Fabrication and characterization of the blend of Polyurethane (PU) and Phase Change Materials (PCM) for energy storage and release

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Abstract
Utilizing thermal energy storage (TES) system having phase change material (PCM) in it is an effective technique for energy conservation and reduction in greenhouse gas (GHG) emission. Fatty acids have the highest energy storage capacity and easy to process in comparison to all other PCM. Eutectic mixture of palmitic acid (PA) and capric acid (CA) was prepared and thermal analysis was done to confirm its latent heat storage capacity for energy storage and release. This eutectic mixture of fatty acids was physically blended in PMMA to avoid leakage. Fatty acid blended PMMA (F-PMMA) was blended with polyurethane (PU) foam. 10% F-PMMA added as an additive in PU offered highest compressive strength with improved energy absorption.

Introduction
Inserting insulation panels into walls, doors, and windows of buildings can reduce energy consumption and lessen greenhouse gas emissions [1]. Thermal insulating materials are used in commercial buildings to improve the energy ingesting of buildings, cooling and heating systems [1]. Polymeric materials such as expanded polystyrene (EPS) and polyurethane (PU) provide good insulation for internal heating and cooling of buildings [2–4]. In PU, the air is entrapped within the honeycomb-like structure, provides high heat absorption capacity [5, 6].

Phase Change Material (PCM) is categorized as a latent heat storage unit that absorbs and releases heat during a phase change by variation in temperature [7, 8]. Fatty acids based PCMs possess efficient properties than other PCM mixtures or compounds such as melting range, great chemical stability, non-toxicity and adequate melting temperature [9]. Fatty acids were encapsulated in epoxy composites as filler for thermal management which resulted in lower mechanical properties due to less interaction between components [10]. PCMs were directly encapsulated in thermoplastic polyurethane (TPU) and results showed good interfacial adhesion and homogenous encapsulation [11]. PCM materials in different proportions can be incorporated directly into PU foam or by encapsulation in another polymer [12, 13]. Organic PCMs are chemically stable, without supercooling and phase segregation [14]. The blend of polyvinyl alcohol (PVA) and fatty acid was prepared for latent heat storage material without encapsulation. Lauric acid (LA), myristic acid (MA), palmitic acid (PA), and stearic acids (SA) were used separately in PVA in 20, 30, 40, 50, 60 wt%. The melting temperatures and latent heat stored by PVA/LA, PVA/PA, PVA/MA and PVA/SA blends were determined as 39.8 °C, 56.2 °C, 50.2 °C, and 67.4 °C and 96.4, 121.6, 105.3, and 132.6 Jg⁻¹, respectively [15].

From literature, it was observed that most of the phase change materials were studied and blended and very less work was done to apply this into an energy storage application. The addition of fatty acids in polymers resulted in reduction of mechanical strength due to poor adhesion between fatty acids and polymer chains. Hence there is a need to prepare such blend of polymer and fatty acids with maintained mechanical properties so that it can be used for structural applications. This paper is, therefore, focusing on preparation of the blends of the binary mixtures of palmitic acid (PA) and capric acid (CA) held by PMMA chains and added in PU foam as additives. The thermal, morphological and mechanical analysis was done on the prepared blend in PU foam.
Experimental

Materials
Capric acid (CA), palmitic acid (PA) were used as PCMs purchased from Sigma Aldrich with >95% purity. Chloroform was used as a solvent and purchased from Dae-Jung with >99.5% purity. PMMA was obtained from Sigma Aldrich with >95% purity. Polyether polyols and isocyanate were used as PU raw materials delivered by Chawla Footwear Pakistan.

Preparation of eutectic mixture blend with PMMA
According to literature the eutectic point of PA and CA is at the ratio of 23.5 wt.% and 76.5 wt.% respectively that’s why both the fatty acids were blended in this ratio to prepare a eutectic mixture of fatty acids [16]. Firstly, both the fatty acids were heated to convert them into liquids. Fatty acids were added in the beaker in specific ratios. Mixing was done using an overhead mixer at 65°C for 5 min. To confirm the eutectic point and latent heat stored by this blend thermal analysis was done using DSC.

To prevent the leakage of the eutectic blend of fatty acids at its melting point from PU foam, the eutectic mixture of fatty acid blend was mixed with PMMA that hold the fatty acid liquid after melting. The sample chart of the blend of PMMA with eutectic mixture of fatty acid is displayed in table 1.

PMMA was dissolved in chloroform at 30 °C temperature and then the eutectic blend was added dropwise. Mixing was done until the homogenous solution appeared. This solution was poured in a petri dish to evaporate chloroform and placed at room temperature for 2 days.

Fabrication of PU foam by adding F-PMMA
From all the prepared fatty acid blended with PMMA (F-PMMA), the sample having high amount of fatty acids with minimum leakage (confirmed from SEM) was selected to make a blend of F-PMMA with PU foam. After the evaporation of chloroform from F-PMMA, the flakes of F-PMMA was obtained. F-PMMA-2 was added in polyol liquid in different proportions as mentioned in table 2 to make a foam. The mixture was mechanically stirred for 2–3 min at room temperature at 500 rpm. Isocyanate was added into polyol mixture in equal proportion of pure polyol and intensive mechanical stirring was done at 1500 rpm for 30–40 s until mixture was uniform and started to generate bubbles. The mixture was poured in a wooden mold to expand with controlled dimensions.

Results and discussion

Thermal properties of CA/PA mixtures
TA Instruments’ Differential scanning calorimeter (DSC) DSC250 was used to check the phase transition temperature and total latent heat stored by the eutectic blend in comparison of pure fatty acids. 6 to 10 mg weight of sample was taken and test was run in nitrogen atmosphere. The samples were heated from 10 °C to

Table 1. Sample Chart of the blend of PMMA with a fatty acid mixture.

| Sample Name | PMMA (wt.%) | Eutectic mixture of PA and CA (wt. %) |
|-------------|-------------|--------------------------------------|
| F-PMMA-1    | 5           | 95                                   |
| F-PMMA-2    | 20          | 80                                   |
| F-PMMA-3    | 40          | 60                                   |
| F-PMMA-4    | 60          | 40                                   |
| F-PMMA-5    | 80          | 20                                   |

Table 2. Formulations of the blends of polyurethane (PU) foam with F-PMMA.

| Sample Name | Isocyanate wt.% | Polyol wt.% | F-PMMA |
|-------------|-----------------|-------------|--------|
| F-0P        | 50              | 50          | 0      |
| F-90        | 45              | 45          | 10     |
| F-80        | 40              | 40          | 20     |
| F-70        | 35              | 35          | 30     |
70 °C and cooled from 70 °C to 10 °C with a ramp of 10 °C per minute. Figure 1 exhibits the heating thermogram of fatty acids blends showing eutectic behavior.

Pure PA melted at 64 °C with latent heat 274 J g⁻¹ and pure CA melted at 32 °C with latent heat 117 J g⁻¹. The blend of PA and CA in a ratio of 23.5 wt.% and 76.5 wt.% melted at 26.9 °C with latent heat 197.5 J g⁻¹. It was observed that the prepared blend of fatty acids has a different melting temperature and the eutectic point of the blend of PA and CA offered the phase change temperature exactly at room temperature hence this blend can maintain the room temperature where applied as insulation. The amount of heat stored during melting in the fatty acid blend is also higher than CA but less than PA. Figure 2 shows the solidification of PA, CA and PA:CA mixture. PA releases 300 J g⁻¹ heat and changes its phase to solid at 56 °C while CA releases 114 J g⁻¹ heat and solidified at 26.5 °C. Eutectic mixture of fatty acids shows solidification at 16.5 °C and releases 140 J g⁻¹ heat. The latent heat of the eutectic mixture was high to be compared to some PCMs such as salt hydrates and polyalcohols1–3.

**Morphological analysis**

Scanning electron microscopy (SEM) Joel JSM 6490A was performed to study the interactions of the fatty acid mixture with the PMMA. First, the eutectic mixture of fatty acid blended PMMA was subjected to heat in oven for the melting of fatty acids and then cooled down before analyzing the morphology of F-PMMA. Heating and cooling of the blend were done to check the leaking of fatty acids from PMMA.
From figure 3, it is clear that after heating still, the mixture of fatty acid has some interaction with PMMA structure. However, at high amount of fatty acid mixture (F-PMMA-1), there was some amount of fatty acids appeared on the surface of PMMA (highlighted in black circles), indicates that there is slight leakage from the PMMA at high loading of fatty acids.

The maximum amount of fatty acid mixture that was able to be held by PMMA was in sample F-PMMA-2. Higher than this ratio caused leakage of fatty acids from PMMA structure and lesser of this concentration was not able to provide effective heat absorption and release capacity. Hence, the best characteristics from all the prepared blends were observed in the sample that holds 80% fatty acid mixture.

Compression testing
Thermal insulation, when applied in construction application, withstands high amount of compression load so compression test was performed to check the mechanical stability of polyurethane (PU) foam by the addition of fatty acids blended PMMA as additive. From SEM the best sample observed was F-PMMA-2 and this sample was added in PU foam as additives in three different concentrations. To conduct a compression test, universal testing machine of ZwickRoell Z-100 was used and sample was designed according to the ASTMD3574. Compression force was applied to sample until the sample approaches to its maximum strain before collapsing and the stress-strain curve was obtained. Each composition was tested 5 times. Figure 4 shows that sample which holds 10% by wt. of F-PMMA-2 provide the high compression strength as compared to other samples having fatty acids.

In pure PU foam (F-0P), the maximum compressive stress absorbed until 33% strain was 0.17 MPa. By adding 10% F-PMMA in PU foam as additive improved the energy absorbed however the there was a slight decrease in the compressive strength (0.16 MPa) and it provided 38% maximum strain. Hence at 10% F-PMMA, we achieved comparable mechanical strength. At a low amount of F-PMMA, interaction between F-PMMA and PU chains is better and due to PMMA chains that have high energy absorption property. By adding a higher amount of F-PMMA in PU foam, the compressive strength was observed to be decreased because the high concentration of fatty acids that enhanced the plasticity of material owing to its plasticizing effect, hence resulted in the weakening of the intermolecular interactions between the PU foam chains [17].

Figure 3. Scanning electron microscopy (SEM) images of fatty acid mixture blended in PMMA after heating (a) F-PMMA-1 (b) F-PMMA-2 (c) F-PMMA-3.
Conclusion

Polyurethane (PU) based thermal insulation can be prepared with the capability of energy absorption and release by inserting fatty acids-PMMA. PMMA is observed to be an excellent material that can hold fatty acids as well as it can be easily blended with PU foam. Eutectic mixture of palmitic acid (PA) and capric acid (CA) can maintain the inside temperature at 26 °C. SEM analysis showed that up to 80% by wt. of the fatty acid mixture has good interaction with PMMA and above this amount resulted in the leakage of mixture from PMMA. F-PMMA was blended with PU during the fabrication of foam, however, greater than 10% by wt. of F-PMMA caused reduction in the compressive strength of PU foam.

Data availability statement

All data that support the findings of this study are included within the article.

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Figure 4. Comparison of compressive strength of PU foam by varying F-PMMA.
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