International Journal of Technology 10(6): 1112-1119
ISSN 2086-9614

EXPERIMENTAL INVESTIGATION OF THERMAL STABILITY AND ENTHALPY OF EUTECTIC ALKALI METAL SOLAR SALT DISPERSED WITH MGO NANOPARTICLES

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(Received: August 2019 / Revised: October 2019 / Accepted: October 2019)

ABSTRACT

In this study, nanocomposites containing a pre-defined mass ratio of solar salt ($NaNO_3$-KNO_3: 60–40 wt.%) dispersed with magnesium oxide (MgO) nanoparticles with nominal sizes of 100 nm were prepared in solid and liquid states. The proposed amounts of sodium nitrate and potassium nitrate were added to certain amounts of ultrapure deionized (DI) water comprising a 5 wt.% concentration of MgO nanoparticles. Afterward, the prepared mixture was placed in a dry oven to mix in a liquid state to obtain well-dispersed nanocomposites. Scanning electronic microscopy (SEM) was conducted to evaluate the uniformity of synthesized, molten salt–based magnesium oxide–nanoparticles, revealing a uniform dispersion. Enthalpy and melting point measurements were performed using differential scanning calorimetry. The experimental results of solar salt–based MgO indicated decreases in melting point and enthalpy by 7% and 12.4%, respectively. The reduction of enthalpy indicated that, with the addition of magnesium oxide to solar salt, the final nanocomposite tends to have more exothermic reactions and enhanced thermal conductivity performance at the melting point. Lower melting points constitute one of the major concerns regarding molten salt–based nanofluids. MgO nanoparticles with a concentration of 5 wt.% have a melting point decreased by 7%. Mass loss and thermal stability measurements were conducted using thermogravimetric analysis (TGA). The experimentally acquired results revealed an increment of decomposition temperature from 734.29°C to 750.73°C, demonstrating the enhancement of thermal stability at high temperatures.

Keywords: Enthalpy; MgO; Solar salt; Thermal stability

1. INTRODUCTION

Renewable energy sources are promising replacements for petroleum resources. Demand for green and renewable energy has significantly attracted the interest of scientists, many of whom have studied solar energy as a clean source of energy (Thirugnanasambandam et al., 2010). The productivity of solar thermal systems depends on the efficient conversion of thermal energy from the sun. Light-to-heat conversion at high temperatures (above 300°C) is more desirable to access a broad range of operation temperatures (Kusrini & Kartohardjono, 2019). In solar thermal systems, storage and transportation of thermal energy occurs using heat transfer fluids

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Permalink/DOI: https://dx.doi.org/10.14716/ijtech.v10i6.3568

(HTFs) and thermal energy storage (TES) materials (Hawachi et al., 2014). Inclusion of nanoparticles in HTFs in volume concentrations (typically lower than 10%) generates nanofluids (NFs). The anomalous increments of NFs in thermal conductivity and thermal storage are well-known. Conventional NFs, such as water-based ones, were initially introduced by Choi and Eastman (1995). Eastman et al. (2004) later obtained a 60% enhancement of NF thermal conductivity over water by the dispersion of CuO nanoparticles at a 5% volume concentration. Carbon-based nanostructures and/or ceramic and metallic nanoparticles (NPs) have been utilized as additives to water-based fluid (Huang et al., 2010). Ethylene glycol, engine oil, and organic oil have all been employed as base fluids for NFs (Kalogirou, 2004). These traditional NFs, however, are not applicable to several industrial processes that require the application of fluids that operate at temperatures higher than those suitable for the aforementioned fluids. Lower thermal stability up to 400°C is another drawback of conventional NFs. These limitations have encouraged scientists to study new classes of NFs, a tendency that might lead to enhancing the efficiency of systems and be suitable in terms of cost effectiveness. Molten salts can operate at high temperatures, thus improving procedural efficiency, as they possess efficient thermal properties to operate as TES materials in concentrated solar power (CSP) systems. The low costs of molten salts and their higher thermal stabilities (up to 600°C) constitute a prominent advantage in these types of applications.

On the other hand, the industrial implementation of molten salts is affected by their low thermal conductivity properties (Mahian et al., 2013). The optimization of these thermophysical properties is the key to applying these salts in TES systems and new HTFs in CSP facilities. With the aim of fulfilling this need, Shin and Banerjee developed a new kind of NF eight years ago at the University of Texas at Arlington (Shin & Banerjee, 2011a) by utilizing a mixture of binary inorganic salt (Li_2CO_3-K_2CO_3: 62-38 by mol) as the base fluid and SiO_2 as the additive. The specific heat capacity (C_p) of the developed mixture revealed more than 100% enhancement with 1% volume concentration of NPs. Shin and Banerjee suggested that applying their NF would reduce costs by 50% with a combination of higher operating temperatures (higher thermodynamic efficiency) and the diminution of materials.

Phase change materials (PCMs) are preferable to TES in terms of large enthalpy changes (Putra et al., 2016). These crucial changes occur during freezing and melting (phase changes). Inorganic eutectic alkali metal PCMs (molten salts) have enormous capabilities as TES (Shukla et al., 2009). Hence, molten salts have been a subject of intense research for scientists around the world. Extensive amounts of researches have focused on organic PCMs, such as paraffin waxes (Huang et al., 2009), but few inorganic PCMs have been investigated for operation in high-temperature applications. Nitrate-based molten salts have received more attention due to their availability in a wide range of temperatures (Lachheb et al., 2016). Solar salt is a eutectic, nitrate-based, alkali molten salt with combination of 60 wt.% sodium nitrate and 40 wt.% potassium nitrate. This type of molten salt has a relatively high melting point and high energy storage density (Vignarooban et al., 2015). According to the literature, solar salt has efficient high thermal stability (Wang et al., 2015). Solar salt has also been utilized as a heat storage medium (Myers et al., 2016). One of its major drawbacks, however, is its relatively low thermal conductivity, which affects its thermal storage performance (Gimenez-Gavarrell & Fereres, 2017).

The present study investigates the effects of magnesium oxide dopant nanoparticles on the thermophysical properties of nitrate-based molten salt. A conventional solar salt ($NaNO_3$-KNO_3: 60–40 wt.%) is utilized as a base fluid, and the suspended nanoparticles are MgO (5 wt.%). Well-dispersed molten salt–based NF was synthesized in a two-phase preparation method. The first step was physically mixing and the second step conducted in a melting state using an oven at high temperature. The melting point and enthalpy of alkali metal molten salt with and without nanoparticles were measured using differential scanning calorimetry (DSC). The measured melting point of the synthesized molten salt was compared with the literature to verify its accuracy. The nanostructures of the synthesized molten salt with and without NPs were observed using scanning electronic microscopy (SEM) images. Adding magnesium oxide nanoparticles at 5 wt.% has increased exothermic reactions are the melting point. The melting point also fell by 7%, which prevented the solidification of the solar salts on the walls of heat exchanger surface. This reduction in melting point is one of the main drawbacks of solar salts.

2. MATERIALS AND METHODS

Sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) were procured from R&M Chemicals Co. and Fisher Chemicals, respectively. Magnesium oxide (MgO) nanoparticles with purities of 99% or greater were procured through Alfa Aesar.

2.1. Preparation of Eutectic Alkali Metal Solar Salt

The average particle sizes of the magnesium oxide nanoparticles were confirmed with the manufacturer to be 100 nm. The method of synthesizing eutectic alkali metal solar salt was similar to that adopted by Shin and Banerjee (2011a) with some modifications. Initially, 28.5 g of sodium nitrate ($NaNO_3$) was measured using a microbalance (TX323L, Unibloc) and was added to a glass beaker (600-ml volume). Then 50 g of ultrapure deionized water (model of direct-Q UV, Merck) was poured into the beaker. The weight of the ultrapure DI water was as same as the final solid mixture of molten salt–based magnesium oxide. The glass beaker with the sodium nitrate and DI water was placed on a hot plate (RCT Basic, IKA) and stirred for 15 minutes at 600 rpm using a magnet stirrer. The temperature of the hot plate was maintained at 50°C to ensure the uniform dissolution of the sodium nitrate in the DI water. Afterward, 19 g of potassium nitrate (KNO_3) was added to the beaker followed by stirring for 15 minutes at 600 rpm. The synthesized molten salt dispersed well in the DI water. Then 2.5 g of magnesium oxide (5 wt.%) was poured into the glass beaker, and the same stirring protocol was repeated. The synthesized molten salt–based magnesium oxide was sonicated for 100 minutes using an ultrasonic probe sonicator (FS-1200N) with an on-time of 7 seconds and an off-time of 3 seconds. The final sample was placed on the hot plate at 120°C and stirred at 200 rpm to evaporate water from the sample. The final stage of synthesizing was performed in an oven (VO 500, Memmert, Germany) at 250°C. The eutectic molten salt mixture with magnesium oxide nanoparticles was heated for 2 hours to remove any chemically bonded (hydrated) water molecules. The pure eutectic of sodium nitrate and potassium nitrate was synthesized with the same protocol (Shin & Banerjee, 2011b).

2.2. Characterization Method

The enthalpy and melting point of the samples were measured by using DSC (1000/C Linseis, Germany). Consistent methods of testing and characterizations were followed for all samples to ensure of the reliability of results, a significant point regarding the characterization of molten salt–based NFs. For DSC measurement, the heating rate of all samples was fixed at 10°C/min from 25°C up to 500°C. The high-density signal carrier (HDSC) value was fixed at 250 ųV to obtain a higher resolution, and mass value was considered 14 mg for all measured samples. Thermal stability analysis was performed using TGA (4000, PerkinElmer) from 30°C up to 800°C. Mass loss assessment and thermal stability evaluation were conducted at a fixed heating rate of 10°C/min under nitrogen gas (flow rate of 20 ml/min). The pans utilized for this measurement were alumina crucibles, considering consistent mass values for all samples to achieve comparable results. The dispersion and homogeneity of the synthesized alkali metal solar salt dotted with magnesium oxide nanoparticles was checked with SEM (model of VEGA3, Tescan) and energy-dispersive x-ray spectroscopy (EDX, Oxford Instruments). A digital ion coater (model of Coxem Co., SPT-20) was utilized for Pt coating of the samples in a fixed current of 3 mA for 300 seconds for the purpose of SEM imaging.

3. RESULTS AND DISCUSSION

Figure 1 shows the experimental results and derivative curves of the melting point and enthalpy values for pure eutectic alkali solar salt and molten salt–based NFs obtained from differential scanning calorimetry. The results are represented as a function of temperature. To verify the accuracy of the measurement method, the melting point of the pure eutectic solar salt was measured and compared with literature data. The measured melting point of solar salt was 225.3°C, which is consistent values reported in the literature (222°C) (Lasfargues et al., 2015). The estimation of measurement uncertainty was 1.5%. Figure 1 shows the decrement of the melting point for synthesized eutectic alkali metal solar salt dotted with magnesium oxide nanoparticles by 7% in comparison with pure eutectic solar salt. The measured melting point obtained through DSC measurement was 210.7°C. One of the main concerns regarding molten salts is their melting and freezing temperatures. In this study, we prove experimentally that, with the inclusion of magnesium oxide (MgO) nanoparticles at 5% concentration in volume, the melting point decreases. The enthalpy of synthesized molten salt–based NF fell from 118.73 J/g, that of pure eutectic molten salt, to 104 J/g. The increment of exothermic reaction at the melting point of the synthesized solar salt-based MgO nanoparticles represents heat release at that point. The enthalpy of a system is favorable when reduction (exothermic reaction) occurs over the reaction. Enthalpy is a central factor in terms of thermophysical properties, because the reduction of the enthalpy value means that new chemically bonds are made. This verifies the validity of the synthesized molten salt–based NFs and the effects of MgO dopant nanoparticles on the base fluid.

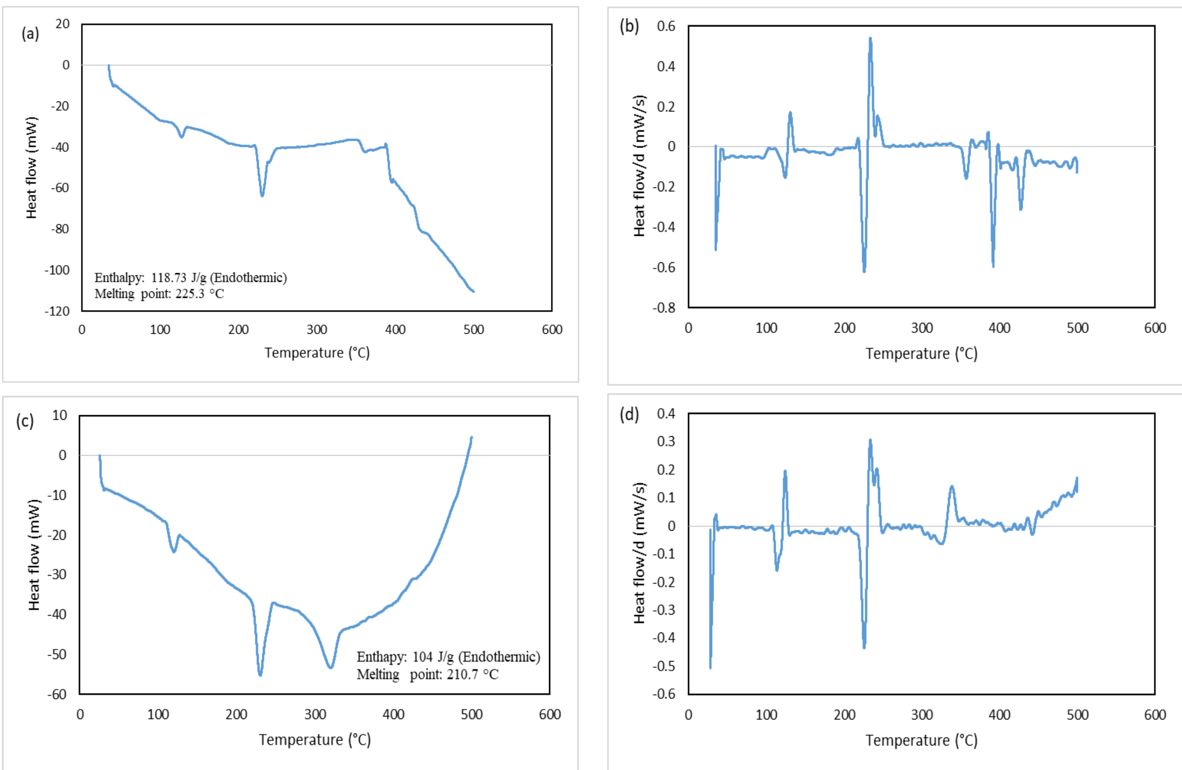

Figure 1 Differential scanning calorimetry (DSC) of: (a) pure eutectic solar salt; (b) the derivative curve of pure eutectic solar salt; (c) the synthesized alkali solar salt dotted with MgO nanoparticles; and (d) the derivative curve of synthesized alkali solar salt dotted with magnesium oxide nanoparticles

SEM and EDX were performed to evaluate the homogeneity and dispersion of nanoparticles in the synthesized eutectic alkali solar salt and elemental analysis, respectively. The existence of globe-shaped nanostructures and a few extended nanostructures is evident from SEM images of magnesium oxide nanoparticles (Figures 2a and 2b). The synthesized pure eutectic solar salt (Figures 2c and 2d) showed good dispersion of the sodium nitrate and potassium nitrate.

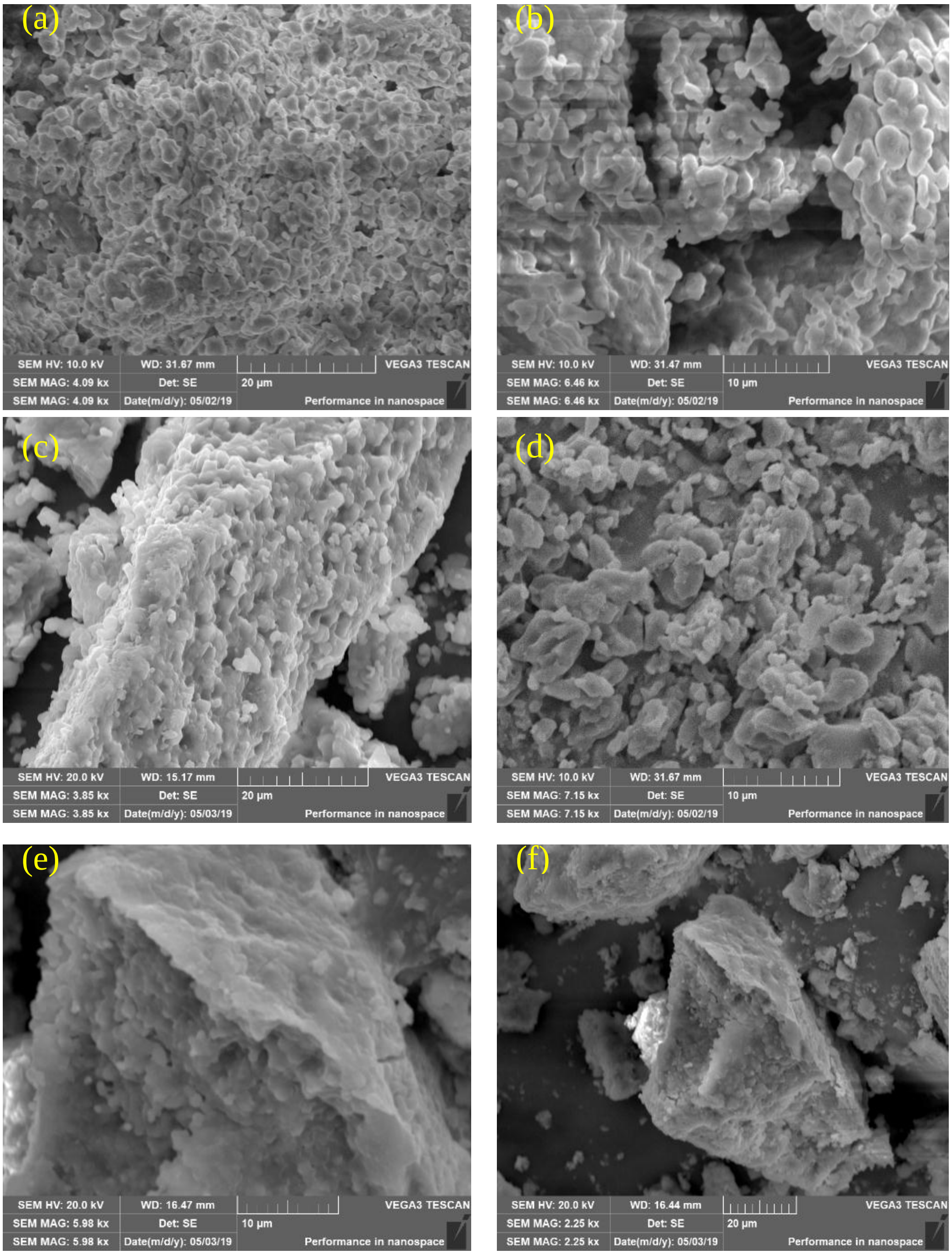

Figure 2 Scanning electronic microscopy (SEM) images for (a, b) magnesium oxide, (c, d) synthesized pure eutectic solar salt, and (e, f) synthesized eutectic alkali metal solar salt dotted with magnesium oxide nanoparticles

EDX spectroscopy analysis of the pure eutectic solar salt showed the existence of 26.04, 13.44, and 60.51 wt.% of sodium, potassium, and oxygen, respectively. The atomic percentages of sodium, potassium, and oxygen were 21.54%, 6.54%, and 71.92%, respectively. Energy-dispersive spectroscopy analysis for the synthesized alkali metal solar salt dotted with MgO nanoparticles indicated a good dispersion of nanoparticles in the matrix of molten salt. Figure 2 (e and f) shows the SEM images of synthesized molten salt–based magnesium oxide NFs (MSBNFs). Chain-like structures due to the presence of MgO nanoparticles are evident in the images. The EDX results for the MSBNFs indicated 21.19, 25.09, 6.99, and 46.73 wt.% for sodium, potassium, magnesium, and oxygen, respectively. The wt.% values of the components were perfectly consistent with the pre-defined mass fraction of utilized materials. The achieved atomic percentages for sodium, potassium, magnesium, and oxygen were 19.32%, 13.45%, 6.03%, and 61.21%, respectively. The synthesized molten salt ($NaNO_3$-KNO_3: 60-40 wt.%) consisting of 5 wt.% MgO nanoparticles was verified with the atomic percentage results acquired by EDX.

Thermogravimetric analysis (TGA) was employed to measure mass loss and thermal stability. The heating rate was fixed at 10°C/min and the measurements were performed at temperature range of 30–800°C. The same mass of samples was placed into alumina crucibles to ensure the comparability of the results. The experimentally achieved results (Figures 3 and 4) indicated the increment of thermal stability for MSBNFs in comparison to pure molten salt from 734.29°C to 750.73°C. The chain-like structures (SEM images) due to the presence of magnesium oxide nanoparticles and the interfacial interacting between molten salt molecules and induced nanoparticles might be the consequence of the enhancement in thermal stability.

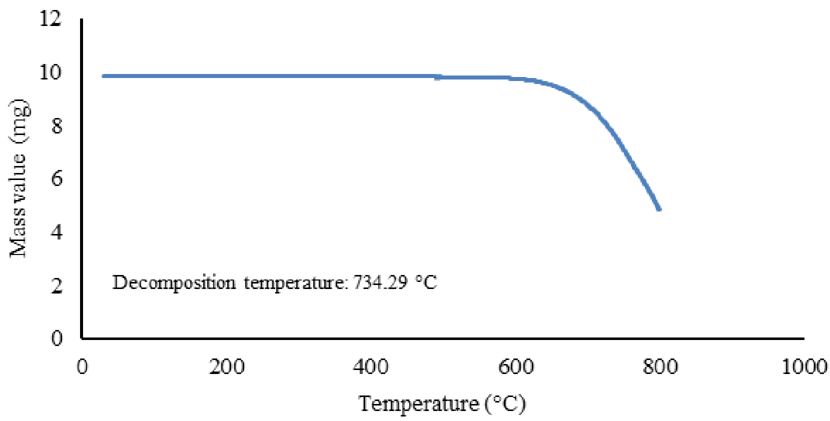

Figure 3 TGA for pure eutectic alkali metal solar salt

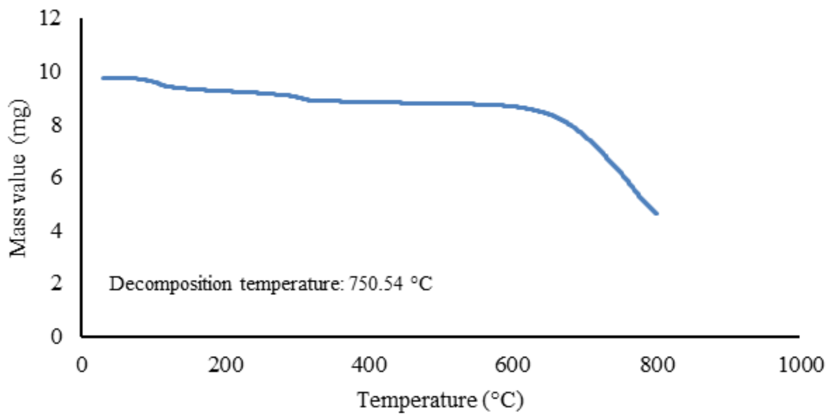

Figure 4 TGA for eutectic alkali metal solar salt dotted with magnesium oxide nanoparticles

4. CONCLUSION

In conclusion, the eutectic alkali metal solar salt dotted with a 5% concentration by volume of MgO nanoparticles and the pure eutectic solar salt were synthesized using a two-phase method. The alkali metal molten salts with and without nanoparticles were mixed physically followed by mixing at melting state in an oven at high temperature. The resultant samples were well-dispersed. Enthalpy and melting point measurements were performed using DSC. The enthalpy of the MSBNFs decreased by 12.4%, which demonstrates a more exothermic reaction at the melting point. The experimentally achieved data indicated a melting point decrement for MSBNFs by 7% in comparison to pure eutectic solar salt. SEM and EDX indicated chain-like structures in the resultant NF, and elemental analysis using EDX showed good dispersion of magnesium oxide nanoparticles. Thermal stability measurements expressed an enhancement of thermal stability in solar salt induced with a 5% concentration by volume of MgO nanoparticles. The experimentally acquired results revealed the increment of decomposition temperature from 734.29°C to 750.73°C.

5. ACKNOWLEDGEMENT

R. Saidur would like to acknowledge the financial support provided by the Sunway University through the project no. STR-RCTR-RCNMET-001-2019.

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