



## Thermal Behaviour of Paraffin Wax/Poly Vinyl Alcohol Composite Material

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### Abstract

Polymer additives binder system provides many properties useful in thermal energy storage (TES) then developed the efficient energy storage materials and green strength bodies system.

This paper studies the thermal energy storage property for polyvinyl alcohol (PVOH) / paraffin wax (WPw) blends. To enhance paraffin wax thermal conductivity, PVOH as a material which high conductivity was employed. A fixed weight of Paraffin wax was dispersed with PVOH heterogeneously at different additive weights ratios of PVOH/Pw (50/50, 67/33, 75/25, and 80/20) wt. ratio respectively. The composite material was prepared using wetted pressing method.

Both base materials (polyvinyl alcohol and paraffin wax) were scanned using differential scanning calorimeter (DSC) under non-isothermal conditions, the result was analysed to determine the thermal transition temperature of PVOH and paraffin wax base material. The thermal decomposition of PVOH and waste paraffin wax proved that high transition temperature (TG) for PVOH reached 209<sup>o</sup>c rather than wax of 60<sup>o</sup>c respectively. This result shows that PVOH suppress the thermal stability of PVOH/waste paraffin wax composites. Afterward examines the thermal conductivity enhancement using Lee- disk techniques. Composite materials PVOH/paraffin wax have a high thermal conductivity which increases thermal conductivity of waste paraffin wax as a heat storage media and this allows to apply change in phase with wide range of temperatures, and the highest decreased ratio of phase-change heat is very low, compared to that of paraffin only. Therefore, PVOH, added to paraffin which has significant potential for enhancing the thermal storage characteristics of paraffin.

A wax/PVOH system acts as strength body resistance to sever contact of both air and moisture then a moisture absorbance percent was achieved by use both Fourier transform infrared spectroscopy (FTIR) techniques and moisture solutions (100% H<sub>2</sub>O) for all pure and composite material system Pw/PVOH, the results shows high resistance to ambient conditions (air/ moisture) for composite system rather than pure materials (PVOH and Pw).

**Keyword:** PVOH/ Pw system, thermal energy storage (TES) property, thermal behaviour, green strength bodies.

### 1. Introduction

Thermal energy storage (TES) materials that applied in solar power have become an important fields of research in recent years, According to their impact of day and night on solar thermal energy storage, therefore, a recent development of professional energy storage materials will directly influence the utilization in solar storage systems [1-3]. In other hand if a single phase thermal

energy storage materials require a large storage space, cause reduces a usefulness of thermal storage property [4,5], therefore, a wide investigation occurred on thermal energy storage materials that focuses on phase-change materials (PCMs), and only several results are applied in these systems [6-10]. PCMs have low thermal conductivity, that prevents any problems of rapid load changes in the charging and discharging processes [11], and obtain excellent thermal

properties. Many studies have proposed various techniques for enhancing the thermal conductivity of PCMs, such as adding metallic or non metallic particles with high thermal conductivity [12-15], inserting fins [16-18], incorporating porous or expanded materials [19-27], inserting fibrous materials [28-31], and incorporating macro-, micro-[32]. These methods are mentioned for enhancing the thermal conductivity of PCM involves adding high-conductivity materials to improve the thermal conductivity of PCMs.

Thermal energy storage (TES) system is considered to be a suitable technology to store excess energy that would otherwise be wasted and used it for another time [1]. The system consists of material that capable to store thermal energy in the form of heat or cold (as insulation system applications). Based on its phase change, the thermal energy storage can be classified as sensible heat, latent heat and thermo-chemical energy storage. Among these types of energy storage, latent heat thermal energy storage (LHTES) system is a more attractive technology due to its higher density of energy storage capabilities, compared with conventional sensible heat thermal energy storage (SHTES) system, that have smaller volume and less weight for a same amount of energy stored. A lot of studies are achieved by researcher in this fields usually use salt hydrates, paraffin and organic compounds as storage material [2]. where less of materials having low thermal conductivity and insufficient time for melting and solidification process that reduces the overall power of the heat storage device and limiting the application of materials[3]. Studies of thermal energy storage materials have been attracting more and more attention from all over the world. And these materials can be categorized into sensible heat storage materials, latent heat storage materials and thermal chemical materials. Latent heat thermal energy storage uses phase change materials PCMs of much higher heat storage density and extremely smaller temperature variation during phase change process, compared with sensible heat storage materials. If a comparison are done between inorganic PCMs, organic PCMs materials that have chemical thermal and a proper phase change temperature range, little or no super cooling, lower vapour pressure, nontoxicity, noncorrosivity, and excellent thermal stability. Therefore, PCM is one of the most preferred forms of thermal energy storage materials of wide applications in this field of solar energy storage. Fatty acids and paraffin wax (PW) are good organic PCMs [18-20] due to their desirable characteristics such as high latent

heat of fusion, negligible super cooling, low vapour pressure in the melt, and stability.

The use of synthetic polymer materials has caused significant environmental problems. Polyvinyl alcohol (PVOH) it is well known as a synthetic biodegradable polymer [8] and possesses excellent mechanical properties [9] its biodegradability in various microbial environments has been reported, and PVOH is one of the best options to be blended with other material [10]. PVOH is a versatile polymer, and it may be the only synthesised polymer with a backbone that consists primarily of –OH bonds that is absolutely biodegradable. PVOH is also an interesting water-soluble synthetic polymer with a broad range of applications. Due to the solubility and biodegradability of PVOH, PVOH films are increasingly used in packaging applications [13] However, the biodegradability of PVOH depends on its degree of hydrolysis and its molecular weight. PVOH has the advantages of good film formation, strong conglutination and high thermal stability. In recent years, PVOH has been increasingly applied in the material industry. Mettawee, et al [21], conduct a study to examine a method of increasing the thermal conductivity of paraffin wax by adding aluminum powder. The average particle diameter of aluminum powder used was 80  $\mu\text{m}$ . Tests performed by varying mass fraction of aluminum powder which are 0.1, 0.3, 0.4, and 0.5 of the total mass of paraffin wax-aluminum for using in a solar collectors system. Hamdani, et al [23] investigated characteristics of melting heat transfer of latent heat thermal storage unit with finned tube. The experimental results show that heat transfer characteristics presenting similarity for heat exchanger tube. Polyvinyl alcohol (PVOH) is a high potential technology material with professional properties as strong, durable and high crystallinity structure [1]. With a high melting point at 230°C compared to polyethylene of temperature ranges 117-135°C according to the high level of hydrogen bonding in the crystals [2]. Polymer blends is a well-used technique to modify their properties, as low in cost [3]. A recent study done by Sreedar et al., 2005 [29] reported that incorporation of PVOH into starch had changed the thermo mechanical properties of the material and thus modified the polymer structure at both molecular and morphological levels [6, 7].

### The aim of this work is to

1. Design and develop efficient thermal energy storage, green strength composite materials system by using waste material to solve this environmental problem.
2. Try different additives content of PVOH of good formation, strong conglutination and high thermal stability with paraffin wax.
3. Optimization the additives content on thermal energy storage composite system (PVOH/WPw) according to their thermal and chemical properties.
4. Scanning their stability point by use DSC, FTIR, and Lee- disk techniques.
5. Applied final optimum system in preparation of solar cells (thermal storage energy materials).

## 2. Experimental

### 2.1. Materials

1. Paraffin wax: waste material collected locally from damping wastes of homes (domestic wastes) high molecular weight hydrocarbon compound of low melting point reached 60-70°C.
2. Polyvinyl alcohol: high purity compound of high hydroxyl active groups (DP 1799, average molecular weight: 145,000; hydrolysis rate: 90%; pH: 4.5-7 and density of 1.3g/cm<sup>3</sup>).
3. Vaseline for ease holding of prepared composite material.
4. Distilled water for chemical absorbance laboratory tests.

### 2.2. Instruments

1. DSC (differential scanning calorimeter) 131EVO – SETARAM: in order to estimate the change in phase for base material paraffin and polyvinyl alcohol (TG).
2. FTIR (Fourier transform infrared spectroscopy) 27- TENSOR/ Bruker : in order to estimate the intersurface morphology of polymers mean active group such as (CO-, OH-, Cl-, etc) for both base materials paraffin and polyvinyl alcohol.
3. Lee- disk technique: in order to estimate the thermal conductivity for thermal energy storage composite system (PVOH/ WPw).
4. Press instrument: for preparation of composite system (PVOH/ WPw) before tests.

### 2.3. Procedures

#### 2.3.1. Preparation and scanning of base material

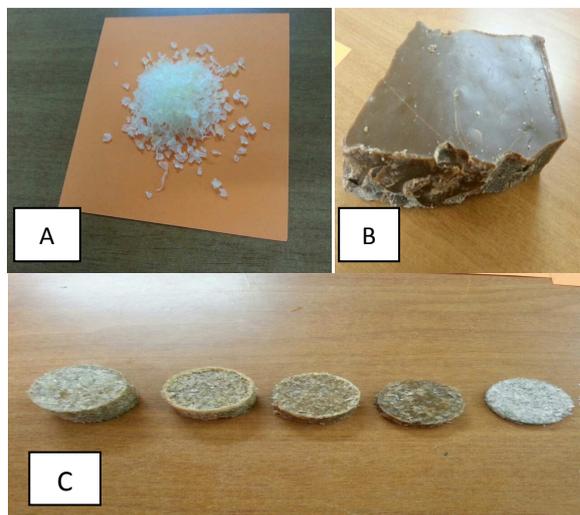
Both base materials were analyzed by using both DSC and FTIR techniques before preparing composite material in order to evaluation thermal stability and ambient resistance conditions where fixed weight for both samples are introduced in above scanning instruments. Non-isothermal crystallization behaviours of PVOH, P using 131EVO – SETARAM DSC and the weight of samples were approximately 7.5 mg. The sample were placed in aluminum pans and initially heated at the rate of 10°C/min from 25°C to 200°C under nitrogen atmosphere and held for 5 minutes to remove previous thermal history. Afterward Non-isothermal crystallization was investigated by cooling these samples from 200°C to 25°C at constant cooling rates of 10°C/min and it was heated again under the same temperature as in the first heating. All the thermograms shown refer to the second heating TG transition temperature .The absorbance (transmittance) inverse wave length cm<sup>-1</sup> in order to give absorbance values for activity groups (CO-, OH-, Cl-, etc).

#### 2.3.2. Preparation of Thermal Energy Storage Materials Composite System

A fixed amount of paraffin wax as (2 g) are exposure to moisture ambient reached (50%) then were mixing with different weight (2, 4,6,8) g of high thermal stability and high active hydroxyl group polyvinyl alcohol (PVOH) by use mechanical mixer for 30 min then heating composite material at 50°C for 15 min afterward putting them in a suitable oily moulds , finally pressing them strongly at 10 ton loading , then output the final efficient energy thermal storage samples , left them for 24 hrs before any tests and an experimental design weight ratios shown in Table (1),also Figure (1) shows abase materials (PVOH, WPw) and composite system (PVOH/ WPw).

**Table 1,**  
Show the experimental design for thermal energy storage composite system

Base material WPw/ g	0	2	2	2	2	2
Base material PVOH/ g	2	2	4	6	8	0
Design composite system PVOH/WPw wt. Ratio	100 / 0	50/50	67/33	75/25	80/20	0/100



**Fig. 1.** show base material (PVOH, Pw) and composite system (PVOH/Pw)  
A: show base PVOH crystals. B: show base paraffin wax (Pw). C: show thermal energy storage composite system (PVOH/Pw)

## 2.4. Methodology

Thermal and chemical properties were achieved for thermal energy storage composite system (PVOH/Pw) as thermal conductivity by using Lee- disk instrument for prepared samples of (1 cm thickness and 3cm dia.) dimensions. The prepared composite system applied between two copper disks then heating these disks afterward reading the change in temperatures by applying accumulated temperature load until failure of specimen occurred from (increasing temperature).

**Chemical properties:** This type of test is determined by immersion of both base and prepared composite system in natural solutions (100% H<sub>2</sub>O) for 0, 24, 48, 72, and 96 hrs respectively at 30°C afterward recorded the change in weight every 24 hrs in order to calculate the moisture percent in each samples and absorbance values to check which of samples is more chemically stable than others (optimum one).use the following relation below:

$$\text{Moisture (\%)} = (W_i - W_d / W_i) \times 100 \quad \dots (1)$$

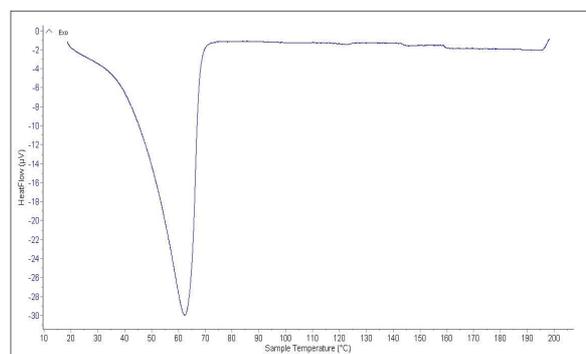
Where:  $W_i$ , and  $W_d$  estimate the weight for samples initially and after immersing in distilled water in (g).

## 3. Results and Discussion

### 3.1. Scanning of Base Material

The scanning of base materials (PVOH and Pw) achieved as heat transfer characteristics of storage in the form of transition temperature, melting or freezing processes. From this result using paraffin wax as a thermal storage material shown in Figure (2). It can be seen from the graph, at the beginning of heating, the measurements at TG point show the temperature increases rapidly until reach the melting temperature paraffin wax and then starts to slow down. It can be stated that at the beginning of heating, hot paraffin wax absorbs sensible and then followed by the absorption of latent heat which takes place at a temperature nearly constant. Paraffin wax is used as core material of latent heat storage media[1-3].

PVOH (100/0) showed relatively large and sharp endothermic peak at about 209°C this related to its experimental melting point of PVOH (100/0) sample while the theoretical melting value of all hydrolyzed PVOH is 230°C. It could see that the melting temperature observed from the result was lower than theoretical one; this may be affected by the plasticizer and other chemical content in the sample [1-3] as shown in Figure (3).



**Fig. 2.** shows a DSC scanning result for paraffin wax base material.

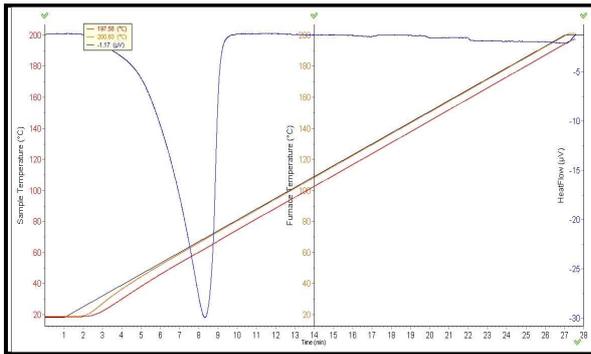


Fig. 3. shows a DSC scanning result for polyvinyl alcohol base material.

### 3.2. Preparation and Characterization of Thermal Energy Storage Materials Composite System

The thermal conductivity is an important property of phase change materials (PCMs) due to the rate of energy storage. PCMs are used for thermal energy storage in environments with wide range in temperature variation. Therefore, the thermal conductivity of these materials in both solid and liquid states at temperature range for experimental results are shown in Figure (4), where the additives of PVOH to paraffin are improved their thermal conduction performance of the paraffin wax, and the additive weight ratio 80/20 PVOH/Pw to the paraffin is the best selection one. Then the thermal conductivity performance of the paraffin wax was mainly enhanced due to the higher thermal conductivity of additives compared with pure PVOH. The PVOH material have higher water uptake than Pw, and this water are increased with increasing immersion time and PVOH ratio. Then the hydroxyl group (4.5- 7%), which is responsible about the absorption water in the prepared composites. Therefore, a higher content weight ratio led to higher water being absorbed, at few days of immersion. Figure (5) shows a rapid moisture uptake, afterward become straight constant relation the optimum samples that give high absorbance to moisture percent were 80/20 PVOH/Pw respectively.

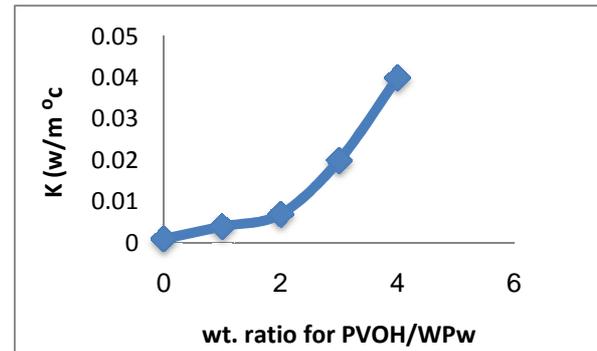


Fig. 4. show the thermal conductivity values for all base PVOH, Pw, and composite system PVOH/Pw.

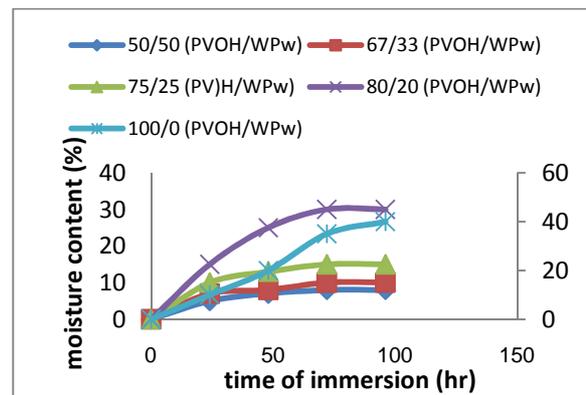


Fig. 5. Show the absorbance for moisture percent for all base PVOH, Pw and composite system PVOH/Pw at different weight ratio of PVOH and immersion time.

### 3.3. FTIR Instrument

The FTIR spectra of PVOH (Figure 6) showed two peaks at  $2955\text{ cm}^{-1}$  and  $2847\text{ cm}^{-1}$  according to -NH stretching, where the C=O stretching at  $1019\text{ cm}^{-1}$ , and -NH bending between  $1462\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  respectively. Also -NH outside the wagging plane has  $572\text{ cm}^{-1}$ , and C-H stretching is  $2955\text{ cm}^{-1}$  and  $2842\text{ cm}^{-1}$  respectively. In other hand the FTIR for PVA material has been showed a broad peak around  $3425\text{ cm}^{-1}$  in structure which indicating the stretching of hydroxyl groups but, peaks  $2955\text{ cm}^{-1}$ ,  $2842\text{ cm}^{-1}$  referred to stretch C-H group. Then peaks appeared at  $1019\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  indicated the C-O stretch as secondary alcohol groups and ester. Finally the appearance for peak at  $2947\text{ cm}^{-1}$  in structure proved that the appearance of hydrocarbon chromophore in the esterified product [33].

According to the FTIR results of paraffin wax (Pw) in Figure 7, it could see that the specialist peaks of the paraffin and polyaniline could be

noticed after 200, 400, 600, 800 and 1,000 cycles. Also the peaks around  $2960\text{--}2850\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  show carbon hydrogen stretching and bending absorption, respectively. The C–H bending group is absorbed as CH<sub>3</sub> group at  $1381\text{ cm}^{-1}$  and CH<sub>2</sub> rocking is absorbed at  $729\text{ cm}^{-1}$  respectively in order confirm the linear saturated aliphatic structure of the paraffin wax [34]. Consequently, these results indicated that the reaction between PVOH materials and the ambient is not significant.

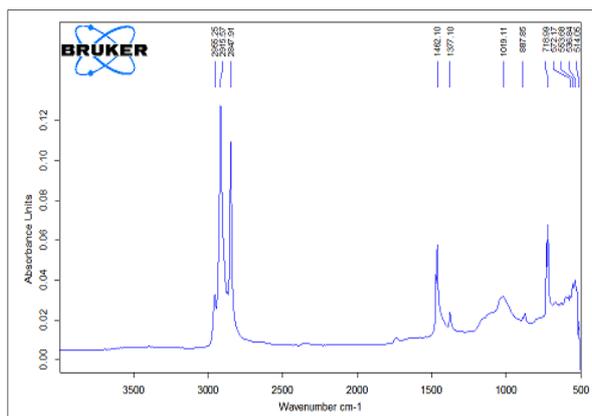


Fig. 6. the FTIR spectra of polyvinyl alcohol (PVOH) base material.

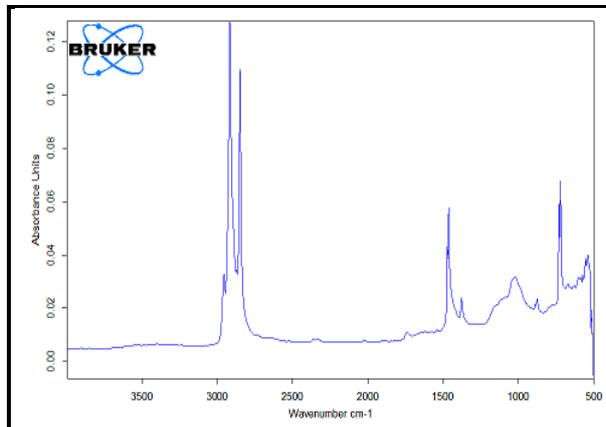


Fig.7. the FTIR spectra of paraffin wax (WPw) base material.

#### 4. Conclusions

1. The addition of high thermal conductivity (PVOH) material could able to increase thermal conductivity of paraffin wax as a heat storage media, and reduce the heat latent of energy storage material this allows the application of phase-change heat to respond to rapid heat load changes and a wider temperature range for paraffin material. Since, it causes predominantly

conduction heat transfer process during melting and freezing processes in heat exchanger and remains stable operations.

2. Crystalline structures are thermally degraded at higher temperature compared to the amorphous structure so it has higher thermal stability than amorphous structure.

3. Thermal stability and chemical activity for thermal energy storage composite system (PVOH/P) results show that composites system suppresses the thermal stability of PVOH.

4. Paraffin wax is used as core material of latent heat storage media, then enhancing the heat conduction and thermal storage performance and this property has great potential for future applications.

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## السلوك الحراري للنظام المترابك من مادة الشمع المدعمة ببولي فينيل الكحول

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### الخلاصة

يوفر نظام المضافات البوليمرية الجديد العديد من الخصائص المفيدة في تخزين الطاقة الحرارية (TES)، فضلا عن ذلك فهي مواد صديقة للبيئة وذات قوة ومثانة عالية.

والدراسة الحالية تعنى بتصميم مواد مترابكة خازنة للطاقة الحرارية وتحضيرها ، حيث تمزج مادة بولي فينيل الكحول PVOH بوصفها مادة ذات الموصلية العالية / (PVOH) مع شمع البارافين (PW)، لتعزيز التوصيل الحراري لشمع البارافين ، تم تصميم المادة المترابكة بمزج وزن ثابت من شمع البارافين (WPW) مع نسب وزانية مختلفة لمادة بولي فينيل الكحول / (PVOH) مادة الشمع وهي على التوالي (٠/١٠٠، ٠٠/٥٠، ٣٣/٥٠، ٢٥/٧٥، ٢٠/٨٠)، وذلك باستخدام طريقة الكيس الرطبة.

وتم على حد سواء اجراء الفحوصات الاولية للمواد الأساسية (بولي فينيل الكحول وشمع البارافين) باستخدام المسعر التفاضلي الماسح (DSC) تحت ظروف تشغيلية غير مثالية، تم تحليل النتيجة لتحديد درجة حرارة التحول الحرارية ( درجة حرارة الانتقال الزجاجية) للمواد بولي فينيل الكحول ( PVOH) وشمع البارافين. ان التحلل الحراري لمادة بولي فينيل الكحول PVOH ونفايات شمع البارافين أثبتت أن ارتفاع درجة حرارة التحول (TG) ل PVOH بلغت ٢٠٩°م مقارنة بالشمع ذي درجة التحول ٦٠°م على التوالي. هذه النتيجة تظهر أن مادة بولي فينيل الكحول PVOH ذات الاستقرار الحراري قد دعمت النظام المترابك لل PVOH / شمع البارافين. وفيما بعد تم دراسة خاصية التوصيل الحراري وذلك باستخدام تقنية قرص- لي. المواد المركبة / PVOH / شمع البارافين ان مادة بولي فينيل الكحول تمتلك الموصلية الحرارية العالية مما يزيد التوصيل الحراري من شمع البارافين بوصفها وسائط التخزين الحرارية وهذا يسمح لهذه المادة لتكون قابلة للتطبيق على نطاق أوسع من درجات الحرارة، وتخلصت هذه المادة من تغير مواصفاتها عند درجات حرارة منخفضة، مقارنة بما كان عليه البارافين من قبل. ولذلك فان مادة بولي فينيل الكحول PVOH أضافت لمادة البارافين التي لديها إمكانات كبيرة لتعزيز خصائص التخزين الحراري الى العمل باستقرارية حرارية عالية.

كما ان مقاومة النظام المترابك للظروف البيئية عند تعرضه لكل من الهواء والرطوبة تم تقييمه للنظام المترابك شمع البارافين / PVOH / وذلك باستخدام فحص الامتصاصية والنسبة المئوية للرطوبة عن طريق استخدام تقنيات الفحص (جهاز فورييه الطيفي بالأشعة تحت الحمراء (FTIR) ، ومحلول الرطوبة ذو تركيز (١٠٠٪) (H<sub>2</sub>O) ، لجميع المواد الاساس (بولي فينيل الكحول ، شمع البارافين ، والنظام المترابك) (PW / PVOH) ، واطهرت النتائج مقاومة عالية للظروف المحيطة (الهواء / الرطوبة) لنظام مترابك مقارنة بالمواد الاساس PVOH و PW .