Development of novel Polymer Phase change material for heat storage application

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Abstract: Polymer Phase change material (PCMs) are materials used to store Energy for a broad range of Applications. Unlike conventional storage materials, PCM absorbs and release heat at a nearly constant temperature. They store 5–14 times more heat per unit volume than sensible storage materials. Increasing demand in solar engineering and spacecraft thermal control applications; require the continuous development of such materials to maximize its efficiency. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. In this paper we can show that combination of low Density Polyethylene (LDPE) paraffin wax and glycerin is an alternative material that can be used as PCMs. Differential Scanning Calorimeter (DSC); Melt Flow Index test and FTIR technique were used to characterize the new developed Compound. Results obtained indicate that a reduction of more than 10°C in melting temperature (Tm) of the pure LDPE-resin was achieved.

Keywords: PCM's, Phase Change Material, Paraffin Wax, LDPE, PP, Heat Storage

1. Introduction

Energy storage technologies offer exciting new possibilities to increase the efficiency and reliability of energy markets. Customers and suppliers of heating and cooling systems will benefit from understanding and utilizing storage technologies. The latent heat of fusion is repeatedly converted between solid and liquid phase to utilize their latent heat of fusion to absorb; store and release heat or cooling during such phase conversion[1,2].

PCMs have been widely used in latent heat thermal storage systems for heat pumps, fibers building etc... It found applications in wall and floor boards to store heat to provide a room with comfortable ambient temperature [3]. The storage of energy in suitable forms, which can conventionally be converted into the required form, is a present day challenge to the technologists. Energy storage not only reduces the mismatch between supplies and demand but also improves the performance and reliability of energy systems and plays an important role in conserving the energy [4,5]. There are large numbers of PCMs that melt and solidify at a wide range of temperatures, making them attractive in a number of applications.

In this project we have investigated, novel non commercial PCMs hybrid composite of low molecular weight materials containing under others low density Polyethylene (LDPE) Polyethylene Oxides, Polyethylene Glycol (PEG) and formulation of their off. Successful development of such material with low melting and freezing point and great latent heat fusion maybe lead to break through in the development of hybrid composites to store and release heat or cooling during such phase conversion.

The continuous increase and the rise in fuel prices is the main driving forces behind efforts to more effectively utilize various sources of renewable energy. Development of heat storage materials are part of this effort to save energy. Scientists all over the world are eager to develop new renewable energy sources [5-8]. One of the options is to develop energy storage devices, which are as important as developing new sources of energy. The storage of energy in suitable forms, which can conventionally be converted into the required form, is a present day challenge to the technologists. Energy storage not only reduces the mismatch between supply and demand but also improves the performance and reliability of energy systems and plays an important role in conserving the energy [7,8].

Developing Polymeric phase change materials for heat storage applications is the challenge of today's research and development. Those technologies is very beneficial for the humans and as well as for the energy conservation.
The development of a latent heat thermal energy storage system hence, involves the understanding of three essential subjects: phase change materials, containers materials and heat exchangers. Atul Sharma and co-authors \cite{7, 8} published a technical review on thermal energy storage with phase change materials and applications, shown in Figure 1.

Phase change materials (PCM) are “Latent” heat storage materials. The thermal energy transfer occurs when a material changes from solid to liquid, or liquid to solid. This is called a change in state, or “Phase.” Initially, these solid–liquid PCMs perform like conventional storage materials; their temperature rises as they absorb heat. Unlike conventional (sensible) storage materials, PCM absorbs and release heat at a nearly constant temperature. They store 5–14 times more heat per unit volume than sensible storage materials such as water, masonry, or rock \cite{6}.

A large number of PCMs are known to melt with a heat of fusion in any required range. However, for their employment as latent heat storage materials these materials must exhibit certain desirable thermodynamic, kinetic and chemical properties \cite{9, 10}. Moreover, economic considerations and easy availability of these materials has to be kept in mind.

In this work we have investigated new PCM’s in this particular field, with the main focus being on the development and assessment of the thermal properties of various PCMs. Combination of high melting point polyethylene and polypropylene with low melting point paraffin waxes, Polyethylene glycol, glycerin and polyethylene oxide in combination with special nano graphene additives and fillers were used in this study. Altering molecular weight of the developed compound has the aim to reduce melt temperature and to increase the specific heat of the material to be developed. Our ideal candidate is a PCM material that will show a eutectic reaction. In this project, the target was to reduce the melting point so that we could reach a better heat observing in energy saving applications.

Solid materials have basically, a higher molecular weight and melting temperature. By heating the material it transforms to the liquid phase. As the molecular weight for the material decreases, we can get a lower melting temperature. Lowering the melt temperature yields a material that can melt upon absorbing lower amount of heat capacity. This heat will be giving off when the atmosphere cools and we can get a better heat cycle in a shorter heating time interval.

![Figure 1: Technical options available for storing low temperature thermal energy materials as shown by Atul Sharma](image)

### 2. Melting Point or First Order Transition

As mentioned, one of our targets was to decrease the range of melting temperature of the compound so that PCM will melt at a low temperatures compared to pure and virgin resin.

Usually melting of a crystalline solid or is associated with change of phase and involvement of latent heat \cite{10-12}. Different polymers have molecular symmetry and/or structural regularity that when crystallizes; produce a solid-liquid phase transition, exhibiting a crystalline melting point. The melting is quite sharp high for crystalline materials, while in semi crystalline and amorphous materials, etc., the phase change takes place over a range of
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Phase transitions of this kind, particularly in low molecular weight materials, being associated with sharp discontinuities in some primary physical properties, such as the density or volume, \( V, \) \( V = (\partial G / \partial P)_T \) and entropy, \( S, \) \( -S = (\partial G / \partial T)_P \), which are first derivatives of free energy, are commonly termed first order transitions.

2.1. Latent Heat

Differential Scanning Calorimeter was performed to measure changes that took place during the compounding and mixing of the different materials. The thermal behavior of the test samples was recorded to analyze the influence of applied ingredient on latent heat storage, using a Netsch instrument type DSC 2920 piloted on PC with TA Advantage control software. The measurements were performed by using constant heating rate of 10 °C/min. The values of latent heat were found equal within the measurement accuracy for both pure paraffin micro particles and polymer. The value of the latent heat was measured and found equal to approximately 116 J/g.

3. Experimental

Materials used throughout this investigation were LDPE and PP as a matrix resin. Blends containing as a single ingredient or multiple ingredient were paraffin wax; Polyethylene- glycol; Glycerol; stearic acid and polyethylene oxide. As nano filler graphene was used. A Brabender plastograph was utilize to prepare the different concentration listed in table 1 and 2 under constant processing conditions (160°C, and 5 minute mixing time). Sheets of 2mm were pressed using carver hot press.

4. Results and Discussions

Differential Scanning Calorimeter (DSC) is an instrument used frequently by our group to measure the thermal characteristics of the phase change materials (PCM). For every sample, heat flows in mW versus temperature were determined. A sample of PCM of known mass is placed in a closed pan with a volume of 50L. Latent heat, Enthalpy and melting point were measured. Figure 2 shows the DSC plots for the sample listed in table 1. It could be seen that some curves indicates two peaks, that’s belong to the polymer resin and the wax. Change in melting point versus wax concentration and enthalpy changes versus glycerin concentration are shown in Figure 3-6. From the plots it’s obvious that a decrease in melting temperature of more than 15 °C was achieved for the formulation containing 40% wax(Figure 3). An increase in latent heat represented in enthalpy change of more than 100% was achieved (Figure 4).

MFI measurements were carried out to investigate the change of flow ability of the different ingredient added to polyethylene to determine changes related to change in Molecular weight. Changes in Molecular weight are related to changes in Melt temperature of the developed compound and as well to the specific heat change that taking place during compounding.

Figure 5 and 6 shows MFI changes versus wax concentration at 0% and 5% glycerin constant concentration whereby the wax concentration was varied. As expected an increase of melt flow index was obvious due to the flow ability of the wax. It’s very obvious that adding of low molecular weight paraffin wax was acting as a lubricant to the resin increasing its flow behavior exponentially from 4 to approximately 30 g@2.16kg and 160°C for 10 minutes. In our selected formulation Glycerin could act in this since. Adding Glycerin combination (2) was unexpected and surprising. Figure 7 shows the result for the formulation contains glycerin. The results indicate less change in MFI. We were not able to measure the MFI for formulations containing high percentage of glycerin. This indication shows that a kind of crosslinking of polymer chains was taking place. Although DSC results confirm an increase in enthalpy of compound containing glycerin compared to virgin resin, the unexpected behavior in MFI leads to the conclusion not to use Glycerin any more in the development of polymeric phase change materials.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>LLPDE</th>
<th>Paraffin WAX</th>
<th>Glycerin</th>
<th>Tm(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>124.4</td>
</tr>
<tr>
<td>2</td>
<td>90%</td>
<td>10%</td>
<td>-</td>
<td>123.5</td>
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<tr>
<td>3</td>
<td>75%</td>
<td>25%</td>
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<td>122</td>
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<td>50%</td>
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<tr>
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<tr>
<td>9</td>
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<td>-</td>
<td>15%</td>
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<tr>
<td>10</td>
<td>75%</td>
<td>-</td>
<td>25%</td>
<td>134.2</td>
</tr>
</tbody>
</table>
Figure 2: DSC plots measured using Netsch DSC 2920 for specimen listed in table 1.

Figure 3: The figure indicates changes in Tm versus wax concentration at const. glycerin concentration.

Figure 4: The figure indicates changes in enthalpy versus glycerin concentration.

Figure 5: The figure indicates relation between enthalpy and glycerin concentration.

Figure 6: The figure indicates relation between Melt index wax concentration.
5. Conclusion

In this paper an attempt was made to develop polymer based phase change materials on the basis of polyolefin's blends. In such a blend small molecular weight species were dispersed in high molecular weight materials to generate latent heat storage materials. Addition of paraffin wax; PEG and ethylene glycol to LDPE; HDPE and PP reduces the melting temperature and increases melt flow index of the material. The addition of glycerin to the polymer resin increases the enthalpy but was acting as a crosslinking agent; so that MFI was reduced significantly and Melt index increases. For future work glycerin should be amended from the formulation. Results on formulation included polyethylene oxides steric acid and graphene nano filler will be reported in next.

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