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# Novel hybrid form-stable polyether phase change materials with good fire resistance

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ABSTRACT

The development of phase change materials (PCMs) with fire resistance is important to improve the application security. Series of novel hybrid materials were synthesized by the simple composite process of phase change polyurethane with flame retardants. The polyurethane functions as phase change segment for thermal energy storage as well as supporting materials of flame retardants. The structure and properties of obtained materials were characterized by FT-IR, DSC, XRD, TG and limiting oxygen index (LOI). The latent heat of the composite reached 86.69 J/g, and the LOI reached 21.3, which indicated that the composite materials had good fire resistance and high thermal energy storage density. Simultaneously, the obtained materials also demonstrated excellent form-stable properties and thermal stability. Judicious application of the novel form-stable PCMs has opened up a rich field of energy materials with enhanced performance in fire resistance and energy storage.

## 1. Introduction

As an important energy utilization mode, thermal energy is closely related to human life and social production. In order to solve the strong timeliness problem of the supply and demand of thermal energy [1–5], numerous researchers have focused on thermal energy storage (TES). TES is an effective way to improve thermal energy utilization efficiency [6–13]. In particularly, phase change energy storage, which can store and release large amounts of latent heat energy within a slight temperature change, has attracted a great deal of interest [5,9,14–20].

Of the various thermal energy storage materials, organic form-stable PCMs are considered to have tremendous potential due to their adjustable phase transition temperature, no precipitation phenomenon, excellent form-stable effect during phase transition, and easy processing and excellent molding [21–27]. However, the fire protection performance of organic form-stable PCMs is very important because of the flammable nature of organic materials.

There are approximately two methods to improve flame retardant performance of organic form-stable PCMs have been reported. The first one is utilizing microcapsules to encapsulate phase change core and flame retardant meanwhile. Qiu et al. [28] prepared microcapsules containing paraffin and diethyl ethylphosphonate (DEEP) flame retardant with crosslinked P(MAA-co-EMA) shell. The crosslinked P(MAA-co-EMA) microcapsule with DEEP had latent heat of 67.2 J/g and improved flame retardant performance. Another more commonly used method is using organic or inorganic supporting materials to support PCMs and flame retardant simultaneously [29–34]. Zhang et al. [29] investigated the thermal properties and flame retardant performance of phase change material which bases on paraffin/high density polyethylene (HDPE), chlorinated paraffin, antimony trioxide and expanded graphite. The microscale combustion calorimeter and cone calorimeter tests indicated the substantial improvement of the flame retardant efficiency. And the enthalpy reached 59.31 J/g.

All these remarkable works were aiming at supporting PCMs and flame retardants to improve shape-stabilized property and fire resistance performance of organic PCMs. However, the introduction of supporting materials resulted in the unavoidable decrease of the latent heat because the supporting materials did not have phase-change behavior. The enthalpies of the reported materials are mostly around 60 J/g. In this study, novel hybrid form-stable polyether PCMs with good fire proofing were prepared by polyurethane with phase change chain segment and organic flame retardants. The polyurethane with phase change chain segment was used as supporting materials for flame retardants as well as phase change section. In contrast to the reported materials, these materials have prominent advantages of high enthalpy (86.69 J/g) and self-extinguishing characteristic. In addition, the phase change segment was inserted into the polyurethane skeleton by chemical bond connection. This characteristic gives the materials excellent shape-stabilized property and cycling ability. These characteristics reveal an extensive prospect in practical application.

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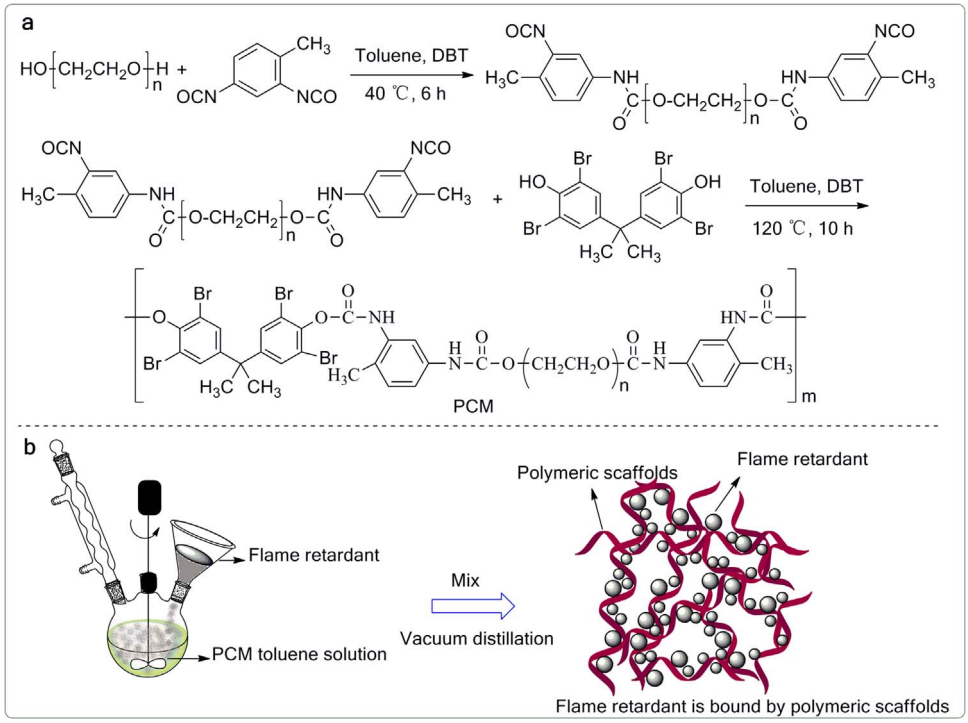


**Scheme 1.** The synthetic route for the phase change composite.

## 2. Experimental

### 2.1. Materials

Analytical-grade polyethylene glycol (PEG, $M_n$=10,000, Xilong Chemical Co. Inc., Ltd). Analytical-grade tetrabromobisphenol-A (TBBP-A, Aladdin chemicals Co., Ltd). Analytical-grade decabrominated-dipheny ethane (DBDPE, Aladdin chemicals Co., Ltd). Analytical-grade toluene (Sinopharm Chemical Reagent Co., Ltd) was distilled and then dried by 5 Å molecular sieve to use. Analytical-grade toluene-2, 4-diisocyanate (TDI, Sinopharm Chemical Reagent Co., Ltd). Analytical-grade dibutyltindilaurate (DBT, Tianjin Kemiou Chemical Reagent Co., Ltd). All other reagents employed in this work were of analytical grade.

### 2.2. Preparation of composites

The synthetic route for the PCM is illustrated in Scheme 1. A stoichiometric amount of dried PEG10000 was dissolved in freshly distilled toluene at 60 °C. A certain amount of TDI and DBT was injected and stirred at 40 °C for 6 h to produce an NCO-terminated prepolymer. A predetermined amount of TBBP-A was added to this mixture, and the reaction was continued for 10 h at 120 °C. The PCM toluene solution was then obtained.

A certain volume of TBBP-A was added in the PCM toluene solution to produce gruel white viscous liquid after vacuum distillation. We obtained PCM/TBBP-A composite materials after vacuum drying. The amounts of TBBP-A added were 0%, 10%, 15%, 10%, and 25%, respectively.

The same method was used for DBDPE and TBBP-A to produce PCM/TBBP-A/DBDPE composite materials, which composite additional amount was 20%.

### 2.3. Characterization

According to a previous report, the viscosity-average molecular weight ($M_v$) of the obtained PCM toluene solution was related to the intrinsic viscosity based on Eqs. (1)–(4).

$$|\eta| = 2.1 \times 10^{-4} \times \overline{M}_v^{0.82} \tag{1}$$

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \tag{2}$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \tag{3}$$

$$|\eta| = \frac{1}{c}\sqrt{2\left(\eta_{sp} - \ln \eta_r\right)} \tag{4}$$

The Fourier-transform infrared (FT-IR) spectra of the samples were obtained using a FT-IR-460 (NICOLET, America) spectrophotometer.

The thermal properties of form-stable PCM composites were measured through differential scanning calorimetry (DSC) technique using a DSC204 (NETZSCH, Germany). Analyses were performed at 5 °C/min heating rate in a $N_2$ atmosphere.

The crystalline products were studied using an X Pert Powder (PANalytical B.V., Netherlands) from 5° to 60° at room temperature.

The shape-stabilized properties of the PCMs were characterized by a hot stage and digital camera. A suitable amount of samples were made into 1 cm diameter circular wafers by tablet press. The circular wafers were placed on a hot stage and heated from 30 °C to 100 °C at a rate of 5 °C/min. The changes in the samples were observed via tracking photography by using a digital camera.

The thermal stability properties were characterized via thermo gravimetric analysis (TGA) by utilizing a TG209C thermal analyzer (NETZSCH, Germany). Approximately 10 mg of the specimen was heated from room temperature to 800 °C at a linear heating rate of 10 °C/min in a $N_2$ atmosphere.

The flame retardant performance was characterized via limiting oxygen index. Limiting oxygen index is defined as the minimum oxygen concentration of flame combustion. Materials can self-quench in air when the LOI is over 21. This experiment used the OJN-9307 digital display oxygen index tester (OJNO, China). The materials were hot-pressed and cut into 14 mm*130 mm*3 mm samples after a hot-compaction process. The sample was fixed by the sample holder and

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