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Organic, cross-linking, and shape-stabilized solar thermal energy storage materials: A reversible phase transition driven by broadband visible light

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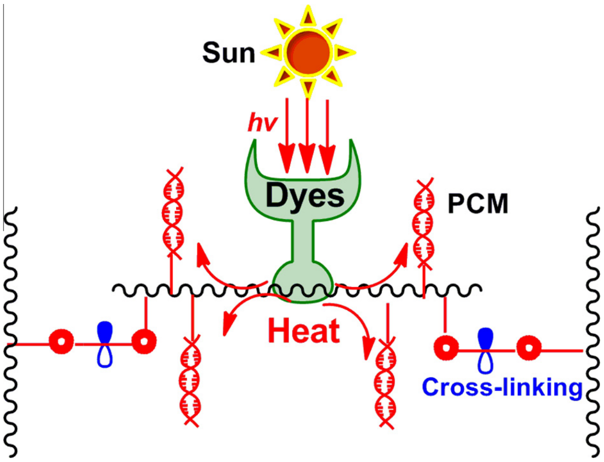
HIGHLIGHTS

- Novel phase change materials (OCSPCMs) were obtained by crosslinking and color matching.
- The η of the OCSPCM was higher than 0.74 (visible light from 400 nm to 700 nm).
- The phase change latent heats of the OCSPCMs were more than 120 J/g.
- The OCSPCM has excellent form-stable effect during phase change process.

GRAPHICAL ABSTRACT

Organic shape-stabilized solar thermal energy storage materials (OCSPCMs) with broadband harvesting for visible light were obtained by crosslinking and color matching, which provided a new platform for improving the efficiency of solar radiation utilization.



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ABSTRACT

Broadband visible sunlight usage and shape-stabilized effect were achieved using organic, cross-linking, and shape-stabilized phase-changed materials (OCSPCMs) with broadband visible light absorption, which were obtained by cross-linking reticulation and color matching (yellow, red, and blue) according to solar irradiation energy density. The obtained OCSPCMs exhibited excellent form-stable phase-change energy storage and broadband visible light-harvesting. Under broadband irradiation (from 400 nm to 700 nm), the light-to-heat conversion and the thermal energy storage efficiency ($\eta > 0.74$) of the OCSPCMs were significantly improved upon solar irradiation by color matching compared with those of OCSPCMs with single-band selective absorption of visible light (yellow, red, or blue). Differential scanning calorimetric results indicated that the phase change temperatures and latent heats of OCSPCMs ranged from 32.6 °C to 60.2 °C and from 120.1 J/g to 132.7 J/g, respectively. The novel materials show a reversible (more than 200 cycles) phase transition via ON/OFF switching of visible light irradiation.

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1. Introduction

Solar energy is clean, inexhaustible, and readily available [1,2]. Thus, harnessing solar energy is one of the most promising ways to address today's energy issues [3–5], which is currently one of the research hot-spot [6,7]. The direct conversion of solar to thermal energy has received significant attention among various technical applications. Given the sunlight intermittent limit, the traditional materials or technologies that rely on sunlight for energy cannot be used continuously [8,9]. Energy storage is required to address the intermittence of time and space in solar irradiation, particularly with high energy density phase-change materials (PCMs) [10–12]. Shape-stabilized PCMs with latent heat storage are one of the most attractive PCMs [13–16]. During the phase-change process, shape-stabilized PCMs retain their original shape and produce no leak after phase transition [17–19]. In addition, low temperature change and an increased amount of energy per weight of materials are obtained [20–22]. Although shape-stabilized PCMs exhibit excellent performance, using visible sunlight directly or effectively is difficult. Visible light, which accounts for approximately 44% of solar radiation, cannot be directly or effectively applied because of low thermal efficiency [23,24]. Thus, PCMs that can harvest and convert visible sunlight into thermal energy have attracted significant attention in modern energy technology.

In our previous study [25], dye was introduced into solid–liquid phase-change materials [organic photothermal conversion-thermal storage materials (OPTCMs)] to improve usage efficiency of solar energy, which proved to be a promising idea. Although the transduction and energy storage efficiency (η) of the OPTCMs with single-band selective absorption of visible light was higher than 0.94 under the corresponding single-band irradiation, the η of the red OPTCM was 0.956 under light irradiation from 550 nm to 650 nm. Capturing and converting the remaining visible solar radiation were difficult because of the limitation of the dye-selectively absorbed visible light. The η of the OPTCMs with single-band selective absorption of visible light was lower than 0.66 under visible sunlight irradiation (from 400 nm to 700 nm). Simultaneously, the solid–liquid phase-transition materials require additional package in the application process to prevent leakage. We developed organic, cross-linking, and shape-stabilized phase-change materials (OCSPCMs) through toluene-2,4-diisocyanate cross-linking reticulation to further achieve a shape-stabilized effect. Moreover, for highly efficient utilization of sunlight, color matching (yellow, red, and blue) was incorporated, providing materials with the ability to harvest broadband visible light (from 400 nm to 700 nm) according to the solar irradiation energy density [26].

The OCSPCMs are advantageous over previously reported materials [25] because of their form-stable and broadband harvesting conversion. No liquid is formed during the transition process of OCSPCMs, although the temperature exceeds 100 °C. Therefore, the plasticity of OCSPCMs is further improved, which broadened their application in other fields. The visible-light-to-heat conversion and energy-storage efficiencies of color-matching OCSPCMs were determined to be $\eta > 0.74$ under full band visible light irradiation conditions (from 400 nm to 700 nm) using photothermal calculation methods. This result was higher than the ($\eta < 0.66$) value of OCSPCMs with single-band selective absorption of visible light (yellow, red, or blue) (Supporting information Fig. S1). Color-matching OCSPCMs are essential prerequisites for the highly efficient use of solar radiation and extending their potential applications in renewable and clean energy sources.

2. Experimental

2.1. Materials

Analytical grade methoxypolyethylene glycol (MPEG) (Mn = 5000) (Sigma–Aldrich Co. Inc., China) was dried at 80 °C under high vacuum (−0.1 kPa) for 48 h. The polyethylene polyamine ($M = 423$) was purchased from Sigma–Aldrich Co. Inc., (China). Analytical grade toluene (Tianjin National Medicines Co. Inc., China) was dried for 48 h using a 5 Å molecular sieve and distilled prior to use. Analytical grade toluene-2,4-diisocyanate (TDI) (Tianjin Kemiou Chemical Reagent Co. Inc., China) and dibutyltin dilaurate (DBT) (Tianjin Kemiou Chemical Reagent Co. Inc., China) were used as received. All the other reagents were of analytical grade and were used as received.

2.2. Synthesis

The synthetic route for the OCSPCMs is illustrated in Scheme 1. The synthesis was conducted in a flame-dried glassware through a step-condensation reaction process under an inert nitrogen (N_2) atmosphere. Predetermined amounts of dried MPEG 5000, TDI, and DBT in freshly distilled toluene were mixed and stirred for 6 h under N_2 at 40 °C to 45 °C to produce an NCO-terminated prepolymer (Compound 1). MPEG 5000 and dyes (Compound 2, Electronic Supplementary information: structural characterizations) were introduced to the polyethylene polyamine ($M = 423$) by NCO groups and chlorosulfonyl or active chlorine (S-triazine) groups. The resulting Compound 4 was vacuum evaporated and further dried for 48 h at 80 °C under vacuum (−0.1 kPa) prior to testing. Compound 4 is called the organic solid–liquid phase-change material (OSPCM). Predetermined amounts of dried color-matching Compound 4, TDI, and triethylamine in freshly distilled toluene were mixed and stirred for 6 h under N_2 at 110 °C to obtain the OCSPCM (Compound 5; Table 1). Color-matching OCSPCMs were vacuum evaporated and further dried for 48 h at 80 °C under vacuum (−0.1 kPa) prior to testing.

2.3. Sunlight irradiation experiment

We showed in our previous study [25] the schematic presentation of the light-to-heat conversion process under solar irradiation. The light-to-heat conversion system consisted of a foam insulation system, OCSPCMs in a weighing bottle ($R = 2.5$ cm), and a light source. A power meter (VLP-2000, Changchun Femtosecond Technology Co., Ltd., Jilin, China) was used to measure and verify the light irradiation power from the solar and simulated light sources (CHF-XM-500 W, Beijing Chang Tuo Technology Co., Ltd., Beijing, China). Data collecting and processing devices consisted of two subsystems, namely, the temperature versus time data collection system and the processing system by a computer. The temperature versus time data collection system comprised a Pt thermocouple, a thermocouple-to-analog connector (RS-232-RS-485, Instrument Co., Ltd., Jiangsu Suke, China), and a data logger (SK-130RD106062560021A1, Instrument Co., Ltd., Jiangsu Suke, China).

2.4. Transduction and storage efficiency (η) of OCSPCMs

The visible-light-to-heat η of OCSPCMs was calculated using Eq. (1) through irradiation from a simulated light source (with a measured light irradiation area of 4.90 cm^2) [25]. The temperature change of the OCSPCMs was measured with foam insulation after simulating light source irradiation (from 400 nm to 700 nm). Using photothermal calculation methods, the parameter η is obtained as follows: