

Synthesis and properties of crosslinking halloysite nanotubes/polyurethane-based solid-solid phase change materials



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ABSTRACT

Polyurethane-based solid-solid phase change materials were first synthesized using polyethylene glycol (PEG) and hexamethylene diisocyanate biuret (HDIB), and the influence of halloysite nanotubes (HNTs) on this system was investigated. HNTs can not only serve as crosslinking agent in synergy with HDIB, which reinforces the solid-solid phase change properties of the system that has no leakage even at the temperature that 40 °C higher above the melting temperature of PEG, but also greatly improve the latent heat of the system from 86.8 to 118.7 J/g, as a result of heterogeneous nucleation effect, which can make up partial latent heat loss caused by crosslinking. Also, HNTs endows the system with excellent thermal stability, where the temperature at 5% weight loss is increased by 53 °C. The synthesized PCMs have extensive applying prospects in thermal energy storage fields.

1. Introduction

Phase change materials (PCMs) are members of green energy that can relieve the energy crisis and improve the utilization of resources and reduce the use of other energy materials that discharge pollutants [1]. Their wide applications in building, solar energy storage, smart textiles, biomedical, surplus heat storage and food packaging etc. [2–7] make them have great research value and bright prospects in exploitation.

Polyethylene glycol (PEG) is a kind of typical solid-liquid PCMs with a great deal of advantages including nontoxic, noncorrosive, good biocompatibility, chemically and thermally stability as well as low-cost [8,9]. However, there is unavoidable leakage with regard to solid-liquid PCMs when they melt, which will lead to large volume change and limit their applications [10]. To solve this problem, solid-liquid PCMs should be turned into solid-solid PCMs, combined with other skeleton substances through physical or chemical method.

Compared with the simple impregnation into porous matrix such as expanded vermiculite, mesoporous silica and aerogel [11–13] as well as the complicated encapsulation with organic or inorganic shells [14–17], solid-solid PCMs prepared by grafting [18] or crosslinking [19–21] have better chemical, thermal stability and reliability. Nowadays, polyurethane-based solid-solid phase change materials (PU-SSPCMs) have attracted a great deal of attention due to various

advantages including no additional containers, easily being processed, no gas or liquid generation etc. [22,23]. Thus, a great number of studies have been carried out to design and synthesize PU-SSPCMs. Usually, PEG serves as working component while polyisocyanate and chain extender act as hard segments which are responsible for maintaining the solid framework. At the very start, researchers synthesized various kinds of linear PU-SSPCMs using PEG and different diisocyanate such as toluene-2,4-diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), hexamethylene diisocyanate (HDI), dicyclohexylmethane-4,4'-diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and bifunctional chain extender including diols [22,24–28]. The hard segments made up of diisocyanate and chain extender can fix the chain ends of PEG by chemical bonds, which can prevent the dissolution of PEG. What's more, the existence of hydrogen bonding between hard segments can form physical crosslinks keeping the solid framework. To get PU-SSPCMs with better shape and thermal stability, some researchers employed multifunctional chain extenders into the PU system. On the basis of the synthesized prepolymer composed of PEG and diisocyanate, the multifunctional extenders like glucose [29], polyhydroxy surfactants [30], β -cyclodextrin (β -CD) [31], multiamino components [32], hyperbranched polyester [33] and so forth are used to establish a chemical crosslinking network, which can maintain the solid framework when phase change components melt. In general, the synthesis requires prepolymerization and

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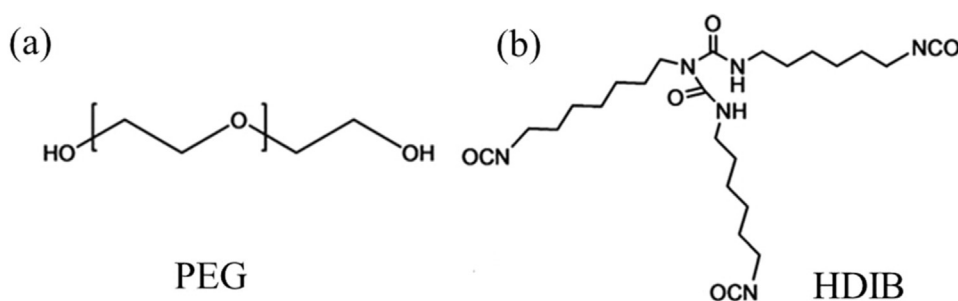
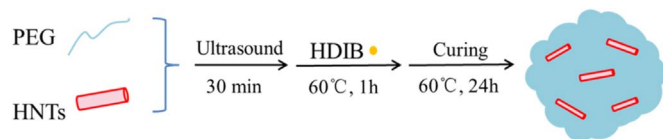


Fig. 1. The chemical structural formula of (a) PEG and (b) HDIB.



Scheme 1. The synthetic route of HPCMx.

chain extending. The hard segments can support the PEG segments well, but they can also severely disrupt and confine the movement of PEG and result in excessive loss of phase change enthalpy. Therefore, PU-SSPCMs without chain extenders, which involve relatively easier synthesis process, are developed to support and seal the solid-liquid PEG. Wu et al. [34] synthesized PU-SSPCMs with PEG and HDI at a stoichiometric ratio of 1:2 and the products had latent heat of 76 J/g. Wang et al. [35,36] fabricated PU-SSPCMs just using PEG as phase change part and triphenylmethanetriisocyanate as supporting skeleton, where the content of PEG can reach 96%. Comparatively speaking, the polyisocyanate serving as crosslinker can realize the supporting of solid-liquid PCM well while avoiding the involvements of other chemicals which may have negative effects on the crystallization of phase change part.

Halloysite nanotubes (HNTs), which have the composition of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, exhibit hollow nanotubular structure like carbon nanotubes and have many desirable properties like environment friendly, easy to disperse, low-cost etc., which make them a popular nanofiller to improve the physical mechanical properties, crystallinity and flame resistance of polymers [37–42].

In this paper, PU-SSPCMs using PEG and hexamethylene diisocyanate biuret (HDIB) were first synthesized and their phase change properties were investigated. The purified HNTs were dispersed uniformly in the reaction system to work in conjunction with HDIB as crosslink agents. What's more meaningful is that HNTs can play the role of nucleation that can increase the rate of crystallization the crystallinity of the confined PEG segments in the system, which is of great significance to increase the density of thermal energy storage and accelerate the response to environment of the products while ensuring the excellent solid-solid phase change properties. Currently, it has been hardly reported in other literatures to employ crosslinkers as nucleation agents into the synthesis of solid-solid phase change system. Meanwhile, the thermal stability of the system got great enhancement with addition of HNTs. Therefore, the synthesized PCMs provide promising application potential in thermal storage systems like solar energy storage devices.

Table 1
The recipes of synthesized PCMs.

Samples	PCM1	PCM2	PCM3	HPCM1	HPCM2	HPCM3	HPCM4	HPCM5	HPCM6
stoichiometric ratio of [PEG/HDIB]	1.50	1.00	0.75	0.75	0.75	0.75	0.75	0.75	0.75
HNTs wt%	0.00	0.00	0.00	0.25	0.51	1.02	1.96	4.26	13.03

2. Experimental

2.1. Materials

Polyethylene glycol, (PEG, analytical grade, $M_n = 4000$, from Sinopharm Chemical Reagent Co., Ltd., Beijing, China) was dried under vacuum at 110 °C for 3 h. Hexamethylene Diisocyanate Biuret (HDIB, N75, with NCO% = 15.6%, which was gotten by “di-*n*-butylamine-toluene” method, from Bayer, Germany) was used as received. *N,N*-Dimethylformamide (DMF, analytical grade, from Beijing Chemical Works, China) was distilled under vacuum after refluxed and stirred overnight. HNTs, mined from Guizhou Province in China. Before use, the as-received HNTs were purified according to the method reported in literature [42]. The detailed purification process was given in Supporting information (SI).

2.2. Preparation of PU-SSPCMs

The crosslinking PU-SSPCMs were synthesized by one-step using PEG and HDIB, whose chemical structural formula are given in Fig. 1. The calculated PEG and HDIB were added into a three-neck round bottomed flask in sequence after the given mass of DMF added. And the synthesis process was conducted at 60 °C for 1 h under the protection of nitrogen. Soon afterwards, the reacted solution was poured into petri-dishes and curing at 60 °C for 24 h to get the final PU-SSPCMs named PCM_x, where *x* represents sample numbers and the following one in HPCM_x is the same.

2.3. Synthesis of HNTs /PU-SSPCMs

The synthetic route of HNTs /PU-SSPCMs, named HPCM_x, which was almost identical to the synthesis of PCM_x, is shown in Scheme 1. The only difference in preparing the former samples was that the PEG and HNTs were first ultrasonically mixed for 30 min to form homogeneous solution. Table 1 lists the products and their recipes, where PCMs refer to all the synthesized PCMs including PCM_x and HPCM_x.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded over the wavenumber range of 400–4000 cm^{-1} using a Vertex 70 FTIR (Bruker, Germany). The morphologies of HNTs and PCMs were visually characterized with a XL-30 field emission scanning electron microscopy (SEM) equipped with an INGA energy dispersive spectroscopy (EDS) instrument from Oxford under an acceleration voltage of 10 kV.

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