Fabrication and characterization of photocrosslinked phase change materials by using conventional and terahertz spectroscopy techniques

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ABSTRACT

A series of novel photocrosslinked shape-stabilized phase change materials (PCMs) based on tetradecanol and lauric acid have been prepared by UV technique for the purpose of thermal energy storage applications. Both lauric acid and tetradecanol were reacted with glycidyl methacrylate to form acrylated structures for covalently integrate into polyurethane (PU) based UV matrix to prevent leakage problem. The heating process phase change enthalpy is measured between 9 and 77 J/g, and the freezing process phase change enthalpy is found between 1,29 and 35 J/g. All the photocrosslinked PCMs improved latent heat storage capacity in comparison with the pristine PU sample. Phase changing properties of the samples were also investigated by THz spectroscopy. Two spectral features were observed for L20 sample at 0.85 THz and 1.1 THz while no feature was observed for the other samples. The results suggest that the THz spectroscopy can be a complementary technique for characterization of the phase changing polymeric materials.

1. Introduction

Energy shortage issues and eco-friendly materials are becoming a impending problem in the world due to rapid economic and industrial improvements and growing population. Hence, it has become a very concerning issue to converse it and improve efficiency and also protect the environment. Thermal energy storage system has become an essential way to match the thermal energy claim and supply [1–3].

Phase change materials (PCMs) are commonly known for their latent heat storage properties. These PCM materials which undergo the solid–liquid and solid–solid phase transformation, more commonly known as the physical state (melting-solidification) cycle, at a temperature within the operating range of a desired thermal application. PCMs are being utilized to absorb, collect, and release thermal energy during the cycles of melting and freezing, turning from one phase to another. In the beginning, these phase change materials operate like any typical storage materials; however, as they absorb energy from heat, their temperature rises. But unlike any other storage materials, phase change materials takes in and releases heat energy at a practical, consistent temperature [4,5]. PCMs can store many times, 5–14, more heat per unit volume than classic storage components such as water, or rock. There are many PCM types can be found, yet they were categorized under three main branches; organic materials, inorganic salt hydrates, and eutectics of inorganic and organic materials [6,7]. Many kinds of organic and inorganic PCMs and their blends have been developed and tested as latent heat storage materials. These organic materials include fatty acids, fatty alcohols, organic eutectics, and paraffin waxes. When we examine the literature leakage problem seems to be main disadvantage of PCMs, once they melt. However, this problem can be eliminated by modifying the PCMs or incorporate them into stable polymer networks [8,9].

One of the advantages of photocrosslinked PCMs is that they hinder even completely prevent the interior PCMs from leaking. Stable shaped PCM is prepared by blending the PCM with a supporting material, generally polymers. Leakage problem can be minimized by coating the fatty alcohols and acids with a photo-crosslinked polymeric matrix. [10,11]. Photo curing (UV) process is a well-established polymerization method which takes place at low or room temperature, under the UV light rays. Most common formulations consist of mixture of more than one monomer and oligomer, but in this method formulations are solvent free; the maximum polymerization time is only few minutes and UV light is the only required energy source needed to form up the polymeric matrix. Thus, the process is well known for being fast and environmentally friendly, as the energy consumption is low and there is no emission of volatile organic compounds [12,13]. When it is investigated, the main advantage of the photocrosslinked PCMs is that

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they restrain the leakage of PCMs. As supporting materials, polymeric materials can be used in or with PCMs and they are obtained by mixing the PCM with this aiding component [14,15].

Generally, latent heat energy properties are measured by using DSC method but in some cases, spectral peaks may be used to identify the temperature at which phase changes occur within these materials. On the other hand, THz spectroscopy is considered to be an emerging new technique as a sensitive and non-destructive tool for identification of phase transition and structural features if any. Terahertz (THz) spectroscopy covers the region from 0.1 to 10 THz that is generally known as far-IR region of the electromagnetic spectrum. THz waves can couple with rotational and low frequency vibrational modes, torsional modes of molecules. In addition, the crystalline phonon modes are generally in this region, which enables THz spectroscopy to identify the various phases of the materials. THz wave can penetrate or transmit through many materials like skin, paper, plastic, many synthetics, textiles etc. With its non-invasive nature and fingerprinting ability, the technique has been applied to many areas like molecular spectroscopy [16], solid state physics [17], biology [18], and pharmaceuticals [19–22] as well as determination of the different morphologies of drugs [19,20]. The physical and chemical investigation of the PCMs are commonly done by techniques like X-ray diffraction, FTIR, SEM, TGA, and DSC. As a newly developing technique, THz spectroscopy is a very promising complementary technique with its unique properties since THz waves are quite sensitive to different polymorphic forms [23–30] and can readily be used for characterization of PCMs.

In this paper, lauric acid and tetradecanol were methacrylated and were integrated into UV curable formulations in various amounts. Photocrosslinked PCMs were prepared by photo polymerization and characterized by various techniques such as ATR-FTIR, TGA, DSC and THz etc.

2. Experiments

2.1. Materials

Lauric Acid, glycidylmethacrylate (GM), polyethylene glycol dialcrylate (PEGDA), Darocure 1173 and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Tetradecanol was purchased from Alfa Aesar and Sartomer CN 1963 was kindly provided from Sartomer. All the materials were used as they received.

2.2. Preparation of tetradecanol series (T series)

5 g of glycidyl methacrylate (35.17 mmol) was put into a 100 ml three-neck flask with of backcooler and heated to 50°. When the solution became completely clear, 5 g of glycidyl methacrylate (35.17 mmol) was added dropwise to the solution. The reaction was monitored by formation of epoxy ring. Fig. 1 shows the methacrylation of T series.

2.3. Preparation of lauric acid series (L series)

7.05 g of lauric acid (35.17 mmol) was put into a 100 ml three-neck flask with of backcooler and heated to 50°. When the solution became completely clear, 5 g of glycidyl methacrylate (35.17 mmol) was added dropwise to the solution. The reaction was monitored by formation of ester peaks at ATR-FTIR and opening of the epoxy ring. Fig. 1 shows the methacrylation of L series.

2.4. Preparation of PCM films

UV curable formulation which was composed of Polyurethanediacrylate oligomer, PEGMA, both methacrylated L/T and Darocure 1173. The composition of PCM films were given in Table 1. To obtain uniform photocrosslinked samples, UV curable resins were put under a 300 W UV lamp and exposed to UV rays (OSRAM, λmax = 365 nm) for 5 min to induce polymerization.

3. Characterization

The chemical characterization of the films was determined by ATR-FTIR spectroscopy. Perkin Elmer Spectrum 100 ATR-FTIR spectrophotometer (PerkinElmer, Waltham, MA, USA) was used to record FT-IR spectrum.

SEM imaging of films were performed on Philips L30 ESEM-FEG/EDAX (Philips, Eindhoven, The Netherlands). The samples were made ready for SEM analysis by freeze fracturing in liquid nitrogen following a gold coating.

The thermal stability of the films was determined in the temperatures between 30 – 750 °C by thermogravimetric analysis (TGA) using a PerkinElmer STA 6000 instrument (PerkinElmer, Waltham, MA, USA) under air atmosphere at a heating rate of 10 °C/min.

The Tg values and phase change properties of films were determined by using differential scanning calorimetry (DSC). The analysis was carried out with a Perkin Elmer Pyris Diamond model instrument (PerkinElmer, Shelton, CT, USA). The samples were analyzed under a nitrogen atmosphere between of –20 – 100 °C at a heating rate of 10 °C/min and cooling rate of 10 °C/min.

Structural changes of samples due to the phase change and its effect on the absorbance of THz frequencies in the frequency range of 0.1–1.4 THz (3.3–46 cm−1) were monitored with THz Time Domain Spectroscopy (THz-TDS). The details of the THz time domain spectrometer has been described elsewhere [31]. In short, an ultrafast mode
3.1. Chemical characterization

Fig. 2 shows the ATR-FTIR spectra of bare GM, tetradecanol and lauric acid. In spectra of GM one can see characteristic epoxy ring peaks between 941 and 904 cm\(^{-1}\) and C=\(\text{C}\) bond of acrylate peaks at near 1638 \(\text{cm}^{-1}\) and 813 \(\text{cm}^{-1}\). Disappearance of epoxy peaks and appearance of C=\(\text{C}\) bond at near 1638 and 813 shows that integration GM into tetradecanol and lauric acid was a success after ring opening reaction. Additionally, appearance of ester peak at 1718 \(\text{cm}^{-1}\) instead of carboxylic acid peak at 1690 \(\text{cm}^{-1}\) in lauric acid shows the integration was successful.

Fig. 3 shows the ATR-FTIR spectra of methacrylated lauric acid and photocrosslinked films of; blank, L series and T series. Appearance of C=\(\text{C}\) bond at 1638 \(\text{cm}^{-1}\) indicates addition of GM to lauric acid successfully. It is shown that stretching vibrations peak at 1638 \(\text{cm}^{-1}\) and 842 \(\text{cm}^{-1}\) have disappeared upon completion of the photocrosslinking process.

3.2. Thermal characterization

Fig. 4 shows the thermograms and Table 2 shows the results of the TGA of L and T series. The thermal decomposition of film series begins around 304 ºC. Between 304 and 470 ºC temperature values, indicator of degradation can be detected. Between these temperatures, two degradation steps can be detected. The first step is, between 304 ºC and 320 ºC, and could be attributed to dealkylation of the fatty alcohol (methacrylated tetradeanol) and fatty acid (methacrylated lauric acid) chain, which leads to the arrangement of saturated carbon-carbon bonds along the fatty alcohol and ester chain. The second step is between 350 and 470 ºC, which could be attributed to thermal degradation of the main polymer chain [32,33].

3.3. DSC

Phase change materials are generally investigated and used in thermal energy storage using, since phase change materials have most of the desired attributes such as chemical stability, high latent heat, and satisfactory phase transition temperatures [34,35]. Phase change properties of the samples were determined by DSC equipment (Figs. 5 and 6). The freezing and melting points were chosen as the peak flect of the DSC curves. Table 3, summarizes all the DSC data of the phase transfer properties of heating and cooling for all the prepared formulations.

Blank sample does not show any endothermic peaks in thermogram, whereas PCMs has only one. Methacrylated tetradeanol containing PCM shows a maximum peak near 35 ºC with an enthalpy value of 9.49, 21.49 and 77.76 J/g, whereas methacrylated lauric acid containing PCM gives a maximum peak around 41 ºC, respectively. Their observed melting enthalpy values are 17.50 J/g, 26.72 J/g and 43.95 J/g, which are generally higher than methacrylated tetradeanol containing PCM. These results shows that the melting temperature and enthalpy of PCMs was increased by the increase of length of n-alkyl chain of fatty alcohol and acid as it was expected due to previous works [36]. This may contribute to the chain movement hindrance of the PCM. The alkyl chains, which are more easily rotatable around their ties, can accumulate more energy than the hard polar groups [37]. As a results, enthalpies of the prepared PCMs were raised from 0 J/g to 77.76 J/g with respect to blank sample.

The DSC freezing results of blank sample, L and T series are shown in Figs. 4 and 5. Blank sample does not have any exothermic/freezing peaks, whereas L series have only one freezing peak while T series have two peaks. Methacrylated tetradecanol containing PCM has a maximum peak values around 32 ºC and 26.5 ºC with an enthalpies of between 1.42 J/g and 2.40 J/g whereas methacrylated lauric acid containing

![Fig. 2. ATR-FTIR spectra of bare GM, tetradecanol, lauric acid and methacrylated materials.](image-url)
peaks around 36.5 °C, respectively. Their freezing enthalpies are between 12.83 J/g and 35.13 J/g which is higher than methacrylated tetradecanol containing PCM. Noticeably these results indicate that the freezing temperature and enthalpy of PCMs were decreased by the increase of length of n-alkyl chain of fatty alcohol and acid [36]. This may contribute to the chain movement hindrance of polar groups. The polar groups, which are hardly rotatable around their ties, can release more energy once they stored than the easy rotatable alkyl chains. Since the free alkyl chains migrate the energy stored in their bonds to a different conformation, the freeze enthalpy is lower than the polar groups. Because they used their energy for chain conformation [38]. As results, freezing thermal energy storage of the materials containing fatty acid were raised from 0 J/g to 35.13 J/g with respect to blank sample.

3.4. Terahertz spectroscopy

The Fig. 7 presents the frequency domain spectra of the blank (host) sample between 0.1 and 1.4 THz. Time domain spectra of the empty sample cell (air) and some selected samples are given in Supporting

### Table 2

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$T_{on}$</th>
<th>$T_{max}$</th>
<th>Char Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>304</td>
<td>363</td>
<td>0.03</td>
</tr>
<tr>
<td>L 5</td>
<td>308</td>
<td>369</td>
<td>3.65</td>
</tr>
<tr>
<td>L 10</td>
<td>311</td>
<td>370</td>
<td>2.96</td>
</tr>
<tr>
<td>L 20</td>
<td>310</td>
<td>371</td>
<td>3.52</td>
</tr>
<tr>
<td>T 5</td>
<td>309</td>
<td>367</td>
<td>4.61</td>
</tr>
<tr>
<td>T 10</td>
<td>303</td>
<td>370</td>
<td>4.85</td>
</tr>
<tr>
<td>T 20</td>
<td>307</td>
<td>365</td>
<td>5.24</td>
</tr>
</tbody>
</table>
As expected the absorption spectra of the host material at 21 °C (RT) and at 70 °C are fairly similar to each other. The observed slight change (increase) in absorption upon heating could be due to thermal expansion of the sample, hence due to slight changes in scattering rather than changes in absorption cross section. The maximum change observed is around 10% at low frequencies where the spectrometer system also has the lowest signal to noise. On the other hand, the average change is about 4% between the 0.1 and 1.4 THz.

Terahertz absorption spectra and the relative change in absorbance with phase change of L series samples (L5, L10, and L20) are given in Fig. 8. These frequency dependent absorption cross sections of the samples were calculated relative to the air reference (solid lines) and relative to the host material reference (dotted lines) at RT and at 70 °C. (Fig. 8a–c) Here, the former shows the frequency dependent changes in the absorption of the sample as the temperature was increased. Thus it is a direct measure of the phase change effect. The latter shows the changes in the absorption of the sample relative to the host material. Since the host material characteristics do not change significantly (Fig. 7) with increase in temperature we expected and observed a similar behavior in each case. With the phase change, a clear difference in the frequency dependent absorption spectra was observed in all three samples. (Fig. 8d–f) A more interesting observation was the decrease in absorption coefficients of the samples with the phase change, except the sample L5.

The absorption spectra of the L5 shows a slight increase in absorbance at all frequencies. Such a non-structured increase in the absorption suggest a change in scattering of the sample with the phase change. This observation is much weaker in the absorbance spectra referenced to host material but it is still observable. A small but an observable part of this increase is due to an increase in scattering cross section of the host material. (Fig. 7) Such a small change is normal for L5 sample given that the additive amount is very small. We have not observed any spectral feature with the phase change in L5 sample.

L10 sample, on the other hand, showed a decrease in the absorbance with the phase change. An increased amount made it easier to observe the phase change effect compared to L5 sample. With the phase change methacrylated lauric acid melts and loses its structured order in the system. This way the scattering effect of the micro structured additive is lost in the sample and scattering cross section reduced in the sample. This resulted in higher transmission through the sample and resulted in lower absorbance as observed. There is no observed feature band prior to phase change or with the phase change of L10 sample. Similarly, L20 sample also showed a decrease in absorbance. As expected, the effect of the phase change is much more pronounced in this sample compared to the L5 and L10 and the sample became significantly more transparent.

Unlike the other two samples, L20 RT spectra has features; a broad band at 1.1 THz and a shoulder at 0.85 THz (blue solid lines in Fig. 8c). Observation of these bands both in air and blank referenced spectra confirms as these being spectral signatures of the L20 sample at RT. Interestingly, these signature features disappear when the temperature was increased to 70 °C and phase changed occurred. This suggests that the solid structure (most probably crystalline structures) that exist at room temperature disappears when the material melts beyond the transition temperature. The trend observed in the L-series samples are consistent with the latent heat results obtained in DSC measurements.

The Fig. 8e,f shows the absolute change in absorbance with the phase change relative to the host material. In L5 it is not possible to suggest any spectral feature due to the low signal to noise level. However, there is small but above the error change in absorption coefficient confirming that the phase change can be observed with the
THz spectroscopy even at these low concentrations. The absolute change in absorption coefficient increases with the additive amount. The observed change in L10 is can be considered featureless, however, the spectral features at 0.85 THz and 1.1 THz are well above the noise levels and dominates the spectra of L20.

The effect of the phase change in the absorption spectra of T series samples were less prominent. (Fig. 9a–c) The absorption increased slightly for T5 and T10 similar to the one observed for L5 while it was slightly decreased for T20. All the observed changes are well above the measurement errors, especially for the frequencies above 0.75 THz. The observed behavior is consistent with the latent heat of freezing measurements with DSC, where the observed latent heat was very low (1–2 J/g). Interestingly, increased addition of the methacrylated tetradecanol does not improved the system. In addition, we do not observe any spectral features even at high concentrations of tetradecanol (T20) in these samples.

The observed spectral features of L20 with high concentrations suggest possible crystal domains of methacrylated lauric acid in L20 sample. Once the sample is heated to 70 °C, the sample is melted down and such ordered regions disappeared. On the other hand, such crystalline domain formation apparently does not exist in any other L series samples or in all of the T series samples. These results suggest that the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melting Temperature (°C)</th>
<th>Latent Heat (J/g)</th>
<th>Freezing Temperature (°C)</th>
<th>Latent Heat (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tetradecanol</td>
<td>42.4</td>
<td>222.7</td>
<td>28.8 and 29.6</td>
<td>219.7 and 60.7</td>
</tr>
<tr>
<td>Lauric Acid</td>
<td>43.2</td>
<td>158.7</td>
<td>41.5</td>
<td>164.6</td>
</tr>
<tr>
<td>T5</td>
<td>35.0</td>
<td>9.5</td>
<td>32.3 and 26.9</td>
<td>1.3 and 1.4</td>
</tr>
<tr>
<td>T10</td>
<td>35.8</td>
<td>21.5</td>
<td>32.4 and 26.3</td>
<td>−1.1 and 2.0</td>
</tr>
<tr>
<td>T20</td>
<td>34.9</td>
<td>77.7</td>
<td>31.8 and 26.5</td>
<td>−2.4 and 2.3</td>
</tr>
<tr>
<td>L5</td>
<td>41.2</td>
<td>17.5</td>
<td>37.0</td>
<td>−12.8</td>
</tr>
<tr>
<td>L10</td>
<td>40.9</td>
<td>26.7</td>
<td>36.9</td>
<td>−19.3</td>
</tr>
<tr>
<td>L20</td>
<td>41.2</td>
<td>43.9</td>
<td>36.2</td>
<td>−35.1</td>
</tr>
</tbody>
</table>

Fig. 7. THz spectrum of the blank sample.

Fig. 8. THz spectra of L5, L10, and L20 samples. The spectra have been obtained with two separate references, blank and air whose spectra are represented by dashed and solid lines, respectively. The measurements with blank reference shows the effect of additive better.
samples are homogeneously dispersed with the host materials. Our results are consistent with the cooling DSC thermogram data since the samples are heated and cooled in cycles prior to our measurements. On the other hand, it is noticeable that each sample has its own unique behavior that varies with the phase change. This indicates that THz spectroscopy can be used to differentiate the phase differences based on their spectral changes.

3.5. Morphology

The morphology of L series and T series were screened and studied by scanning electron microscopy (SEM). Fig. 10 shows the SEM images of the fragmented surface morphology of both series. As it can be seen in Fig. 10, methacrylated tetradecanol and methacrylated lauric acid were dispersed homogenous in the matrix and bead-like structures that appear is due to the methacrylated fatty alcohol and methacrylated acid.

4. Conclusion

Methacrylated lauric acid and tetradecanol were synthesized and put into UV curable recipe. Photocrosslinked PCMs were prepared by photo polymerization to prevent leakage problem. TGA analysis demonstrated these PCMs could keep high thermal stability under 304 °C, which is higher than fatty alcohols and acids. DSC results indicates that higher methacrylated lauric acid content increase the enthalpy (17.5,
26.7 and 45.9 J(g) value aside from T20 (77.7 J(g) sample. Thermal energy properties of PCMs are determined by DSC. In addition to common characterization techniques, THz spectroscopy was also used to measure phase change behavior of photocrosslinked PCMs in this study. Being a non-destructive tool that is sensitive to the phase and structural ordering, THz spectroscopy technique was also utilized for identification of phase change as a complementary technique in this study. Results of DSC and THz are consistent considering that the samples are heated and cooled in prior to THz measurements. THz spectroscopy studies were not only successfully showed the phase change of the material, but also resulted information of possible structural ordering with the observed spectral features in L20 sample at 0.85 and 1.1 THz. THz spectroscopy is an emerging new technique in characterization of phase changing polymeric materials and can be considered as a complementary technique to the conventional ones.

Declaration of Competing Interest
None

References