Novel (Organic Phase-Change Materials−Ceramics) Nanocomposites for Solar Energy Storage and Release

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In this paper, preparation of novel organic phase-change materials−ceramics nanofluids with high efficiency for thermal-energy storage and release is carried out, namely, the (PVA−PAA−NbC−H$_2$O) nanofluids' and (PVA−PAA−NbC) nanocomposites' films are fabricated. The structural and dielectric properties of (PVA−PAA−NbC) nanocomposites are studied. The results show that the dielectric constant and dielectric loss of nanocomposites decrease with increase in frequency, while the electrical conductivity increases with increase in frequency. The dielectric constant, dielectric loss and electrical conductivity of (PVA−PAA) blend increase with increase in NbC nanoparticles' concentration. The results of thermal-energy storage and release for (PVA−PAA−NbC−H$_2$O) nanofluids show that the melting and solidification times decrease with increase in NbC nanoparticles' concentration.

У даній роботі здійснюється підготовка нових органічних фазово-змінних матеріялів — нанофлюїдів кераміки з високою ефективністю для зберігання та вивільнення теплової енергії, а саме, виготовлено плівки нанокомпозитів ПВА−ПАА−NbC−H$_2$O та ПВА−ПАА−NbC. Вивчаються структурні та діелектричні властивості нанокомпозитів ПВА−ПАА−NbC. Результати показують, що діелектрична проникність і діелектричні втрати нанокомпозитів зменшуються зі збільшенням частоти, хоча електропровідність збільшується зі збільшенням частоти. Діелектрична проникність, діелектричні втрати й електропровідність суміші ПВА−ПАА збільшуються з підвищенням концентрації наночастинок NbC. Результати зберігання та вивільнення теплової енергії для нанофлюїдів ПВА−ПАА−NbC−H$_2$O показують, що часи топлення і твердіння скорочуються з підвищенням концентрації наночастинок NbC.

Key words: nanofluids, phase changes, ceramics, nanocomposites, conductivity.

1. INTRODUCTION

Several studies are carried out on phase change materials over the last three decades. Phase-change materials (PCM) are very interesting due to their absorbing of large amount of energy as latent heat at a constant phase-transition temperature. These materials can be used for passive heat storage. Major disadvantage of the PCM is related to their low thermal conductivity, which impedes high rate of charge and discharge of heat flux. These types of materials have many useful properties including heat source at constant temperature, heat recovery with small temperature drop, high storage density, melting point that matches the applications, low vapour pressure at the operational temperature, and chemical stability and noncorrosiveness. These properties allow the PCM to be used in many industrial applications such as thermal storage of solar energy, thermal management of electronic devices, thermal storage in buildings, cooling of engines, *etc.* An ever-increasing world population combined with a strong rise in energy demand has led to a significant environmental crisis that already shows its clear beginning. Energy demands in the commercial, industrial and utility sectors vary on daily, weekly and seasonal bases, *e.g.*, solar heating, waste heat recovery, building space heating and cooling, thermal comfort, electronic cooling, and reducing the HVAC equipment size by levelling or shifting the peak load demand. These demands can be satisfied by smoothing the temporal variations with the help of thermal-energy storage (TES) systems. Energy storage is an effective approach to increase energy efficiency and energy savings, since many energy sources are intermittent in nature. It is the most appropriate way and method to correct the gap between the demand and supply of energy. Energy storage is not only plays an important role in conservation of the energy but also improves the performance and reliability of wide range of energy systems, and become more important where the energy source is intermittent such as solar. The TES is recognized as one of the key technologies for energy storage in the future. Three major methods are currently considered for thermal storage: sensible heat, latent heat, and thermochemical heat. To store/release passively thermal energy, builders have used sensible heat storage for centuries, but a much larger volume of material is required to store the same amount of energy in comparison to latent heat storage. Latent heat energy storage, using the

PCM, is the most effective technique because of its advantages of high energy-storage density and isothermal characteristics [1].

With the rapid development of construction industry, more and more lightweight building materials are applied in high-rise buildings. Because of the low thermal capacity of lightweight materials, indoor temperature tends to fluctuate under climate change. PCMs with their high heat storage capacity have been considered as potential latent storage materials widely studied in building thermal storage. PCMs absorb redundant heat in daytime, the stored thermal energy release into indoors at night. Through this thermal energy circulation, the indoor temperature maintains in a relative comfortable temperature range. The traditional PCMs are mainly divided into organic materials and inorganic materials. Several reviews have concluded a large category of candidate materials for latent heat storage. Organic materials such as fatty acids and their eutectic mixtures have superior properties over inorganic materials like litter super cooling, high latent heat, less volume change, good thermal, and chemical stability after repeated cycles [2].

Abundance of renewable energies available in nature should be harnessed and utilized to meet the growing power demand for sustained future. Renewable energy systems play a vital role in energy savings and reduction of global gas emission to have a pollution free environment for future generations. Solar energy claims to be the primary source among various renewable energy sources, which is intermittent and uncertain by its nature. Henceforth a need arises to develop thermal storage systems to store the available excess energy for later use. Thermal energy storage system should possess good storage capacity, high efficiency, quick charging/discharging, cost effective, and hazard free. The PCM with their heat storage and releasing behaviour have found suitable for latent heat storage systems that can be operated at wide range of temperatures. High-energy process of PCMs (latent heat of vaporization) is not preferred due to their large density changes, which need additional support equipment. Hence, latent heat of fusion of PCMs is utilized for thermal applications. Incorporation of nanomaterials could possibly increase the thermal conductivity of the PCMs with their high surface area-to-volume ratio. Aluminium oxide (Al_2O_3), copper (Cu), copper oxide (CuO), gold (Au), silver (Ag), silicon carbide (SiC), titanium carbide (TiC), titanium oxide (TiO_2), and carbon nanotubes were some of the nanoparticles used for thermal applications [3].

The low heat flux achieved due to the low thermal conductivity of most PCMs, which drastically affects the melting and solidification performance of the system, and widespread use of latent heat stores have not yet been realised. A larger heat flux can be achieved by enhancing the effective thermal conductivity. Different ap-

proaches have been proposed to overcome this problem: use of metal thin strips, porous metals, porous graphite, metal foam matrix and carbon fibres are among the common techniques used to enhance the effective thermal conductivity of PCMs. The presence of the nanoparticles in the PCMs increases significantly the effective thermal conductivity of the fluid and consequently enhances the heat transfer characteristics [4].

2. MATERIALS AND METHODS

The (PVA−PAA−NbC) nanocomposites are prepared by dissolving 1 gm of polyvinyl alcohol (PVA) and polyacrylic acid (PAA) in 30 ml of distilled water with concentrations of 0.85 wt.% PVA, 0.15 wt.% PAA by using magnetic stirrer to mix the polymers for 1 hour to obtain solution that is more homogeneous. Niobium carbide nanoparticles (NbC NPs) were added to polymer blend with different concentrations of 1.5, 3, 4.5 and 6 wt.%. The thermal energy storage and release include analysing the melting and solidification characteristics of nanofluids during heating and cooling processes. The water and nanofluids were used as the heat-transfer fluid, whose temperature can be varied from 20°C to 90°C with stirrer and measuring the temperature of nanofluids during the heating and cooling processes by digital device. The casting method is used to prepare the films of nanocomposite samples in the template (Petri dish has diameter of 10 cm). The dielectric properties of samples were examined with frequency range from 100 Hz to $5 \cdot 10^6$ Hz by using LCR meter type (HIOKI 3532-50 LCR HI TESTER).

The dielectric constant (ε') of (PVA−PAA−NbC) nanocomposites is determined by the following equation [5]:

$$\varepsilon' = C_p/C_o \, , \tag{1}$$

where C_p is parallel capacitance and C_o is vacuum capacitor.

The dielectric loss (ε'') of nanocomposites is given by the following equation [6]:

$$\varepsilon'' = \varepsilon'D, \tag{2}$$

where D is dispersion factor of (PVA−PAA−NbC) nanocomposites.

The A.C. electrical conductivity is calculated by the following equation [6]:

$$\sigma_{A.C.} = w\varepsilon''\varepsilon_o, \tag{3}$$

where w is the angular frequency.

3. RESULTS AND DISCUSSION

The dielectric measurements have been carried out by a capacitive arrangement technique using LCR meter in the frequency range from 100 Hz to 5 MHz at room temperature. The polarized molecules or atoms in dielectric medium can align in accordance with the applied electric field, which implies electromagnetic energy to be transferred into materials. Figure 1 shows the behaviour of frequency-dependent dielectric constant of PVA–PAA and NbC/PVA–PAA at room temperature. At lower frequencies, high values are noticed, which indicate that the four polarizations are active, whereas at higher frequencies, due to the high periodic field, reversal resulting in an inertia of the dipolar moments causes the reduction in the values. An independent frequency trace is noticed beyond 1 kHz but a substantial modification is achieved by the incorporation of NbC nanoparticles in the matrix. A giant polarizability is noticed because the particles are relatively free to move in extended trajectories between the electrodes. The NbC exhibits a strong ionic polarization and has a high value of static permittivity, so, the increment in the values of relative permittivity for the nanocomposites due to these mobile charge carriers is expected.

Figure 2 illustrates the frequency-dependent dielectric loss of PVA–PAA and NbC/PVA–PAA at room temperature. This curve possessed a similar trace as the plot of dielectric constant, and the changes in steepness are observed at the same frequency region. The phenomenon can be identified as interfacial polarization (IP) where the high values are presented at the low frequency region. At higher frequencies, the dipoles cause an inertia results from the electri-
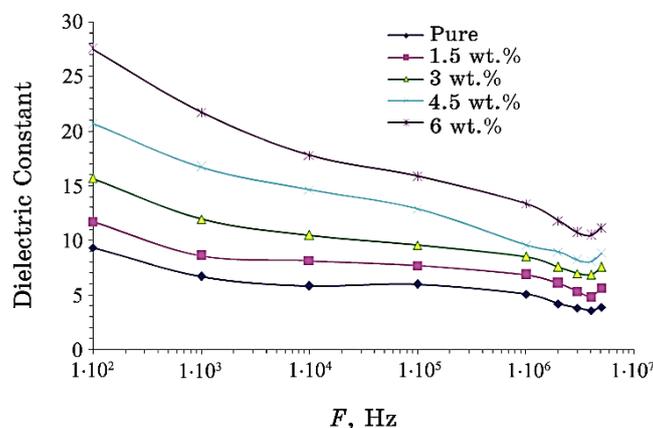
Fig. 1. Behaviour of frequency-dependent dielectric constant of PVA–PAA and NbC/PVA–PAA at room temperature.
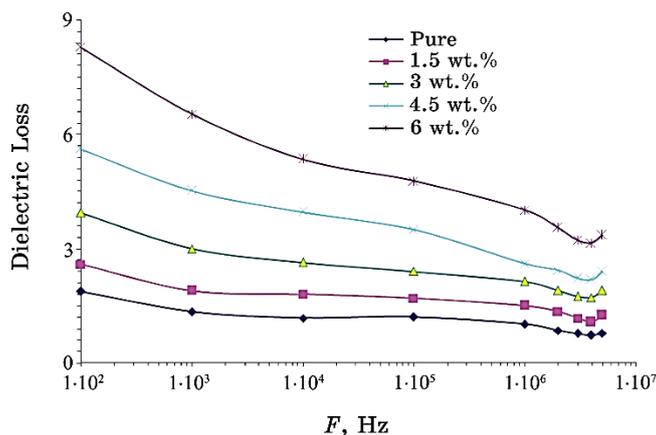
Fig. 2. Frequency-dependent dielectric loss of PVA−PAA and NbC/PVA−PAA at room temperature.
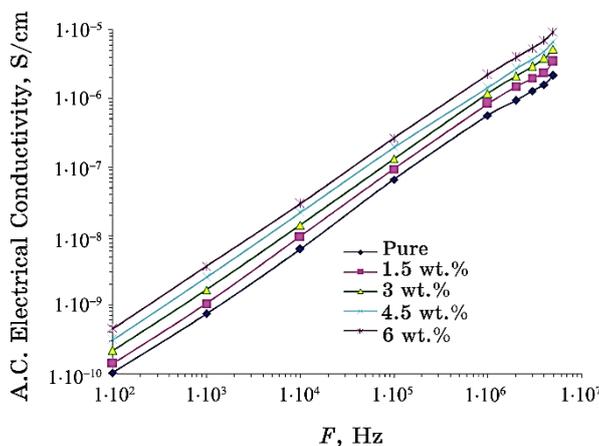
Fig. 3. Variation of the A.C. electrical conductivity of the (PVA−PAA−NbC) nanocomposites with frequency at room temperature.

cal heterogeneity known as Maxwell−Wagner−Sillars effect [7−10].

Figure 3 shows the variation of the A.C. electrical conductivity of the (PVA−PAA−NbC) nanocomposites with frequency at room temperature.

As the frequency decreases, the more and more charge is accumulated at the electrode and electrode interface that leads to a decrease in the number of mobile ions and, eventually, to a drop in the conductivity at low frequencies. In the high frequency region, the conductivity increases with the frequency due to the mobility of charge carriers and the hopping of ions from the infinite cluster.

As a result, the ion exchange process occurs effectively in the high-frequency region.

From Figures 1–3, the dielectric constant, dielectric loss and electrical conductivity increase as niobium carbide nanoparticles' concentration increases. This result can be attributed to the increase in conductivity as a result of the increase charge-carrier density in polymer matrix. At low niobium carbide nanoparticles' concentration, the dielectric constant and dielectric loss values are low. The increase of niobium carbide nanoparticles' concentration caused
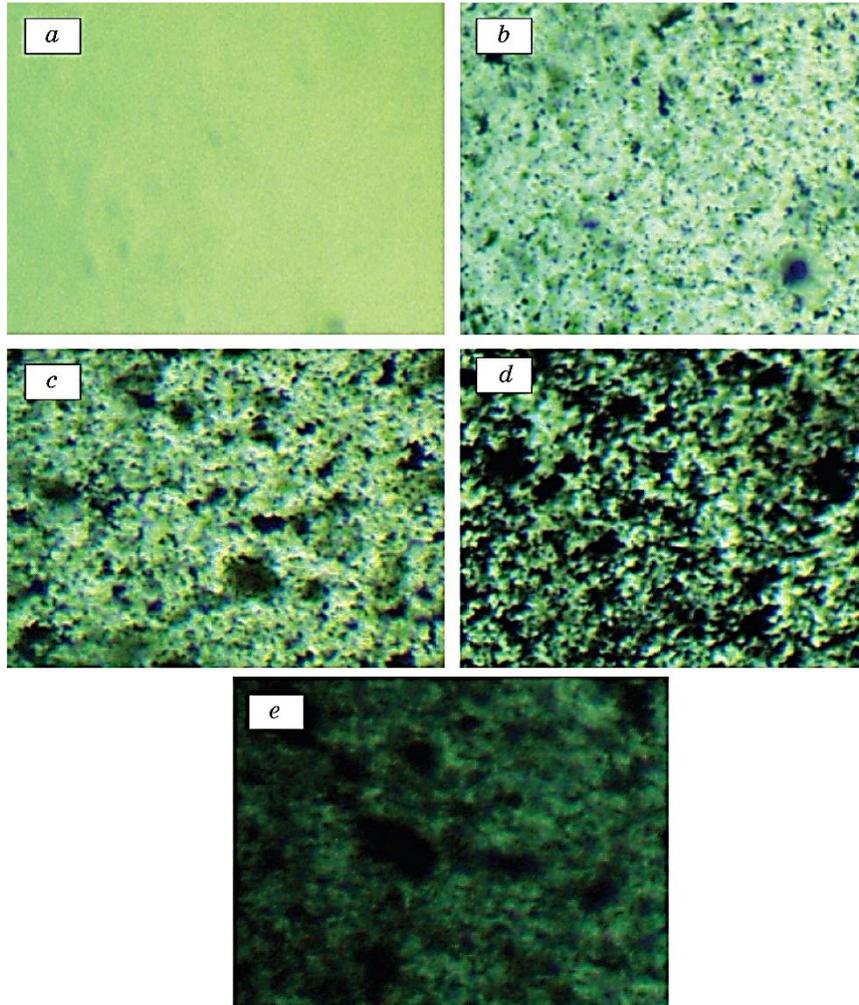
Fig. 4. Photomicrographs (×10) for (PVA–PAA–NbC) nanocomposites: (*a*) for (PVA–PAA); (*b*) for 1.5 wt.% NbC; (*c*) for 3 wt.% NbC; (*d*) for 4.5 wt.% NbC; (*e*) for 6 wt.% NbC.

an increase in the average number of concentrations among the niobium carbide nanoparticles. At high concentrations of niobium carbide nanoparticles, the dielectric constant and dielectric loss are due to formation of a continuous network of nanoparticles through the nanocomposite [11−14], as shown in Fig. 4.

The thermal-energy storage and release were investigated during the melting and solidification processes, as shown in Figs. 5 and 6. From these figures, the melting and solidification times decrease with increase in NbC nanoparticles. We see that there is an apparent heat-transfer enhancement effect by introducing NbC nanoparticles into the (PVA−PAA) blend, because NbC nanoparticles im-
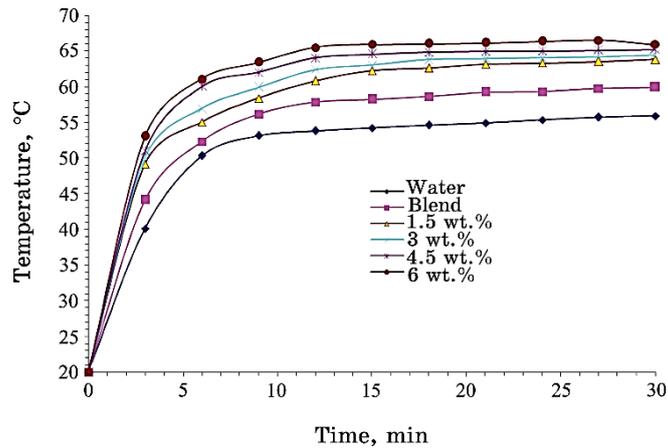

Fig. 5. Melting curves of (PVA−PAA−NbC−H_2O) nanofluids.
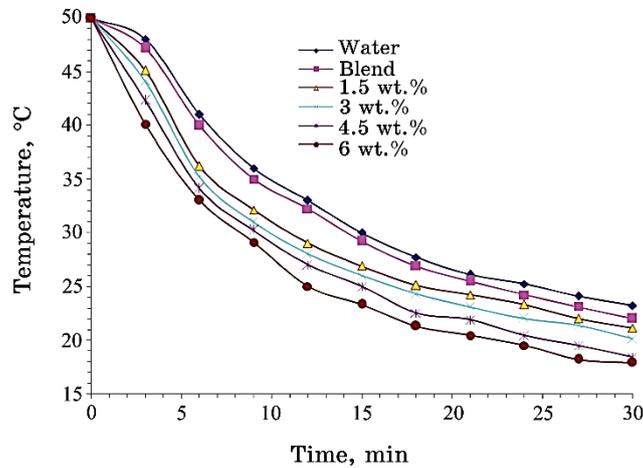

Fig. 6. Solidification curves of (PVA−PAA−NbC−H_2O) nanofluids.

prove the thermal storage/release performance of the (PVA–PAA) blend. Based on the afore-mentioned results, (PVA–PAA–NbC–H₂O) nanofluid can be considered as a potential building thermal-energy storage material to keep comfort indoor environment and save energy. This is a useful method to improve completely the thermal conductivity of organic materials. Furthermore, faster rates of melting and solidification of nanocomposites would be evident to the thermal conductivity enhancement of base material [15–22].

4. CONCLUSIONS

1. The dielectric constant, dielectric loss and A.C. electrical conductivity of (PVA–PAA) blend increase with increase in niobium carbide nanoparticles' concentration.
2. The dielectric constant and dielectric loss of (PVA–PAA–NbC) nanocomposites decrease with increase in frequency, while the A.C. electrical conductivity increases with increase in frequency.
3. The (PVA–PAA–NbC–H₂O) nanofluids have high efficiency for solar-energy storage and release with low cost. The melting and solidification times decrease with increase in NbC nanoparticles' concentration.

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