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Shape-stable composite of synthetic phase change materials from balsa wood by epoxy/PEG through alkaline method

Le Duc Tho[1,*], Le Thi Duyen[1], Nguyen Thi Huong Ly[1], Nguyen VanTeo[1],
Nguyen Thi Thanh Bao[2], Trinh Dac Hoanh[3], Tong Thi Thanh Huong[1,*]

[1] *Faculty of Petroleum and Energy, Hanoi University of Mining and Geology, 18 PhoVien, Hanoi*
[2] *Institute of Physics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi*
[3] *Institute of Chemistry and Material, Academy of Military Science and Technology, 17 Hoang Sam, Hanoi*
**Email: leductho.tk@gmail.com; tongthithanhhuong@humg.edu.vn*

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ABSTRACT

Phase change materials have excellent thermal energy storage capacity, making them an appealing option for energy management applications. Stabilizing the form of phase change materials enhances their practical effectiveness. This research focuses on sustaining the shape of low molecular weight PEG phase change materials in wood structures made from natural balsa wood. The alkalization process is used to modify the wood, after which the PEG/epoxy polymers are infused into the wood structure to form a synthetic phase change material. The process of treating wood with alkali involves partially removing lignin from the wood, creating specific spaces. Results from optical transmittance analysis demonstrate that wood treated with alkali and wood infused with phase change polymer exhibit high optical transmittance. SEM images also illustrate the presence of spaces in delignified wood treated with Epoxy/PEG 400 and Epoxy/PEG 600. The synthetic phase change material remains stable at temperatures below 310°C and possesses a ΔH_c of 170.1J/g to 162.8 J/g. The phase transition temperatures during heating are 56.4°C and 57.2°C, cooling is 25.7°C and 30.1°C.

1. Introduction

Wood is an ecologically conscious renewable resource that is beneficial for the environment. The components of natural wood consist of cellulose, hemicellulose, and lignin, which are organized in a hierarchical and layered structure [1]. There are numerous pores in the wood structure that are both water and air filled. Synthetic phase change composites are made by managing and expanding porosity in wood structure, which is essential for establishing a stable reinforced phase [2]. By modifying the lignin content of the wood, one can regulate its porosity and brightness. Lignin is known for its role in connecting cellulose fibers and stabilizing the natural wood structure. Once the lignin is removed, the cellulose-based material framework provides a stable structure for the synthetic phase change material (PCM) [3-5]. A appropriate phase change material has been determined and infused into the wood frame to make a synthetic phase change material composite, which will stabilize and connect the cellulose fibers.

PCM can be used to store laten heat energy [6, 7]. To carry out the heat storage and release process, PCM undergoes a phase transition by changing its crystal

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structure in response to external temperature [8, 9]. PCMs are classified into numerous categories based on their qualities and states [10]. Examples include solid-solid, solid-liquid, solid-gas, and liquid-gas. Liquid PCM forms provide substantial heat storage capacity, but their poor formability limits practical applicability [11, 12]. By establishing a liquid phase change material in a stable solid framework, a composite phase change material can be created that is both practical to use and performs well in heat storage. Solid-liquid phase change materials exhibit high chemical reactivity and significant, controllable latent heat storage [13, 14].

Polyethylene glycol (PEG) is a phase change agent that is low in cost, corrosion-free, has excellent chemical characteristics, and is non-toxic. PEG's melting temperature ranges from 4°C to 70°C, and the latent heat of phase change ranges from 100 J/g to 200 J/g, depending on the length of the polymer chain [15]. This makes it appropriate for combining with wood to form a synthetic phase change material with Thermal Energy Storage (TES) heat-storing qualities. However, low molecular weight PEGs exist in liquid form, making the product formation process unattractive. To form the product, in addition to shaping in the modified porous wood structure, some curing ingredients, such as epoxy, can be added to stabilize the shape [16].

The objective of this paper is to stabilize the shape of low molecular weight and mobile PEG (PEG 400, PEG 600) in wood frameworks modified by alkylation. This determines the shape stability and heat storage capabilities of the TES wood-based PCM material

2. Experimental

Materials and Chemicals

Balsa wood was supplied from San Ho Timber Pte Ltd, Singapore, with a density of 0.113g/cm^3. Sodium sulfite (Na_2SO_3) and acetone (99.5%) were sourced from Xilong Company, China. Sodium hydroxide (NaOH) and ethanol (C_2H_5OH, 96%), H_2O_2 (30%) were purchased from Duc Giang Chemical J. S. Company, Vietnam. Polyethylene Glycol PEG 600, PEG 400 were purchased from Shanghai Zhanyun Chemical Company.

Fabrication of Wood-based Synthetic PCM

Preliminary Treatment of Balsa Wood

The 1 mm thickness of longitudinal grained balsa wood was cut into small pieces with a cross-section of 30x30 mm. The wood samples were dried at 100°C for 24 hours to completely remove water from the wood. Fabrication of synthetic phase change materials follows two steps below.

Step 1: Lignin Treatment

Lignin was treated by an alkalinization method using 1M Na_2SO_3 and 2M NaOH solution in a volume ratio of 3:7. After drying, the balsa wood sample was soaked in the lignin treatment solution, heated to 90°C, and maintained at this temperature for 6 - 15 hours. Then the sample was taken out, soaked in 1 M NaOH, soaked in a 30% H_2O_2 solution, and placed in a UV chamber for 15 hours. After lignin treatment, the samples were washed with distilled water, then ethanol, and finally soaked in acetone.

Step 2: Manufacturing Synthetic Phase Change Materials from Balsa Wood

Lignin-treated wood samples were impregnated with Epoxy/PEG 400 and Epoxy/PEG 600 in specified proportions. The polymer impregnation process was carried out in a vacuum chamber. The resulting composites were wood based synthetic PCM composites: (TES_epoxy_PEG 400 and TES_epoxy_PEG 400). The phase change composite samples were sandwiched between two silicon sheets and dried at 70°C for 24 hours, resulting in a composite phase change material products.

Material Characterization

The properties of wood during the modification process are determined by specific analytical methods. Infrared spectroscopy was used to determine the bonds in the wood structure before and after treatment on an IRAffinity-1 instrument (Shimadzu). FTIR spectra were recorded by the KBr method, with a measuring range from 4000 to 500 cm^{-1}. Optical transmittance was determined on a Shimadzu UV-2600 ultraviolet spectrometer with a wavelength range of 300 - 800 nm. The surface structure of the sample was determined using a FE-SEM machine: Regulus 8100 (Hitachi). Differential scanning calorimetry (DSC) curves were recorded on a NETZSCH DSC 204F1 Phoenix 240-12-0416-L. Thermogravimetric analysis (TG, N_2) was conducted on a Toledo TGA/SDTA851 instrument.

3. Result and Discussions

Fabrication of Wood Based Synthetic PCM

Balsa wood was used as the material source. The nature wood is light yellow of color and was treated using the alkalinization method with NaOH/Na_2SO_3. Following lignin treatment, the wood sample exhibited an opaque white color, indicating partial removal and processing of lignin and chromophores, thereby leaving a porous structure suitable for lignin-type wood products. When polymer as epoxy or PEG is impregnanted into the wood fibers, it fills the empty spaces left by the lignin, creating a transparent wood product. These observations were clearly identified when analyzing the optical transmittance of the wood samples (Figure 1).

Figure 1 shows that in the wide wavelength range from 300 to 800 nm, the optical transmittance of epoxy/PEG-impregnated wood samples increased significantly compared to balsa wood. Balsa wood has a dense structure due to the close bonding of cellulose, lignin, and hemicellulose fibers, which reduces optical transmission. Lignin wood samples appear whiter and brighter than natural balsa wood. However, the optical transmittance of delignified sample is relatively low in the wavelength range of 300–500 nm and increases to 25% in the wavelength range of 500–800 nm. Although the lignin in this wood sample has been removed in large quantities, the pores left behind are filled with air, making the wood sample opaque and reducing its optical transmittance. When the optical transmittance of wood samples impregnated with epoxy/PEG polymer is measured, a significant increase is observed. Epoxy-impregnated wood samples showed optical transmittance as early as the 350 nm wavelength region, with a significant increase from 500 nm onwards.

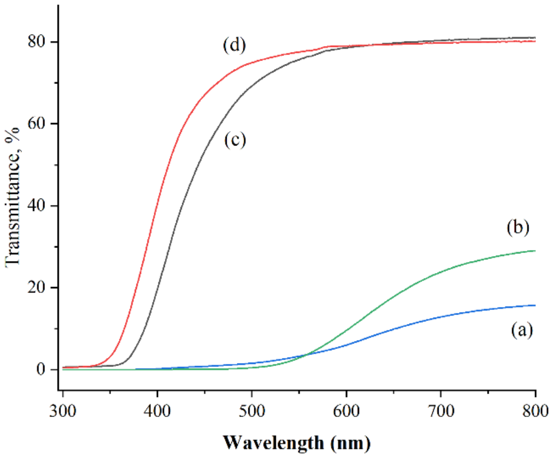

Figure 1. Optical transmittance of: natural balsa wood (a), delignified balsa wood (b), composite TES_epoxy_PEG_400 (c) and TES_epoxy_PEG_600 (d)

Thus, the optical transmittance study of wood samples with lignin removed using an alkaline approach, as well as synthetic phase change material samples, demonstrates that NaOH/Na_2SO_3 is successful at removing lignin from natural balsa wood. This allows for the efficient impregnation of phase change materials into wood structures.

Infrared spectrum examination of the samples revealed that lignin has been eliminated from the natural wood samples. The infrared spectrum reveals peaks at 3332 cm^{-1} and 2927 cm^{-1}, indicating the valence vibrations of -OH and C-H bonds. These bonds are present as single bonds in the structures of cellulose and hemicellulose. The infrared spectrum clearly shows a peak at 1730 cm^{-1}, which represents the valence vibration of C=O. This peak is clearly apparent in the natural balsa sample but only weakly present in the delignified sample's infrared spectrum (Figure 2a, b). The peak at 1242 cm^{-1} indicates the valence vibration of the C-O bond as conect to the aromatic ring in the balsa wood, but it is absent in the delignified sample. The 1610 cm^{-1} peak of the C=C bond in the aromatic ring was observed in both natural and delignified wood samples, suggesting that lignin was not completely eliminated from the natural balsa wood.

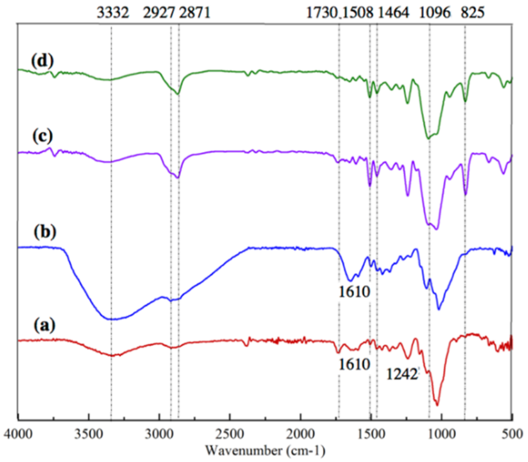

Figure 2. FT-IR spectrum of natural balsa wood (a), delignified wood (b), composite TES_epoxy_PEG_400 (c) and TES_epoxy_PEG_600 (d).

In the composite of synthetic phase change materials (Figure 2 c, d), distinctive signals reflecting the valence vibration of C-H on alkyl groups at 2871 cm^{-1} were detected. The peaks at 1508 cm^{-1}, 1464 cm^{-1}, 1096 cm^{-1}, and 825 cm^{-1} correspond to C=C aromatic vibration in epoxy, the =C-H bond, the aliphatic ether C-O-C in PEG and the bending out of plane for para subtitution benzene ring, respectively. As can be observed, the epoxy structure has an ether group and a C=C double bond due to the presence of vinyl monomers, which are grafted onto the wood matrix during the polymerization process. The presence of the above peaks indicates that epoxy and PEG have blended into the wood's inner frame, forming a wood/epoxy/PEG composite. The two-steps technique eliminates lignin from natural wood and incorporates the epoxy/PEG polymer deep into the wood structure, resulting in a shape-stable synthetic phase change material product.

SEM was used to image the inner surface of wood before and after treatment. As shown in Figure 4, the porosity of the natural wood sample along the cross-sectional surface changed during the modification process. Figure 3a clearly shows the wood structure's hollow tubes, which have thick and smooth tube walls. After lignin removal, it is clear that the wood's microstructure is unbroken; the tube walls remain stable within the structural frame (Figure 3b). Essentially, the tube walls of the delignified samples are nearly identical.

Through epoxy/PEG impregnation, a synthetic phase change material (PCM) composite is formed. SEM images of the synthetic PCM composite indicate that the contact surface between the polymer and the wood cell wall is extremely tight. Epoxy and PEG polymers are tightly packed into the hollow tubes of delignified wood. PEG 400 and PEG 600 are shape-stabilized using epoxy within a wooden frame that has had its lignin removed. The cross-sectional surface of the composite phase change material samples is stable, with no cracks (Figure 3 c, d).

SEM image analysis of wood samples during the manufacture of composite phase change materials indicates that lignin is eliminated through alkalinization (Na_2SO_3/NaOH), resulting in tiny holes. This is clearly illustrated in Figure 3 (b, b_1, b_2), an expanded SEM image of a delignified wood sample. Following the elimination of lignin, the inner wall of the tube exhibits the formation of tiny pores and thin fibers on the surface of the tube wall (Figure 3 e, f). This process makes the wood structure more porous, and the rough surface of the tube walls ensures that the PEG polymer dispersed in epoxy fills in, resulting in a durable alternating structure.

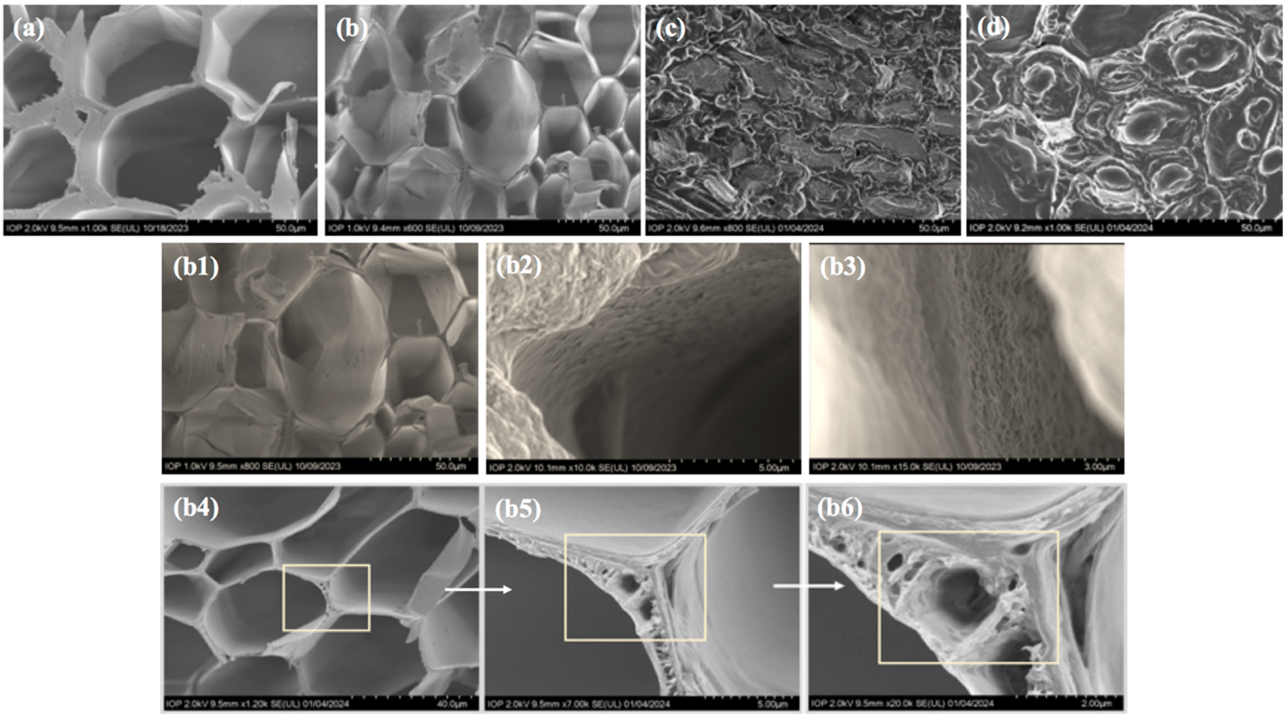

Figure 3. SEM images of wood samples: natural balsa wood (a), delignified balsa wood (b), composite TES_epoxy_PEG_400 (c) and TES_epoxy_PEG_600 (d), delignified balsa wood is emphasized of 800 times (b1)10000 times (b2), 15000 times (b3), 1200 times (b4), 7000 times (b5) and 20000 times (b6).

Thermal Properties of Wood Based Synthetic PCM

Thermogravimetry Differential Thermal Analysis (TG/DTA)

The thermogravimetric analysis results of the composite samples TES_epoxy_PEG400 (Figure 4a) and TES_epoxy_PEG600 (Figure 4b) indicate that surface water loss is responsible for the first stage in the temperature range of 70 to 110°C. The material experiences a weight loss of 6.25% in the TES_epoxy_PEG400 composite sample and 8.42% in the TES_epoxy_PEG600 composite sample at this stage of the dehydration process, caused by the release of free-state water molecules. The second stage, from 110°C to 310°C, corresponds to the release of chemically bonded water molecules in the sample. Specifically, the TES_epoxy_PEG400 sample loses 36.98% of its mass, while the TES_epoxy_PEG600 sample loses 37.84% of its mass during this phase. The next step involves the breakdown of PEG and epoxy, as well as the breaking of hemicellulose, cellulose, and lignin linkages, between 320°C and 410°C. As a result, the TES_Epoxy_PEG400 composite loses 40.5% of its weight, while the

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TES_Epoxy_PEG600 composite loses 36.3%. The final mass loss results from the complete breakdown of the C-C, C-O, and C-H bonds within the wood structure's framework. For the composite samples of TES_epoxy_PEG400 and TES_epoxy_PEG600, this causes a mass loss of approximately 16.2% and 17.5%, respectively. After that, the samples completely decompose.

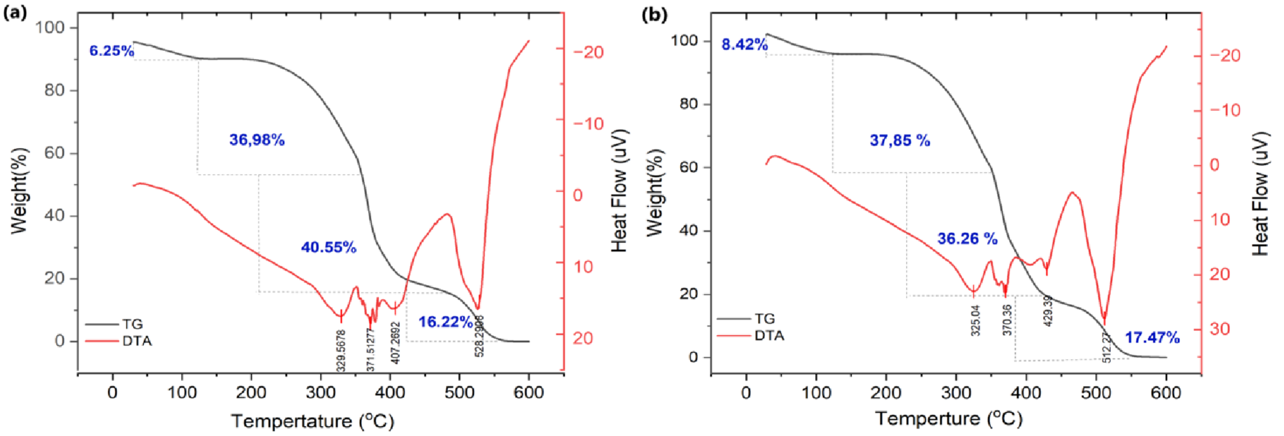

Figure 4. Thermogravimetric analysis of samples TES_epoxy_PEG400 (a) and TES_epoxy_PEG600 (b)

Diferential Scanning Calorimetry (DSC) Analysis

This technique determine the difference in the amount of heat require to increase the temperature of sample and reference is measured as a function of temperature.

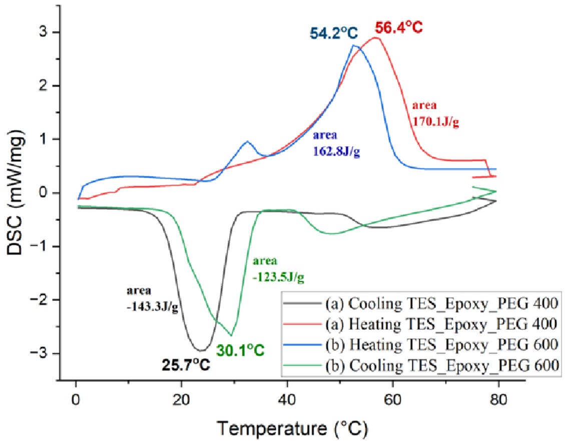

Figure 5. DSC analysis of TES_Epoxy_PEG 400 (a) và TES_Epoxy_PEG600 (b)

According to the results of DSC (Figure 5), the latent heat values of the heating process for the two samples, TES_Epoxy_PEG400 and TES_Epoxy_PEG 600, are ΔHm = 170.1 J/g and 162.8 J/g, respectively. The cooling process values for TES_Epoxy_PEG400 and TES_Epoxy_PEG600 are ΔHc = 143.3 J/g and 123.5 J/g, respectively. The DSC curve clearly shows that the phase transition begins at 25.5°C and achieves Tm values of 56.4°C and 57.2°C for TES_Epoxy_PEG400 and TES_Epoxy_PEG600, respectively, as the temperature increases. Phase transitions are caused by heating. The material stores energy corresponding to the latent heat value above the vitrification temperature, Tm. Upon observing the cooling process of the two samples, it is evident that the material experiences a phase transition upon reaching the crystallization points, which are observed to be 25.7°C and 30.1°C, respectively. Heat is released at this stage.

Thus, it is evident that heat storage is an inherent feature of the synthetic phase change material TES_Epoxy_PEG. Consequently, the application of these materials in thermal energy storage can be directed.

4. Conclusions

According to research findings, synthetic phase change materials can be effectively produced from balsa wood in two steps: (i) treating lignin with NaOH/Na_2SO_3 and (ii) impregnating the modified wood with phase change polymers such as PEG 400 and PEG 600. The process of impregnating the polymer in a vacuum chamber ensures even distribution throughout the wood structure. Additionally, epoxy is used to stabilize the shape of low molecular weight PEG, resulting in synthetic phase change materials. These materials, known as TES_Epoxy_PEG 400 and TES_Epoxy_PEG 600, are capable of storing latent heat. Specifically, the latent heat value during the heating process of TES_Epoxy_PEG400 is ΔHm = 170.1 J/g, while TES_Epoxy_PEG600 is 162.8 J/g. During the cooling process, the latent heat value of TES_Epoxy_PEG400 is ΔHc = 143.3 J/g, while TES_Epoxy_PEG600 is 123.5 J/g. This difference in latent heat values indicates that

TES_Epoxy_PEG400 has better latent heat storage and release capacity than TES_Epoxy_PEG600.

Depending on the fabrication process, synthetic phase change materials can effectively manage latent heat storage values, thereby promoting the efficient use of natural fuel sources. These materials optimize energy consumption processes and are used as energy storage materials in construction.

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