

# Енергозберігаючі технології

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## Heat accumulation with montmorillonite / carnauba wax nanomaterials

A thermal energy latent accumulation using phase change materials attracts interest in energy storage under an isothermal condition. An introduction of the green chemistry principles in the creation of form-stable phase change materials occupies its justified technological niche. Information about the behavior of the molecules of materials obtained using physicochemical methods including NMR spectroscopy can be used to optimize the choice of material. The materials are required longer general thermal, chemical stability and according to the thermal cycling test for the extended performance of a system. The phase change materials with a phase transition were obtained from melts by mixing nanosized montmorillonite with carnauba wax. As a result, a number of wax/nanomaterials solid samples were prepared by grinding with a mass ratio of 70/30, 60/40 and 50/50 %. The created composite materials had the latent heat, respectively 115.5 J/g for 70/30, 107.8 J/g for 60/40 and 91.4 J/g for 50/50 samples. There is a correlation between the wax content in the phase change materials (PCMs) 70, 60 and 50 % and the percentage of heat accumulation relative to pure wax, namely 61, 57 and 48 %. The black-grey material obtained makes it possible to reduce the time intervals of the cycle of accumulation and return of heat. The profiles of heat absorption curves for all materials break off at 100 °C and the cooling curves have two regions of heat loss. The area under the DSC curves during the first heating of the powders is more on 42 % of whole pieces of PCMs. The PCMs (50/50) <sup>13</sup>C resonances were at around 20–40 ppm, which are the typical chemical shifts for the methylene carbons of the aliphatic region, at 62.82, 63.46 ppm for the oxygenated species, at 114.05, 116.11 ppm for the alkenes at 130.68, 133.44 ppm for the aromatic rings and at 172.92, 178.72 ppm for the carboxylic groups. <sup>27</sup>Al spectrum has the maximum at 2.90 ppm of octahedral aluminium and at 26.53 ppm may belong to a distorted tetrahedral site. *Bibl. 43, Fig. 3.*

**Keywords:** energy, storage, nanoclay, wax, phase transition material.

The thermal energy latent accumulation using a high density of lateral energy storage in isothermal conditions. The introduction of the green phase change materials (PCMs) attracts interest in

chemistry principles in the creation of form-stable phase change materials occupies its justified technological niche. The increasing energy demand in conjunction with greater environmental concern has lifted the development of sustainable energy sources [1, 2].

The ideal PCMs should be characterised by: adequate phase transition temperature to meet the needs of practical use, high melting enthalpy ensuring the high latent heat storage capacity, faster discharging and charging due to high thermal conductivity, persistent chemical and thermal properties to provide the rigid thermal storage capacity, non-toxic, non-flammable, non-corrosive and, non-explosive to provide safety and avoid harm to surroundings, compatibility with the construction materials, small enough supercooling, subtle volume variation during phase transition, high nucleation rate range, adequate rate of crystallisation, high latent heat of phase transition per unit volume, high specific heat for sensible thermal changes, fully reversible freeze/melt cycle storage, low vapour pressure at the operating temperatures for safety, positive phase equilibrium, abundant and easily available low cost, good recyclability for environmental and economic reasons [3].

To create dimensionally stable composites, clays are often added to organics that meet the criteria of “green” chemistry. Meanwhile, the clay mineral materials have relatively high thermal conductivity and excellent adsorbability. Nine kinds of mineral materials were summarized [4], that is kaolin, diatomite, sepiolite, montmorillonite, perlite, SiO<sub>2</sub>, attapulgite, vermiculite and fly ash. The large specific surface area and prominent porous structure of clay mineral materials can successfully prevent the flow and leakage of PCMs [5, 6]. Publications have persistently suggested the use of nanoparticles and nanomaterials to solve the phase change materials' low thermal-conductivity, supercooling, leakage, phase segregation and inflammability problems amongst others. This has not only shown promise of improved heat transfer and phase transition performance but also, reduced charging time and phase transition temperatures amongst many other benefits with limited distortion of other material properties. They also have a number of other advantages, such as high adsorption capacity, good thermal stability and ease of use, which gives the potential for practical application in heat-storing materials. Halloysite nanotubes are an oxide clay

silicate mineral that is abundantly available worldwide. Cavities can be filled with various molecules to create effective functional materials [7–9].

The montmorillonite (bentonite) is promising additive to phase change material. Paraffin/bentonite composite was prepared by a solution intercalation process. The XRD results show that the layer distance of bentonite has been increased from 1.49175 nm to 1.96235 nm through organic modification. The latent heat capacity of the composite is 39.84 J/g. The heat transfer rate of prepared PCMs was enhanced by bentonite [10]. Composite phase change materials were prepared by blending butyl stearate, dodecanol with an organically modified montmorillonite. It is established that due to the high thermal conductivity of bentonite, the heat transfer rate of PCMs is exactly higher than without clay [11, 12]. The solid-solid phase change polyurethane materials were successfully prepared when the molar ratio of polyethylene glycol to 4'4-diphenylmethane diisocyanate was 0.75, and the organic montmorillonite acted as a crosslinking heterogeneous nucleating agent to improve the temperature control capacity, the crystallization ability and the thermal stability of the solid-solid phase change polyurethane material. When the addition of montmorillonite was 0.5 %, the phase change enthalpy of PCMs increased from 95.46 J/g to 106.8 J/g. The relative crystallinity increased from 66.5 % to 74.8 % and the initial thermal weight loss temperature was increased from 348 °C to 368 °C [13].

The phase change enthalpies of the reduced graphene oxide-montmorillonite-poly(vinyl alcohol) PCMs composite were 189.4–191.2 J/g, along with a satisfactory structural and thermal cycle stability over 2000 thermal cycles. The thermal conductivity of PCMs reached 0.418 W/(m·K), which was almost 157% that of pure polymer. At the same time, the sunlight absorbability of the composite PCMs increased from 40 % to 90 % upon loading with a 5 % content of graphene oxide [14]. The adsorption rate experiment results show that the mass ratio of capric-stearic acid/montmorillonite is 35:65, which can effectively prevent the leakage of PCMs. The thermal conductivity of PCMs with 2 % graphene increases by 156.4 % [15]. A composite phase change material comprised of organic montmorillonite/paraffin/grafted multi-walled nanotube is synthesized via ultrasonic

dispersion and liquid intercalation. The latent heat is 47.1 J/g, and the thermal conductivity of the PCMs composites is 65% higher than that of paraffin [16]. It used a vacuum impregnation method to prepare shape stabilized PCMs that contained sodium montmorillonite and exfoliated graphite nanoplatelets, to improve the thermal conductivity of PCMs, and prevent leakage of the liquid state of ones [17].

The montmorillonite framework has been exfoliated into two-dimensional montmorillonite nanosheets it provides super porosity and huge specific surface area to encapsulate more than 95 % stearic acid without leakage, resulting in the highest latent heat capacity 198.78 J/g among clay mineral based composite PCMs. Besides, the composites provided rapid heat transfer paths, leading to outstanding thermal transfer ability and excellent photo-thermal conversion performances [18]. The most successful organoclay composite sample, prepared by intercalating 9 mmol *n*-hexadecane per gram of Na-montmorillonite, displayed a high heat capacity 126 J/g and good thermal durability [19].

The paraffin (petroleum) wax is a soft colorless solid derived from petroleum, coal or oil shale has good performance of PCMs due to the melting temperature range of 60–75 °C, high latent heat capacity, satisfactory thermal and chemical stability, no supercooling during phase transition, non-toxicity and non-corrosive to metal containers. However, they are produced from non-renewable sources and their carbon footprint and associated environmental impact cannot be overlooked [20]. Besides, paraffin wax has a low thermal conductivity, hindering its heat charging and discharging process. It is found that the maximum thermal conductivity enhancement 48 % is exhibited by paraffin wax/0.06 % carbon nanotubes compared to pure wax [21, 22]. The best performance with regards to thermal conductivity is given by 2 % graphene-paraffin wax nanocomposites, which has been improved 66.15 % when compared with pure paraffin [23]. The paraffin wax composites with different loading levels 0.5–2 % of  $\alpha$ -nanoalumina were successfully synthesized as PCMs [24]. The 8 % aluminum foils in paraffin wax doubled the thermal conductivity, achieving values of 0.63 W/(m·K) [25]. Phase change materials based on graphite-filled Fischer-Tropsch wax/polyethylene blends could find application as thermal energy storage materials.

Expanded graphite enhanced the thermal conductivity by more than 200 % at a loading of 10 % [26].

Researchers use for the synthesis of wax PCMs of natural origin. The heat storage-dissipation performance and thermal stability of the sugarcane wax-based composite PCMs layer with the heat capacity of 2.86 J/g-was influenced by its thickness [27]. Shellac wax storage efficiency is comparable to existing paraffin wax, stearic acid and palmitic acid-based latent heat thermal energy storage unit. In this regard, shellac wax can be a potential bio-PCMs for medium temperature range 60–80 °C solar thermal applications such as domestic water heating and food drying [28]. Of the by-products, coffee wastes were effectively vacuum impregnated into each natural wax, which is currently consumed and abandoned as coffee as a drink, was used as the supporting material for PCMs. The use of bio-compatible PCMs by-products is economical as well as environmentally friendly and is sufficient for building applications [29]. The use of carnauba wax with a melting point above 80 °C (higher than in paraffin) in PCMs can lead to a significant increase in heat capacity of materials [2].

PCMs are implemented by primarily in the construction industry for the microclimate creation. The application of these systems in thermo-regulating systems such as refrigeration, air conditioning, personal thermal comfort, and other construction, has been widely accepted too. Finding new materials and improving traditional constructive solutions for more efficient building envelopes leads to significant application opportunities to decrease the energy demand for heating and cooling, as well as to reduce global energy consumption and greenhouse gas emissions at the buildings' level. For example, the reduction of 24 % was attained, for the thermal conductivity, and the specific heat capacity was increased 17 % with the PCMs incorporation. Another one proved to be the most conductive, with a 71 % increase in the thermal conductivity value, and also the one with the highest specific heat, that increased 60 %. By using the clay-straw construction integrating PCMs instead of the cement construction, the interior heat flux density is reduced by 72 % [30–32].

Knowledge of the mechanism of PCMs exploitation is important for the creation of efficient energy storage systems. Information about the behavior of the molecules of materials obtained using

physicochemical methods including NMR spectroscopy can be used to optimize the choice of material. PCMs are required longer general thermal, chemical stability and according to the thermal cycling test for the extended performance of a system [33, 34]. Changes in the structure of the material can be detected by spectroscopy, which allows us to assert the materials stability. Compounding organic materials with other materials can effectively improve the thermal conductivity, the faster discharging and charging and the fully reversible freeze/melt cycle storage [35, 36]. The improvement in thermal conductivity correlates with a greater intensity of interaction between molecules, atoms through chemical bonds and other types of attraction.

### Experimental part

Montmorillonite K10 nanoclay (Sigma-Aldrich 281522, surface area according the quality certification is 220–270 m<sup>2</sup>/g) was mixed with Carnauba wax (Nature Product, it is in the form of yellow-brown flakes) at 110–120 °C using a magnetic stirrer for 30 min and rapidly cooled with cold water to prevent sedimentation of nanoclay. The particles of the montmorillonite are plate-shaped with an average diameter around 1 μm and a thickness of 0.96 nm. As a result, a number of black solid samples of wax/nanoclay with 50/50, 60/40 and 70/30 mass ratios were prepared from the melt. Big pieces of materials were ground during 20 min to obtained the polydisperse powders.

Differential scanning calorimetry was performed using Perkin Elmer 8500 equipment with a linear heating rate of 10 °C/min within 0–200 °C. The samples of polydisperse powder weighing about 10 g were placed in a cuvette and the recording of spectra began from zero temperature. The standard for calculating the experimental curves of differential thermal analysis was the carnauba wax with a melting enthalpy of 189.09 ± 2 J/g.

All solid-state NMR spectra were recorded on a Bruker Avance 400 DSX NMR spectrometer at a <sup>13</sup>C frequency of 100.55 MHz, <sup>27</sup>Al frequency of 535.16 MHz and <sup>1</sup>H frequency of 399.87 MHz. A commercial three-channel 4 mm Bruker probe head at 10 kHz MAS was used for all experiments. The <sup>1</sup>H NMR spectra were recorded averaging 32 transients with 8 s recycle delay. For all solid-state <sup>13</sup>C CP MAS NMR experiments, an initial 90° pulse with 4.0 μs length and 5 s recycle delay were used.

A ramped CP pulse (64–100 %) with duration of 3 ms. Transients of 2 k were averaged for the CP experiments. The spectra were baseline-corrected, and a broadening of 50 Hz was applied. The spectra were referenced to external adamantane at 38.5 ppm (<sup>13</sup>C), 1.63 ppm (<sup>1</sup>H) and to solution of AlCl<sub>3</sub> at 0 ppm.

### Results and discussion

Carnauba (palm) is a wax of the leaves of the carnauba palm *Copernicia prunifera*. It is obtained by collecting and drying the leaves which are a renewable source of raw materials, beating them to loosen the wax, then refining and bleaching the wax. Carnauba consists mostly of aliphatic esters (≈ 40 %), diesters of 4-hydroxycinnamic acid (≈ 21 %), ω-hydroxycarboxylic acids (≈ 13 %) and fatty alcohols (≈ 12 %). The compounds are predominantly derived from acids and alcohols in the C<sub>26</sub>–C<sub>30</sub> range. The wax has other compounds in less concentrations including unsaturated ones. Montmorillonite 2 : 1 type clay is hydrated sodium calcium aluminium magnesium silicate hydroxide (Na,Ca)<sub>0.33</sub>(Al,Mg)<sub>2</sub>(Si<sub>4</sub>O<sub>10</sub>)(OH)<sub>2</sub>·*n*H<sub>2</sub>O. The clay has two tetrahedral sheets of silica sandwiching a alumina central octahedral sheet. The water can intervene in the sheets of clay causing the one to swell.

Montmorillonite characterized as having greater than 50 % octahedral charge. Its cation exchange capacity is due to isomorphous substitution of Mg<sup>2+</sup> for Al<sup>3+</sup> in the central alumina plane. The substitution of lower valence cations in such instances leaves the nearby oxygen atoms with a net negative charge that can attract cations. The variable colors of nanoclays are the results interlayer cation substitution by iron, manganese, titanium and other within the lattice structure and depend upon the concentration and valence state of cations.

The montmorillonite we used had a light gray color. After converting the wax into the liquid state according to the synthesis procedure, it retained its original (Figure 1, a) yellow-brown color. The nanoclay was added to the liquid while stirring. Visual observation revealed a rapid color change towards a black shade (Figure 1, b). The polydisperse powder of the PCMs has a dark gray color with areas of the black shade. One of the reasons for the drastic color change can be the intercalation of organic molecules in the layers of the montmorillonite [18, 19]. Ion-exchanged cations

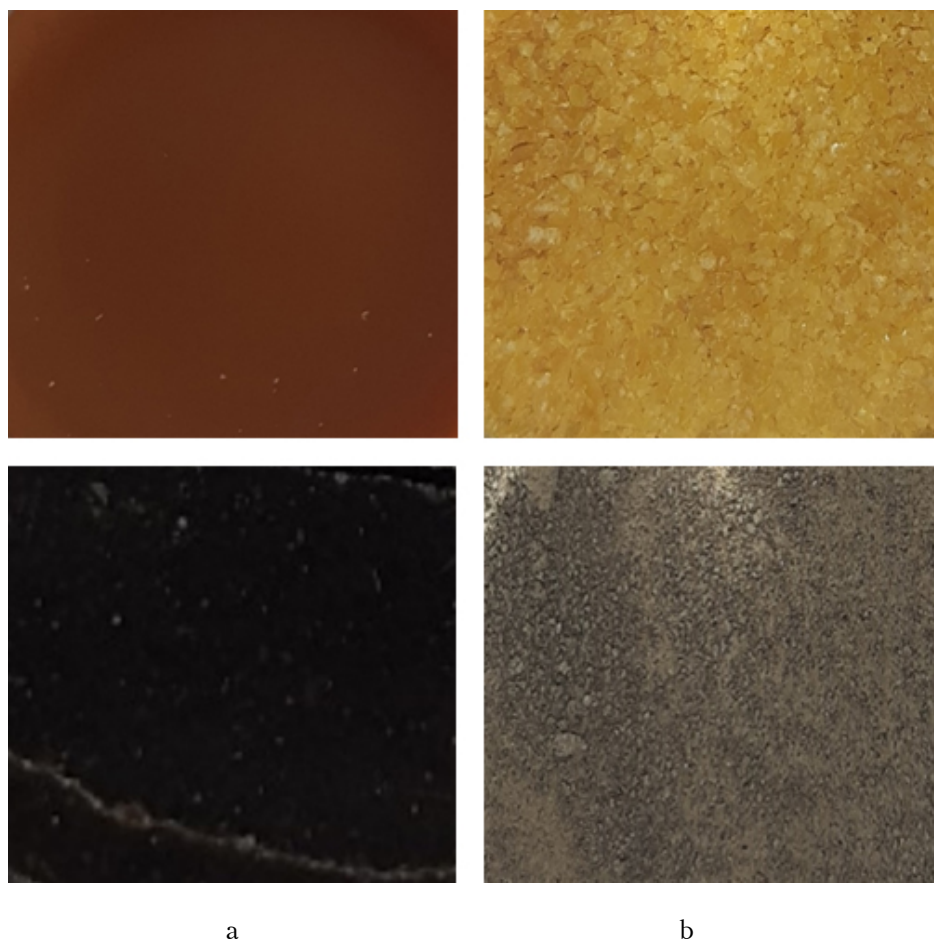


Figure 1. Optical images of the pure wax (a) and 50/50 synthesized materials (b), the whole pieces surface (left) and polydisperse powders (right).

can enter into chemical reactions with components of the wax to change the composite color. It is well known that the black color of the PCMs allows to quickly absorb solar radiation. The material makes it possible to reduce the time intervals of the cycle of accumulation and return of heat.

All obtained powder samples on the DSC curves have one asymmetric maximum at 86.8-87.9 °C, which corresponds to heating and the transition from solid to liquid state. The visible onset of endothermic heat absorption occurred at above 50 °C, with sharp heat absorption at temperatures above 75 °C. The profiles of heat absorption curves for all materials break off at 100 °C (Figure 2). The cooling curves have two regions of heat loss. The pure wax showed two distinct peaks at 68.4 and 63.2 °C. After added the clay in PCMs it observed the shift of the high temperature peak to 71.5–

72.5 °C. The 3–4 °C shift behavior can be due clay, which has the higher thermal conductivity than wax. The heat desorption occurs faster the presence of clay. Another phenomenon was observed, namely, a decrease in the heat transfer intensity at the low-temperature peak with a significant change in the profile from the maximum to the shoulder (Figure 2).

After the first cycle of heating and cooling, polydisperse powders will transform into a solid state. The reheating curves are slightly different in shape and have a down-temperature shift of maxima 0.7–4.8 °C to 83.1–86.1 °C compared to the first one (Figure 2). Carnauba wax is the most refractory melting point 80–91 °C and hard of waxes of plant origin. Our experiments confirm the high melting point above 80 °C of wax in PCMs composites. Paraffin wax has a melting point of 45–65 °C [10].

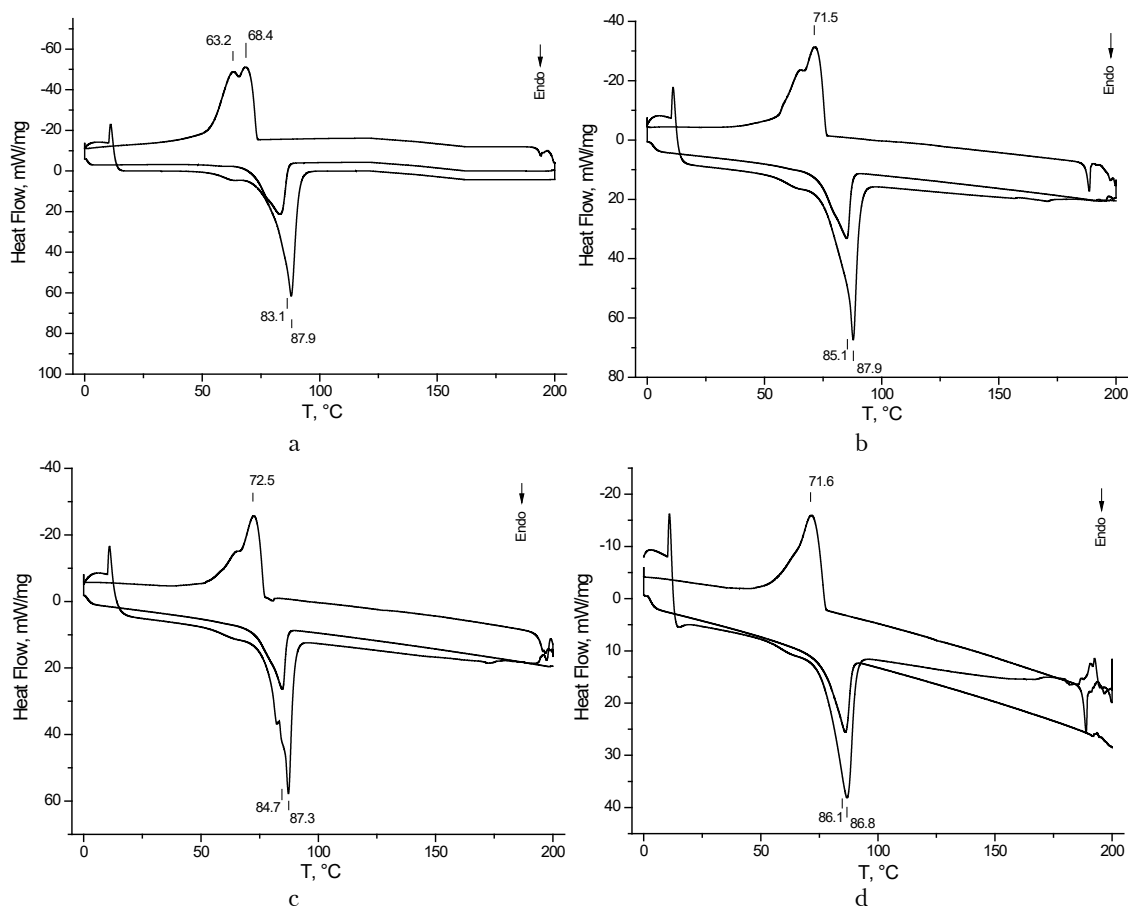


Figure 2. DSC curves of heat absorption-desorbption of pure wax (a) and composite materials 70/30 (b), 60/40 (c), 50/50 (d) %.

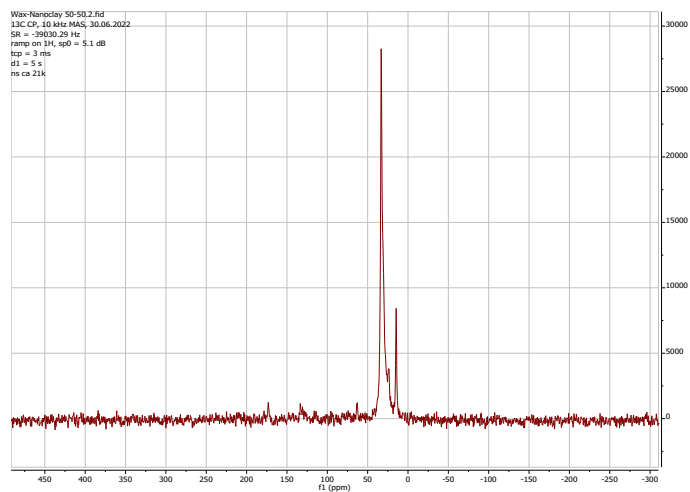
The materials have a much lower heat of fusion than pure wax, respectively 115.5 J/g for 70/30, 107.8 J/g for 60/40 and 91.4 J/g for 50/50 samples. There is a correlation between the wax content in the PCMs 70, 60 and 50 % and the percentage of heat accumulation relative to pure wax, namely 61, 57 and 48 %. The higher the wax content, the greater the amount of thermal energy accumulation – the higher the productivity of PCM products. Obviously, clays with a heat of melting 1250–1300 °C do not significant participate in the accumulation of heat and serve primarily as a molding material.

The area under the DSC curves during the first heating of the powders is more on 42 % of whole pieces of PCMs. The lower storage capacity of the solid body relative to the powders is probably due to the peculiarities of the powder melting process, which requires more energy. It takes more energy to assemble particles of material into a whole body.

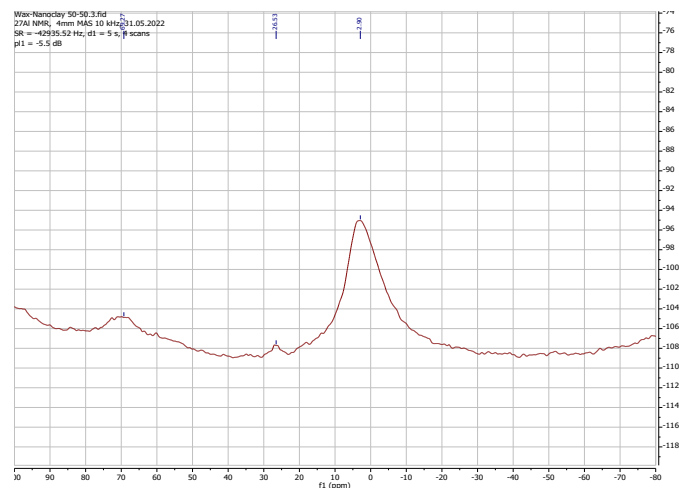
Other factors related to the 3D structure of the samples can also influence this process.

The different electronic environment of carbon atoms in the natural wax, consisting of dozens of molecules types, causes the appearance of many signals. We can see the resulting signal from energetically close functional groups of atoms. All clear signals are a superposition of molecular responses. In the same region, signals from different structural fragments of molecules can be observed. Based on the data of correlation tables NMR spectra and related publications were analyzed the signals [37–39].

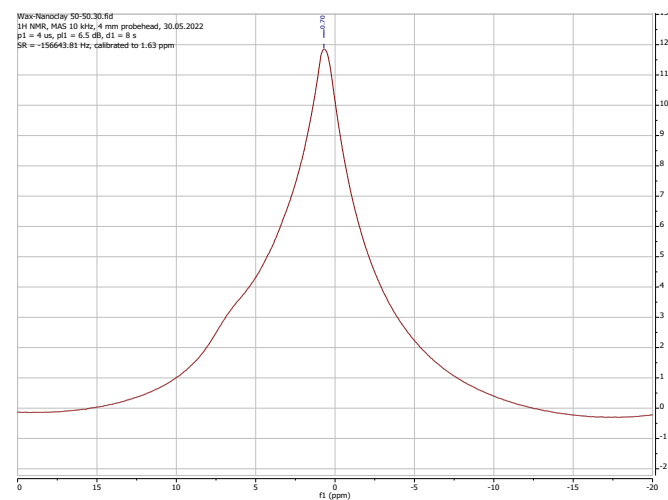
The  $^{13}\text{C}$  CP/NMR spectrum of native wax at room temperature has the peak at 14.63 ppm unambiguously corresponds to the methyl carbons  $(-\text{CH}_2)_n-\text{CH}_3$  at the terminal chain of hydrocarbon radicals. The strongest resonances were at around 20–40 ppm, which are the typical chemical shifts for the methylene carbons  $(-\text{CH}_2)_n-$  of the



a



b



c

Figure 3. <sup>13</sup>C (a), <sup>27</sup>Al (b) and <sup>1</sup>H (c) NMR spectra of composite material 50/50 %.

aliphatic region. The peaks are observed at 62.82 and 63.46 ppm in the  $^{13}\text{C}$  spectrum can be assigned as an oxygenated species of the fatty alcohols  $\text{C}-\text{O}-\text{H}$  and the simple ethers  $\text{C}-\text{O}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ,  $\text{C}^{\text{arom}}-\text{O}-\text{CH}_3$  groups, respectively. The weak  $^{13}\text{C}$  signals 114.05 and 116.11 ppm were assigned to the alkenes 130.68 and 133.44 ppm to the aromatic rings. The wax chemical composition has two significant groups of carbonyl atoms – esters ( $\text{R}-\text{COO}-\text{R}^1$ ) and free acids ( $-\text{COOH}$ ). Therefore, the  $^{13}\text{C}$  signals in the carbonyl region from the opposite side of the spectrum with a high probability can be interpreted as the esters 172.92 and the carboxylic acids 178.72 ppm. The chemical shifts of the methylenes are slightly neither in the solid wax than those in liquid phase by the packing of the alkene chains in the solid one and additional van der Waals force [38, 39].

$^{27}\text{Al}$  spectrum has the maximum at 2.90 ppm of one octahedral aluminium site ( $^{\text{VI}}\text{Al}$ ). The signal at 26.53 ppm may belong to a distorted tetrahedral site ( $^{\text{IV}}\text{Al}$ ) or fifth coordinated aluminium ( $^{\text{V}}\text{Al}$ ).  $^{27}\text{Al}$  spectrum has the broad profile signal of tetrahedral site 69.27 ppm of aluminium of  $\text{Q}^3(3\text{ Si})$  structure. The  $\text{Q}^4(4\text{ Si})$  unit signal did not clear appear on the spectrum in the region 52–68 ppm [40]. Figure 3 shows the  $^1\text{H}$  NMR spectrum of the sample which displays one major water signal centered at 0.70 ppm. The clay has a broader signal between 0 and 4 ppm associated with the framework hydroxyl groups [41].

The interaction between clay particles and the wax matrix significantly depends upon the hydroxyl groups, defects and charges of CPMS surface. Electrical conduction pathways of nanoclay should be considered as a potential mechanism for thermal conduction. The electrical conductivity of the montmorillonite porous material is the combination of conductivities of the matrix material and the pore fluid. Molecules and ions in the pores can create additional heat transfer channels. NMR spectroscopy makes it possible to reveal the presented mechanisms of heat transfer. During thermal heating, the mobility and conformation of groups of atoms changes, which is reflected in the NMR spectra.

According to the theory of phonon propagation, huge gaps between two different materials in a mixture can lead to serious surface scattering of phonons and, consequently, to a decrease in thermal productivity. To successfully reduce the thermal resistance, it is important that chemical bonds

are formed to create additional heat transfer paths at the interface of materials and increase thermal conductivity. The thermal conductivity of different waxes is low and is about 0.3–0.4  $\text{W}/(\text{m}\cdot\text{K})$ , with the addition of nanomaterials there is an increase in heat transfer rate in composite materials with increasing content of ones to 0.7–0.9  $\text{W}/(\text{m}\cdot\text{K})$  [2, 42].

There are a number of companies on the market that need to improve existing PCMs materials. They are used to create technical solutions for building, electronic product, textile, cooling accessory [43].

## Conclusions

A number of shape-stable materials with a phase transition were obtained from melts by mixing nanosized montmorillonite with carnauba wax. As a result, a number of wax/nanomaterials solid samples were prepared by grinding with a mass ratio of 70/30, 60/40 and 50/50. The materials have a lower heat of fusion than wax, respectively 115.5 J/g for 70/30, 107.8 J/g for 60/40 and 91.4 J/g for 50/50 samples. There is a correlation between the wax content in the PCMs 70, 60 and 50 % and the percentage of heat accumulation relative to pure wax, namely 61, 57 and 48 %. The PCMs (50/50) resonances were at around 20–40 ppm, which are the typical chemical shifts for the methylene carbons of the aliphatic region, at 62.82, 63.46 ppm for the oxygenated species, at 114.05, 116.11 ppm for the alkenes at 130.68, 133.44 ppm for the aromatic rings and at 172.92, 178.72 ppm for the carboxylic groups.  $^{27}\text{Al}$  spectrum has the maximum at 2.90 ppm of one octahedral aluminium site and at 26.53 ppm may belong to a distorted tetrahedral site.

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## **Аккумуляция тепла наноматериалами монтморилонит / карнаубский воск**

Скрытое накопление тепловой энергии с использованием материалов с изменением фазы привлекает интерес к накоплению энергии в изотермических условиях. Свою оправданную технологическую нишу занимает внедрение принципов «зеленой» химии при создании формоустойчивых фазоизмененных материалов. Информация о поведении молекул материалов, полученная с помощью физико-химических методов, включая ЯМР-спектроскопию, может быть использована для оптимизации выбора материала. Материалы требуют более длительной общей термической и химической стабильности для расширенной продуктивности системы. Формоустойчивые материалы с фазовым переходом получали из расплавов вследствие смешивания наноразмерного монтморилонита с карнаубским воском. В результате измельчения был получен ряд твердых образцов воска/наноматериалов с массовым соотношением 70/30, 60/40 и 50/50 %. Черный цвет материалов позволяет быстро поглощать солнечное излучение. Созданные композиционные материалы имели скрытую теплоту соответственно 115,5 Дж/г для образцов 70/30, 107,8 Дж/г — для 60/40 и 91,4 Дж/г — для 50/50. Существует корреляция между содержанием воска в материалах с фазовым переходом 70, 60 и 50 % и процентом накопления тепла относительно чистого воска, а именно: 61, 57 и 48 %. Полученный черно-серый материал позволяет сократить временные промежутки цикла аккумуляции и отдачи тепла. Профили кривых теплопоглощения для всех материалов обрываются при 100 °С, а кривые охлаждения имеют две области потери тепла. Площадь под кривыми ДСК при первом нагревании порошков на 42 % больше, чем у целых кусков материалов. Материал с фазовым переходом (50/50) имеет <sup>13</sup>C резонансы около 20–40 м.д., что есть типичным химическим сдвигом для метиленовых углеродов алифатической области, а также для оксигенированных форм — 62,82, 63,46 м.д., для алкенов — 114,05, 116,11 м.д., для ароматических колец — 130,68, 133,44 м.д., для карбоксильных групп — 172,92, 178,72 м.д. Спектр <sup>27</sup>Al имеет максимум при 2,90 м.д. октаэдричного алюминия и при 26,53 м.д. может принадлежать к тетраэдричному алюминию глины. *Библ. 43, рис. 3.*

**Ключевые слова:** энергия, сбережение, наноглина, воск, материал фазового перехода.

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## **Акумуляція тепла наноматеріалами монтморилоніт / карнаубський віск**

Приховане накопичення теплової енергії з використанням матеріалів зі зміною фази привертає інтерес до накопичення енергії в ізотермічних умовах. Свою виправдану технологічну нішу займає впровадження принципів «зеленої» хімії при створенні формостійких

фазозмінних матеріалів. Інформація про поведінку молекул матеріалів, отримана за допомогою фізико-хімічних методів, включаючи ЯМР-спектроскопію, може бути використана для оптимізації вибору матеріалу. Матеріали вимагають довшої загальної термічної та хімічної стабільності для розширеної продуктивності системи. Формостійкі матеріали з фазовим переходом отримували з розплавів шляхом змішування нанорозмірного монтморилоніту з карнауцьким воском. У результаті подрібнення було отримано ряд твердих зразків воску/наноматеріалів із масовим співвідношенням 70/30, 60/40 та 50/50 %. Чорний колір матеріалів дає можливість швидко поглинати сонячне випромінювання. Створені композиційні матеріали мали приховану теплоту відповідно 115,5 Дж/г для зразків 70/30, 107,8 Дж/г – для 60/40 та 91,4 Дж/г – для 50/50. Існує кореляція між вмістом воску в матеріалах з фазовим переходом 70, 60 та 50 % та відсотком накопичення тепла відносно чистого воску, а саме: 61, 57 та 48 %. Отриманий чорно-сірий матеріал дає можливість скоротити часові проміжки циклу акумуляції та віддачі тепла. Профілі кривих теплопоглинання для всіх матеріалів обриваються при 100 °С, а криві охолодження мають дві області втрати тепла. Площа під кривими ДСК при першому нагріванні порошоків на 42 % більше, ніж у цілих шматків матеріалів. Матеріал з фазовим переходом (50/50) має <sup>13</sup>С резонанси близько 20–40 м.д., що є типовим хімічним зсувом для метиленових вуглеців аліфатичної області, а також для оксигенованих форм – 62,82, 63,46 м.д., для алкенів – 114,05, 116,11 м.д., для ароматичних кілець – 130,68, 133,44 м.д., для карбоксильних груп – 172,92, 178,72 м.д. Спектр <sup>27</sup>Al має максимум при 2,90 м.д. октаедричного алюмінію та при 26,53 м.д. може належати до тетраедричному алюмінію глини. *Бібл. 43, рис. 3.*

**Ключові слова:** енергія, зберігання, наноглина, віск, матеріал фазового переходу.

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