Enhanced Thermal Stability and Degradation Kinetics of Xylitol-Based Phase Change Materials Reinforced with Activated Peanut Shell Biochar and Aluminum Nanoparticles

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ABSTRACT

Phase change materials (PCMs) made with xylitol have large latent heat which is useful in medium temperature energy storage, but they have poor thermal stability and moderate degradation resistance, limiting the high-cyclic operation. The test in this research involved the addition of activated peanut shell-derived biochar (15 wt% and 0.3 wt% and 0.6 wt%) and aluminum nanoparticles (0.3 wt% and 0.6 wt%) to xylitol to promote thermal performance. The composites would be prepared in two stages by dispersion and structural stability, phase transition properties, and degradation kinetics non-isothermal TGA at 20, 25, and 30 C/min would be analyzed by use of XRD and FTIR, respectively and activation energies measured using KAS, FWO and Starink iso-conversional models. DSC findings indicated that pure PCM contained a melting onset temperature of 85.7 o C, a peak temperature of 94.6ºC and a latent heat mass of 358.4 J/g, PCM +0.3%Al+15%BC and PCM +0.6%Al+15%BC contained latent heats of 345.2 J/g and 332.8 J/g respectively. TGA established insignificant loss of mass below 200ºC which is a sign that it has thermal reliability within the operating range. Kinetic analysis indicated that pure PCM had average activation energy of about 8390 kJ/mol, PCM+0.3%Al, +15-percent-BC was between 358268.4 kJ/mol, and PCM+0.6%Al, +15-percent-BC was between 188268.7 kJ/mol, which confirmed reduced degradation resistance. The highest thermal stability and degradation delay behavior was observed in the hybrid composite with 0.3% aluminum hence developed materials can be considered promising materials to use in solar thermal storage, waste heat recovery, and medium-temperature energy storage systems.

Keywords: Thermal stability, Energy storage, Phase change material, Kinetic analysis, Latent heat.

1. Introduction

Due to the energy crisis and the growing environmental concerns, there is a drive towards the application of renewable energy and reclamation of the waste heat released in the industrial processes. The biochar composites were prepared by the use of peanut shells and the results were structurally verified by XRD and FTIR methods and confirmed the high surface area and functional group enrichment. The porous architecture was optimized to increase adsorption efficiency and thermal characteristics, which means that it can be used in environmental remediation systems and energy storage systems [1]. Biochar was produced in nano form made of peanut shell that was integrated into polymer matrices by use of XRD and TGA that confirmed crystallinity and thermal stability. Mechanical reinforcement and better thermal properties are shown to be suitable to structural components in advanced frameworks of energy storage [2]. Heterojunction form led to enhanced photocatalytic performance, hydrogen evolution and thermal performance of built-in environmental-energy frameworks [3]. Xylitol-based phase change materials were nano-enhanced to enhance thermal conductivity and storage efficiency that were tested with DSC and TGA. The engineered system had better thermal characteristics that could be applied in high-performance latent heat energy storage [4]. DSC and TGA thermal characterization of xylitol defined melting temperature, enthalpy and stability parameters. The measured thermal performance of it proves it to be viable in use as an effective phase change material in latent heat energy storage systems [5].

Experimental characterization was done of pure and eutectic sugar alcohol phase change materials in terms of melting, latent heat, and thermophysical properties. Optimized thermal behavior of medium-temperature energy storage systems was found to be confirmed using performance benchmarking [6]. The biochar skeletons obtained using peanut shells were designed to trap phase change materials to increase the porosity and latent heat holding capacity. Evaluation of thermal properties established better storage of energy when compared to raw biomass matrices [7]. The EVA composites with peanut shell fiber and aluminum oxide nanopowder were made and structurally proven through FTIR, XRD, and TGA. They are improved by better mechanical integrity and thermal performance to enable their use in sustainable composite that is durable [8]. The peanut shell hydrochar composites with MnO_2 were prepared and characterized using the FTIR, XRD, BET, and TGA. Functional versatility in environmental and improved material systems in respect to improved catalytic efficiency and stable thermal properties [9]. Composites of peanut shell-derived cellulose acetate were electrospun and analyzed using FTIR, XRD and TGA. Sustainable filtration and advanced functional material development is enabled by the stable structural and thermal performance [10].

This study involved the fabrication of four samples: pure PCM and nano-enhanced PCM samples (PCM + 15% BC, PCM + 0.3% A + 15% BC, and PCM + 0.6% A + 15% BC) for medium temperature thermal storage devices. The focus of this work is on the production of biochar-based PCM composites with enhanced thermal conductivity and chemical and thermal stability, which is to be used in the process of desalination. The findings highlight the effect of aluminum/ biochar on the thermal properties of phase change materials (PCMs). To determine the effects of nanoparticles and biochar on thermophysical properties, the synthesized samples have been examined by the use of XRD, FTIR, DSC and TGA. Kinetics of the degradation of both the materials were evaluated with the help of the KAS, FWO and Starink models.

2. Materials and Methods

2.1. Fabrication of Activated Biochar Using Peanut shell

This paper focused on the production of biochar using the peanut shells as shown in Figure 1. The process started with crushing of the remaining peanut shells into 15mm-20mm pieces, after which it was washed three times with deionized (DI) water to eliminate dust, dirt, and surface impurities. The shell particles were dried in vacuum oven at 130ºC within 1 day after the washing process to remove all the moisture. To transform the biomass to an energy form in the form of carbon-rich char the dried shell waste was carbonized under an inert atmosphere of nitrogen (N_2) at 1000ºC in a tube furnace. This was followed by controlled thermal decomposition (pyrolysis) of the biomass at 500ºC in a tubular furnace under a constant flow of nitrogen (75 $cm^3 min^{-1}$). Controlled heating of 10ºC per minute was applied to the temperature to allow evenly produced biochar. Zinc chloride ($ZnCl_2$) was employed as an activating agent to improve porosity and surface area to achieve chemical activation. Test tubes containing a solution of $ZnCl_2$ and biochar in 1:4 mass (biochar:$ZnCl_2$) were thermally treated at 800º C in a nitrogen atmosphere of 1 h to form activated biochar. The material was then dried in the oven after washing in deionized water to eliminate the remnants of $ZnCl_2$. A two step reduction size procedure was used to make the carbonized material get the nano-scale particle size. Mechanical grinding was initially done to get micron sized particles (approximately 1.5–1.8 µm). Wet planetary ball milling of the same was then carried out at 300 rpm and 36 h with a 10 min rest period following every 20 min of milling to ensure that excessive heat was not accumulated. The analysis of particle size after milling showed that the size distribution was found in 500-700 nm range which justified the successful nano-scale fabrication. Synthesized biochar nanopowder (BNP) was eventually kept in an airtight and moisture-free container to avoid oxidation and contamination. This preparation technique is such that the activated biochar nanopowder (BNP) has the characteristics of a high surface area, increased porosity, and nano-scale particle dimension, which is ideal in future experimental studies.

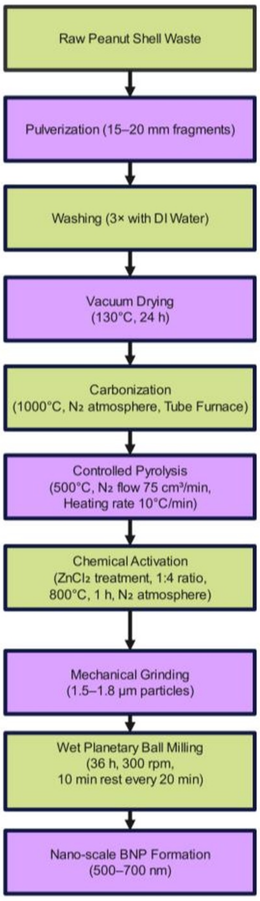
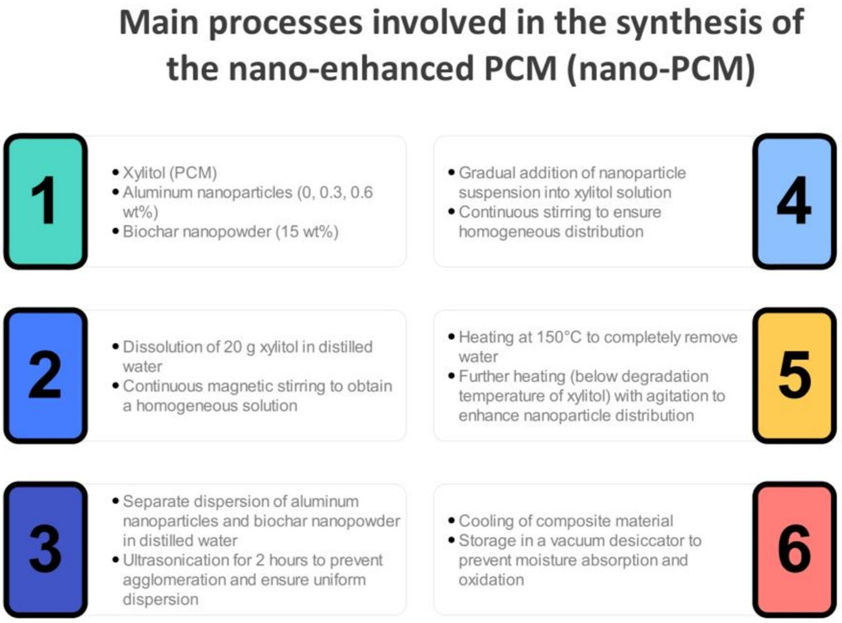


Figure 1. Representation of preparation of biochar

2.2. Preparation of the Nano-PCM Materials

Xylitol, a bio-based phase change material (PCM) with an average melting temperature of 93–96 °C was used. High-purity aluminum nanoparticles with 99% purity is also employed.

The aluminum nanoparticles possessed a particle thickness of 5–10 nm, a lateral size in the micrometer range (approximately 5–10 µm), and a specific surface area of 200–210 $m^2\ g^{-1}$. The particles consisted of approximately 4–8 stacked layers, indicating a lamellar nanostructure. A two-step dispersion method was employed for the fabrication of nano-enhanced phase change material (nano-PCM) samples. Initially, 20 g of xylitol was dissolved in distilled water under continuous magnetic stirring to obtain a homogeneous solution. Aluminum nanoparticles at 0 wt.%, 0.3 wt.%, and 0.6 wt.%, along with a fixed 15 wt.% biochar nanopowder (BNP), were separately dispersed at deionized water and subjected to ultrasonication for 2 h. The nanoparticle suspension were gradually introduced into the xylitol solution under continuous stirring, followed by heating at 150 °C to facilitate complete evaporation of water and obtain a dry composite mixture. Subsequently, the micro-PCM mixtures were heated to a temperature slightly above the processing temperature (below the degradation temperature of xylitol) under continuous agitation to ensure uniform nanoparticle distribution within the PCM matrix. The prepared nano-PCM samples were finally stored in a vacuum desiccator to prevent moisture absorption and preserve the chemical integrity of the composite material. The schematic representation of the nano-PCM synthesis procedure is presented in Figure 2.



Main processes involved in the synthesis of the nano-enhanced PCM (nano-PCM)

1
- Xylitol (PCM)
- Aluminum nanoparticles (0, 0.3, 0.6 wt%)
- Biochar nanopowder (15 wt%)

2
- Dissolution of 20 g xylitol in distilled water
- Continuous magnetic stirring to obtain a homogeneous solution

3
- Separate dispersion of aluminum nanoparticles and biochar nanopowder in distilled water
- Ultrasonication for 2 hours to prevent agglomeration and ensure uniform dispersion

4
- Gradual addition of nanoparticle suspension into xylitol solution
- Continuous stirring to ensure homogeneous distribution

5
- Heating at 150°C to completely remove water
- Further heating (below degradation temperature of xylitol) with agitation to enhance nanoparticle distribution

6
- Cooling of composite material
- Storage in a vacuum desiccator to prevent moisture absorption and oxidation

Figure 2. Synthesis of nano-PCM

2.3. Characterization of the Prepared Samples

The phase composition of pure PCM and nano-improved PCM samples was analyzed using X-ray diffraction (XRD) by linearly scanning a 2θ range of 5°–80° at a rate of 1°/min. The Cu-Kα radiation emitted by the Ultima IV Rigaku diffractometer, operating at 40 kV and 30 mA was utilized for the study. A Debye–Scherrer equation were used to determine crystallite size of both pure PCM and nano-improved PCM samples. The phase identification of samples was performed with standard JCPDS cards. The study of functional groups at PCM samples were conducted by Fourier transform infrared spectroscopy. The FTIR analysis was conducted within a spectrum range of 4000–500 cm^{-1} utilizing the FTIR-4200, employing pellets composed of a 1:200 combination of PCM and spectroscopic potassium bromide. The background scan was conducted utilizing the sample holder in the absence of a sample. TGA is an effective method for analyzing the thermal stability and degradation characteristics of

PCM and nano-composite PCM materials. TGA data, when integrated with model-free kinetic approaches, yield significant insights into the deterioration dynamics of phase transition materials. TGA tests were performed on Xylitol PCM and NEPCM materials with the PERKIN-ELMER TGA 8000. Approximately 5–10 mg of PCM was subjected to heating from 25°C to 900°C at different speeds 15, 20, and 25°C/min. Nitrogen gas was used at flow rate of 20 mL/min to inhibit oxidation. The phase change temperature and latent heat capacity of the PCM samples were assessed using a DSC with an accuracy of ±0.6°C. The DSC examination was conducted by heating samples in an aluminum crucible at regulated rates of 20, 25, and 30°C/min.

2.4. Kinetic Analysis of the Composite PCM Samples

Thermogravimetric analysis (TGA) is a sophisticated thermo-analytical method utilized to assess the thermal stability and breakdown characteristics of materials, particularly nano-structured phase change materials (PCMs). TGA data, when integrated with kinetic approaches offer a significant insight into the deterioration dynamics of phase change materials.

$$\frac{d\Phi}{dt} = k(T)G(\Phi) \tag{1}$$

where Φ denotes degree of conversion in the reaction, k(T) signifies temperature-dependent rate constant, and G(Φ) corresponds to the model of the reaction mechanism.

The FWO, KAS, and Starink methodologies are the predominant techniques utilized for evaluating kinetic parameters. Kinetic techniques enable the determination of the activation energy (Ea), the minimum energy required for a reaction to occur, without presupposing a particular reaction mechanism. This is especially beneficial for intricate events such as the breakdown of nano-PCMs, where the precise mechanism may be unidentified. These approaches ascertain the activation energy as a function of the degree of conversion (Φ) by examining the temperature dependence of the reaction rate at various conversion levels.

The FWO method were also involved in iso-conversational methodology, which was used to measure the activation energy of a thermal breakdown process. This method is quite beneficial in TGA. FWO method calculates the activation energy (Ea) based on the temperature dependence of the reaction rate with different heating rate (γ). It uses the following equation.

$$\ln(\gamma) = \ln\left[\frac{A\times E_\mathrm{a}}{R_\mathrm{g}\times G(\Phi)}\right] - 1.0516\times\frac{E_\mathrm{a}}{R_\mathrm{g}\times T} \tag{2}$$

with Rg being the universal gas constant. The slope of ln(1-T) profile versus 1/T of the samples of PCM may be used to determine the activation energy (Ea) of the sample.

The KAS technique is an iso-conversational technique that is used in determining the activation energy of a thermal decomposition or transformation process. KAS method is particularly beneficial in TGA and DSC studies, providing the possibility to study thermal reactions kinetics without the assumption of a specific reaction model. The KAS method calculates the activation energy (Ea) by evaluating how the reaction rate varies with temperature at different heating rates (γ).[11]. It employs the subsequent equation.

$$\ln\left(\frac{\gamma}{T^2}\right) = \ln\left[\frac{A\times E_\mathrm{a}}{R_\mathrm{g}\times G(\Phi)}\right] - \frac{E_\mathrm{a}}{R_\mathrm{g}\times T} \tag{3}$$

The activation energy (Ea) of the PCM samples may be determined by calculating slope of ln $(\frac{\gamma}{T^2})$ vs 1/T plots for different samples.

The activation energy was calculated with Starink method, which were analogous to FWO and KAS techniques. The Starink technique assesses the activation energy of a material's thermal breakdown or transformation using the following equation, which evaluates the activation energy (Ea) as a function of the degree of conversion (γ).

$$\ln\left(\frac{\gamma}{T^{1.8}}\right) = C_{\mathrm{s}} - 1.0037 \times \frac{E_{\mathrm{a}}}{R_{\mathrm{g}} \times T} \tag{4}$$

The model-free methodologies were chosen in this work due to the complexity of the thermal degradation process in phase change material which is often driven by a number of, unknown factors. Unlike model-fitting procedures, model-free methods, such as the KAS, FWO, and Starink methods do not require any initial assumptions on the reaction mechanism. These techniques allow determination of activation energies as a function of conversion without the need to assume a particular degradation model, so the techniques are ideal in materials like PCMs, where degradation behaviour depends on a variety of factors, including material composition, temperature, and phase changes.

Besides, model-free methods provide a more convenient and solid evaluation of the activation energy that will enable a better understanding of thermal stability of PCMs. Such methods are widely utilized in kinetics studies of the degradation of complex materials such as biochar-PCM composites, in which the mechanisms of breakdown can change with different additions. With the help of these methodologies, we will be able to determine the accurate activation energies of each stage of the thermal degradation process which will be important in determining the effectiveness of the material in application in the storage of thermal energy. On the other hand, model-fitting methodologies require a pre-defined mechanism that may also be the cause of over-simplification and representation of the thermal degradation process of these composite materials. Model-free techniques are better and reliable to measure the kinetic parameters of thermal deterioration because the materials under study are complex and have no clear-cut method to measure such parameters. To summarize, model-free kinetic methods were selected due to their ability to provide model-independent, accurate estimates of the activation energies as well as more clearly reflect the complex nature of the degradation process in the composite phase change materials studied.

3 | Results and Discussion

3.1 | XRD Assessment of the Samples

Figure 3 illustrates XRD patterns of pure PCM biochar–PCM and biochar–PCM combined with aluminum samples. The XRD patterns of PCM samples containing 0%, 0.3%, and 0.6% aluminum, together with 15% biochar were analogous, revealing no new peaks or significant peak changes, so affirming chemical stability of composite PCM. The chemical stability verified the absence of any chemical interaction between PCM, biochar, and aluminum. Activated biochar possesses microcrystalline structure and exhibits wide XRD pattern spanning from 2θ=17.9° to 44.6°. A XRD pattern of biochar displays prominent peak at 22.2°, identified as natural peak (002) of aluminium, along with modest peaks at 31.5°, attributed to peaks (100). The peak intensities of the PCM composite are inferior to those of the pure PCM sample. The rationale for this is that the patterns of moisture-absorbent phase change materials (PCMs) in composites were poorly characterized, resulting wide pattern, possibly of their surface area and extensive pore, which promotes liquid's reversion to its original form within the cavity. According to the earlier literature, the XRD patterns of the peanut shell-derived activated carbons revealed a broad peak of the crystal forms at approximately 23-26 and 43° which represents the (002) and (100) planes of amorphous turbostratic carbon [12]. This thermal stability is essential in thermal behavior since it directly determines the properties of phase change of the material and the ability of the material to survive multiple melting and solidification cycles without significant degradation. Thermal cycling can alter phase transition temperatures or alter values of latent heat or reduce the thermal conductivity of the material and thus impair its thermal performance. The investigation we have conducted shows that the absence of significant changes or new peaks in the XRD patterns confirms that the chemical integrity of the composite PCMs had stayed intact even when subjected to moderate temperatures. This stability ensures that the PCMs retain their high latent heat capacity and thermal conductivity with time leading to a more reliable and efficient energy storage.

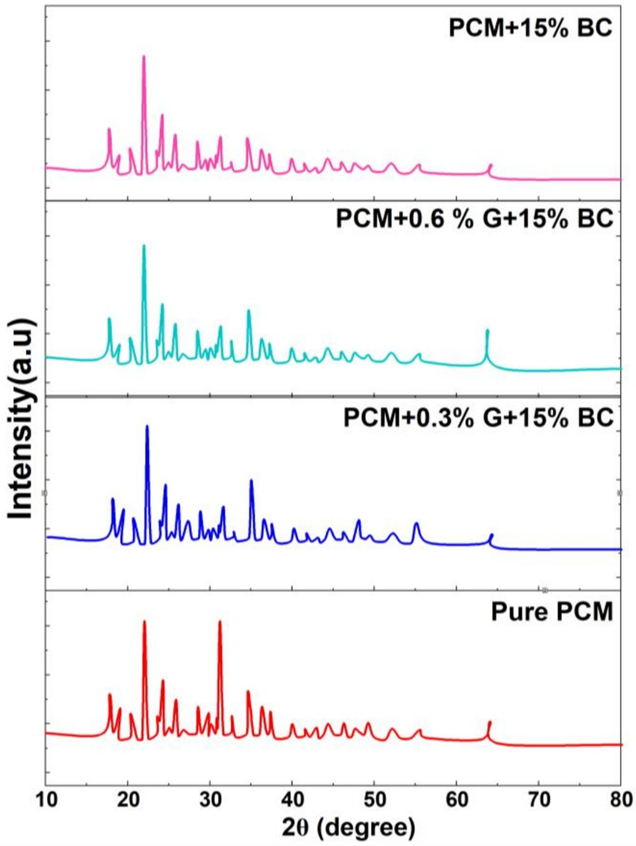


Figure 3. XRD analysis of PCM and composite samples

3.2. FTIR Analysis of the Prepared Samples

The functional groups of PCM and nano-improved PCM samples, namely PCM+15% BC, PCM+0.3% A+15% BC, and PCM+0.6% A+15% BC, were evaluated using FTIR spectroscopy, with the resulting spectrographs illustrated in Figure 4. The absorption bands between 2955 and 2850 cm^{-1} are attributed to the symmetrical stretching vibrations of CH3 and CH2 functional groups at PCM and PCM samples containing aluminum and charcoal. The bands between 1730 and 1700 cm^{-1} are attributed to the C O vibration in pure PCM and PCM samples containing aluminum and charcoal. The bands between 1470 and 1370 cm^{-1} correspond to vibration of O-H group. A in-plane and out-of-plane bending vibrations OH groups are attributed to the bands ranging from 1250 to 1050 cm^{-1}. FTIR examination corroborated the absence of any chemical interaction between PCM and charcoal or aluminum, as seen by the lack of additional bands in composite PCM samples. The comparison to pure PCM sample, the biochar–PCM samples (PCM+15% BC, PCM+0.3% A+15% BC, and PCM+0.6% A+15% BC) exhibit no novel functional groups. Therefore, it is clear that bio-composite samples exhibit chemical stability. Previous research revealed the presence of the -OH, Si-O-Si, and C=O functional groups in the biochar composite of the modified zeolite peanut shell through the use of the FTIR spectra. The results of observed peak shifts revealed an increase in the interaction with the surface and increased phosphate adsorption capacity [13].

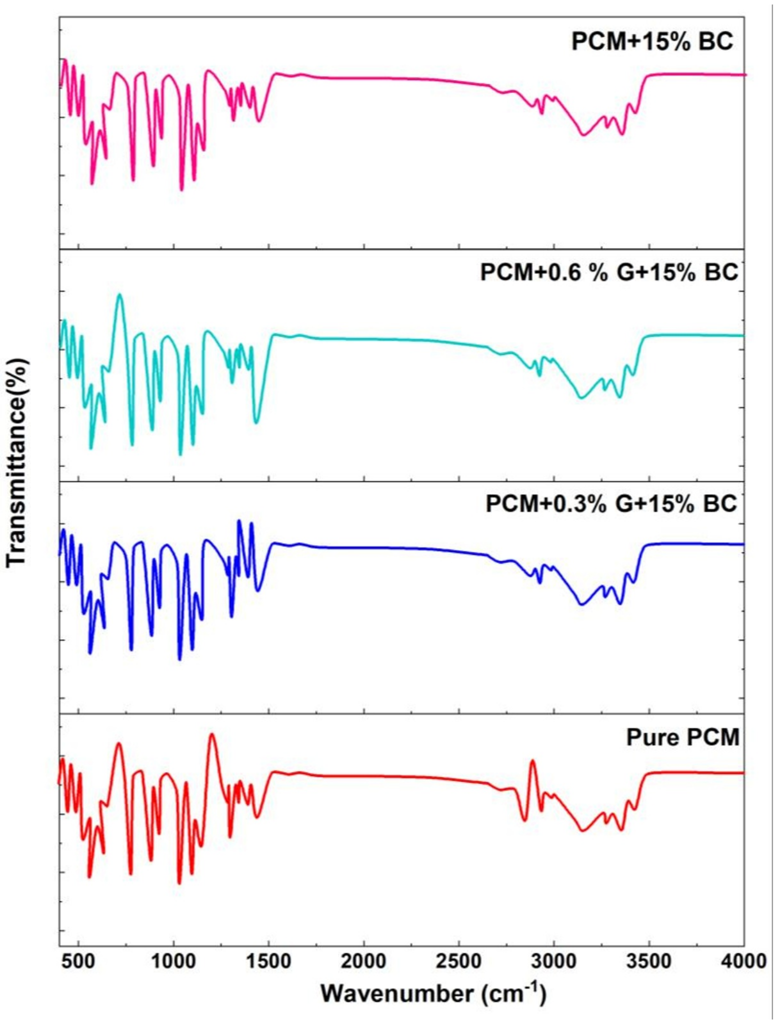


Figure 4. FTIR spectrum of PCM and composite samples

3.3. TGA Analysis of the Composite PCM Samples

Figure 5 illustrates the TGA curves of Xylitol PCM with varying aluminum nano powder weight fractions (0%, 0.3%, and 0.6%) and a constant peanut shell powder weight fraction of 15%, heating speeds of 20, 25, and 30°C/min. A weight loss percentage of PCM samples are represented as a function of temperature by subjecting the samples to different heating rates with temperature range of 30°C to 500°C. TGA analyses were performed by positioning a 2±0.6m PCM specimen in an alumina crucible within a flowing nitrogen atmosphere. The TGA data indicate that no samples experienced degradation before to the phase change, with an insignificant total weight loss of under 2%. Xylitol PCM demonstrates a phase transition temperature of around 190°C at 20°C/min. As heating rates escalated, the phase transition temperature rose. At increased phase transition temperatures, the TGA curves demonstrated a singular, sequential breakdown step. The use of biochar has led to a notable enhancement at thermal stability, accompanied by decrease in percentage weight loss. The weight reduction percentages PCM, PCM+15% BC, PCM+0.3% A+15% BC, and PCM+0.6% A+15% BC are as follows. This method enables direct assessment of thermal stability and underscores the variations in breakdown patterns among the produced materials. The results indicate that addition of biochar and aluminum leads to a significant improvement in the thermal stability of PCM as indicated by high activation energies and delayed decomposition behavior as evidenced in the TGA experiment. The enhanced thermal stability is needed to sustain the performance of phase change materials (PCMs) especially in medium-temperature energy storage systems because it ensures that its material is not affected by repeated thermal cycling. In the literature shows that, hydroxyapatite was utilized to functionalize the biochar peanut shells and TGA to investigate the stability of the structure and adsorption mechanism. These are underscored by excellent thermal performance that render these materials useful in the remediation and sustainable energy material design [14]. The raised activation energy values, especially for the composite containing 0.2% aluminum and 14% biochar, imply that the material necessitates considerably more energy for breakdown, hence signifying enhanced structural integrity at high temperatures.

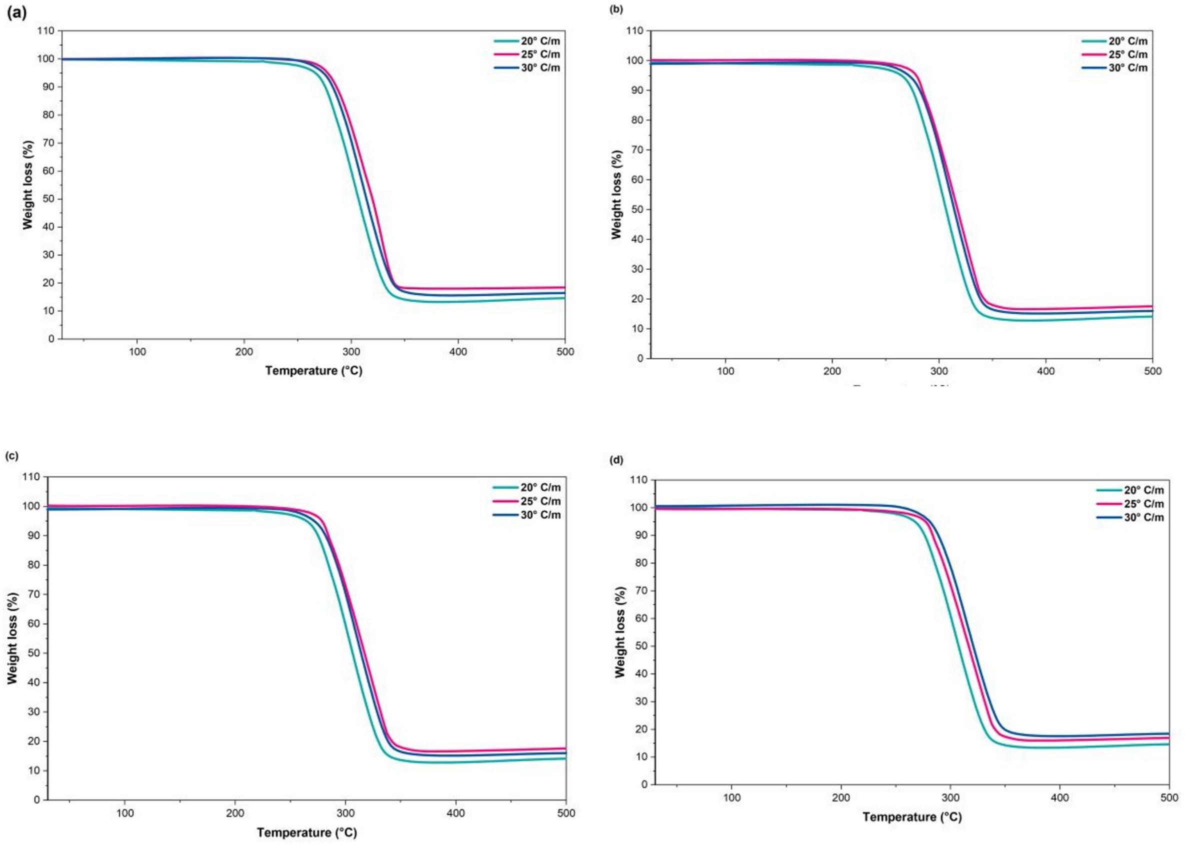


Figure 5. TGA plots (a) PCM, (b) PCM+0.3% A+15% BC, (c) PCM+0.6% A+15% BC, and (d) PCM+15% BC

3.4. DSC of the Composite PCM Samples

A DSC graphs of PCM and PCM with aluminum nanopowders and BNP composites demonstrate the thermal characteristics of these materials throughout the melting process. The phase transition temperature, denoting the shift between solid and liquid states, determined by drawing a tangent line at DSC heat flow curve at the transition point. The latent heat, or the energy necessary for the phase transition, may obtained by integrating area beneath these DSC heat flow graphs. Fig. 6 demonstrates that integration of charcoal and aluminum into the PCM induces significant alteration at phase transition temperature. The phase transition temperature varies from 78.5°C to 86.2°C, whereas the melting temperature escalates markedly from 95.6°C to 104.3°C. This alteration indicates that the additives affect thermal stability and transition characteristics of the PCM. Table 1 presents the latent heat values derived from the DSC curves. DSC analysis has been used in the prior to establish the melting temperature and transition enthalpy of sugar alcohol based phase change materials such as xylitol. The acquired heat capacity curves allowed the precise assessment of the thermodynamic properties that can be applied to storage thermal energy [15].

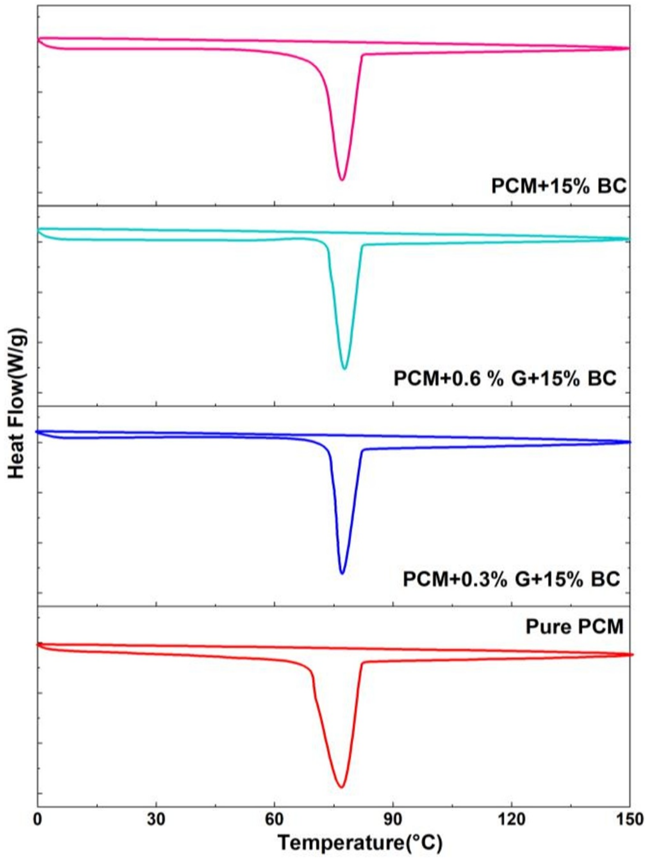


Figure 6. DSC of PCM, biochar–PCM, and biochar– PCM with aluminum

Table 1. Thermal properties of pure PCM, biochar–PCM, and biochar–PCM with aluminum

	T_{onset} (°C)	$T_{\max}$(°C)	Latent heat, ΔH_{m}(J/g)	T_{end} (°C)
PCM	85.7	94.6	358.4	103.8

PCM + 0.3%G + 15%BC	82.4	92.1	345.2	100.5
PCM + 0.6%G + 15%BC	80.3	89.7	332.8	98.4
PCM + 15%BC	79.8	88.4	325.6	96.9

3.5. Kinetic evaluation of the Composite PCM

A degradation kinetics of Xylitol PCM following the incorporation of charcoal and aluminum nanoparticles was examined using TGA. A non-isothermal method was utilized to investigate degradation kinetics of PCM by heating them 600°C at rates of 20, 25, and 30°C/min, while recording the percentage of weight loss. The kinetics of thermal breakdown were evaluated by analyzing the correlation between activation energy and the degree of conversion. A reduced activation energy indicates that less energy is necessary to decompose PCM molecules, hence enhancing the reaction rate. At 15% conversion, the disintegration rate of PCM was minimal, but it escalated swiftly to 60% when the activation energy increased from 10% to 60% conversion. The breakdown rate then escalated until it attained a stable state at 80% conversion, attributed to little reduction at activation energy. Table 2 indicates that PCM samples including nano-powder and biochar had an elevated breakdown rate at 15% conversion, which significantly diminished by 80% conversion. The unadulterated PCM had average activation energy of 83 kJ/mol. Conversely, PCM samples with 0.3% and 0.6% aluminum exhibited elevated activation energy values of 415.4 and 339.3 kJ/mol, respectively. TGA indicated that there was no notable weight loss for pure PCM or PCM samples containing 0.3% or 0.6% aluminum and 15% bio-nano-powder between room temperature and 200°C. Evaporation contributed insignificantly to thermal deterioration within this temperature range.

Table 2. Activation energy analysis of PCM using kinetic models

Conversion (5)	**Activation energy (E_a) (KI/mol)**		
	KAS technique	**FWO technique**	**Starink technique**
PCM			
0.2	90.8	96.2	91.5
0.3	88.6	94.1	89.3
0.4	85.4	91.3	86.1
0.6	80.9	87	81.7
0.6	78.5	85.2	79.4
0.7	77.6	84.6	78.7
0.8	83.4	89.1	84.2
PCM +0.3% aluminium+15% BC			
0.2	358.2	332.5	360.1
0.3	396.7	368.9	394.4

0.4	412.9	384.6	410.8
0.6	401.5	372.3	399.2
0.6	415.4	386.8	413
0.7	368.1	341.7	366
0.8	339.4	318.2	337.6
PCM +0.6% aluminum+15% BC			
0.2	188.4	170.3	186.9
0.3	197.2	179.6	195.8
0.4	212.6	193.4	210.9
0.6	226.8	207.5	225.2
0.6	244.9	223.6	243.1
0.7	268.7	241.2	266.4
0.8	264.3	238.9	262
Pure PCM + 15% BC			
0.2	27.5	17.5	26.5
0.3	28	17.9	27
0.4	27.8	17.6	26.8
0.6	27.2	17	26.2
0.6	26.5	16.3	25.5
0.7	25.5	15.5	24.6
0.8	24.8	14.8	23.8

Figure 7 illustrates the conversion (α) function of temperature for PCM and PCM composites with aluminum (G) and charcoal (BC) at several heating speeds (20, 25, and 30°C/min). All prepared materials demonstrate a significant increase in conversion within the thermal degradation range (240°C–250°C), with pure PCM exhibiting a more pronounced transition and nearly total conversion, whereas the composites reveal diminished maximum conversion and an expanded transition range, especially for PCM+15% BC, suggesting improved thermal stability and slower degradation kinetics. Biochar and aluminum addition can modify degradation behavior because of the effects of physical barriers, porous structure, and reorganization of surface functional groups, which reduce PCM chain mobility, alter crystallinity, and increase heat resistance. The hybrid system especially PCM+0.3% A+15% BC takes advantage of the high workability of aluminum and its high nucleating power and the stabilizing effect of biochar, resulting in delayed decomposition. This slight rise of the onset temperature observed with high heating rates is also consistent with kinetic theory, as more energy is required to initiate degradation, which supports the results in the literature of biochar and aluminum-enhanced PCM composites. The results reveal that the degradation characteristics of PCM can be adjusted with customized hybrid filler in order to enhance the efficiency of thermal energy storage.

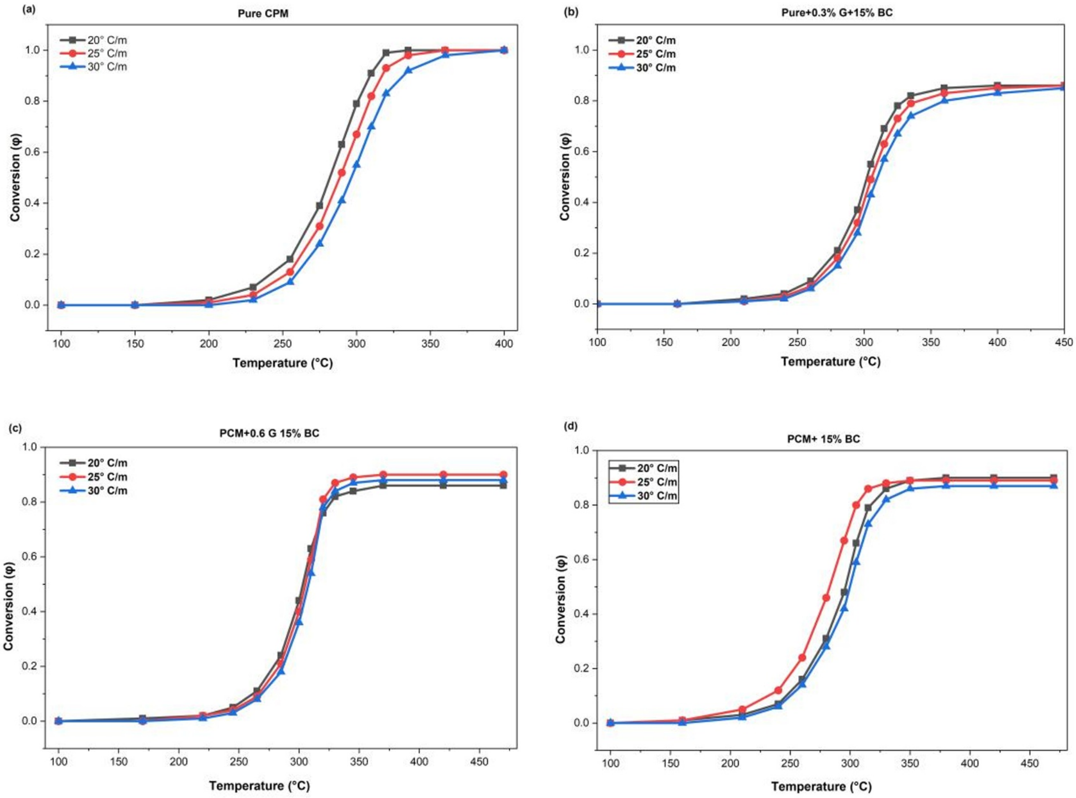


Figure 7. Conversion plots (a) PCM, (b) PCM+0.3% A+15% BC, (c) PCM+0.6% A+15% BC, and (d) PCM+15% BC

Figure 8 illustrates the activation energy curves for pure PCM and its composites including varying amounts of aluminum and charcoal as a function of conversion. As conversion rises, the activation energy of the pure PCM progressively diminishes, which is characteristic of a phase change material undergoing thermal deterioration. The addition of aluminum and charcoal, seen in Figure 8 (b & c) reveals activation energy patterns with pronounced peaks at intermediate conversions, indicating complex degradation processes likely facilitated by the structural and catalytic attributes of the additives. The activation energy of pure PCM determined to range from 95 to 400 kJ/mol for both pure and composite PCM, utilizing the Friedman, KAS, FWO, Vyazovkin, and Starink methodologies for conversion (α) values between 0.1 and 0.9, as seen in Figure 8. Nonetheless, the reduction is shown to be quite minimal. The average activation energy of PCM and composite PCM is about same across the Friedman, Vyazovkin, and Starink methodologies.

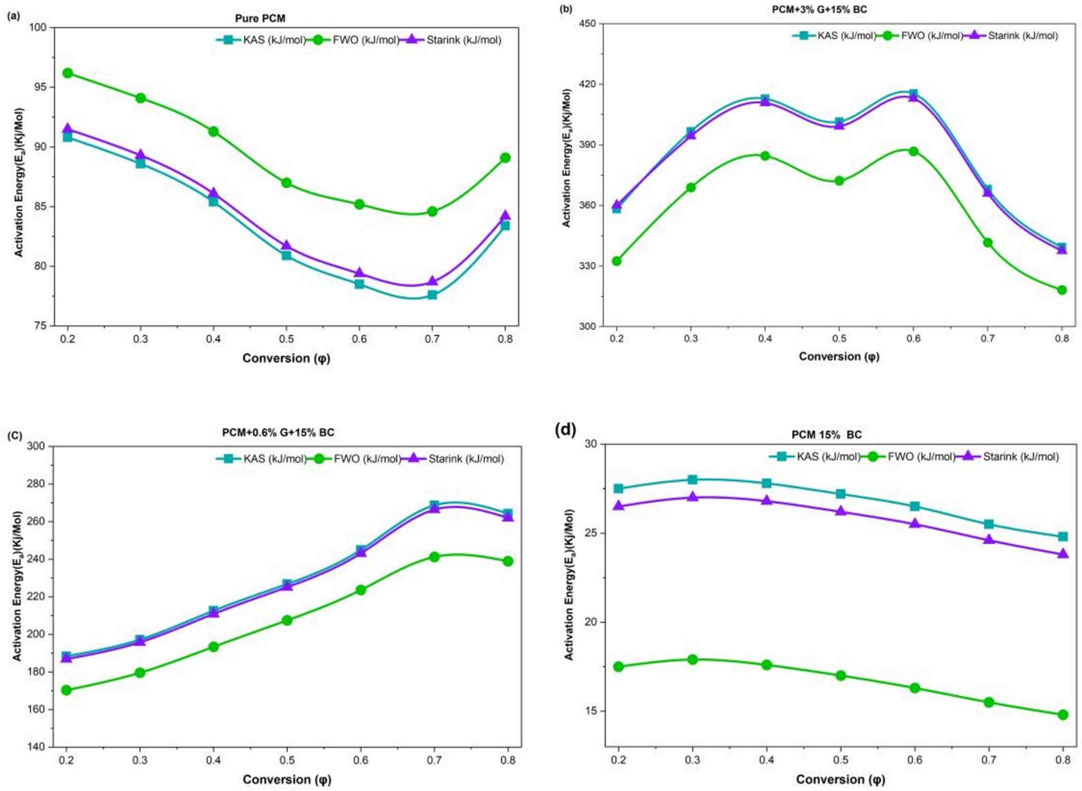


Figure 8. Activation energy to various conversions. (a) PCM, (b) PCM+0.3% A+15% BC, (c) PCM+0.6% A+15% BC, and (d) PCM+15% BC

4. Conclusion

The limited thermal stability and moderate degradation resistance of sugar alcohol–based phase change materials (PCMs), particularly xylitol, restrict their long-term applicability in medium-temperature thermal energy storage systems. To address this issue, xylitol was reinforced with 15 wt% peanut shell–derived activated biochar (BC) and aluminum nanoparticles at 0.3 wt% and 0.6 wt% concentrations to form hybrid nano-enhanced PCM composites. The materials were synthesized using controlled pyrolysis for biochar preparation followed by a two-step dispersion technique for composite fabrication. Structural stability was verified using XRD and FTIR, while thermal characteristics were examined using DSC and non-isothermal TGA at 20, 25, and 30°C/min, and degradation kinetics were evaluated using KAS, FWO, and Starink iso-conversional models. The DSC analysis indicated that pure PCM had a melting onset temperature of 85.7ºC, peak temperature of 94.6ºC, and latent heat of 358.4 J/g, PCM + 0.6% Al + 15%BC, and PCM + 0.3% Al + 15%BC had latent heat of 345.2 J/g and 332.8 J/g, respectively. TGA ensured that there was insignificant loss of mass below 200 o C and kinetic analysis revealed that pure PCM had an average activation energy of 83-90 kJ/mol, PCM+0.3%Al+15%BC and PCM+0.6%Al+15%BC had average activation energies of 358.2-415.4 kJ/mol and 188.4-268.7 kJ/mol respectively, which were very higher and confirmed that both had much The 0.3% aluminum composite was the best of the prepared samples because it exhibited the greatest resistance to thermal degradation and decomposition retardation. These results prove that biochar aluminum hybrid reinforcement is a viable process to improve the thermophysical stability of xylitol PCM and hence the developed composites can be used in medium-temperature thermal energy storage system like solar thermal, industrial waste heat recovery and desalination processes.

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