Preparation and characterization of thermal conductivity enhanced shape stabilized phase change composite for thermal energy storage

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Abstract. Thermal energy management is fetching more importance, recently in many sectors including chemical/petrochemical, automotive, aerospace, and electronics. An attempt has been done on the investigation in thermal energy storage (TES) applications using phase change composites. To make the composite material suitable for potential devices the thermal conductivity should be high. For achieving this, fillers with higher thermal conductivity can be incorporated into polymers to form polymer composites. In the light of background study on the recent researches in this area, nanocomposites are expected to show good thermal conductivity behavior. In this work, ZnS/PMMA nanocomposites are used as the conductive polymer for thermal energy storage in which the ZnS nanoparticles are used as the fillers. The solution casting method is used to prepare the nanocomposites. Samples based on the weight percentage of filler are used for characterization. The thermal stability and conductivity of the composite material are evaluated using TGA and Thermal Conductivity Apparatus. The SEM analysis of ZnS particles shows the nanoscale size and morphology suitable for filler components. An enhancement of 72% in thermal conductivity is noted for the 6% (ZnS) sample with PMMA.

Keywords – nanocomposites, thermal energy storage.

1. Introduction

The effective goal in energy management lies in balancing the challenges between producing and utilizing various forms of energy. Thermal energy management has been a subject of an issue in numerous researches for a long time. Loss of energy in the form of heat is happening in many of the sectors varying from electronic gadgets to process industries. The minute losses as we consider, collectively form into a large quantity of energy loss in our daily life. Phase change materials (PCM) are such materials that could store and discharge heat likewise. The proper application of PCM’s can thus resolve this particular research gap in thermal energy management. In any case, the significant issue in regards to the PCM is their shape stability while phase change. Numerous examine in regards to the structure dependability prompts encapsulation of the PCM with appropriate composite.
Consequently building up a novel composite material with good thermal conductivity and better shape stability for TES is of great enthusiasm to the research world. Various methodologies in the investigation of ideal TES are progressively discussed. In this work, we use the latent heat storage procedure in which the thermal energy is stored inside the phase change material. This work is concerned with the planning of form-stable composite by utilizing the solution casting technique. The ZnS nanoparticles for the composite are first synthesized and different weight percentage of them is used for the composite preparation. The acquired PMMA/ZnS nanocomposites are characterized by scanning electron microscopy (SEM) and thermogravimetric (TGA) analysis. The thermal conductivity tests are conducted and the outcomes are brought down to acquire the better composite for thermal energy storage applications. 

PCM's are broadly utilized in thermal energy storage frameworks. Solid-liquid PCMs have an inadmissibly high liquid leakage. Shape stabilized phase change composites are a type of novel PCM. They have the major features including large specific heat for the particular phase change temperature area, reasonably good thermal conductivity, maintaining its shape stabilized in the process of phase change, and no requirement for containers to handle. Subsequently, shape settled Phase Change Composites are getting importance in thermal energy storage applications. Interest in heat-dissipating materials is expanding and further advancement is expected around these areas.

In the preparation of Zinc Sulfide (ZnS) / Polymethyl Methacrylate (PMMA) nanocomposite by the solution casting method, different samples of composite films is prepared based on the weight percentage of nanoparticles (ZnS). By analyzing the thermal properties, a better composite will be used for the PCM encapsulation. Characterization includes SEM analysis for nanoparticles prepared to identify the surface morphology of the composite and the thermal conductivity analysis and TGA for the nanocomposites. A better composite is used to encapsulate the phase change material by using the hot press method.

1.1. Objective
1. To develop a novel shape stabilized PCM composite.
2. To evaluate the thermal properties of the shape stabilized PCM developed.
3. To investigate the application of the shape stabilized PCM in thermal energy storage.

1.2. Methodology
1. Preparation of ZnS nanoparticle filler material.
2. Addition of filler material to PMMA host material by solution casting method.
3. Characterization of the Nanocomposite.

2. Literature survey
Ahmet Sarı, Cemil Alkan, (2017) “Poly (ethylene glycol)/poly (methyl methacrylate) Blends as Novel Form-Stable Phase-Change Materials for Thermal Energy Storage”. This work focused on the preparation and characterization of poly(ethylene glycol) (PEG)/poly(methylmethacrylate) (PMMA) blends as novel form-stable phase-change materials (PCMs) for latent-heat thermal energy storage (LHTES) applications. Jaume Gasia, Laia Miró, Alvaro de Gracia, Camila Barreneche and Luisa F. Cabeza (2016) "Experimental Evaluation of a Paraffin as Phase Change Material for Thermal Energy Storage in Laboratory Equipment and a Shell-and-Tube Heat Exchanger". The thermal behavior of commercial paraffin with a melting temperature of 58 ℃ is analyzed as a phase change material (PCM) candidate for industrial waste heat recovery and domestic hot water applications. A complete characterization of this PCM is performed based on two different approaches: a laboratory characterization (mass range of milligrams) and an analysis in a pilot plant (mass range of kilograms). Hyunwoo Oh, Jooheon Kim (2019) “Fabrication of polymethyl methacrylate composites with silanized boron nitride by in-situ polymerization for high thermal conductivity”. In this study, BN/PMMA composites were fabricated using the in-situ
polymerization process and hot-pressing method. The BN was silanized by VTES to introduce double bonds that could covalently link with PMMA chains during the polymerization step. The BN/PMMA composites were successfully fabricated using VTES-BN and MMA monomers. Mohammad Mehrali, Sara Tahan Latibari (2018) "From rice husk to high-performance shape stabilized phase change materials for thermal energy storage". A novel shape-stabilized phase change material (SSPCM) was fabricated by using a vacuum impregnation technique. The lightweight, ultra-high specific surface area and porous activated carbon was prepared from waste material (rice husk) through the combination of activation temperature approach and sodium hydroxide activation procedure. Shaokun Song, Tingting Zhao (2018) "Natural microtubule-encapsulated phase change material with simultaneously high latent heat capacity and enhanced thermal Conductivity". Thermal energy storage (TES) systems that use phase-change materials (PCM) store, transport, and use large amounts of latent heat via a reversible phase transition. PCM have been considered potential candidates to relieve the energy crisis and environmental pollution. Y Munusamy, S Shanmugham (2018) “Development of form stable Poly (methyl methacrylate) (PMMA) coated thermal phase change material for solar water heater applications”. In this work, form-stable PCM was prepared by coating myristic acid with Poly (methyl methacrylate) (PMMA) to prevent leakage of PCM. The various tests conducted are leakage tests, differential scanning calorimetric, and thermal conductivity tests along with characterization using FTIR and TEM. Yuanyuan Deng, Lujiang Yang (2017) “Preparation and characterization of polyethylene glycol (PEG) hydrogel as shape-stabilized phase change material”. A kind of PEG8000 hydrogels as shape-stabilized phase change materials (SSPCMs) was prepared by using a simple sol-gel technique. Their thermal characteristics were studied under the modified mass ratio of PEG and water.

3. Materials and methods

3.1. Preparation of Nanoparticle Composites
Step 1: Coprecipitation technique for ZnS nanoparticles
ZnS nanoparticles are prepared by co precipitation method using zinc acetate and sodium sulfide (Na₂S). 0.1 M Zinc Acetate is added and mixed along with polyvinyl alcohol (1% by weight) using a magnetic stirrer. Then Na₂S was added dropwise under vigorous stirring for 1 hour. A white color precipitate formed was separated by centrifugation process. The precipitate was further washed, filtered, and dried in an oven at 80 °C.

Step 2: Solution Casting Method for ZnS/PMMA:
The solution-based casting method was used to prepare Polymethyl methacrylate (PMMA) nanocomposite with different weight percentages (0, 2, 4, 6 and 8) of ZnS nanoparticles. PMMA is dissolved in the Tetrahydrofuran (THF) solution by stirring with a magnetic stirrer for 2 hours. Then the ZnS nanoparticles with different weight % were dispersed into the THF solution. The obtained solution was agitated by ultrasonicator for 20 minutes to get uniform distribution. The solution was poured into the Petri dishes to obtain the ZnS/PMMA nanocomposite films. After 24 hours, the nanocomposite films are taken out from the Petri dishes and dried in a vacuum for 6 hours to remove the solvent. All the chemicals used for the work were of laboratory grade. Deionized water and reagents were used directly throughout the experiment.
4. Result and discussion

4.1 Synthesis of Nanoparticles

Figure 1. ZnS Nanoparticles  
Figure 2. ZnS/PMMA composite

4.2 Preparation of Nanocomposite Samples

Figure 3. Sample 1 (2% ZnS)  
Figure 4. Sample 2 (4% ZnS)  
Figure 5. Sample 3 (6% ZnS)

4.3 Thermogravimetric Analysis
Thermal decomposition ranges of the different samples were obtained and are compared with that of pristine PMMA using TGA curves. The curve trend in figure 4.6 to 4.9 shows that the thermal stability of the composites increases with an increase in the amount of nanoparticles in the composite.
Table 1. Degradation Temperature of Samples

| SAMPLE                | TEMPERATURE (℃) |
|-----------------------|------------------|
| PMMA                  | 230              |
| PMMA / ZnS(2%)        | 240              |
| PMMA / ZnS(4%)        | 260              |
| PMMA / ZnS(6%)        | 260              |

4.4. SEM Analysis
The morphology of the prepared sample was analyzed by SEM. SEM analysis of the prepared Zinc Sulfide nanoparticle sample shows that the materials were spherical in shape and size is found to be in the range of 40 nm.
4.5 Thermal Conductivity Analysis
The study of properties such as thermal conductivity is crucial for any possible innovation since the environmental and thermal stability of material must be described with great precision to determine the ideal conditions for the performance of a system. Thermal conductivity ($k$) is the measure of a substance's ability to conduct heat. The process of heat transfer and, consequently, the thermal conductivity depends on the structure of the material. In metals, heat is transferred using free electrons, while in non-metallic materials, for example in polymers, heat is conducted through phonons or lattice waves, which are emitted by the vibratory energy of the particles. For our situation, a two-phase system like polymer/filler composite, interfacial physical contact among polymer and filler is critical, since phonons assume a significant job in choosing the thermal conductivity through their mean free path. The temperature dependence of effective thermal conductivity of pure PMMA and ZnS/PMMA nanocomposites is shown in the following tables.

Sample 1: PMMA

| Temperature | 30  | 40  | 60  | 80  | 100 | 120 |
|-------------|-----|-----|-----|-----|-----|-----|
| $k$         | 0.11| 0.12| 0.14| 0.17| 0.185| 0.185|

Sample 2: PMMA / ZnS (2%)

| Temperature | 30  | 40  | 60  | 80  | 100 | 120 |
|-------------|-----|-----|-----|-----|-----|-----|
| $k$         | 0.17| 0.18| 0.19| 0.21| 0.22| 0.23|

Sample 3: PMMA / ZnS (4%) 

| Temperature | 30  | 40  | 60  | 80  | 100 | 120 |
|-------------|-----|-----|-----|-----|-----|-----|
| $k$         | 0.18| 0.185| 0.21| 0.22| 0.25| 0.25|

Sample 4: PMMA / ZnS (6%) 

| Temperature | 30  | 40  | 60  | 80  | 100 | 120 |
|-------------|-----|-----|-----|-----|-----|-----|
| $k$         | 0.19| 0.21| 0.23| 0.24| 0.27| 0.27|
The results of the thermal conductivity analysis showed that the thermal conductivity of nanocomposite is higher than that of virgin material. Therefore, the inclusion of ZnS nanoparticles in PMMA has a synergistic influence on thermal conductivity. Figure 5.13 shows that the thermal conductivity of PMMA without nano addition at room temperature (30 °C) is 0.11 W/mK and increases with increasing temperature. Comparable behavior is observed for all ZnS/PMMA nanocomposite. The thermal conductivities of ZnS/PMMA nanocomposite with 2, 4, and 6 wt% ZnS nanoparticles at 30 °C are 0.17, 0.18, and 0.19 W/mK. Similarly, the thermal conductivity of the pristine PMMA test at 100 °C is specified as 0.185, and that of nanocomposite as 2, 4, and 6 weight percent is individually specified as 0.22, 0.25, and 0.27.

The observed variation in thermal conductivity of PMMA and ZnS/PMMA nanocomposite with temperature can be elucidated using various phonon dispersion components like dissipation of chain deformity, structural dispersion, and dissipation of the empty site. As the temperature rises from room temperature, the polymer chains become increasingly fixed and expand the relative mean free path. This leads to a minimization of the errors of the chain and, thus, the obligation to compare the thermal resistance directly with the increase in temperature decreases and, therefore, increases the thermal conductivity.

Figure 4.11 also shows that the effective thermal conductivity of nanocomposite is higher than that of pristine PMMA. This behavior can be clarified using the compact structure of composite materials. When nanoparticles are incorporated into the network, they occupy the empty lattice positions and reduce free volume, resulting in a compact composite structure that improves the thermal conductivity of nanocomposite compared to virgin PMMA. As the ZnS nanoparticle cluster increases to 6% by weight, the free volume continues to decrease and makes the nanocomposite less than the compound with 2 and 4% by weight of ZnS. In any case, this is the ideal conservative structure for which the feasible thermal conductivity is the highest in the entire temperature range examined.

5. Conclusion
In this work, the effect of ZnS nanoparticles on the thermal properties of PMMA which is used to encapsulate the phase change materials were investigated. Experimental procedures were carried out for the preparation of nanoparticles, nanocomposites, and further encapsulation techniques. Characterization of nanoparticles and tests for thermal properties of the composites were conducted. The outcomes showed
that the thermal properties of the nanocomposites were strikingly improved in comparison with the virgin polymer material. The added nano-sized particles occupied the pores of PMMA became advantageous for the thermal conductivity of the composite. The upgrade of thermal properties of phase change composites is a promising method to accomplish high energy storage proficiency in a different area of thermal energy storage applications, like solar oriented energy storage and energy conservation in buildings and structures.

The pristine sample of PMMA at room temperature has the thermal conductivity value of 0.11 W/m K and the 6 % sample composite has the value of 0.19 W/m K. This result indicates the enhancement of thermal conductivity by 72 %. Because of the enhanced thermal conductivity and stability, the phase change composite has far-reaching potential in applications, for example, solar-based thermal energy storage and waste heat recovery process. The benefits of exemplified PCM over the others are essentially about the all-around upgraded thermal conductivity and longer lifetime because of the conductive shell which additionally shields the PCM from direct contact with the outside environment. Additionally, it decreases the issues related to phase separation and spillage.

Phase change composites hence open another way for researchers to investigate and find in-depth to the better application level of materials and procedures so that the phase change materials can be utilized with much better values.

References
[1] Amit Kumar Mishra, B.B. Lahiri, John Philip, Thermal conductivity enhancement in organic phase changematerial(phenol-watersystem)uponadditionofAl2O3,SiO2andTiO2nano-inclusions.Molliq
[2] Atul Sharma, C. R. Chen, Solar Water Heating System with Phase Change Materials, International Review of Chemical Engineering (I.RE.CH.E.), Vol. 1,280-289(2009)
[3] E. Abu-Nada , Z. Masoud, A.Hijazi, Natural convection heat transfer enhancement in horizontal concentric annuli using nanofluids, International Communications in Heat and Mass Transfer 35 657–665(2008)
[4] Hyunwoo Oh, Jooheon Kim, Fabrication of polymethyl methacrylate composites with silanized boron nitride by in-situ polymerization for high thermal conductivity, in composites science and technology, Renewable and Sustainable Energy Reviews 11 797–817.172(2019)
[5] JaumeGasía, LaiaMiró, Alvaro de Gracia, Experimental Evaluation of a Paraffin as Phase Change Material for Thermal Energy Storage in Laboratory Equipment and in a Shell-and-Tube Heat Exchanger, Department of Materials Science and Metallurgical Engineering, Universitat de Barcelona, International Journal of Heat and Mass Transfer 46. 3639–3653.(2016).
[6] Miqdam T Chaichan, Shaimaa H Kamel, Abdul-Mohsen N M Al-Ajeely, Thermal conductivity enhancement by using nano-material in phase change material for latent heat thermal energy storage systems. saussureaissn: 0373-2525 vol. 5(6):pp 48-55, research article(2015).
[7] Mohammad Ali Fazilati and Ali Akbar Alemrajabi, “Phase change material for enhancing solar water heater, an experimental Approach”, Department of Mechanical Engineering, Isfahan University of Technology, Isfahan 84156-83111: pp 1-8(2013)
[8] Mohammad Mehrali, Sara TahanLatibari, “From rice husk to high-performance shape stabilized phase change materials for thermal energy storage”, Advanced Material Research Center, Department of Mechanical Engineering, University of Malaya, Kuala Lumpur, Malaysia, Renewable and Sustainable Energy Reviews 11 512–523.(2016)
[9] MoloudNourani, Nasser Hamdami, JavadKeramat, Ahmad Moheb, Mohammad Shahedi, Thermal behavior of paraffin-nano-Al2O3 stabilized by sodium stearoylactylate as a stable phase change material with high thermal conductivity Department of Food Science and Technology, College of
[11] Mushtaq Ahmad, Kamran Rasool, Structural and Electrical Properties of Zinc Sulfide Nanoparticles, Micro and Nano Devices Group, Department of Chemical and Materials Engineering Pakistan Institute of Engineering and Applied Sciences Islamabad, Pakistan, Applied Thermal Engineering 27 1327–1337. (2015)