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Abstract

Thermal behavior of nanocomposite phase change materials, Myo-inostol (MI) (a sugar alcohol)added with graphene nanoplatelets (GNN) as a solar thermal energy storage system,for use in the temperature range of 100°C to 260°C was studied.GNN isadded to MIwithmass fraction of 1.0, 2.0 and 3.0wt. %. Thermal and chemical stability of MI and MI-GNNwere investigatedbefore and after 50 thermal cycles. Results showed that thedispersion of GNN into pure MI was effective, no crystal change andchemical reaction had taken place between GNN and MI before and after thermal cycling,only physical interaction between them had taken place.GNN particles were dispersed throughout the MI with small aggregates. Theheat of fusion was found to decrease by 14.13%, 15.06% and 17.63% and heat of solidification by 13.02%, 23.12% and 29.68% for MI-GNN with 1.0, 2.0 and 3.0 wt. % of GNN added to MI respectively

Keywords	Phase change materials, Thermal cycling, Latent heat of fusion, Latent heat of solidification, Graphene nanoplatelets
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From   28th December2016

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To

The Editor-in-Chief

Thermal Science and Engineering Progress.

Respected Sir,

I am pleased to submit the manuscript entitled **"Graphene nanoplatelets enhanced myo-inositol for solar thermal energy storage"** by Durgesh Kumar Singh, S. Suresh, H. Singh for consideration in publishing in the esteemed journal of **"**Thermal Science and Engineering Progress**"**. The manuscript has been updated with the suggested technical checks. It is certified that this manuscript has not been published and is not under considered for publication elsewhere.
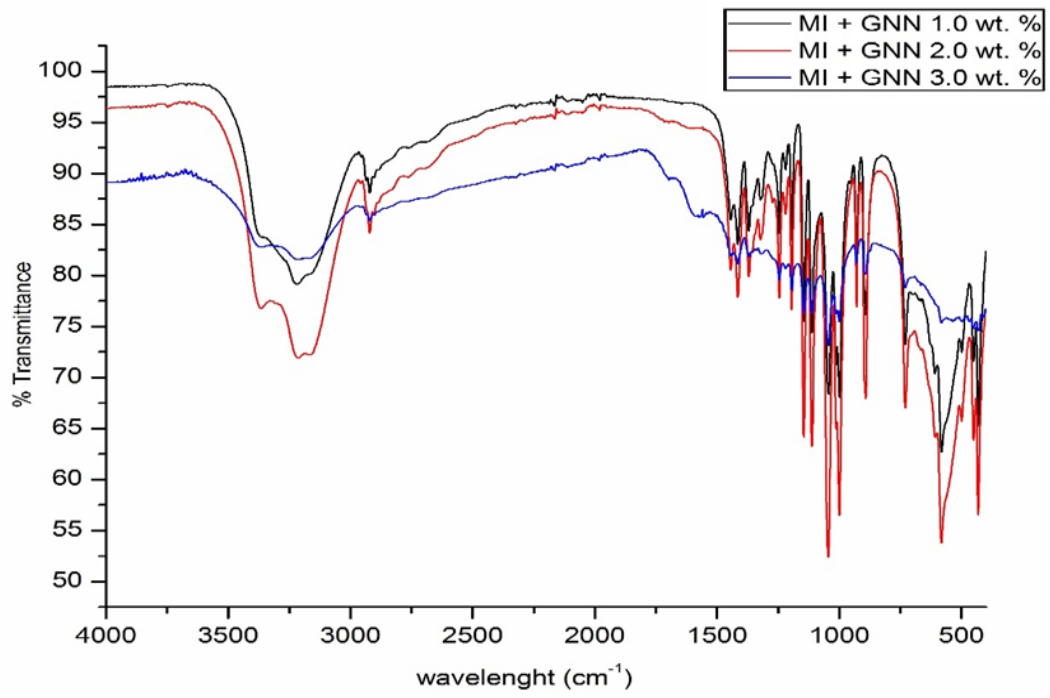
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Sincerely,

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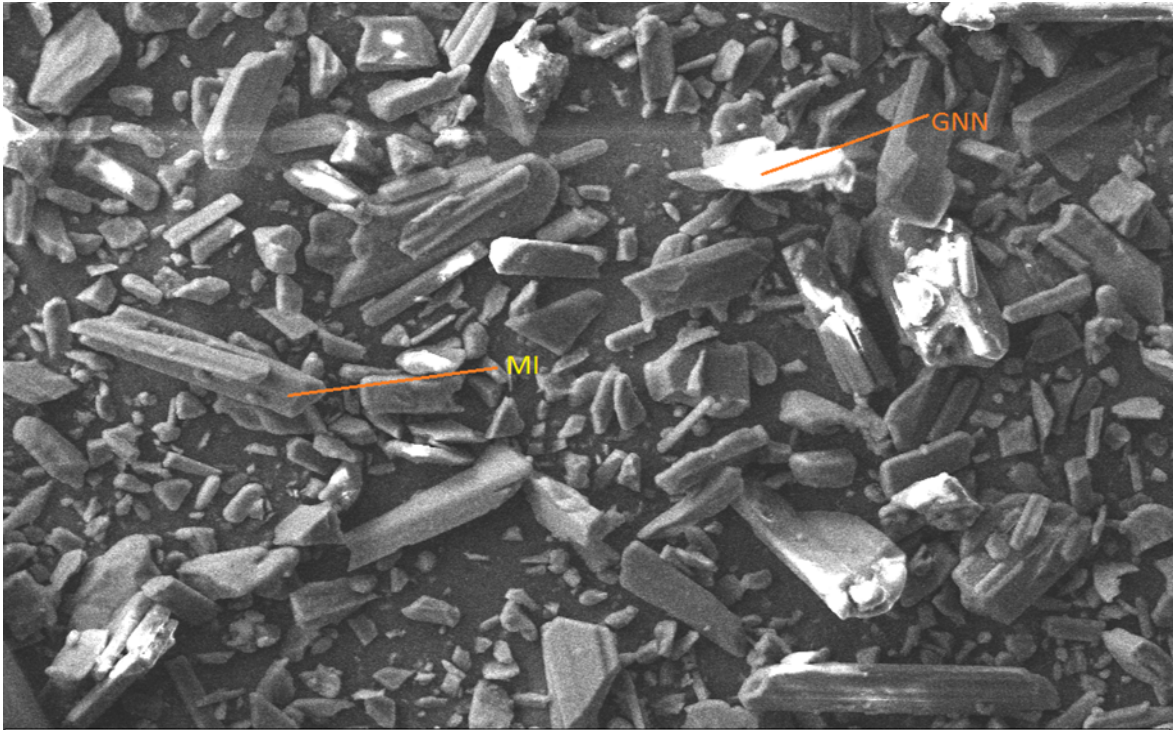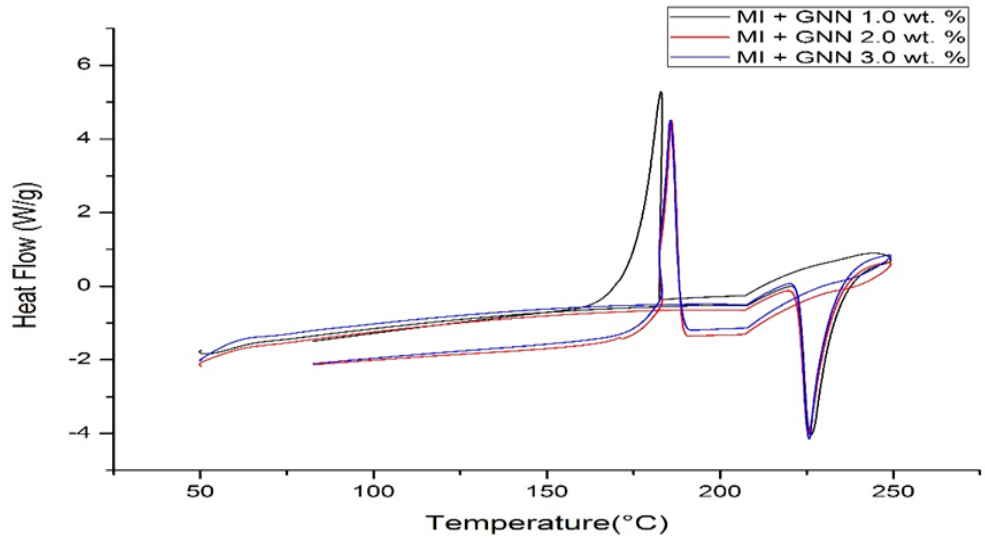
Graphene nanoplatelets enhanced myo-inositol for solar thermal energy storage

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Abbreviation

PCM	**Phase change material**
GNN	**Graphene nanoplatelets**
MI	**Myo-inositol**
DSC	**Differential scanning calorimetry**
TGA	**Thermo gravimetric analysis**
FT-IR	**Fourier transform infra-red**
SEM	**Scanning electron microscopy**
wt.	**Weight**

Greek symbols

λ	**Lambda**
θ	**Theta**
α	**Angle between a and b**
β	**Angle between b and c**
γ	**Angle between c and a**

Abstract

Thermal behavior of nanocomposite phase change materials, Myo-inostol (MI) (a sugar alcohol)added with graphene nanoplatelets (GNN) as a solar thermal energy storage system,for use in the temperature range of 100°C to 260°C was studied.GNN isadded to MIwithmass fraction of 1.0, 2.0 and 3.0wt. %. Thermal and chemical stability of MI and MI-GNNwere investigatedbefore and after 50 thermal cycles. Results showed that thedispersion of GNN into pure MI was effective, no crystal change andchemical reaction had taken place between GNN and MI before and after thermal cycling,only physical interaction between them had taken place.GNN particles were dispersed throughout the MI with small aggregates. Theheat of fusion was found to decrease by 14.13%, 15.06% and 17.63% and heat of solidification by 13.02%, 23.12% and 29.68% for MI-GNN with 1.0, 2.0 and 3.0 wt. % of GNN added to MI respectively.

Introduction

Growing contribution of renewable energy resources has reduced the dependence of non-renewable energy resources. Solar energy has theproblemof intermittency and hence continuous utilization of solar energy is not possible, so to address this problem phase change materials can be asuitable candidate to improve its efficiency and reliability. The goal is to utilize the solar radiation available during day time to store thermal energy in phase change material, where they undergo phase transformation and absorbing huge amount of heat in the process. During night time operation, the reverse occurs and the release heat is utilized for various processes.Several previousresearches have been done on phase change materials, Abhat [1]stated that amongst the various heat storage techniques of interest, latent heat storage is particularly attractive due to its ability to provide a high energy storage density and its unique capacity to store heat at a constant temperature corresponding to the phase transition temperature of the heat storage substance. Shukla et al. [2] conducted aneconomic feasibility study employing a latent heat storage material as a solar thermal energy storage system as the life of the heat storage material, i.e. there should not be major changes in the melting point and latent heat of fusion with time due to the melt/freeze cycles of the storage material.There are several types of phase change materials like organic, inorganic, sugar alcohols etc. Liu et al. [3] investigated thermal performance of paraffin in thermal energy storage mixed with graphene and exfoliated graphite sheet and found that the mass fraction of graphene or exfoliated graphite sheet varied between 0–2.0 wt. %, the enthalpy of phase change material (PCM) composites rose firstly and then dropped down.Wang et al. [4] dispersed TiO_2 nanoparticles of 20 nm diameter in paraffin wax and found that when the NPs loading was not over 1.0wt. %, the phase-change temperature drops, and the latent heat capacity

increased and when the loading was over 2.0wt. %, the phase-change temperature increases, and the latent heat capacity drops. Barreneche et al. [5] found that D-mannitol has good thermo-physical properties for energy storage,the polymorphism was to be taken into account, and this polymorphism was not found to affect the thermal behavior (melting temperature, enthalpy of fusion) for temperature range of 135°C to 175°C. Gill et al. [6] have done an experiment with D-mannitol and found thatby varying the rate of cooling D-mannitol undergoes polymorphic changes and concluded that it wassuitable for pilot plant experiments because temperature variation was inside the working range of 135°C and 175°C. Zhichao et al. [7] studied erythritol with nano-titania and found that heat capacity enhanced by 45% in solid state and 14% in theliquid state compared to pure erythritol when the nano-titania dosage was 0.2%. Seul et al. [8] investigates erythritol with expanded graphite (EG) and showed that composite with highest interlayer distance had the best thermal conductivity (3.56 W/mK) and its latent heat value was 90% of pure erythritol and a 10.80% loss of initial latent heat occurred for thesame composite after thermal cycle tests.Aran et al. [9] studied thermal cycling and chemical stability of D-mannitol, myo-inositol and galacitol, theyshowed that formyo-inositol phase change enthalpy values decreases by 10% and 20% for heating and cooling process respectively after 50 cycles.

It is clear from the literature review that not much research has been done on the use of sugar alcohols (myo-inositol,D-mannitol, erythritol etc.) as phase change materials for solar thermal energy storage though they have ahigh storage capacity and relative non-toxicity.Sugar alcohols have varying phase change temperature and phase change enthalpies which makes them suitable for solar energy storage in the temperature range of 100°C to 250°C. Myo-Inositol as a phase change material can be a better candidate for solar energy storage amongst all other sugar alcohols, because of its high melting temperature, high density, and high phase change

enthalpies[9]. Carbon-based nanostructures like carbon nanotubes, carbon nanofibers etc. are playing asignificant role indevelopment of nanostructured composite phase change materials for energy storage[10]. The family of graphene nanomaterials (graphene nano-platelets, graphene nanosheets etc.) has been seen as thermal conductivity enhancer for nanofluids [11]. Therefore graphene nanomaterials have been used for high-performance composite phase change materials[12,13].GNN is able to reduce the thermal resistance of nano composites due to its planar structure, and its high thermal conductivity. This serves as a background for this investigation. The thermo-physical and chemical properties of MI and MI-GNN have been investigated. Crystal structure changesand surface morphology of MI and MI-GNN were also investigated.

2. Experiments

2.1. Materials

A 99% pure MI (chemical formula $C_6H_{12}O_6$) was obtained from Spectrochem Pvt. Ltd Mumbai (India). It has a mass density of 1.75 gm/cm^3, molecular weight of 180.16, melting range of 222°C to 227°C. Graphene nanoplatelets (sub-micron particles with surface area 500 m^2/g) were procured from Alfa Aesar, USA.

2.2. Sample preparation and thermal cycling

Different PCMs was prepared by the addition of GNN to MI with mass fraction of 1.0, 2.0, 3.0 wt. % and mixed in low energy ball mill, milled at 200 rpm for two hours. Three stainless steel balls were used to provide centrifugal force during rotation for uniform mixing of GNN in MI. Thermal cycling was done on a custom fabricated hot plate (Fig. 1).For every melting and freezing process, 30 g samples of MI and MI-GNN cycled in the temperature range of 50°C to

260°C. J-type thermocouples calibrated in a constant oil bath with temperature accuracy ±1°Cwere used to measure the temperature of PCM in conjunction with data acquisition system(KEYSIGHT 34972A LXI data acquisition/Switch). Visual inspection was used for visualizing complete melting (approximately at 230°C) and solidification process (approximately at 170°C) for every thermal cycle. The temperature was recorded at every 30 secondsintervals during melting and solidification. After 50 cycles pure MI has changed its color from white to black and the same was observed for MI-GNN.

2.3 Characterization methods

The crystal size of MI, MI-GNN was studiedby aX-ray diffractometer (Rigaku Ultima III) having Cu K-alpha radiation (λ = 1.54060 Å).The scanning rate was maintained at 6° s^{-1}.Mass loss characterization was done by Perkin-Elmer (TGA 4000) thermogravimetric analysis system in the range of 100°C to 260°C at 20°C/min under a nitrogen atmosphere for heating and cooling process.Surface morphology was studied by scanning electron microscopy (SUPRA25) device.

Perkin-Elmer FT-IR spectrophotometer (FT-IR spectrum two) was used for studying the chemical stability by observing the Fourier-transform infrared spectra in the wavenumber range of 4000-500 cm^{-1}. Phase change enthalpies and phase change temperature were analyzed by using Perkin-Elmer differential scanning calorimetry (DSC 6000) in the heating-cooling temperature range of 100°C to 260°C at a rate of 6 °C/min with samplesweighing 10 mg sealed in aluminum crucible in N_2 atmosphere.

3. Results and discussion

Surface morphology studies have shown that MI has highly irregular shape and have sharp edges as shown in Fig. 2(a), GNN was uniformly distributed throughout MI with aggregates at some places in MI as shown in Fig. 2 (b).

The X-ray diffraction pattern of pure MI and MI/GNN are shown in Fig. 3. The average crystallite size (D) has been calculated from the line broadening using Debye–Scherer's relation of $D = 0.9\lambda/W \cos\theta$, where λ is the wavelength of X-ray and W is the full width at half maximum (FWHM). MI was foundto have unit cell parameters of a = 6.62 (3), b= 12.89 (4), c= 17.94 (8), $\alpha = 90.00$, $\beta = 93.98$, $\gamma = 90.00$. In pure MI two strong diffraction peaks were observed at 28.88 and 31.10 while other peaks observed at 14.72, 17.46, and 18.76 and 20.25. The crystalline size was calculated to be 35 nm and lattice strain as 0.0062 for pure MI. It can be concluded that the addition of GNN to MI has changed the intensity of peaks and no crystal change has occurred.

Fig. 4 (a) shows the DSC curve it can be seen that,pure MI has alatent heat of fusion of 351.6kJ/kg. The addition of GNN to MI with 1.0, 2.0 and 3.0 wt. %lead to a decrease of 0.99%, 7.87% and 8.90% respectively, in latent heat of fusions as compared to pure MI.The heat of solidification of MI was found as 325.8kJ/kg. A decrease in heat of solidification of1.78, 4.02, and 4.88% decrease was observed for 1.0, 2.0 and 3.0 wt. %MI-GNN as compared to pure MI (Fig.4 (b)). A slight decrease in melting point was observed for all concentration of MI-GNN. A decrease of 2.8°C with 1.0 wt. %, and MI-GNN an increase of 4.19°C and 2.69°C wereobserved for 2.0 and 3.0 wt. %MI-GNN for solidification temperatures as compared to pure MI shown and results summarizes in table 1.

The thermal stability of the PCM mixture was analyzed by thermal cycling in a test plate and sample was characterized again. The results of the analysis are summarized in table 2. After 50

thermal cycles, MI showed 37.31 and 38.58% decrease in latent heat of fusionand solidification respectively compared to Pure MI before thermal cycling. It was observed that latent heat of fusion decreased by 14.13, 15.06 and 17.63% for MI-GNN with 1.0, 2.0 and 3.0 wt. %respectively, after 50 thermal cycles as compared to MI-GNN before thermal cycling.Latent heat of solidification of MI-GNN were decreased by 7.62, 23.12 and 29.68% after 50 thermal cycles as compared to MI-GNN for 1.0, 2.0 and 3.0 wt. % respectively as shown in fig 4 (c).The reason for thedecrease in latent heat of fusion could be attributed to the difference inmelting points of GNN and MI. GNN had not undergone phase transformation during the melting of MI which caused theheat of fusion to decrease in MI. During solidification process, MI was changing its phase from liquid to solid but GNN was still in solid state and absorbing heat from MI during this process,hence the latent heat of solidification is decreased after adding of GNN.

The chemical stability of MI and MI-GNN, itwas characterized by FT-IR, the FT-IR spectra is shown in fig. 5 (a-c). The vibrational peak observed at 3229.89 cm^{-1} was associated to stretching frequency of O-H functional group. The peaks observed at 2922.14, 1445.05, and 1416.84 cm^{-1} were attributed to stretching vibration of C-H group, bending vibration of –C-H group and stretching vibration of C=C group respectively. These groups confirmed the presence of MI and GNN.

Table 1. Phase change properties of pure MI and MI-GNN before thermal cycling

MI-GNN wt. %	Phase change peak temperature (°C)		Latent heat (kJ/kg)	
	Melting	solidification	Melting	Solidification
0.0	225.47	185.73	351.6	325.8
1.0	226.4	182.93	348.1	320.0
2.0	226.3	189.92	323.9	312.7
3.0	226.1	188.42	320.3	309.9

Table 2. Phase change properties of pure MI and MI-GNN after 50 thermal cycles

MI-GNN wt. %	Phase change peak temperature (°C)		Latent heat (kJ/kg)	
	Melting	solidification	Melting	Solidification
0.0	223.4	182.4	220.4	200.1
1.0	224.9	181.21	298.9	295.7
2.0	223.18	170.84	275.1	240.4
3.0	223.9	168.9	263.8	217.9

In the fingerprint region (1500 cm^{-1} to 500 cm^{-1}) peaks were observed at 1370.79 cm^{-1}, 1323.94 cm^{-1}, 1246cm^{-1}, 928.87 cm^{-1}, 732.22 cm^{-1},and 584.87 cm^{-1}which indicates stretching vibration of C-F group, stretching vibration of C-N group, stretching vibration of C-O group, bending vibration of =C-H group, stretching vibration of C-Cl group and stretching vibration of C-Br group respectively. It was observed that reaction of MI with F, N_2, Cl_2, Br_2 and O_2 took place but they had no effect on thermo-physical properties of MI and MI-GNN. It can be concluded that the addition of GNN to MI there was no new group generated. The same was observed for MI-GNN after thermal cycling. Therefore we can say that MI and MI-GNN were chemically stable, as only physical interaction had taken place between MI and GNN, and it can be used onlong-term basis. From fig. 5, a decrease in transmission was observed on addition of GNN, due to the increased infra-red absorptivity of GNN. After thermal cycling, the phase change material lost its optical property gradually, hence the absorptivity was found to decrease.

Thermogravimetric analysis showed (Fig. 6) that in pure MI the mass reduction were 0.81% and 2.43%during melting and solidification respectively. MI-GNN with 1.0, 2.0 and 3.0 wt. %showed about 1% decrease in mass during melting process and solidification process.MI-GNN with 3.0 wt. % which exhibits 1.37% decrease in massduring melting process in the temperature range of 100°C to 260°C. After 50 thermal cycles, MI showed 0.719 and 1.26 % decrease in mass in heating and solidification process. MI-GNN with 1.0, 2.0 and 3.0 wt. % exhibited about 2% and 3% decrease in mass for heating and solidification respectively after 50 thermal cycles in

the temperature range of 100°C to 260°C, so it indicates that MI-GNN was thermally stable in terms of mass change.

4. Conclusions

Thermal properties of MI laden GNN wereinvestigated in terms of phase change temperatures and enthalpies and found following conclusions as follows:

MI has high heat of fusion and solidification enthalpieshowever 50 thermal cycles its phase change enthalpies were decreased at large extents.

Addition of GNN to MI showed slight decrease in phase change enthalpies and increased latent heat of solidificationafter conducting thermal cycled MI, which ishighly advantageous for solar thermal energy storage system.

The only physical interaction between MI and GNN had taken on addition of GNN and during thermal cycling, no chemical bonding occurred, hence making it suitable for long term thermal energy storage.

MI-GNN showed less mass change after 50 thermal cycles (approximately 2 to 3%) which make it suitable for solar thermal energy storage.

Improved thermal properties, less mass change and only physical interaction makes MI-GNN phase change composites a suitable candidate for solar thermal energy system in temperature range of 100°C to 260°C.

Acknowledgement

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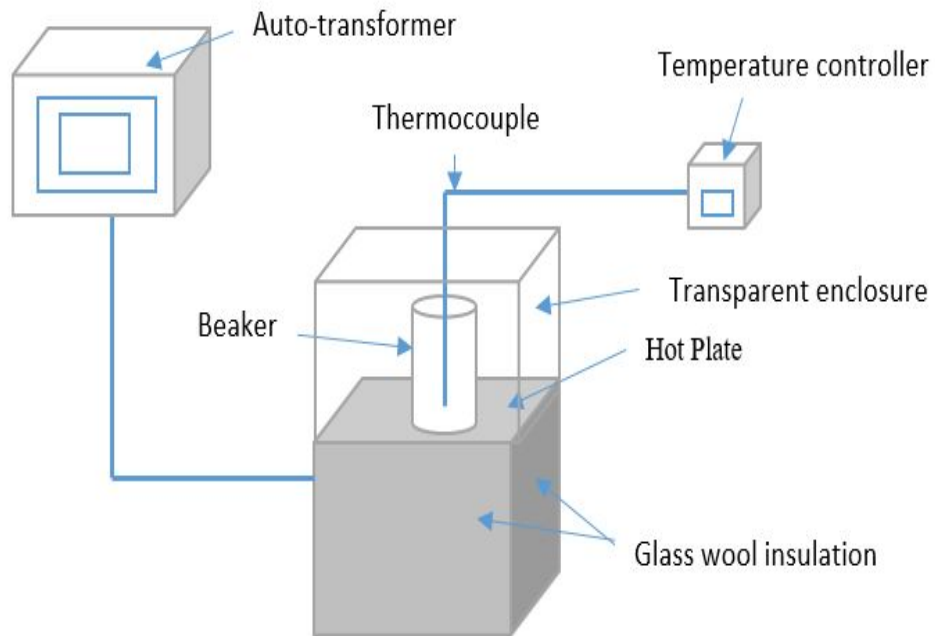
Fig. 1. Schematic diagram of complete experimental set-up of thermal cycling

(a)
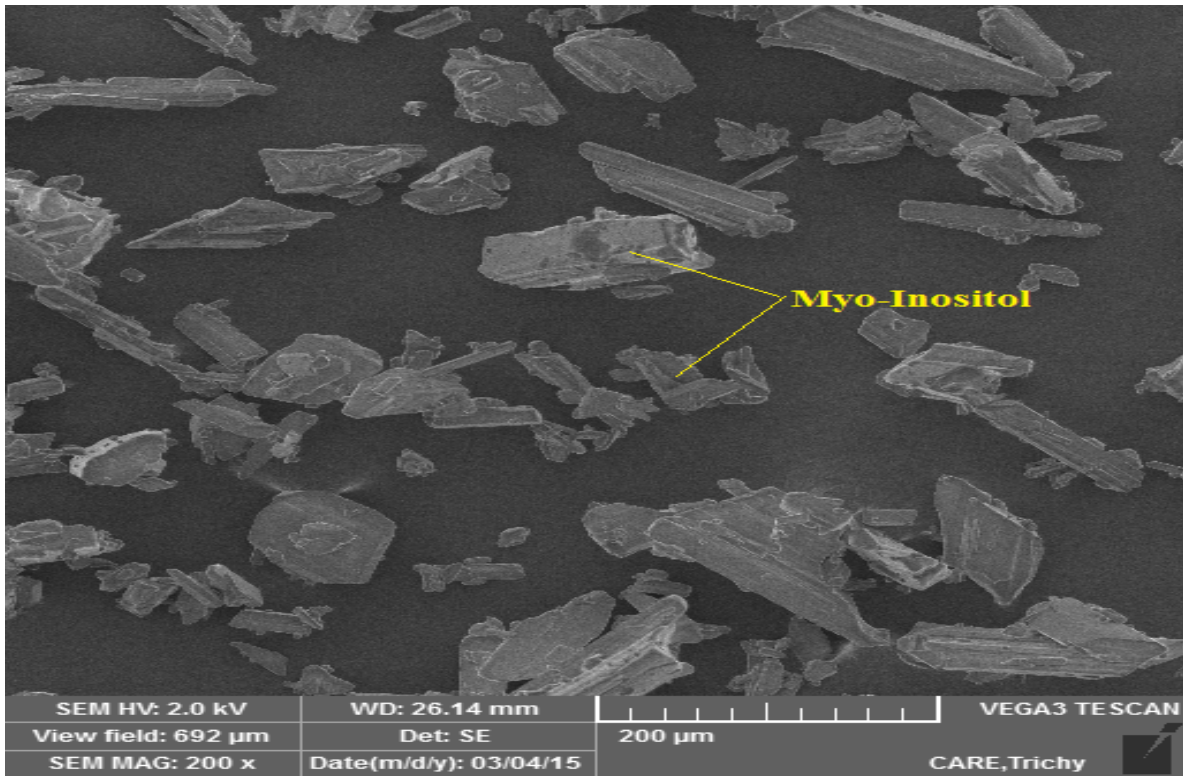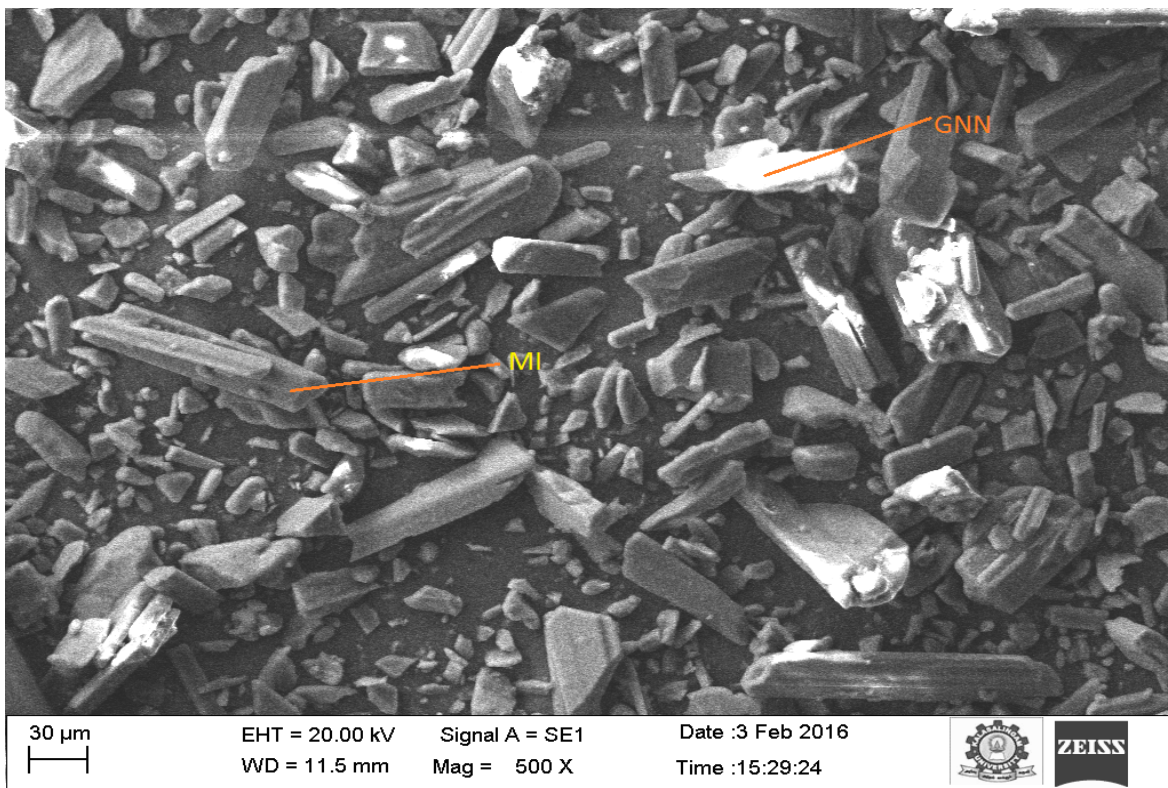
Fig. 2 SEM images at ×5,000 magnifications (a) Pure MI and (b) MI with 1 wt. % GNN before thermal cycling
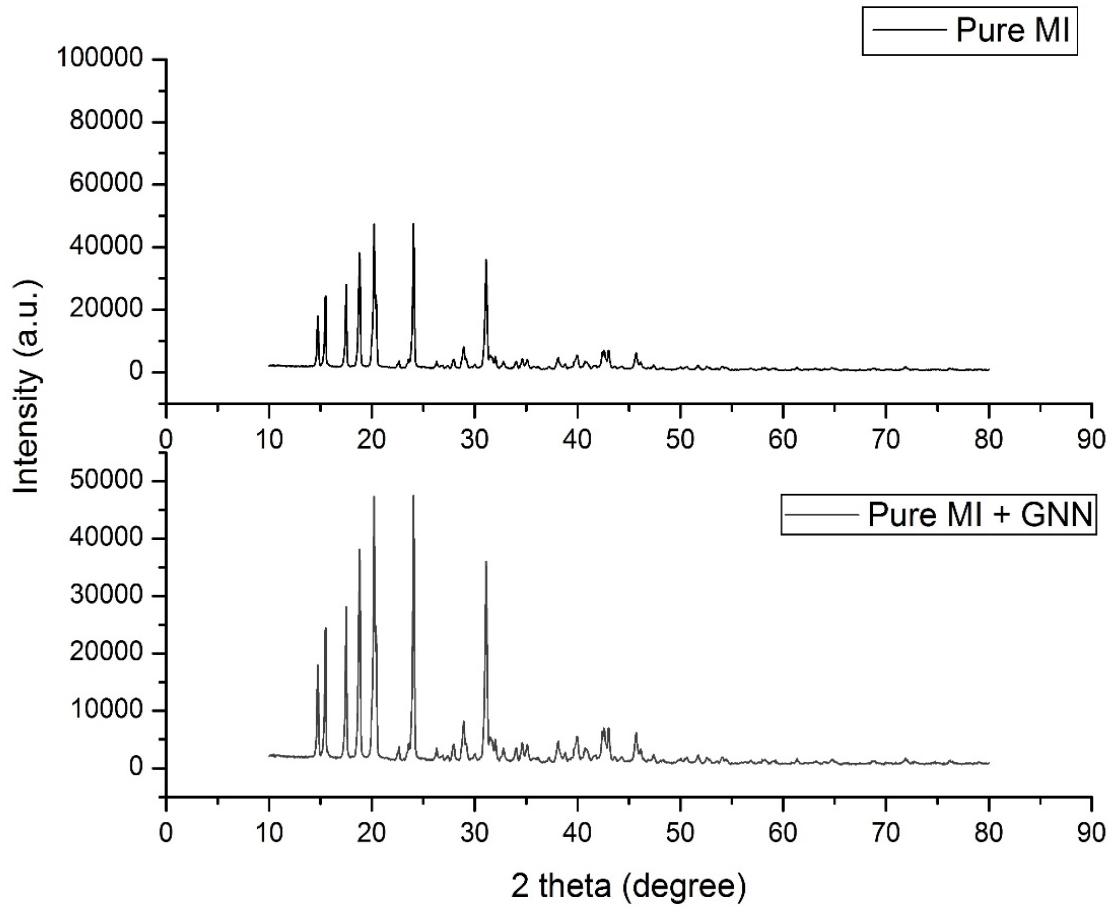
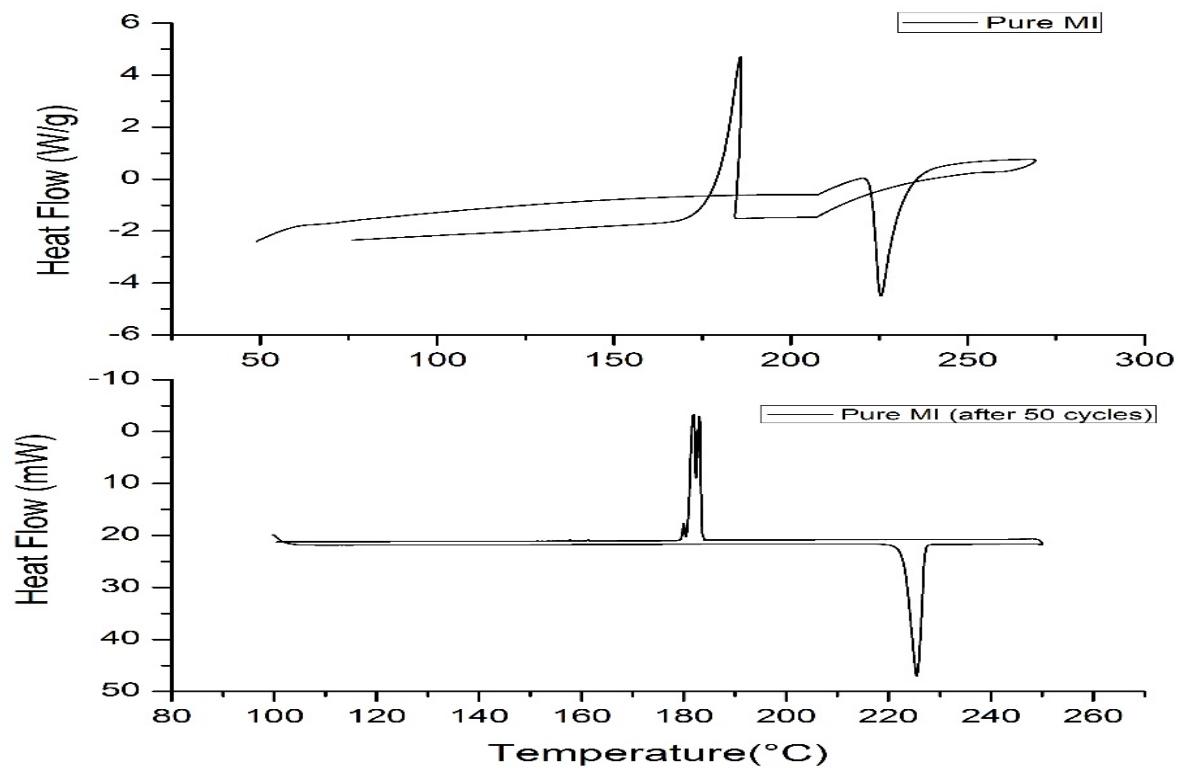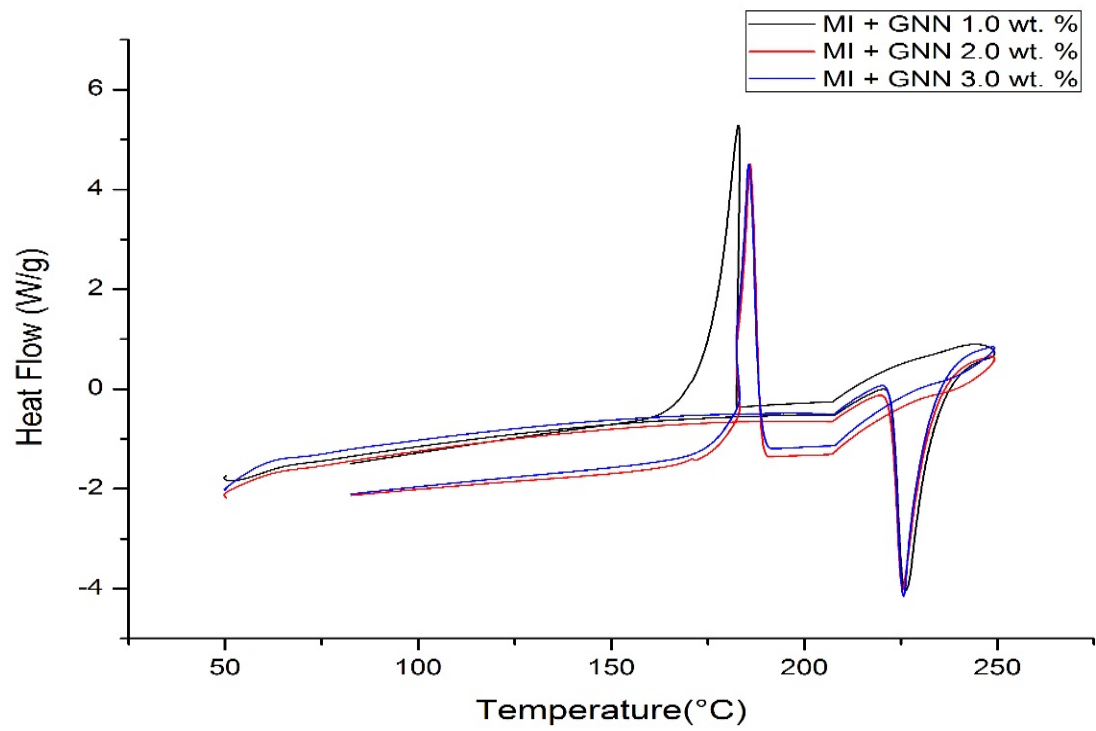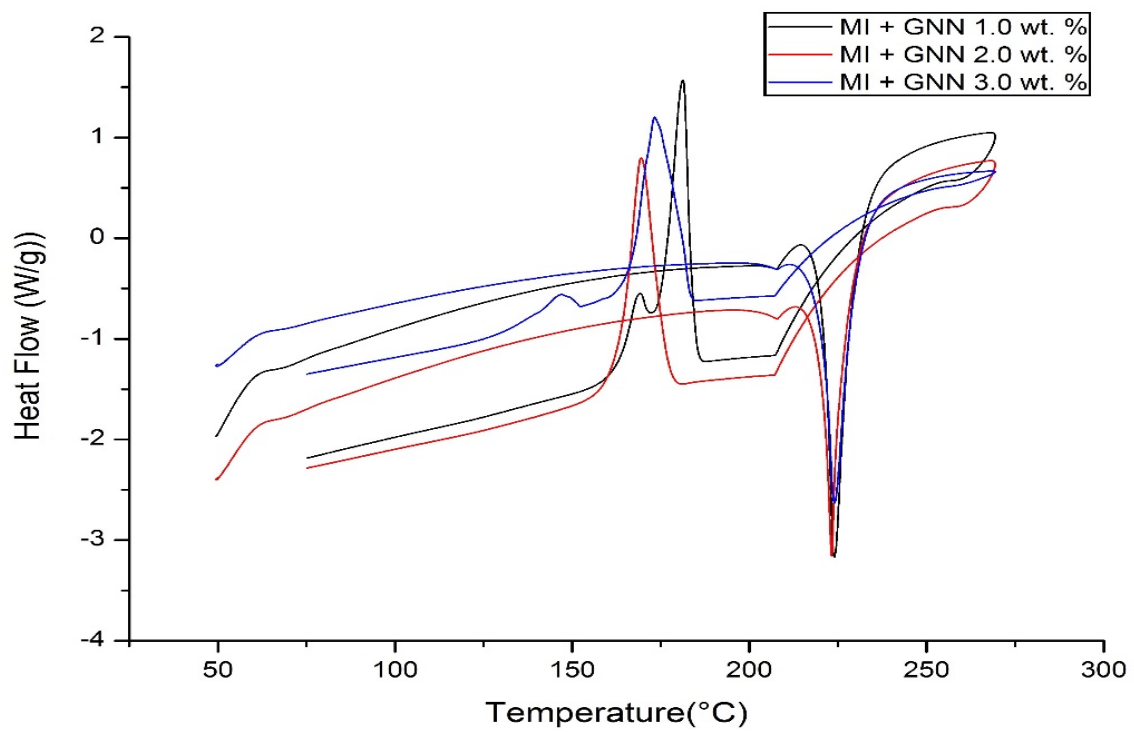**Fig. 3 XRD pattern of (a) Pure MI and (b) MI-GNN (1.0 wt. %) before thermal cycling**
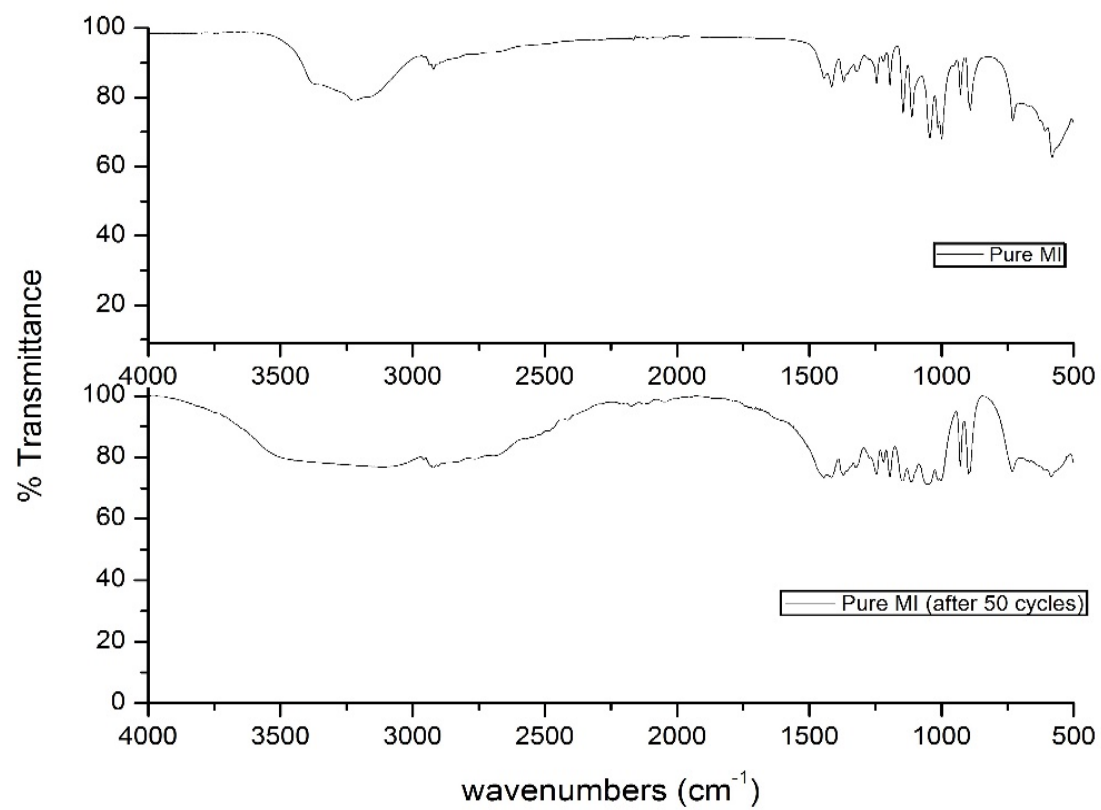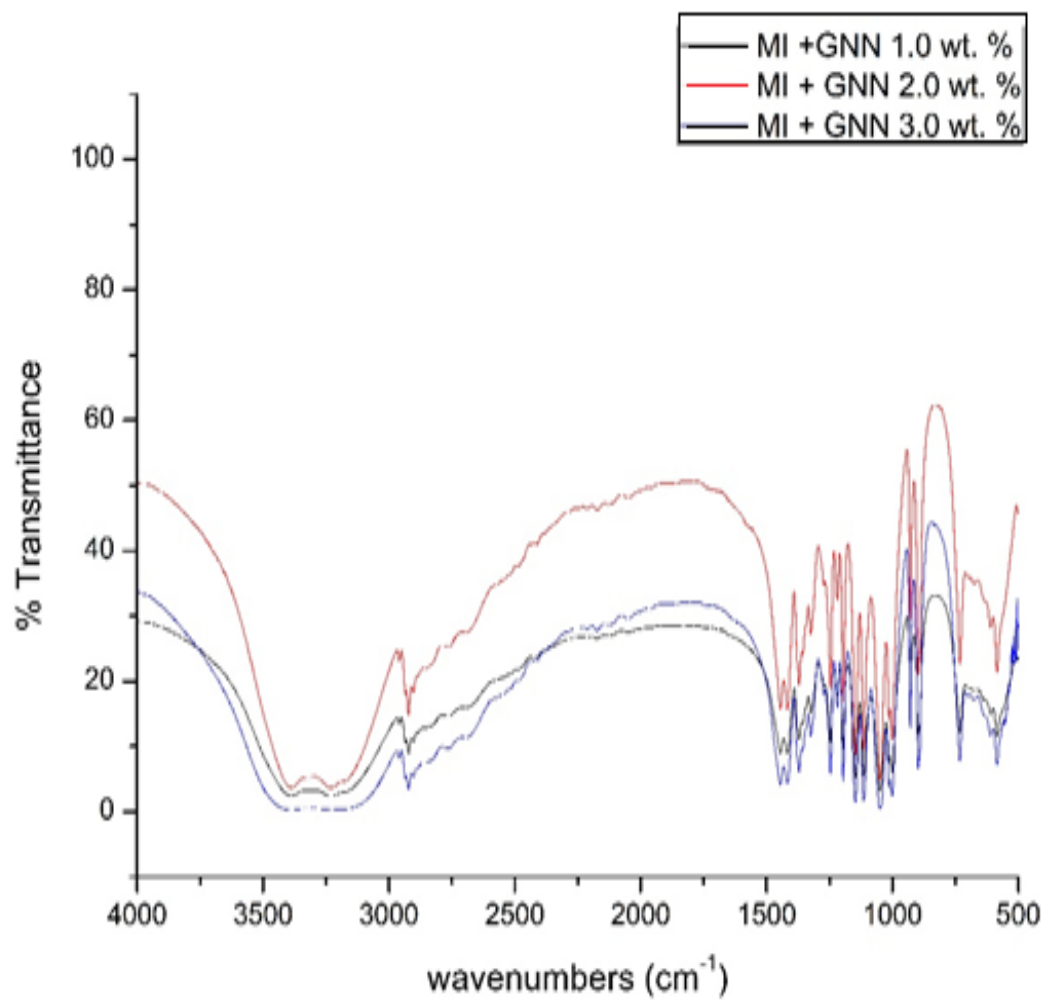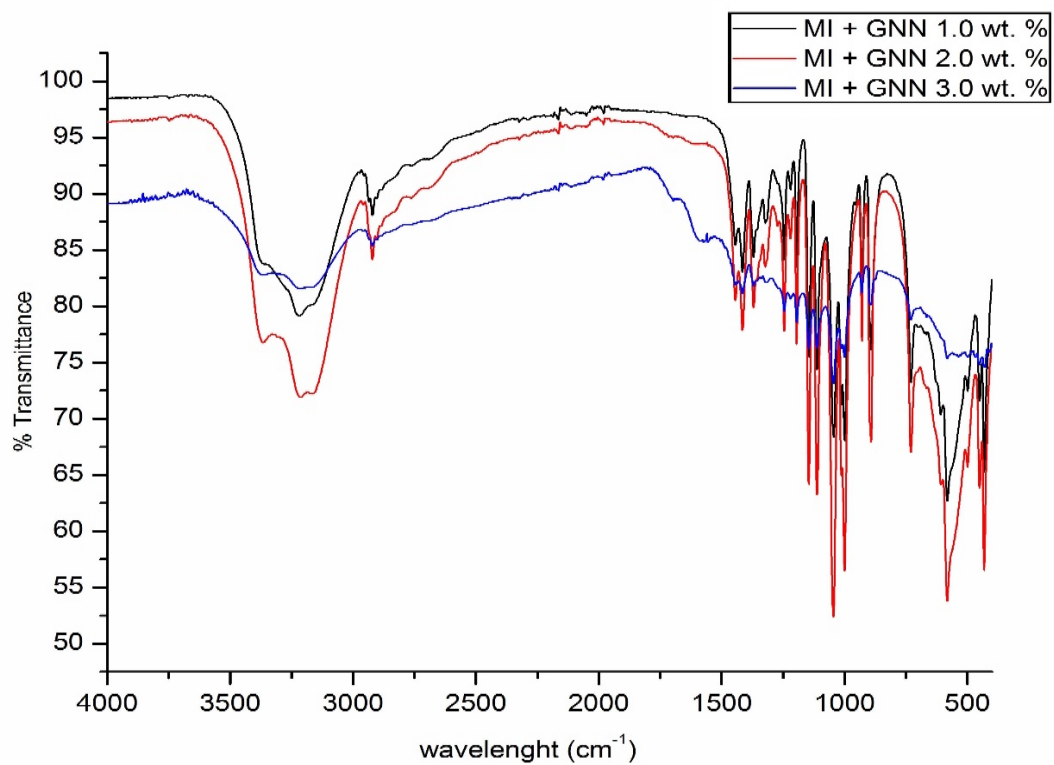
(a)

(b)

(c)

Fig. 4 DSC curve of (a) Pure MI before and after 50 cycles (b) MI–GNN before cycling and (c) MI-GNN after 50 cycles
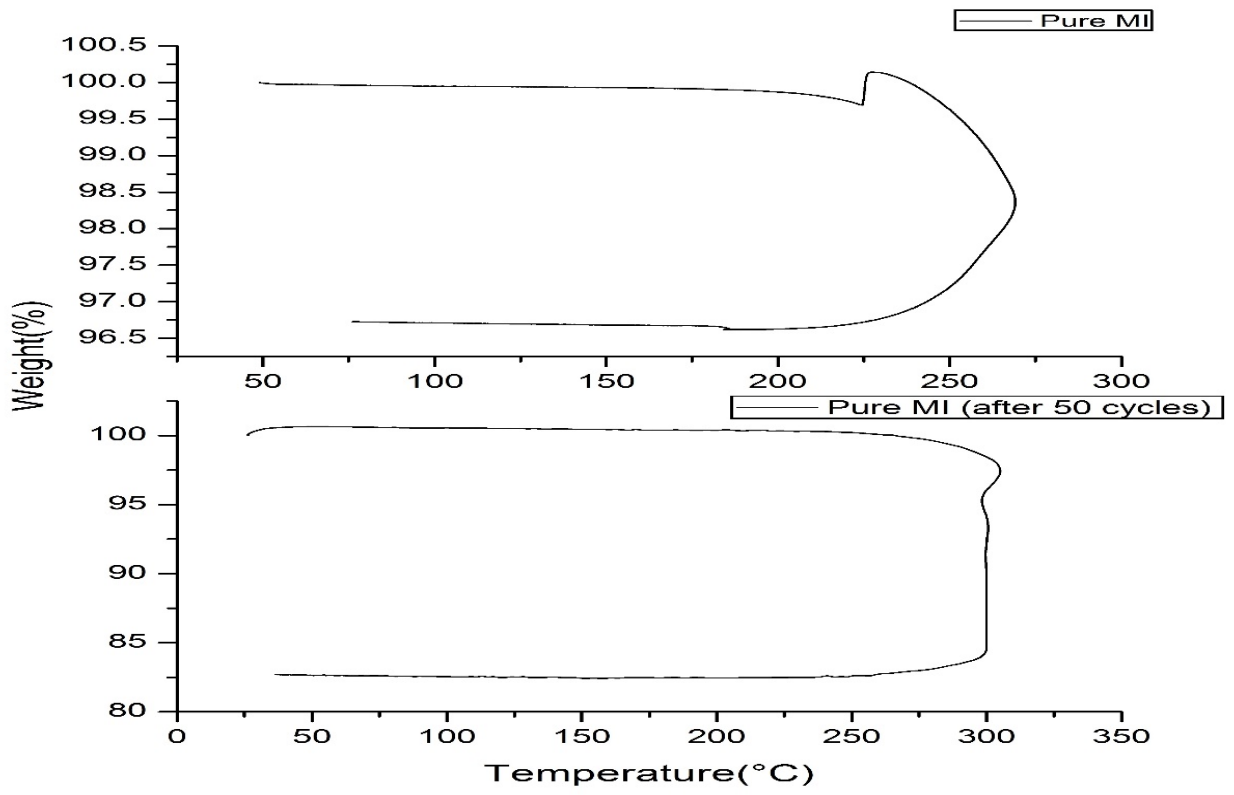
(a)

(b)

(c)

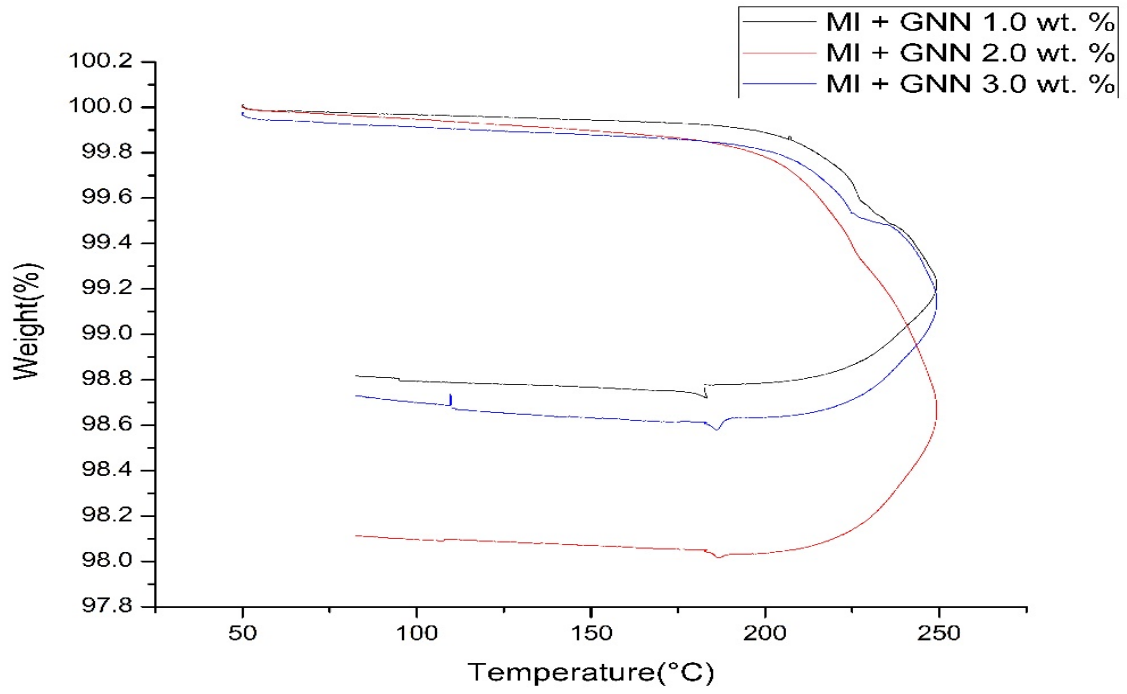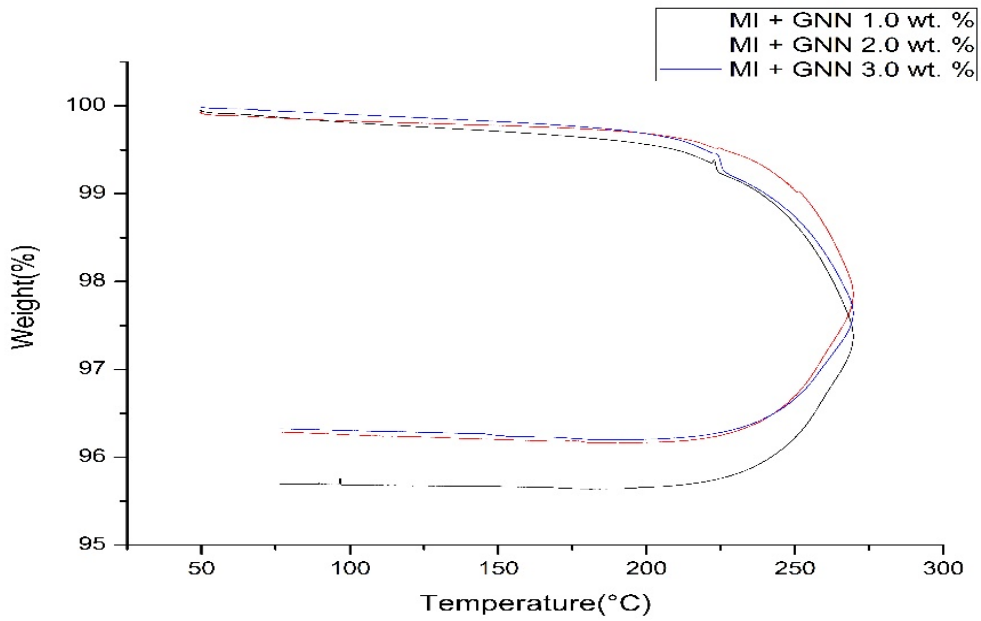**Fig. 5 FT-IR spectrum of (a) Pure MI before and after 50 thermal cycles (b) MI-GNN before thermal cycling and (c) MI-GNN after 50 thermal cycles**

(a)

(b)

(c)

Fig. 6 (a) Pure MI before and after 50 thermal cycles (b) MI- GNN before thermal cycling and (c) MI-GNN after 50 thermal cycles

Highlights

- MI-GNN were investigated physically and chemically.

- Good thermal stability was shown by MI-GNN.

- MI only physically interacted with GNN.

- MI-GNN mass change was very less during thermal cycling.