatures) of these composites for use in various building applications. The method of incorporation is rapid and economically feasible, hence desirable.

I. METHODS AND MATERIALS

In the theoretical study of phase change materials, Paraffin wax from ACROS Organics was utilized due to its high operating temperature (58 - 62 $^{\circ}$ C) to observe its entire phase change process. The determination of its thermal conductivity was

carried out via analysing one-dimensional heat conduction in a cylinder, a method already established by Delaunay [11]. The melting of Paraffin wax was observed by heating up a 500g sample in a glass beaker with a heat rod embedded in the middle region that was heated up to 60° C and 70° C respectively. The heating process was about 5.5 hours at an ambient temperature of 25°C. The process of phase change was monitored using an infrared camera connected directly above the beaker.

The experimented phase change material incorporated subsequently in concrete was Octadecane, from ACROS Organics [12], with an operating temperature of 28 - 31°C. Octadecane was not directly used in the theoretical study since its operating temperature is low and close to ambient temperature, hence, the study of the start of the phase change process was extremely challenging. Octadecane was microencapsulated with Copper nanowires in а PMMA/polystyrene shell using BUCHI Mini Spray Dryer B-290. An image of the encapsulated product was captured using a SEM (Scanning Electron Microscope). The microencapsulated PCM presented itself in a powder form, as opposed to its initial crystalline appearance. 3 samples were used in our experiments, namely; 0% PCM- cement composite (P0) as control, 25% PCM -cement composite (P0.25) and 50% PCM-cement composite (P0.5).

To conduct the hotbox test, panels with different compositions were made. Varying composite concentrations were created via manipulation of the proportions of PCM and Portland cement used. In the synthesis of P0, 400g of Portland cement was used. In the synthesis of P0.25 and P0.5, 100g of micro-encapsulated PCM and 200g of micro-encapsulated PCM was mixed with 300g of Portland cement and 200g of Portland cement respectively. All samples were then mixed manually using a spatula and water was added during the mixing process in minute amounts, until desired consistency and viscosity was obtained. The resulting mixture resembled a highly viscous paste. This mixture was then poured into a 20x20 cm mould, and the surface was subsequently smoothened out using a paint scraper. Thereafter, the mixture was placed in the oven at 61°C for 16 hours.

Hotbox testing was then conducted by placing sensors on the top and bottom of the concrete slab obtained and was tested alongside the control sample, at temperatures of 60, 70 and 80° C.

TGA (Thermo gravimetric analysis) was subsequently conducted on all samples at temperatures ranging from 100 $^{\circ}$ C to 900 $^{\circ}$ C to observe their thermal stability at ambient temperature.

II. RESULTS AND DISCUSSION (THEORETICAL STUDY)

The first sign of melting was observed after around 2 hours and 3 hours at 70 °C and 60 °C respectively. Even after subjecting the material to high temperatures above its melting point (40-45 °C), only half melted at 70 °C after 5.5 hours of testing. On the other hand, only 1/8 melted at 60 °C in the same duration. The heat transfer as monitored by a real time infrared camera was slow. Hence, it was concluded that the thermal conductivity of PCM will be too weak if it was to be directly incorporated into concrete for application purposes since heat cannot be spread out and absorbed promptly to lower surface temperatures. The organic PCM also displayed volume expansion effect upon melting, which is undesirable since cracks and defects may appear on concrete slab if incorporated directly. This has dangerous implications on the stability of building structures over time. In addition, it was also noted that a noticeable odour was produced upon melting, which can result in decreased comfort for individuals in potential building applications.

Microencapsulation hence serves as a good way to overcome such challenges. The process of coating individual particles with a continuous film for the production of a micrometer sized microcapsule [13] can successfully prevent leakage of melted PCM during phase change, increase thermal conductivity, improve chemical stability, and can control changes in volume during phase change, all in a cost effective way [14].

Due to the extremely poor thermal conductivity of PCM, further enhancement of heat transfer rate is necessary. Various methods have been proposed earlier [15, 16, 17]. In particular, the method of incorporating Copper nanowires [18]

is promising as thermal conductivity of organic PCM was reported to show a 9 fold increase. Such metal particles also do not degrade the thermal behavior of organic PCMs, hence maintaining high thermal stability [19].

Visual observance of the melting process of Paraffin wax offered good insights on the behavior of Octadecane in a cost

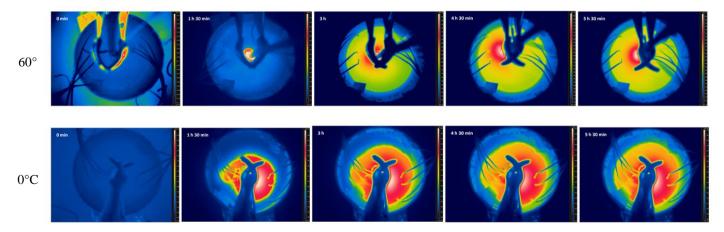


Fig 1: Infrared images of melting of paraffin wax over 5.5 hours at 60°C and 70°C

effective manner, as both are organic PCMs with similar characteristics and limitations in use [20].

III. RESULTS AND DISCUSSION (PCM INCORPORATION IN CONCRETE)



Fig 2: Scanning Electron Microscope image of encapsulated PCM

The SEM image showed that microencapsulation of both Octadecane and Copper nanowires in PMMA/polystyrene shells was successful as there were little leakages or breaks observed. Furthermore, the size of capsules is very uniform and around 50 um.

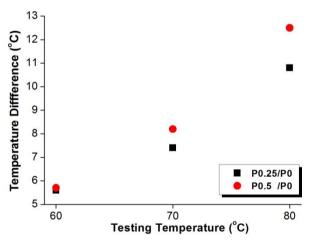


Fig 3: Hotbox testing results for P0.25 and P0.5

Results from hotbox test showed that there was a negative temperature difference between the control sample and the PCM-cement composites at temperatures between 60-80°C. This implies that at these temperatures, the composites can reduce the interior surface temperature of buildings and achieve cooling effect. Since it will be difficult to observe significant changes in temperatures at low ambient temperature of 25°C in a short duration, the hotbox testing was done at higher temperatures of 60-80°C. However, it can be hypothesized that similar effects will be observed at room temperatures. Hence, PCM-cement composites are effective in energy reduction.

The graph also showed that there was an increasing temperature difference between the control sample and the PCM-cement composites as the testing temperature increases. The highest temperature difference recorded was 12.5 °C at testing temperature of 80 °C, achieved by sample P0.5. At 80 °C, P0.5

also registered a 2.5 $^\circ \mathrm{C}$ higher temperature difference than P0.25.

At lower temperatures, such as 60 °C however, the temperature difference between both P0.25 and P0.5 was lower at 5.5 °C and did not vary as much. This suggest that at ambient temperatures of 25°C, both P0.25 and P0.5 may produce similar energy savings effects and can both be used, but for applications involving temperatures ranging from 80 °C and above, P0.5 should be utilised for more efficient energy saving results.

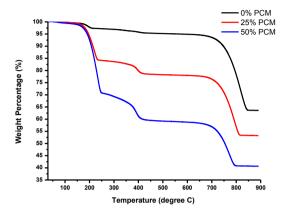


Fig 4: Thermo gravimetric analysis (TGA) analysis of P0, P0.25, and P0.5

TGA results concluded that a sharp drop in weight percentage only occurred at 200 °C for both P0.25 and P0.5. This data proves the high thermal stability of our sample composites, as thermal degradation was only initiated at 200 °C. For application purposes, this suggests that the PCM-cement composite can be widely used, even in industrial applications.

Our team based in the Institute of Materials Research and Engineering, also tested the energy saving potential of the composites in real life simulated applications in mini HDB chambers and concluded that 8-15% energy savings was achieved in comparison with normal concrete. Therefore, our phase change material technology is very promising in green building applications.

IV. CONCLUSIONS AND RECOMMENDATIONS

In retrospect, the theoretical study did offer good insights on the performance and behaviour of non-microencapsulated Octadecane during phase change. Along with literature research, it was concluded that microencapsulation of PCM is indeed essential for building applications. Hotbox testing conducted on the PCM-cement composites also showed significant reduction in inner surface temperatures consistently. In addition, TGA demonstrated the high thermal stability of the composites. As such, there is undoubtedly great potential in microencapsulated PCM-cement composites for application in wallboards, ceilings and roofs alike in Singapore's hot climate.

Subsequent to our research, the incorporation of PCM into other materials such as wood, metal and other construction materials can be explored. In addition, since our research did not fully investigate how the addition of conductive materials like copper nanowires can boost performance of the PCM composites, an indepth study of the behavior of PCM under the influence of varying concentrations of these materials can be conducted. Furthermore, only one type of PCM (Octadecane) was used in our experimental study. Hence, we can look into how different PCMs, organic and inorganic, can form composites to maximise energy saving potential.

V. ACKNOWLEDGMENT

We would like to thank our mentors, Dr Zhu Qiang and Dr Tang Tao from IMRE for their support and guidance throughout the research project. We would also like to thank IMRE for the warm reception and providing us with cutting edge equipment for our project. On top of that, we would like to thank our teacher in charge, Mr Wee Chorng Shin and the school management for giving us an opportunity to try our hands at a research project through the CenTaD programme.

VI. REFERENCES

1 Baetens R, Jelle BP, Gustavsen, A. (2010) Phase change materials for building applications: A state-of-the-art review. Energy and Buildings. 42: 1361-1368

2 Singapore's Submission to the United Nations Framework Convention on Climate Change (UNFCCC). (n.d.). Retrieved December 15, 2015, from http://www.mfa.gov.sg/content/mfa/overseasmission/gen eva/press_statements_speeches/2015/201507/press_20150703. html

3 Singapore's Second National Communication: Under the United Nations Framework Convention on Climate Change (November 2010), NEA. (taken from website https://www.nccs.gov.sg/sites/nccs/files/Aircon%20Primer.pdf)

4 CONSTRUCTION. (2010). In Economic Survey of Singapore 2010 (Vol. 8.2, pp. 40-43). SINGAPORE: MINISTRY OF TRADE AND INDUSTRY.

5 Green concrete â an important innovation for resource-scarce Singapore. (n.d.). Retrieved December 15, 2015, from http://sbr.com.sg/buildingengineering/commentary/green-concrete----important-

innovation-resource-scarce-singapore

6 A Guide on CONCRETE USAGE INDEX. (2012). In BCA Sustainable Construction Series (SUSTAINABLE CONSTRUCTION ed., Vol. 6, pp. 1-85). Singapore: Building and Construction authority.

7 Lane GA. Encapsulation of heat of fusion storage materials. In: Proceedings of 2nd Southeastern Conference on Application of Solar Energy, 1976. p. 442–50. 8 SimenEdsjøKalnæs. 2015 Phase change materials and products for building applications: A state-of-the-art review and future research opportunities. Energy and Buildings 94 (2015) 150–176

9 Obtaining an energy storing building material by direct incorporation of an organic phase change material in gypsum wallboard

10 M.M. Shapiro. D. Feldman. D. Hawes and D, Banu, in: Proc. Solar/87: Joint Conference of ASES and SESCI. Portland, OR, July 12 16, 1987, pp. 45-58.

11 D. Delaunay, P. Carre, Dispositifs de mesure automatique de la conductivit_e thermique des mat_eriaux _a changement de phase, R. Physique Appliqu_ee 17 (1982) 209–215.

12 SAFETY DATA SHEET. (2015, February 10). Retrieved December 15, 2015, fromhttps://www.fishersci.com/shop/msdsproxy?productNam e=AC416770020&productDescription=PARAFFIN WAX (GRANULAR)

2KG&catNo=AC416770020&vendorId=VN00032119&storeI d=10652

13 FangG, ChenZ, LiH. Synthesis and properties of microencapsulated paraffin composites with SiO2 shell as thermal energy storage materials. ChemEngJ 2010;163:154–9.

14 TyagiVV, KaushikSC ,TyagiSK, AkiyamaT .Development of phase change materials based microencapsulated technology for buildings :a review. RenewSustainEnergyRev2011;15:1373–91.

15J. Fukai, Y. Morozumi, Y. Hamada, O. Miyatake, Transient response of thermal energy storage unit using carbon fibers as thermal conductivity promoter, Proceedings of the 3rd European Thermal Sciences Conference, Pisa (Italy), 2000.

16 L.F. Cabeza, H. Mehling, S. Hiebler, F. Ziegler, Heat transfer enhancement in water when used as PCM in thermal energy storage, Appl. Thermal Eng. 22 (2002) 1141–1151.

17 X. Tong, J. Khan, M.R. Amin, Enhancement of heat transfer by inserting a metal matrix into a phase changematerial, Numer. Heat Transfer, Part A 30 (1996) 125–141.

18 Ju-Lan Zeng, Effects of copper nanowires on the properties of an organic phase change material. Solar Energy Materials and Solar Cells 105 (2012) 174-17

19 B.M. Gibbs, S.M. Hasnain, DSC study of technical grade phase change heat storage materials for solar

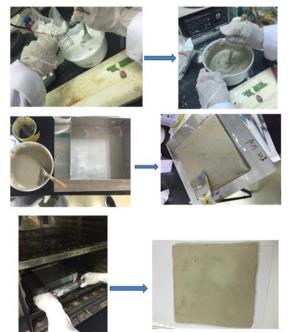
heating applications, Proceedings of the 1995 ASME/JSME/JSEJ International Solar Energy. Conference. Part 2,1995. 20 S. Himran, A. Suwono, G.A. Mansoori, Characterization of alkanes and paraffin waxes for application as phase change energy storage medium, Energy Sources 16 (1) (1994) 117–128.

VII. APPENDIX

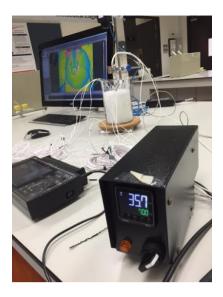
Appendix A- Pictorial Illustration of encapsulated PCM ______in powder form _____



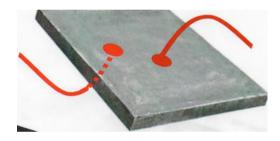
Appendix B- Incorporation process of PCM in concrete



Appendix C- Experimental setup for theoretical study of PCM (paraffin wax)



Appendix D- Position of sensors on PCM-cement composites during hotbox testing



Appendix E- Hotbox testing results at 80°C for P0 and P0.5 showing 12.5°C temperature difference

