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Thermo-mechanical behaviors of the expanded graphite-phase change material matrix used for thermal management of Li-ion battery packs

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ABSTRACT

In this paper, blocks for the thermal management of Li-ion battery are prepared. The blocks are made of paraffin wax, which is used as a phase change material (PCM), and graphite flakes. The process starts by compacting expanded graphite into the desired modular shapes and then impregnating it into molten paraffin wax. The modular pieces were assembled together, followed by finishing operations to achieve a desired packaging geometry.

Thermo-mechanical properties of the produced phase change material–expanded graphite (PCM/EG) composites have been studied. The tests include thermal conductivity, tensile compression and bursting test. The results showed that as mass fraction of paraffin wax increases in the composite material, the thermal conductivity, tensile strength, compression strength, and burst strength were improved while tested at low operating temperatures. In contrast, the results showed reverse behaviors when tested at relatively high operating temperature.

1. Introduction

Thermal energy storage systems (TES) have the ability to store high or low temperature energy for later use (Krupa et al., 2007). For example, the solar energy can be stored for overnight heating, the summer heat stored for winter use, etc. Thus, these systems have potential applications in active and passive solar heating, water heating, air conditioning, etc., and are regarded as an economical and safe energy storage technology.

The idea to use phase change materials (PCM) for the purpose of management of thermal energy is to make use of the latent heat of a phase change, usually between the solid and the liquid state. Since a phase change involves a large amount of latent energy at small temperature changes, PCMs are used for temperature stabilization and for storing heat with large energy densities in combination with rather small temperature changes. Passive thermal management using PCMs is suitable for applications where heat dissipation is intermittent or transient. In principle, materials should fulfill different criteria in order to be suitable to serve as a PCM (Kandasamy et al., 2007; Krupa et al., 2007; Mills et al., 2006):

- Suitable melting temperature
- High melting enthalpy per volume unit (kJ/m^3)
- High specific heat [kJ/(kg K)]
- Low volume change due to the phase change
- High thermal conductivity
- Cycling stability
- Not flammable
- Not poisonous
- Not corrosive

Among the advantages of PCM are: high latent heat of fusion giving high energy density, high specific heat, controllable temperature stability, and small volume change on phase change. Heat is stored (withdrawn from the hot component) during melting and is released to the ambient during the freezing period (Kandasamy et al., 2007). Some of the physical properties that determine the thermal energy storage capacity of materials are (Krupa et al., 2007; Kandasamy et al., 2007):

- The Specific heat capacity (c_p)
- The melting point (T_m)
- The latent heat of fusion (L_f)

Thermal management is recognized as one of the most significant bottlenecks in the development of advanced microprocessors for mobile electronic devices (Luyt and Krupa, 2007), such as

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personal digital assistants (PDAs), mobile phones, notebooks, digital cameras, etc. Considering the effects of temperature on the reliability of the electronic components, the thermal design must be able to keep the working temperature of such devices below their respective allowable maximum temperatures (generally ranging from 85 to 120 °C) at all times during normal operation (Wang et al., 2008).

Reliability of electronic packages is another challenging factor in the design of mobile electronic devices. However, thermal management of Li-ion batteries plays a significant role in large power applications in addressing the thermal safety apart from improving the performance and extending the cycle life. The electrochemical performance of the Li-ion battery chemistry, charge acceptance, power and energy capability, cycle life and cycle life cost are very much controlled by the operating temperature (Mills et al., 2006). One of the side effects of exposure to high temperature is fast aging and accelerated capacity fades (Khateeb et al., 2005).

Sarı and Karaipekli (2007) found that thermal conductivity of paraffin wax could be improved by incorporating expanded graphite into the wax matrix. They found that thermal conductivities of the composite PCMs with mass fraction of 2%, 4%, 7%, and 10% EG indicated that the thermal conductivity of paraffin (0.22 W/m K) increased as 81.2%, 136.3%, 209.1%, and 272.7%, respectively. This was attributed to high thermal conductivity of the EG (Sarı and Karaipekli, 2007). Zhang et al. (2006) investigated the effect of additives on thermal conductivity of shape-stabilized phase change material. Their results showed that incorporating graphite into molten wax tend to improve thermal conductivity of paraffin wax about 52.7%. These results were obtained by Mills et al. (2006) as they pressed EG into sponge-like texture, which they then impregnated into molten paraffin wax at 80 °C for about 60 min. Thermal conductivity of the produced PCM/EG composites produced by this method have tremendous thermal conductivity up to 16.6 W/m K (Mills et al., 2006; Mills and Al-Hallaj, 2005).

Although many thermal properties of PCM/EG are discussed, no results are available about mechanical properties of these composites or their behaviors at relatively elevated temperatures. Hence, the aim of this work is to perform a systematic experimental study to analyze the important effects of the thermo-mechanical properties of the produced samples, like tensile and compression behaviors, bursting and thermal conductivity.

2. Materials and methods

2.1. Expanded graphite

The graphite matrix is made by compacting expanded graphite (EG) to a desired bulk density. EG is easily produced from flake graphite. Flake graphite is characterized by stacked sheets of carbon where the carbon making up the sheet is held together by strong covalent bonds and the stacked sheets are held together by weak van der Waals bonds (Mills et al., 2006). Detailed description of expanded graphite production method is discussed comprehensively in literature (e.g. Mills and Al-Hallaj, 2005; Sarı and Karaipekli, 2007). The following is a brief description of the production method of EG, as outlined by Sarı and Karaipekli (2007). In this process, EG was prepared from graphite to maximize mass fraction of paraffin to be absorbed into its porous structure. The graphite sample was first converted to intercalated, or expandable, graphite through chemical oxidation in the presence of a mixture of sulfuric and nitric acid, and then dried in a vacuum oven at 65 °C for 24 h. EG was then obtained by rapid expansion and exfoliation of expandable graphite in a furnace over 900 °C for 60 s. In this study, EG was supplied by All Cell Technologies, LLC (Chicago, IL).

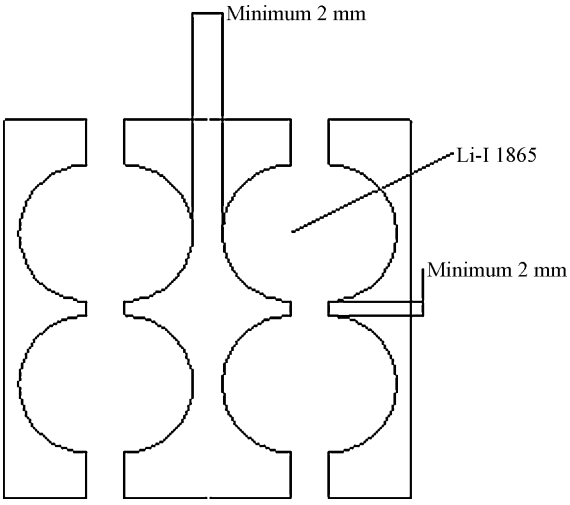

Fig. 1. Modular pieces and their dimensions.

2.2. Manufacturing process

The manufacturing method was based on the presented by Mills et al. (2006). The only main difference is that the EG was initially compacted into desired modular pieces (dimensions are shown in Fig. 1) which reduces the amount of waste material during the drilling processes. The green compacts density is 0.04375 g/cm^3. Technical grade paraffin (melting point = 58–60 °C and thermal conductivity = 0.2 W/m K) was used as PCM. The produced green compacts were then impregnated in the molten paraffin wax at 80 °C for about 12 h. The density of the composite is about 0.83 g/cm^3, which is 17–18×, the density of green compacts in order to get a high thermal conductive matrix (Mills and Al-Hallaj, 2005). The modular pieces were assembled using commercial binder available in the markets (widely used for joining PVC pipes). The inscribed hole diameter was about 16 mm which was enlarged using CNC drilling center to produce holes with diameter of 18.2 mm (the diameter of Li-ion battery). After drilling the holes, the complete block was subjected to finishing operation before usage. Final dimensions of block are 3.7 cm × 5 cm × 6.5 cm. The complete block is then used as a Li-ion battery case in which commercial, type 18650 Li-ion cells could be placed (see Fig. 2).

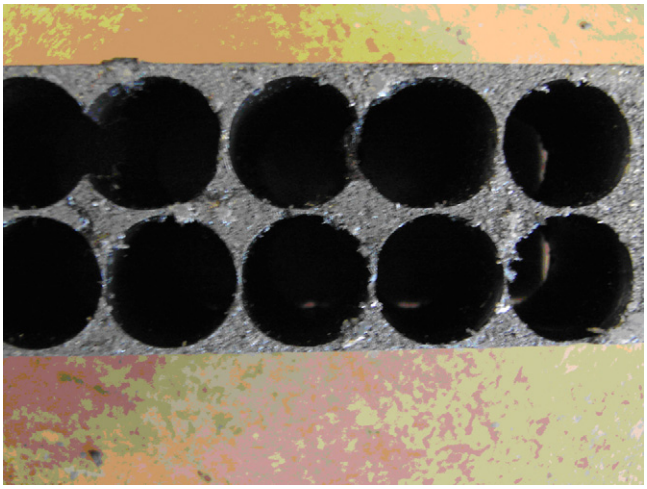

Fig. 2. PCM/EG block.

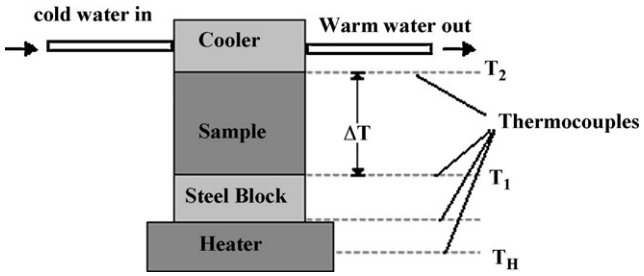

Fig. 3. Thermal conductivity setup for determinination of λ.

2.3. Impregnation of the graphite matrix into paraffin wax

The next step after producing the modular pieces is the impregnation into molten paraffin wax. The matrices were submerged in a liquid paraffin bath at 80 °C. The small samples were removed from the paraffin bath after 1, 3, 6, 9, and 12 h to measure their weights. The bulk density, and therefore the porosity, determines the total volume available for PCM storage.

2.4. Thermal conductivity

The thermal conductivity of the samples was measured using a steady state apparatus illustrated in Fig. 3 Grade 304 stainless steel block (k_{ss} = 16.3 W/m K, 10 mm thick) with a cross-sectional area equal to the area of the graphite matrix composites was placed on a heater at about 80 °C. To enhance diffusion of heat, continuous cold water was maintained through a heat exchanger placed over the sample. The temperature drop across the stainless steel and graphite matrix was measured using three K-type thermocouples, placed at the center of each surface (Mills et al. 2006). The apparatus was insulated to ensure one-dimensional heat transfer. Fourier's law of heat conduction was then used to determine the thermal conductivity of the graphite sample. No attempt was made to quantify the effects of thermal resistance between each unit. Thermal conductivity of sample was calculated according to the following formula (Mehling et al., 2000):

$$\lambda = \frac{Q_{\text{therm}}\,\Delta x}{A\Delta T} \quad (1)$$

where λ is thermal conductivity of sample (W/m K), Q_{therm} is the heat flux from the surface of steel block, Δx is the sample thickness (m), A is the area of sample (m^2) and ΔT is the temperature difference between two sides of the sample (K).

2.5. Tensile and compression tests

Commercial Li-ion battery packs are usually packed with a separator made of thin film placed between cells. Different commercial materials are used with a tensile strength generally ranges between 5 and 10 MPa. From manufacturing point of view, the tensile strength of the separator is 6.8 MPa (Newman et al., 2006).

Tensile strength was performed only on the PCM/EG block shown on Fig. 2. A sample cut from the block in the direction parallel to the compaction is used. The squared cross-sectional specimens were cut to the required dimensions as shown in Fig. 4. The gage length was 60 mm and cross-sectional area was 100 mm^2. The sample was drilled from both ends and fixed in their fixtures vertically to ensure uniaxial loading. A universal Instron testing machine was used to obtain the load-deflection diagrams which then converted to their corresponding stress–strain diagrams. The cross-head speed was set to 1 mm/min.

The compression test was performed at room temperature and at 45 °C to study the effect of temperature on the strength of PCM/EG composites. Cylindrical samples with 20 mm in length and 10 mm in diameter were subjected to uniaxial compressive load using a universal Instron testing machine. Also, the cross-head speed was set to 1 mm/min.

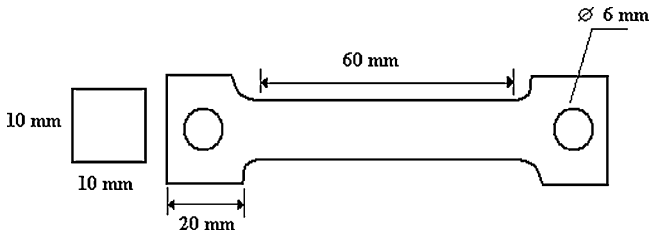

Fig. 4. Tensile specimen with squared cross-section.

2.6. Burst test

The specimens were turned into small cylinders to simulate the single Li-ion case with an inner diameter of 18.2 mm and a wall thickness of 2.5 mm (2.5 mm represents the average value of wall thickness in *x*- and *y*-directions). At the open side of the specimen, a Teflon inlet valve was used to pressurize the selected specimens. The internal pressure was gradually increased to different levels with compressed air and tested at the two different temperature settings (i.e. room temperature 22 ± 1 °C and 45 °C). Burst testing was performed using a sustained gas pressurization system capable of gas pressurization to around 12 bar.

3. Results and discussions

3.1. Impregnation process

Paraffin has an excellent stability concerning the thermal cycling, i.e. a very high number of phase changes can be performed without a change of the material's characteristics (Heinz and Streicher, 2006; Zalba et al., 2003). The PCM is loaded into the graphite matrix through capillary forces between liquid PCM and the graphite (Mills et al., 2006). For example, the produced composite impregnated for about 12 h consists of roughly 80 vol.% PCM, 10 vol.% highly porous EG and 10 vol.% remaining air. Experimental impregnation curve could be established by weighing the total weight of the impregnated sample at different time periods. Such curve is shown in Fig. 5.

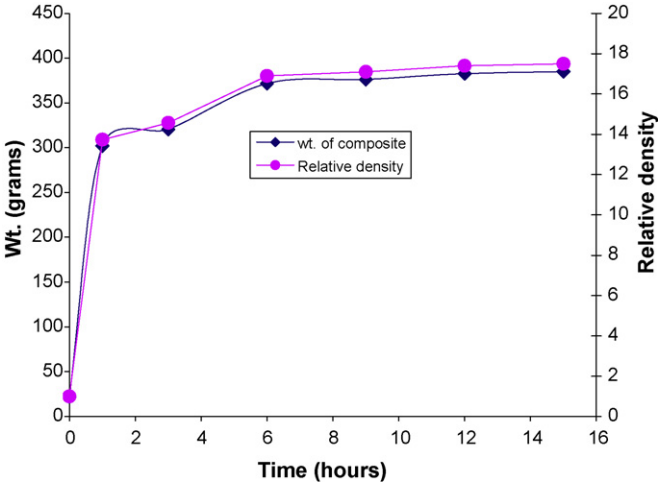

Fig. 5. Typical saturation curves for PCM impregnation process.

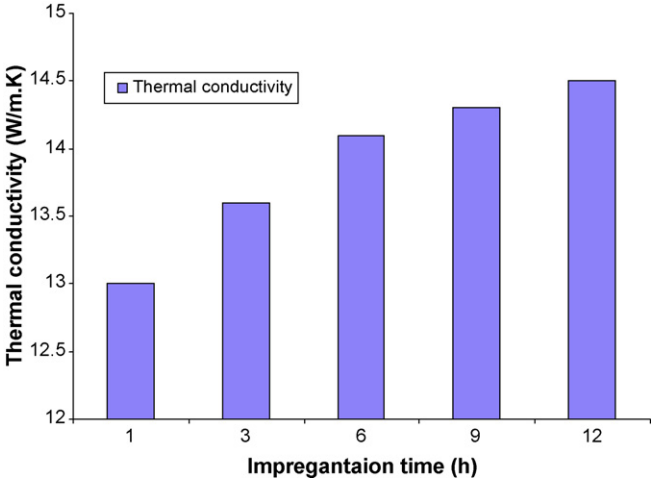

Fig. 6. Thermal conductivity values for samples with different impregnation times.

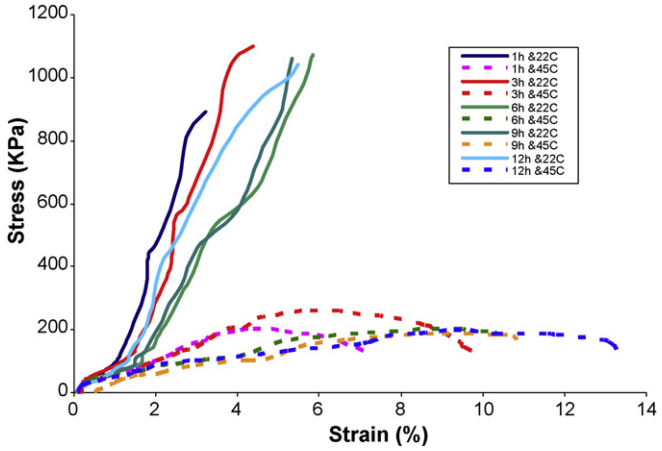

Fig. 8. Stress–strain diagram for different samples impregnated for different times and tested at room temperarature and at 45 °C.

Other interesting aspects of PCM impregnation in the graphite matrix are that natural convection within the matrix does not play a role in the heat transfer, the thermal conductivity of the composite is only due to the thermal conductivity of the matrix, and the capillary forces are strong enough to hold the PCM in the matrix even in the liquid phase (Mills et al., 2006).

3.2. Thermal conductivity

Thermal conductivity is always considered as the main parameter associated with use of PCM's. The apparatus and setup shown in Fig. 3 were capable for determination of thermal conductivity of the PCM/EG. Different samples with different impregnation periods were tested for estimating their thermal conductivity. The results showed that as the mass fraction of the paraffin wax increases, the thermal conductivity of the PCM/EG composite will increase. Thermal conductivity was increased from 13 W/m K for samples impregnated for 1 h to about 14.5 W/m K for samples impregnated for 12 h (corresponding to about 111.5% increase in thermal conductivity). Fig. 6 represents thermal conductivity values for samples with different impregnation time.

Another important purpose of this test was the determination of the thermal conductivity, especially at disjoints and barriers. In this test, both types of composites (those with impregnation time of 12 h) were subjected to this test to estimate the effect of PCM/EG-commercial binder on the continuity of thermal conductivity of PCM/EG composites. The first sample was made from PCM/EG only and its thickness was about 4 cm, while the second sample was made from PCM/EG, cut into two similar pieces (2 cm thickness) then attached together using the binder. It was found that thermal conductivity values for both samples were similar, and the effect of the binder seemed negligible on the continuity of heat diffusion through the PCM/EG matrix. Thermal conductivity values for both samples were about 14.5 W/m K.

3.3. Tensile and compression tests

In the tensile and compression tests, the maximum machine loads were set on 200 N. The specimens subjected to tensile test showed moderate brittleness and they fractured in a brittle manner. It is known that brittle materials fracture along 90° to the tension axis, while ductile materials fracture at 45° forming a cup-and-cone structure. The tested specimens at room temperature (22 ± 1 °C) behave as brittle materials and fractured along 90°. The corresponding specimens tested at 45 °C were fractured in semi-ductile manner. Fig. 7 shows two types of tensile specimens tested at room temperature and at 45 °C, respectively.

The specimens with high volume percentages of paraffin wax are more ductile when they compare to those of low volume percentages of paraffin wax. Extensive elongation was observed in the case of samples impregnated for 12 h (about 13.26% strain) compare to 7.1% strain for samples impregnated for 3 h (Fig. 8). Two samples were selected and tested at 35 °C in order to get a complete observation of these composites behavior. The selected composites were then impregnated for 1 and 12 h, respectively. The selection was based on the impregnation curve in Fig. 5. It was found that the specimens tested at 35 °C tensile properties are between those tested at room temperature and 45 °C. As shown in Fig. 9, the

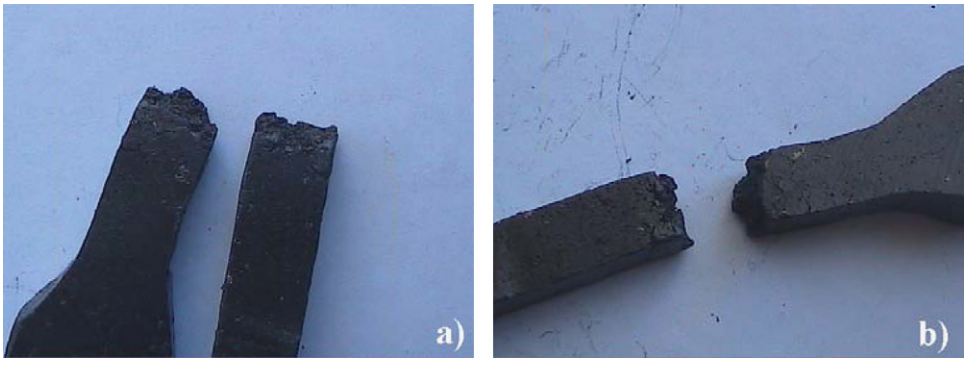

Fig. 7. fractured samples in the tensile test: (a) Sample impregnated for 12 h and tested at room temperature (Brittle fracture); and (b) sample impregnated for 12 h and tested at 45 °C (Ductile fracture).

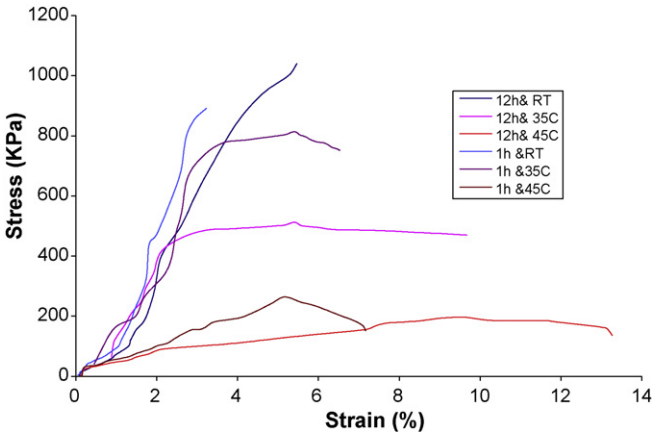

Fig. 9. Stress–strain diagram for different samples impregnated for different times and tested at room temperarature, at 35 °C, and at 45 °C.

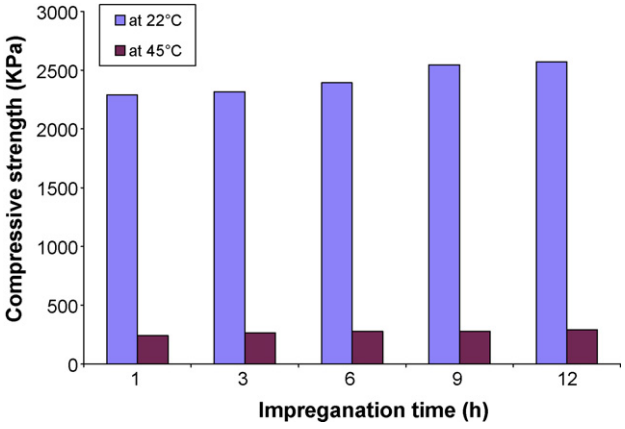

Fig. 11. Compressive strength of samples at room temperature and at 45 °C.

specimens become fractured after they strained for about 6.5% and 9.67% for samples impregnated for 1 and 12 h, respectively.

In the compression test, the incremental load was established until the material failed and fractured. The fracture load was about 80 N (corresponding to 800 kPa) at room temperature (22 ± 1 °C) for most specimens. Most of the samples became weaker and more ductile at elevated temperature (45 °C). At elevated temperatures, the paraffin becomes a semi-solid state and this affects the mechanical behavior of the composites, since it becomes viscoelastic rather than rigid material. Fig. 10 show photos of the tested samples at room temperature and at 45 °C for samples impregnated for 12 h.

The lack of smoothness of the stress–strain curves is due to the behavior of such composites. As the material becomes more deformed, the voids and flaws are combined together, causing slipping and local failures inside the matrix. These voids and flaws are then stacked together to form localized necking effect, and as a result, failure will occur.

On the other hand, the samples subjected to compression test at room temperature failed in a brittle manner (i.e. the fracture occurs at angle of 45°). The compressive load was about 200 N corresponding to 2700–2800 kPa. At 45 °C the samples became viscoelastic and softer. This means that the samples can not withstand any high compressive loads. The compressive load as low as 20–23 N was measured for such samples (i.e. the compressive strength dropped to 1/10 compared to samples at room temperature). Also, the samples bulged before they failed, which means there was more ductility in the matrix. Fig. 11 shows complete results of the compression test. Some tests were conducted at a higher temperature range (55–60 °C). Unfortunately, the machine could not read any compressive load since the samples instantaneously failed upon the application of the load. The samples tested at 35 °C show compression behavior in between the two above mentioned testing temperatures. These samples failed at compressive loads of 712 kPa for sample impregnated for 1 h, and 730 kPa for sample impregnated for 12 h.

3.4. Burst test

The burst test is usually performed for examining the pressure vessels and closed pipes. Usually, the stacked modules become tight and closed inside a high-temperature environment. Here, the burst test was used to show how the modules in the Li-ion battery packs perform under both temperature and pressure.

The results showed that the PCM/EG is stronger at relatively low temperature (say room temperature at 22 ± 1 °C), but it is weaker at relatively high temperatures. For example, the modules impregnated for 12 h withstand pressure up to 650 MPa at room temperature and they fractured in a brittle manner (Fig. 12a). On the other hand, similar modules tested at 45 °C failed at 160 MPa as ductile materials (Fig. 12b). Similarly, the samples impregnated for 1, 3, 6 and 9 h have such type of failure when they tested at room temperature at 22 ± 1 °C and at 45 °C. Fig. 13 shows the burst pressures for different composites investigated through present study. The results show incremental values of bursting pressure for samples tested at room temperature (from 530 to 630 MPa for samples impregnated for 1 and 12 h, respectively). On the other hand, the trend is inversed at 45 °C, in which the bursting pressure was decreased from 160 to 110 MPa for samples impregnated for 1 and 12 h, respectively. This may be attributed to the strengthening behavior of paraffin wax at relatively low temperatures as it acts as a cemented agent. Unlike its behavior at room temperature, paraffin

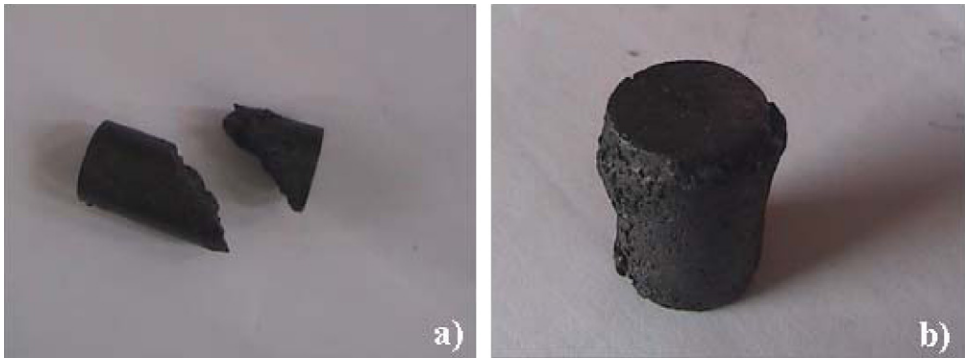

Fig. 10. Photos of the samples after compression test: (a) at room temperature and (b) at 45 °C.

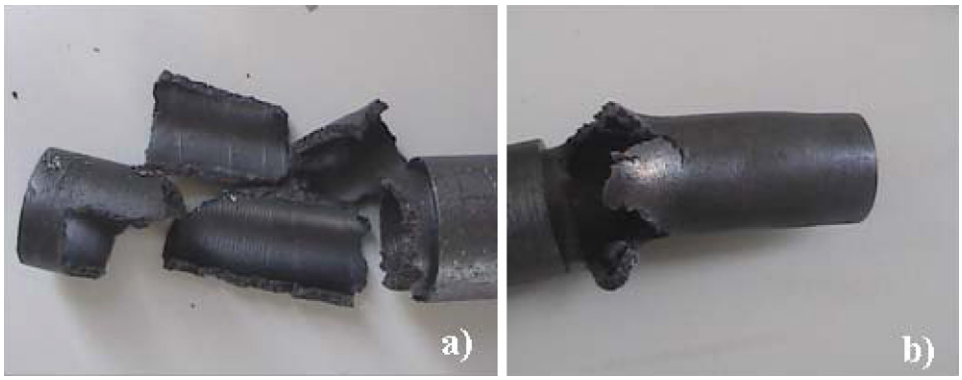

Fig. 12. Photos of the samples after burst test: (a) at room temperature and (b) at 45 °C.

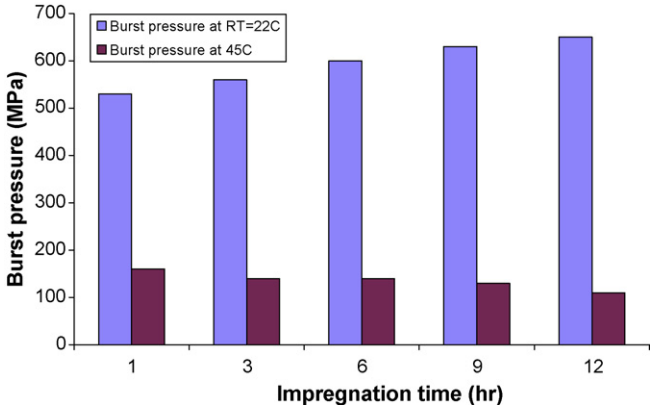

Fig. 13. Burst pressure of samples at room temperature and at 45 °C.

Table 1
Thermo-physical properties of PCM/graphite composites with different impregnation times.

Property	Specification				
	12 h	9 h	6 h	3 h	1 h
Thermal conductivity (W/m K)	14.5	14.3	14.1	13.6	13.0
Bulk density of composite (kg/m^3)	789	775.4	766.3	660.4	622.5
Bulk density of graphite (kg/m^3)	210	210	210	210	210
Tensile strength (22 °C) (kPa)	1040	1060	1072	1100	892
Tensile strength (45 °C) (kPa)	196	186	194	260	264
Compressive strength (22 °C) (kPa)	2571	2546	2394	2317	2292
Compressive strength (45 °C) (kPa)	292	280	280	267	241
Bursting strength (22 °C) (MPa)	650	630	600	560	530
Bursting strength (45 °C) (MPa)	110	130	140	140	160

wax tends to soften the matrix of PCM/EG composites and reduce their bursting strength. It was found that the samples tested at 35 °C withstand burst pressure of 250 MPa for sample impregnated for 1 h and 400 MPa for sample impregnated for 12 h. Table 1 summarizes major results of the present study.

4. Conclusion

The use of phase change materials (PCM) for the purpose of management of thermal energy is a promising idea. PCM's are widely used as passive thermal management tools in Li-ion batteries. On one side, it is important to get higher thermal conductive materials, but on the other side, it is also important to get a stable and stronger battery module to withstand thermo-mechanical effects while in operation. The results of this study show that the PCM/EG composites are strongly affected by their ambient temperatures and the presence of different dynamic loadings like tensile, compressive and explosive loadings. While the percentage of paraffin wax increases in the PCM/EG composite, both tensile and compressive strength are increased at room temperature, but become weaker at relatively elevated temperatures. This is somewhat different during the burst test, where it was found that as the percentage of paraffin wax increases, the burst strength increases at room temperature. This is opposite to burst strength at elevated temperatures in which the percentage of paraffin wax adversely affects the burst strength of such composites.

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