Development of Eutectic Phase Change Materials for Solar Thermal Energy Storage

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Abstract. This paper presents the findings on preparation and thermal analysis of binary eutectic mixture of polyethylene glycol 2000 and 6000. Their measured latent heat are 165.3 J/g and 220 J/g respectively. Eutectic mixtures of these materials were prepared by weight percentage composition with an increment of 10% i.e. compositions of PEG 2000 : PEG 6000 with 0:100, 10:90, 20:80 and so on till 100:0 were prepared. The thermal properties, melting temperatures and latent heats of fusion of these mixtures were measured by DSC analysis. The eutectic mixture with 50:50 composition was kept in a thermal cycling test rig to perform an accelerated thermal cycle test up to 1500 cycles. The melting temperature and latent heat of fusion of this thermally cycled mixture were obtained by DSC analysis on 0th, 100th, 500th, 1000th and 1500th cycle. There was a drop of 1.9 °C in the melting temperature and 8% degradation in latent heat of fusion was observed in comparison to 0th cycle. Considering these values it can be deduced that the eutectic mixture is thermally stable.

1. Introduction
Thermal energy storage as sensible or latent heat is an effective way of using waste heat in industrial processes or excess energy available such as solar radiation. Using phase change materials for storage of sensible heat and latent heat gained importance after the energy crisis of 1973-1974 [1]. With rapid depletion of fossil fuels because of our over dependence on them and greenhouse emissions having adverse effect on our climate the effective utilization of energy became a key issue. Therefore new ways of integrating conventional sources of energy with recovering waste heat and excess energy came into the limelight and became focus of research. In the last three decades extensive research has been carried out in PCMs and their use in LHTES (latent heat thermal energy storage systems). PCMs find applications in the building industry, textiles, the automotive sector and solar energy installations. In recent years an increasing number of applications, including those in electronics and medicine has emerged. The traditional sectors, such as the construction industry, are being advanced by novel, more sophisticated TES materials for smart textiles and thermo regulated biomaterials etc. [1-5].

One way of storing heat is by using the latent heat of phase change of a substance, usually from solid to liquid, as it can provide high energy densities. Then, when this stored heat is needed, it can be released by leaving the material temperature decrease, becoming a solid again. Materials used for this purpose are known as phase change materials (PCM). PCM are being implemented in different systems, active or passive, and for several applications, cold storage, building comfort, medium and high temperatures [2, 6]. As the PCMs are used repeatedly over time their chemical stability is very important for prolonged periods. They should also be compatible with the encapsulation material. For the safety of the TES and to avoid any mishaps, the PCM should be non-toxic, non-flammable and non-explosive [3, 7].
Organic PCM show negligible supercooling during the freezing process and provide congruent melting without phase change segregation. Organic PCM are further classified as paraffin and non-paraffin. Hence organic materials are more suitable to be used as PCM and numerous research studies have been conducted focused on organic PCM’s [8]. Hasan et al., [9] studied the thermal properties of myristic acid, palmitic acid and stearic acid, with melting temperatures between 50° and 70°C for 450 melt/freeze cycles. Sari et al., [5, 10] has conducted extensive research on fatty acids, namely, stearic, palmitic, myristic and lauric acid for 910 cycles. He has also studied the eutectic mixtures of these fatty acids such as eutectic mixture of lauric and palmitic acid, stearic and myristic acid [11].

Eutectic mixture are beneficial as the melting point can be tailored for PCM’s having higher melting temperature which make their use difficult for solar applications. Polyethylene glycol (PEG) also known as polyoxyethylene (POE) or polyethylene oxide (PEO) is having the hydroxyl group at the end, they are soluble in water as well as in organic compounds. It is an important semi-crystalline polymer with a repeating unit of –CH2–CH2–O–. The melting point of PEG depends on its molecular weight and may vary from 4 °C to 70 °C with the heat of fusion in the range of 117 to 174 J/g. the melting temperatures increase with the corresponding increase in the molecular weight. Although PEG’s of different molecular weight have been used along with other materials in binary or ternary mixtures as a PCM, there is not much research done on PEG and its eutectic mixtures as a PCM and its thermal stability till now. Sharma et al., [12] studied the thermal properties of PEG 6000 MW over 500 melt/freeze cycles. It was concluded that PEG 6000 proved to be thermally stable and its melting temperature changed in the range of 55 – 60 °C with a maximum deviation of 6.5%.

In view of the literature reviewed this project will be focused on thermal cycling test of eutectic mixture of PEG 2000 and PEG 6000 molecular weights.

2. Material Preparation
One step method was adopted to prepare the eutectic mixture of PEG 2000 and 6000. They were procured from Merck Company. The mixture compositions by weight % are shown in Table 1. They were mixed in a beaker kept on a hot plate above the melting point of both PCMs. This mixture was stirred using magnetic stirrer at 500 RPM for 30 minutes in order to prepare a homogeneous mixture.

| Sample name | PEG 2000 MW (%) | PEG 6000 MW (%) |
|-------------|-----------------|-----------------|
| PEG 6K      | 0               | 100             |
| U1          | 10              | 90              |
| U2          | 20              | 80              |
| U3          | 30              | 70              |
| U4          | 40              | 60              |
| U5          | 50              | 50              |
| U6          | 60              | 40              |
| U7          | 70              | 30              |
| U8          | 80              | 20              |
| U9          | 90              | 10              |
| PEG 2K      | 100             | 0               |

3. Results and Discussion
3.1. Thermal properties of eutectic PCMs
The lower and the higher temperature range for the accelerated thermal cycle test in the tester for all the samples were kept as 30 °C and 120 °C respectively. The values of the melting temperature and
latent heat of fusion of the eutectic mixtures were measured by DSC at the flow rate of 10 °C/min and the results are presented for various mixtures in Figures 1-8. For the thermally cycled U5 (50:50 composition by weight %), samples were collected and further tested at 500th and 1000th cycles. The values of melting temperature and latent heat of fusion for the eutectic mixtures have been presented in Table 2. The values of the melting temperature from these DSC curves are found on the intersection point of the tangent to the peak and the extrapolated baseline. This value obtained is actually the onset melting temperature of the material. The temperature corresponding to the peak is the maximum peak temperature. The latent of fusion is given by the area under the peak in the DSC curves. The values of latent heat are obtained in J/g.

| Sample name | COMBINATION PEG 2K:PEG 6K (by weight %) | MELTING TEMPERATURE (°C) | LATENT HEAT OF FUSION (J/g) |
|-------------|----------------------------------------|--------------------------|-----------------------------|
| PEG 6K      | 0:100                                  | 59.5 °C                  | 220.0                       |
| U1          | 10:90                                  | 57.5 °C                  | 205.4                       |
| U2          | 20:80                                  | 56.5 °C                  | 208.2                       |
| U3          | 30:70                                  | 54.5 °C                  | 200.5                       |
| U4          | 40:60                                  | 54.0 °C                  | 196.6                       |
| U5          | 50:50                                  | 53.5 °C                  | 190.0                       |
| U6          | 60:40                                  | 52.0 °C                  | 184.7                       |
| U7          | 70:30                                  | 51.5 °C                  | 179.5                       |
| U8          | 80:20                                  | 51.0 °C                  | 174.0                       |
| U9          | 90:10                                  | 50.5 °C                  | 169.5                       |
| PEG 2K      | 100:0                                  | 50.0 °C                  | 165.3                       |

Table 2. Melting temperatures and latent heat of fusions

Figure 1. DSC curve for PEG 2000
Figure 2. DSC curve for PEG 6000

Figure 3. DSC curve of U2 eutectic mixture

Figure 4. DSC curve of U3 eutectic mixture
Figure 5. DSC curve of U4 eutectic mixture

Figure 6. DSC curve of U5 eutectic mixture

Figure 7. DSC curve of U6 eutectic mixture
For PEG 2000 the obtained value of melting temperature is 50ºC, which lies in the melting temperature range of 50 – 55 ºC, as quoted by Sigma Aldrich company and the measured latent of fusion is 165.3 J/g. for PEG 6000 the melting temperature found out from the DSC analysis was 59.5 ºC, which again lies in between the temperature range of 59 - 64 ºC as specified by Merck company and the latent heat of fusion was 220.0 J/g.

For the eutectic mixtures, the melting temperatures and latent heats of fusion lie in between the melting temperatures and latent heats of fusion of PEG 2000 and PEG 6000 as given in Table 1 and Fig 1-8. The compositions by weight percentage of PEG 2000 and PEG 6000 have been arranged in ascending order with respect to the weight percentage of PEG 2000 in the said Table. Hence we see a downward trend in the values of the melting temperatures as the percentage of PEG 2000 increases in the mixtures. This is justified as the melting temperature of PEG 2000 is less than that of PEG 6000. The same is true for the values of latent heats of fusion. The maximum reduction of the melting temperature is seen from pure PEG 6000 to U1 (composition - 10% PEG 2K: 90% PEG 6K) of 2 ºC. No sudden changes or exceptions in the values of the melting temperatures as well as the latent heats of fusion were observed as can be observed from the DSC curves as well.

The eutectic mixture, U5, (Fig. 6) of composition 50% PEG 2000 and 50 % PEG 6000 was selected for the accelerated thermal cycle test. When a substance undergoes repeated melt/freeze cycles consecutively it is known as an accelerated thermal cycle test.

The values of melting temperatures and latent heats of fusion of U5 measured by DSC at 0th, 100th, 500th, 1000th and 1500th cycle are given in Table 5. The values of U5 at the 0th cycle were taken as reference to evaluate and analyze the changes that took place after the material was thermally cycled. The un-cycled U5’s (0th cycle) DSC analysis showed that it has a melting temperature of 53.5 ºC and its latent heat of fusion was obtained as 190.0 J/g.

3.2. Accelerated thermal cycle test of selected eutectic PCM
An accelerated thermal cycle test for U5 was conducted on inhouse designed cycle tester. The minimum and maximum temperature in the tester was set as 30 ºC and 80 ºC. As can be seen from Table 2, the variation in the melting temperature of U5 after 1500 cycles is 1.9 ºC, from 53.5 ºC to 51.6 ºC which amounts to 3.55 % change from the 0th cycle. This is the maximum variation. It can be noted there is a very minute increase in the melting temperature after 100 cycles from 53.5ºC to 53.8 ºC. The variation after 100th, 500th and 1000th cycle is 0.56%, 1.12% and 2.61% respectively as compared to 0th cycle. It can be noted that there is no substantial variation in the melting temperature after accelerated thermal cycle test.

For the latent heats of fusion, a regular decrease in the values is observed as is evident by data given in Table 2. There is slight degradation of latent of fusion after the first 100 cycles is 1.84% from 190
J/g to 186.5 J/g in comparison to fresh PCM (U5) at 0\textsuperscript{th} cycle. After 500 cycles the latent heat is reduced by 2.84% and after 1000\textsuperscript{th} cycle a 4.68% reduction is observed. After 1000\textsuperscript{th} cycle, there is a sharper decrease in the value of latent heat i.e. from 181.1 J/g to 174.3 J/g, a reduction of 3.75% from the 1000\textsuperscript{th} cycle. This is the maximum variation in the value of latent heat. The overall variation from the 0\textsuperscript{th} to the 1500\textsuperscript{th} cycle is that of 8%.

**Table 3.** Melting temperatures and latent heats of fusion of thermally cycled U5

| US - No. of cycles | Melting temperature (ºC) | Latent heat of fusion (J/g) |
|--------------------|--------------------------|-----------------------------|
| 0                  | 53.5                     | 190.0                       |
| 100                | 53.8                     | 186.5                       |
| 500                | 53.9                     | 184.8                       |
| 1000               | 52.1                     | 181.1                       |
| 1500               | 51.6                     | 174.3                       |

The binary system of PEG 2000 and PEG 6000 form eutectic mixtures with sufficiently high latent heats of fusion to be used for various solar thermal applications. The results of the accelerated thermal cycle test show that U5 with 50:50 composition is stable up to 1500 melt/freeze cycles with no substantial decrease in the thermal properties.

4. Conclusion
The objective was to develop a eutectic Phase Change Materials (PCM) mixtures of PEG 2000 and PEG 6000, which are organic materials with melting temperature range of 50 – 55 ºC and 59 – 64 ºC respectively. The melting temperatures of the binary system fall in between that of the constituents i.e. PEG 2000 and PEG 6000 and same is true for the values of latent heats of fusion. An accelerated thermal cycle test was conducted on the mixture of 50:50 composition by weight percentage (U5) between the temperature ranges of 30 - 120 ºC to determine the thermal stability of the eutectic mixture. The results showed that the melting temperature of the PCM had a maximum variation of 3.55 % after 1500 melt/freeze cycles as compared to that of the 0\textsuperscript{th} cycle. A regular degradation in the values of latent heat was observed and had a total variation of 8% after the material had undergone 1500 cycles. These changes are inconsequential to the potential of the PCM and hence the eutectic mixture can be said to be thermally stable after 1500 melt/freeze cycles. As per the result of this project, it can be assumed that, if 300 melt/freeze cycles are considered to occur in a year, then this material can be effectively used as a phase change material for thermal energy storage for a minimum of 5 years.

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