Phase change material focus

Today, thermal energy storage systems have become one of the necessary means for reducing reliance on fossil fuels and contributing to more efficient, environmentally-friendly energy usage by utilising waste heat from solar and other energy sources. In this study, the passive integration of phase change material (PCM) in cement was analysed, and the thermal and mechanical effects on cement properties assessed. The experimental results provide important data on how PCMs affect cement as part of a concrete mixture.

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Phase change materials (PCM) are combined (sensible and latent) thermal storage materials that can store and dissipate energy in the form of heat. There are a range of PCMs available on the market that are classified as organic, inorganic and eutectic materials, depending on their composition and characteristics. PCMs can be added to the concrete mix by using different methods such as direct application, micro/macro encapsulated particles, immersion, or as part of lightweight aggregates.

In the study conducted by Yapichem Kimya Sanayi and presented in this article, the thermal and mechanical phase change behaviours of hardened cement paste were investigated. Firstly, the method of using mixed H_2SO_4/HNO_3 acids to functionalise carbon black (f-CB) is described. Following that, Yapıchem adapted the f-CB to epoxy resin and its hardener. Finally, cement paste compositions containing the PCM in various concentrations were prepared.

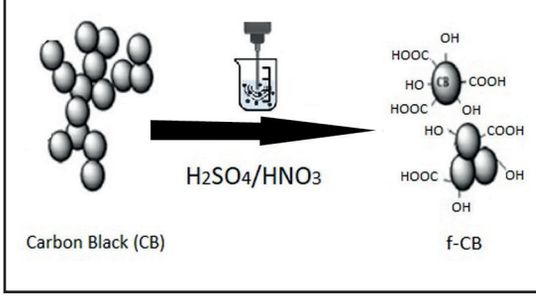
Materials used in the study

An ordinary Portland cement (CEM I 42.5R) was used with a Blaine surface area of 3364cm^2/g (see Table 1 for the chemical composition). Carbon black (Powcarbon ® 24209-G20) with an average particle size of 20±2nm and a BET surface area of 180±20 m^2/g and paraffin wax were supplied by a Turkish company. Paraffin wax, also known as petroleum wax, is obtained from coal and petroleum and contains a mixture of hydrocarbon molecules. Epoxy resin and its hardener, nitric acid and sulphuric acid, were also purchased from a local company and used as obtained without further purification. The resin and hardener ratio was stochiometric: 100/100 weight per cent /weight per cent.

Table 1: chemical composition of the Portland cement used in the study

Compound	Composition (wt %)
CaO	66.04
SiO_2	21.47
Al_2O_3	4.76
Fe_2O_3	3.16
MgO	1.17
SO_3	1.96
Na_2O	0.08
K_2O	0.53
Other (water, impurities)	0.83

Figure 1: functionalised carbon black (f-CB) product



Methods

Preparation of f-CB

HNO_3 and H_2SO_4 were used to synthesise the f-CB. To this end, a few millilitres of H_2O_2 were added to the carbon black and stirred vigorously for 2h. Stochiometric amounts of H_2SO_4 were then slowly added and the mixture was magnetically stirred for 60min. The product obtained was called 'partially functionalised CB', which was then filtered and washed with deionised water. The partially functionalised CB obtained was dried in an oven to remove the water content.

A few grams were taken from the dried product and dissolved in stochiometric amounts of nitric acid and stirred to oxidise the CB once again. The solution was filtered and washed. The oxidised product was dried in an oven. This dried product was called f-CB (see Figure 1).

Preparation of ER-f-CB

To increase thermal conductivity, epoxy resin was dissolved in acetone solvent, and f-CB corresponding to 15 per cent was added to the epoxy resin solution and stirred for 60min to disperse uniformly. The required amount of epoxy hardener was added to the solution and mixed well. The final mixture was transferred into a mould and stored for drying. This dried product was called ER-f-CB (see Figure 2).

Morphologies of the obtained ER-f-CB were observed using scanning electron microscopy (SEM). It was clear that the obtained ER-f-CB has a regular powder structure with uniform morphology (see Figure 3a). Nevertheless, some particles accumulated on the surface of the resin, attributed to the fact that carbon black particles could not separate from each other. The sizes of these particles are shown in Figure 3b.

Preparation of encapsulated PCM

To prepare the encapsulated PCMs, ER-f-CB and paraffin were added to the epoxy resin, along with acetone solvent and stirred vigorously, then hardener was added. The solution was transferred to the mould and stored for drying. In this part of the study, a paraffin content in

Figure 2: the final dried product was called ER-f-CB

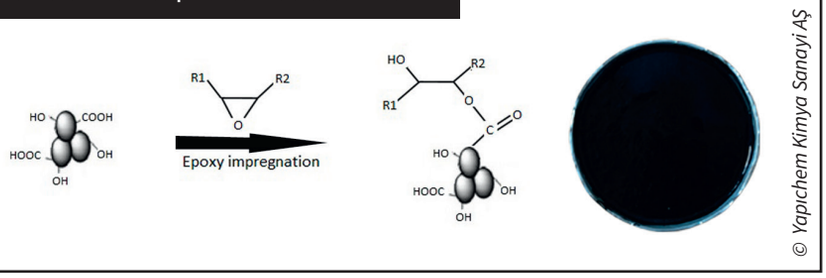


Figure 3: SEM surface images of ER-f-CB

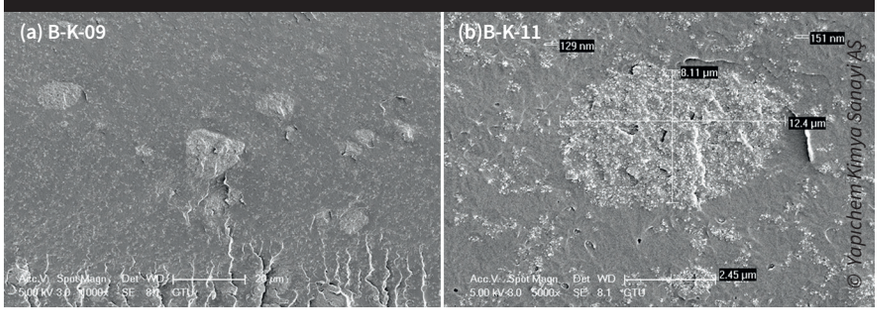


Table 2: mix proportion of hardened cement paste with encapsulated PCM

Codes	Mass ratio of PCM by weight of cement (%)	Cement	Water	Paraffin content in PCM (wt %)
PCM-0	0	1	0.28	0
PCM-I	4	1	0.28	1
PCM-II	4	1	0.28	1.2
PCM-III	4	1	0.28	1.6

the PCM compositions of one, 1.2 and 1.6 per cent was prepared. During the phase transition, PCMs melt into viscous/semi-viscous forms. Therefore, to avoid leakage, Yapıchem used low amounts of paraffin within a shell. The microcapsules used in the study were composed of a paraffinic phase change core and an epoxy shell.

Preparation of the cement paste

The cement pastes were mixed in accordance with EN 196-3:2005+A1:2008 (E) using a Hobart mixer. First, the cement and PCM composite were placed in a bowl and water was added within 10s. This was followed by mixing for 90s at a low speed. The mixer was then stopped for 30s, during which time all the paste adhering to the wall and the bottom part of the bowl was scraped using a metal scraper and added to the mix. Mixing then resumed for an additional 90s. The total mixer running time was 3min. The mix was then cast in a cubic mould with an inner diameter of 40mm and a height of 40mm.

The mix proportions of the cement paste with a different mass paraffin percentage of PCM are given in Table 2. As can be seen, the mass percentages of PCM were four per cent and the paraffin content in the PCM was zero, one, 1.2 and 1.6 per cent by weight of cement, while the water-cement ratio was 0.28.

Discussion

PCMs can store and release latent heat by making phase transitions between solid-solid or liquid-solid phases at specific temperature ranges.

The latent heat and phase change temperature of hardened cement pastes containing PCM were characterised by differential scanning calorimetry (DSC) in the range of -10-80˚C. The results are listed in Table 3.

As clearly observed in the DSC curves shown in Figures 4-7, PCM-0 (hardened cement paste without PCM) has no phase change peak at both heating and cooling. However, PCM-I, PCM-II and PCM-III (hardened cement pastes containing one, 1.2 and 1.6 per cent paraffin in encapsulated PCM, respectively) have melting and crystallisation peaks. The mass fraction of the paraffin affects the latent heat of phase changes but has little effect on the phase change temperatures.

PCM-I exhibits single phase change at 48,73˚C. The latent heats of melting is 0.4446J/g. However, PCM-II and PCM-III showed two melting peaks at 25˚C and 48˚C. As can be seen in Figure 6, the melting temperature peaks (Tm) of PCM-II were 25.07 and 48.14˚C. The latent heat of melting was 0.0943 and 0.3792J/g. At the end of the freezing process, the latent heat of PCM-II was -0.0292 and -0.8538J/g. When increased to 1.6 per cent from 1.2 per cent adding paraffin, the melting peaks of PCM-III were found to be 25.73 and 48.13˚C. The melting points of PCM-II and PCM-III were almost the same. However, the total latent heat of PCM-III was 0.1721 and 1.0106J/g, which increased 2.6 times after increasing to 1.6 per cent from 1.2 per cent.

The results of the compressive strength of hardened cement paste with different mass percentages of encapsulated PCM are presented in Table 4.

The results show that considerable changes in compressive strength were observed by adding the functionalised carbon black reinforced epoxy resin

Table 3: mix proportion of hardened cement paste with encapsulated PCM

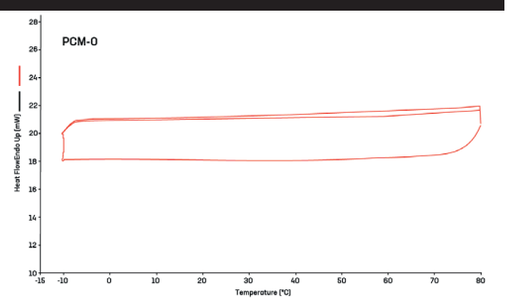
Thermal parameters	PCM-0	PCM-I	PCM-II		PCM-III	
Melting point (Tm1 and Tm2), (˚C)	0	48.73	25.07	48.14	25.73	48.13
Latent heat of melting (ΔHm1 and ΔHm2) (J/g)	0	0.4446	0.0943	0.3792	0.1721	1.0106
Freezing point (Tc1 and Tc2) (°C)	0	41.15	20.83	42	22.67	41.17
Latent heat of freezing (ΔHc1 and ΔHc2) (J/g)	0	-0.2722	-0.0292	-0.8538	-0.1153	-0.6038

(ER-f-CB) to the cement paste. Contrary to literature, investigated the effect of the incorporation of different percentages of encapsulated PCM (zero, one and 1.2 per cent paraffin by weight of cement total mass) on the compressive strength of hardened cement paste and found that the inclusion of one and 1.2 per cent encapsulated PCM increased the compressive strength by up to 18 per cent. Unfortunately, the addition of more resulted in a significant loss of concrete compressive strength. After adding 1.6 wt per cent paraffin of encapsulated PCM, the compressive strength of PCM-III decreased by approximately 10 per cent. This can be attributed to compressive strength having a larger and faster degradation with the increase of encapsulated PCM content and unbalanced distribution among them.

Table 4: results of the compressive strength of hardened cement paste with different mass percentages of encapsulated PCM

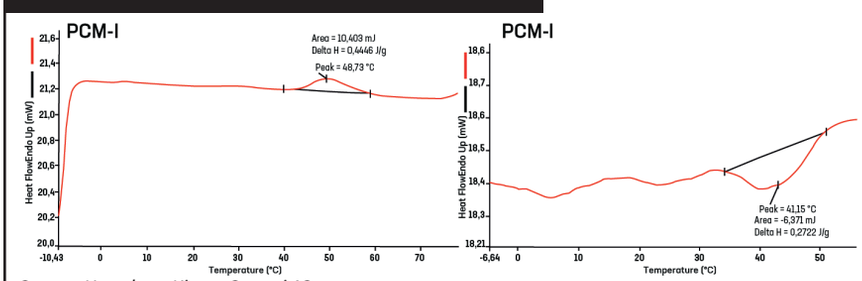
Codes	2-days
PCM-0	43.41
PCM-I	47.49
PCM-II	51.24
PCM-III	46.29

Figure 4: differential scanning calorimetry curve of PCM-0



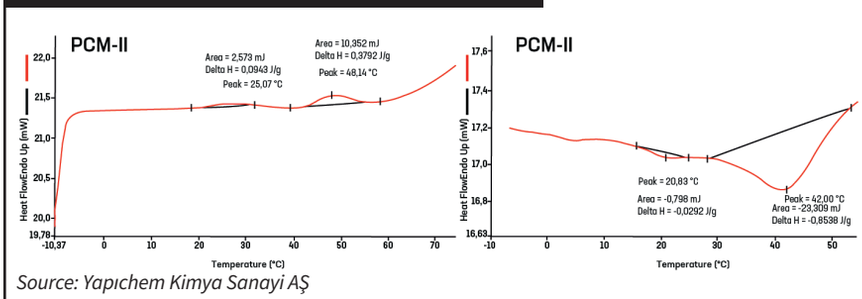
Source: Yapıchem Kimya Sanayi AŞ

Figure 5: differential scanning calorimetry curve of PCM-I



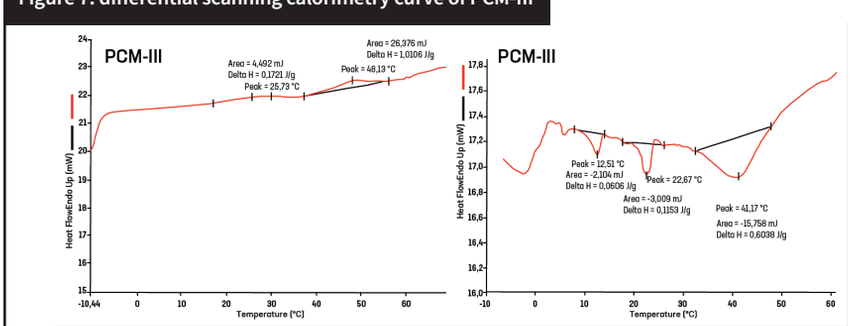
Source: Yapıchem Kimya Sanayi AŞ

Figure 6: differential scanning calorimetry curve of PCM-II



Source: Yapıchem Kimya Sanayi AŞ

Figure 7: differential scanning calorimetry curve of PCM-III



Source: Yapıchem Kimya Sanayi AŞ

Conclusion

In this study, PCM was successfully prepared through oxidising conditions applied on carbon black and subsequent using epoxy resin and paraffin. For the development of cement-based materials, this research not only focused on the thermal properties of hardened cement paste with different mass percentages of PCM, but also discussed their mechanical properties. From a lab scale experimental investigation, the following conclusions can be drawn:

- The prepared MPCM has a melting temperature of 48˚C and total latent heat of 1.18J/g.
- The thermal energy storage (TES) capacity of hardened cement paste with 1.6 per cent encapsulated PCM (PCM-III) by weight of cement was found to be 2.6 times higher than that of hardened cement paste containing one and 1.2 per cent encapsulated PCM (PCM-II).
- The compressive strength of hardened cement paste with encapsulated PCM increased with the increase in the content of encapsulated PCM in cement paste, and then it decreased.

By obtaining the optimal amounts of each of these encapsulated PCMs on a laboratory scale, future studies will continue on a semi-industrial scale.

Challenges

Over the last decade, TES has emerged as a promising technology to achieve a low-carbon future. However, the following challenges limit the widespread use of PCMs in concrete on field projects:

- Some PCMs may interact with certain admixtures used in the manufacture of concrete, changing its mechanical properties or posing compatibility problems.
- The inside environment of concrete is quite alkaline by nature, and in some circumstances, this high alkali causes the PCMs to degrade.
- During phase transitions, some PCMs can experience volume changes, which may cause microcracking in the matrix.
- In contrast to conventional concrete materials, PCMs for concrete are not always inexpensive or easily obtainable on the market. ■