COMPATIBILITY OF PLASTIC WITH PHASE CHANGE MATERIALS (PCM)

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ABSTRACT

Solid-liquid phase change materials (PCM) are used in latent heat thermal energy storage systems. Even though paraffin interactions with plastics are known by industry, plastics are commonly proposed as container materials for encapsulating PCMs in many applications. It is not possible to find in the literature experimental studies of organic PCM migration in plastics and its effects on plastic properties. These interactions are a case study of environmental stress cracking ESC, which is considered one of the most common causes of plastics failure. The main objective of this work is an experimental study of interactions of some PCM typically used for thermal energy storage with a melting point around 26 ºC, and some plastic materials currently used as encapsulating materials. As a consequence of the results, the best plastic to be used with each PCM, and combinations that should be avoided are described.

1. INTRODUCTION

Thermal energy storage systems provide several alternatives for efficient energy use and energy conservation. Solid-liquid phase change materials (PCM) are used in latent heat thermal energy storage systems. The use of phase change materials in building products has rendered it feasible to store significant amounts of thermal energy in the building envelope without the uncomfortable temperature swings and large structural mass associated with sensible heat storage. More detailed information can be found in Zalba (2003) and Khudair (2004)

In thermal energy storage systems, costs are a very important factor of viability. Therefore, even though paraffin interactions with plastics are known by industry, plastics are commonly proposed as encapsulated materials for PCM in many applications. It is not possible to find in the literature experimental studies of organic PCM migration in plastics and its effects on plastic properties. Some behaviour predictions can be found in Lane (1986). These interactions are a case study of environmental stress cracking ESC, which is the simultaneous exposure to a chemical environment under a stress or strain, leading to a reduction of time of failure respect to air environment. ESC is considered one of the most common causes of plastics failure.

Environmental stress cracking mechanism is a physical interaction involving highly localised plasticisation via stress enhanced fluid absorption, which does not involve chemical change or molecular degradation of the plastic. Absorption of paraffins like organic PCM plasticises the polymer and reduces its yield strength being this reduction directly related with the concentration of absorbed fluid. Non-hydrogen bonded fluids such as aliphatic hydrocarbons are reported by Smithers Rapra (2008) as mild stress cracking agents compared with other
severe or moderate stress cracking agents such as aromatic hydrocarbons, halogenated hydrocarbons, ethers, ketones, aldehydes or esters.

In general semi-crystalline polymers such as polyethylene or polypropylene have better ESC resistance than amorphous polymers such as polystyrene. This is attributed to crystalline regions where closely packed crystals act as barrier to fluid penetration also limiting crack propagation. Thus, structural features that condition also the crystallinity like molecular architecture, density, length and degree of entanglement of molecules, have been found to strongly influence ESC resistance.

2. OVERVIEW OF THE PREVIOUS WORK

First experiments of plastic compatibility with PCM were performed and presented by Lázaro (2005), where samples of PCM were introduced in different plastic bottles. The PCMs tested were molecular alloy C16-C18, RT20, RT25, RT26 and TH24, and plastic materials tested are PP, LDPE, HDPE, and PET. An oven was used to cycle the plastic bottles thermally so that melting and solidification processes took place. The experiment consisted of repeated melting and solidification cycles during a period of ten months, giving at least 150 thermal cycles.

Visual inspection and gravimetric analysis were performed. Two effects have been detected, organic PCM migration in plastic and moisture sorption. LDPE bottles had the highest mass variation and big deformation. Therefore, LDPE was discarded as encapsulate material. Attending to the results of the test, when organic materials were used as PCM, the best encapsulate material is PET. If moisture sorption is taken into account, PP could also be recommended. When the hydrated salt was used as PCM and water sorption is not desired, the best encapsulate material is HDPE.

The objective of this work is focused on the interactions of some PCM typically used for thermal energy storage with a melting point around 26 ºC, and some plastic materials currently used as encapsulating materials. In this study, plastic bottles were replaced by plastic samples (Figure 1). Therefore, visual inspection and gravimetric analysis were performed. The mechanical performance of plastic specimens was characterized to evidence the ESC phenomena. As a consequence of the results, the best plastic to be used with each PCM and combinations that should be avoided are described.

2. EXPERIMENTAL METHODOLOGY

Three plastics typically used in the industry were chosen: high density polyethylene (HDPE EGYPTENE HD6070UA), low density polyethylene (LDPE RIBLENE FM34), and polypropylene (ExxonMobil PP 7011L1). The three organic PCM used were: RT20, RT25, and RT27. The inorganic PCM was DC24. Properties of these PCM are shown in Table 1.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting point (ºC)</th>
<th>Manufacturer</th>
</tr>
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<tbody>
<tr>
<td>RT20</td>
<td>22</td>
<td>Rubitherm</td>
</tr>
<tr>
<td>RT25</td>
<td>25</td>
<td>Rubitherm</td>
</tr>
<tr>
<td>RT27</td>
<td>28</td>
<td>Rubitherm</td>
</tr>
<tr>
<td>DC24</td>
<td>24</td>
<td>Cosella Dörken</td>
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</table>
The plastic specimens were immersed in different PCM contained in glass beakers, that were placed in an oven and repeated melting and solidification cycles were performed. The oven was switched on with low power during the melting process using a set point of 40 °C. This temperature was kept around 3 hours. For the solidification process it was enough with switching off the oven and let the plastic specimen reach room temperature. The plastic specimens were removed every 20 days from the glass beakers, during 400 days. Every 20 days the plastic specimens were evaluated with the following procedure:

- Gravimetric analysis prior to and after cycling test provides mass variation:
  Where \( m(to) \) the total mass prior to the compatibility test, and \( m(t) \) total mass at the moment the test is made.

\[
\Delta m(\%) = \frac{m(t_0) - m(t)}{m(t_0)}
\]

- The plastic specimens were cleaned with an absorbent paper and their change in appearance was evaluated visually.
- Measurement prior to and after the test provided variation in sample thickness, and length (mm) using a micrometer and a scale calliper.
- The standard ISO-527 “Determination of Tensile properties” was used to perform the experiments. Mechanical test were performed (deformation test, stiffness test) using a strength tester MT-LQ (INSTRON): deformation test consisted in applying five cycles of 10 N to every specimen, and measuring its deformation; stiffness test consisted in applying a given force to the specimen, and measuring bending, Young’s modulus were calculate with this results.
- Differential Scanning Calorimeter was used to corroborate the PCM absorption by the plastics specimen in a range of temperature of 10 to 200 °C, and the measurements were performed at 5 K/min; Atmosphere: Nitrogen 80 cm³/min.

3. RESULTS AND DISCUSSION

The differences in thickness were not significant enough to be taken into consideration. This is why comparison among samples was made with the mass variation and the mechanical tests.

**Gravimetric Analysis:** from mass measurements, a lower mass variation means poor migration into the plastic material and thus a better container material.
In Figure 2 and Figure 3 (left) it can be seen that when immersed in the organic PCM the mass increased in all plastic materials, but when immersed in the inorganic PCM the plastics show a lower increase (Figure 3 right). Differences by using one or other organic PCM were not significant.

LDPE samples showed the highest rate of mass variation achieving the maximum value during the 80-100 days (100 temperature cycles). Otherwise, PP showed a lower rate of mass absorption but the total mass gained is the highest for the three organic PCM. HDPE samples showed the lower mass absorption for organic PCM. These results agree with the polymer characteristics as HDPE has the higher density which is directly related with an elevated crystallinity. Otherwise, LDPE has the lowest density and mechanical properties, being the most susceptible to paraffin absorption. Results of LDPE corroborates the previous results presented by Lázaro (2005), where LPDE is not a suitable encapsulate material for any PCM. It should be highlighted the mass increase of PP when mixed with any organic PCM. This result also corroborates previous results, showing a clear interaction between PP and the paraffins. Inorganic PCM acts with a different mechanism as no significant interactions were found. Therefore, from the thermoplastic materials studied, HDPE has the best ratio of mass absorption with the organic and inorganic PCMs.

Moreover, with these experiments we could see that this mass increase is not due to moisture absorption, as hypothesized previously, because in these experiments, the plastic specimen was never in contact with moisture, but was only in contact with PCM.

**Mechanical tests:** results of the deformation test after applying five cycles of 10 N to every specimen were not significant. The behaviour of HDPE (figure 4, left) after immersion in any PCM, shows a little final deformation up to 0.1 mm (2.5% of thickness compared to 0.1% deformation for reference HDPE). Variations up to 0.7 mm (17.5% of thickness compared to...
2.8% of reference sample) were found with LDPE (Figure 4, right). Deformation of PP samples varies up to 5% of thickness while the reference sample had a deformation of 0.2% of thickness. These deformation results agree with the lower density, yield strength and crystallinity of LDPE that leads to a higher interaction with organic paraffins.

![Figure 4. Left: Deformation test (mm) with the HDPE; Deformation test (mm) with the LDPE](image)

Results of Young’s modulus of the different plastic materials are presented in the next illustrations (Figure 5 and Figure 6). The three materials become softer than the reference samples as a reduction in Young Modulus is observed after the interaction with paraffin. This reduction is higher for PP with organic PCM (around 60% of reduction).

![Figure 5. Left: Young’s modulus of HDPE; Right: Young’s modulus of LDPE.](image)

![Figure 6. Left: Young’s modulus of PP](image)

**DSC:** Thermal analysis of the plastic specimen is shown in the next illustrations. Three samples of different days (41, 86 and 157 days) were analyzed and compared with a sample reference. DSC profiles for HDPE and the different PCM (Figure 7 and Figure 8); evidences that the little amount of absorbed PCM do not affect the thermal behaviour. Differences in the melting peaks, especially the peak width depends on the sample size (increasing mass → increasing melting time → wider peak). A result of LDPE and the different PCM (Figure 9 and Figure 10) shows a peak before of the LDPE melting peak. This peak corresponds at the melting peak of the PCM corroborating the PCM absorption by the plastic.
Results of the PP and the different PCM corroborate the PCM absorption by the plastic, melting peaks of 20 °C, 25 °C and 27 °C can be seen in the different illustrations of the PP with the organics PCM (Figure 11 and Figure 12: Left). DSC profile for PP and hydrated salt (DC24) evidences that the little amount of absorbed PCM do not affect the thermal behaviour.

Figure 7. Left: DSC analysis of HDPE with RT20; Right: DSC analysis of HDPE with RT25

Figure 8. Left: DSC analysis of HDPE with RT27; Right: DSC analysis of HDPE with DC24

Figure 9. Left: DSC analysis of LDPE with RT20; Right: DSC analysis of LDPE with RT25

Figure 10. Left: DSC analysis of LDPE with RT27; Right: DSC analysis of LDPE with DC24
4. CONCLUSIONS

LDPE immersed in different PCM showed the highest rate of mass variation achieving the maximum value during the 80-100 days. In mechanical test (deformation test) LDPE had a significant deformation respect to the reference sample with the organic and inorganic PCM. Young’s modulus results show a reduction using organic or inorganic material. Thermal analysis of the LDPE immersed in different PCM corroborates the PCM absorption by the plastic.

PP immersed in different PCM showed the highest mass variation for the three organic PCM. Thermal analysis of the PP immersed in organic PCM showed a PCM absorption by the plastic, but immersed in inorganic PCM do not affect the thermal behaviour. As PP has higher yield strength than HDPE and LDPE deformation for PP is less affected by the absorption of paraffin. However Young’s modulus results showed the highest reduction.

HDPE immersed in different PCM showed the best behaviour with a lower mass variation. Thermal analysis of the HDPE immersed in different PCM evidences that the amount of absorbed PCM do not affect the thermal behaviour. In mechanical test (deformation test) HDPE with organic and inorganic PCM had also the lowest deformation. Young’s modulus results also show a significant reduction when using organic PCM. Therefore, with the materials tested until now it can be concluded that LDPE and PP showed worse behaviour than HDPE for encapsulating PCM.

Future work is a material selection looking for semicrystalline polymers with improved resistant to ESC. Constant-tensile-stress method to determine Environmental Stress Cracking with the selected polymers should be performed, to evaluate changes in yield strength, the other key parameter for selecting the best alternative material for long term encapsulation of organic PCM.
ACKNOWLEDGMENTS

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REFERENCES


