Solar Energy 197 (2020) 222–228

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Thermo-optically responsive phase change materials for passive temperature regulation

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ARTICLE INFO

Keywords:
Solid-liquid phase change material
Polymeric phase change materials
Transparency shift
Thermal conductivity
Passive thermal energy

ABSTRACT

Many phase change materials (PCMs) experience a change in transparency when undergoing a phase transition. These thermo-optically responsive materials can be used to generate passive temperature control systems for building enclosures. The integration of optical and thermal switches into smart temperature-controlling elements requires rationally designed PCMs featuring tunable optical and thermal properties. Two polymers, poly (Octadecyl methacrylate) (PSMA) and poly(2-(2-(octadecyloxy) ethoxy) ethyl methacrylate) (PE2SMA) were synthesized and evaluated for their potential use in passive thermal energy storage systems. UV–Visible Spectroscopy, Near Infra-Red Spectroscopy, and Differential Scanning Calorimetry were used to evaluate the effect that changes in the polymer chemical structure had on the optical and thermal properties of the resulting materials. Insertion of a 6-atom flexible spacer (diethylene glycol) between the pendant crystalline motif and the polymer backbone of PSMA resulted in increases of latent heat storage capacity from 62 J/g to 94 J/g and thermal conductivity from 0.218 W/mK to 0.318 W/mK. Notably, insertion of a flexible spacer also resulted in a melting transition temperature increase from 37.7 °C for PSMA to 48 °C for PE2SMA. The visible transmittance of the polymers increased from 0% to 90% upon transition from crystalline to amorphous state. This study presents a synthetic strategy to control thermal and optical properties of polymeric PCMs materials. The material properties and structure-property relationships derived from this study will enable the refinement of the models used to predict the performance of passive temperature-regulating systems. More accurate models will guide the development of the thermo-responsive polymeric materials required for better perfoming temperature-regulating building enclosures.

1. Introduction

Worldwide energy demand has grown significantly during the last century and has prompted researchers worldwide to develop energy systems that are more efficient, sustainable and resilient. The building sector is one of the largest energy consumers and accounts for approximately 30% of the energy used in many countries (International Energy Agency, 2018). A significant fraction of this energy is used for the thermal conditioning of buildings to offset thermal losses or gains occurring through the building envelope (Sadineni et al., 2011). Many new technologies have been introduced to reduce building thermal energy usage and improve their efficiency (Sun et al., 2018; Samuel et al., 2013; Saadatian et al., 2012; Ye et al., 2012). A promising implementation of sustainable energy systems at the building or building envelope scale consists in the integration of Phase Change Materials (PCMs) into building components to increase their thermal storage capacity.

PCM's typically offer higher latent heat storage capacity than sensible heat storage systems allowing them to absorb and release larger amounts of energy per unit mass when there is a thermal surplus or deficit. Below their melting transition temperature, the PCMs used in this study are semi-crystalline due to ordered domains formed by the alkyl side chains of the polymer. The order is disrupted by absorption of thermal energy as illustrated in Fig. 1. The reported advantages of using PCMs in buildings lie primarily in the shift of heating and cooling peak loads (Kalnæs and Jelle, 2015), the improvement of indoor thermal comfort (Kalnæs and Jelle, 2015; Soares et al., 2013), and the reduction of environmental impact due to decreased energy consumption in

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https://doi.org/10.1016/j.solener.2019.12.064
Received 15 August 2019; Received in revised form 26 November 2019; Accepted 23 December 2019
Available online 11 January 2020

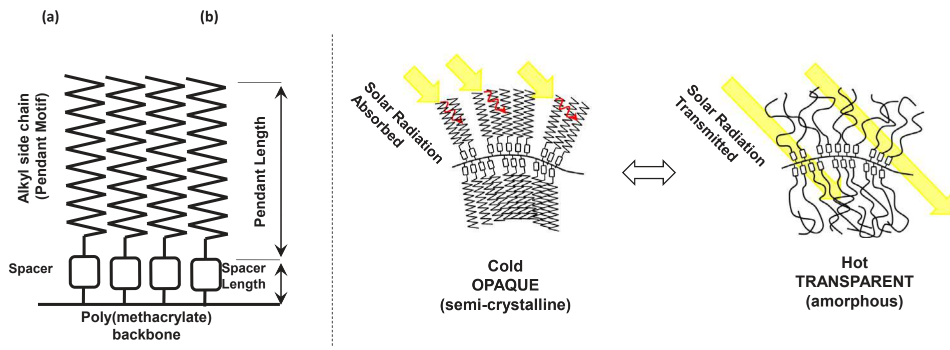

Fig. 1. PCMs showing phase transition from crystalline to amorphous state by absorption of heat and reverse while cooling.

buildings. Many different types of PCMs have been studied or are already commercially available including solid-liquid, liquid-gas, and solid-solid PCMs (Fallahi et al., 2017; Baetens et al., 2010). PCMs can also be blended with other materials to create composite systems with enhanced properties (Sarı, 2012; Chung et al., 2015; Jeong et al., 2013). For example, PCMs can be blended with polymers to stabilize their shape (Inaba and Tu, 1997), or they can be mixed with fillers to improve their thermal conductivity (Jeong et al., 2013; Inaba and Tu, 1997; Yu et al., 2014).

One example of promising PCM use to regulate building envelope temperature includes their blending with building materials for roofs and walls. The roof of the building is alone responsible for 70% of its heat exchange, thereby increasing heating and cooling load. Widely used bituminous roofs can reach temperatures as high as 60–70 °C during summer, thus significantly increasing the cooling load (Liu and Baskaran, 2003; Teemusk and Mander, 2009). Several studies have been done on PCMs modified roofs and walls to minimize the undesirable heat exchange. Gypsum modified PCM and form stable PCM walls have been reported to reduce the inner temperature swing by 50% (Zhou et al., 2007). The thermal inertia of a modified roof was reported to improve significantly by using fatty acid-derived PCMs sealed inside an array of tubes (Lu et al., 2016). In another example a concrete roof containing cylindrical holes filled with PCMs reduced the heat flux inside the building by as much as 17% (Alqallaf and Alawadhi, 2013).

Many PCM's experience a change in transparency when changing phase. For example, most solid-liquid PCMs (like paraffin) are opaque when solid and become transparent while liquid (Kalnæs and Jelle, 2015). Such feature offers new opportunities to improve the performance and expand the application scope of PCMs. See Fig. 1.

To explore the use of transparency changes, adaptive building envelope systems have been studied that rely on changes in a PCMs optical properties to regulate the amount of solar energy admitted into a building enclosure system (Guldentops et al., 2018; Li et al., 2016; Bianco et al., 2017; Bianco et al., 2017). The integration of optical and thermal features into smart solar thermal control systems demands the development of new PCMs featuring tailored optical and thermal properties. Previous work indicates that only PCMs with a phase transition close to the thermal comfort temperature and with a specific chemical composition can be used at the building level (Kalnæs and Jelle, 2015). Solid-liquid PCMs composed of paraffin, fatty acids and salt hydrates are promising candidates for such applications (Fallahi et al., 2017).

In an effort to evaluate the benefits of combining PCM's thermal and optical transitions to enhance the thermal regulation efficiency in building envelopes, we have performed a finite element modelling study (Guldentops et al., 2018). Notably, this study indicates that a combination of a thermo-responsive outer PCM roof coating with a reflective backing layered on top of an insulating layer can significantly decrease the heat flux through the roof during the peak mid-day hours. These systems, once optimized, will lead to decreases of the building's surface temperature of approximately 10–15 °C during the summer months (Guldentops et al., 2018). Accurate prediction of the performance of these temperature-regulating elements requires the experimental evaluation of physical properties such as latent heat storage capacity, thermal conductivity and temperature dependent transmittance for potential candidate polymers. This study describes a viable synthetic route to produce long-term thermally and photochemically stable PCMs exhibiting the required latent heat values (melting enthalpy higher than 90 J/g) and thermally-induced change in optical properties (contrast ratios higher than 500) as found in our FEM study (Guldentops et al., 2018). The experimental data for the PCMs in this work will enable closure of the design loop for thermo-optically responsive building enclosures and facilitate the production of the first prototype systems.

Inspired by an approach commonly used to prepare side-chain liquid crystalline polymers (Shibaev et al., 1979; Freidzon et al., 1985; Yamaguchi et al., 1989; Plate et al., 1985; Finkelmann et al., 1978; Hu et al., 2003; Zhang et al., 2005; Zhang et al., 2006; Zhang et al., 2007; Liu et al., 2008; Ahn et al., 2009), we have synthesized polymeric phase changing materials with thermo-responsive optical properties. These macromolecules exhibit relatively high heat storage capacity and were prepared using simple, easily-scalable chemistry. The chemical structures selected based on previous reports produce thermally stable (Qiu et al., 2014) and thermally cyclable (Tang et al., 2012) materials that can be rendered resistant to photodegradation using commercially available additives (Wypych, 2015). Once most promising chemical compositions have been identified, this approach can be easily adapted to produce form-stable bulk or highly porous phase change materials. Our results indicate that insertion of flexible, non-crystallizable, spacers between the backbone and the alkyl pendant motif of polyalkylmethacrylate (Fig. 2) produced a slight decrease in optical transmittance but caused a 1.5-fold increase in the latent heat storage capacity and 50% increase in thermal conductivity. The correlation between spacer length and bulk crystallinity with thermal and optical properties was established using NMR, X-Ray diffraction, Differential Scanning Calorimetry, UV–Visible spectroscopy, Near Infra-Red and ATR-FTIR measurements. The trends identified in these compounds can be used as a guide for the development of a new generation of thermo-optically responsive building envelopes capable of passive temperature regulation.

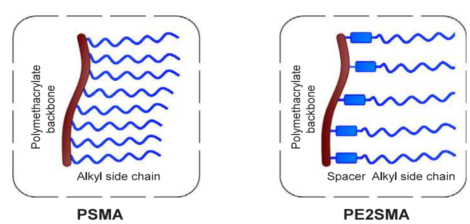

Fig. 2. Schematic illustration of two polymers with flexible amorphous backbone (red) and crystalline pendant moities (blue). The blue rectangular box represents the spacer inserted in PE2SMA.

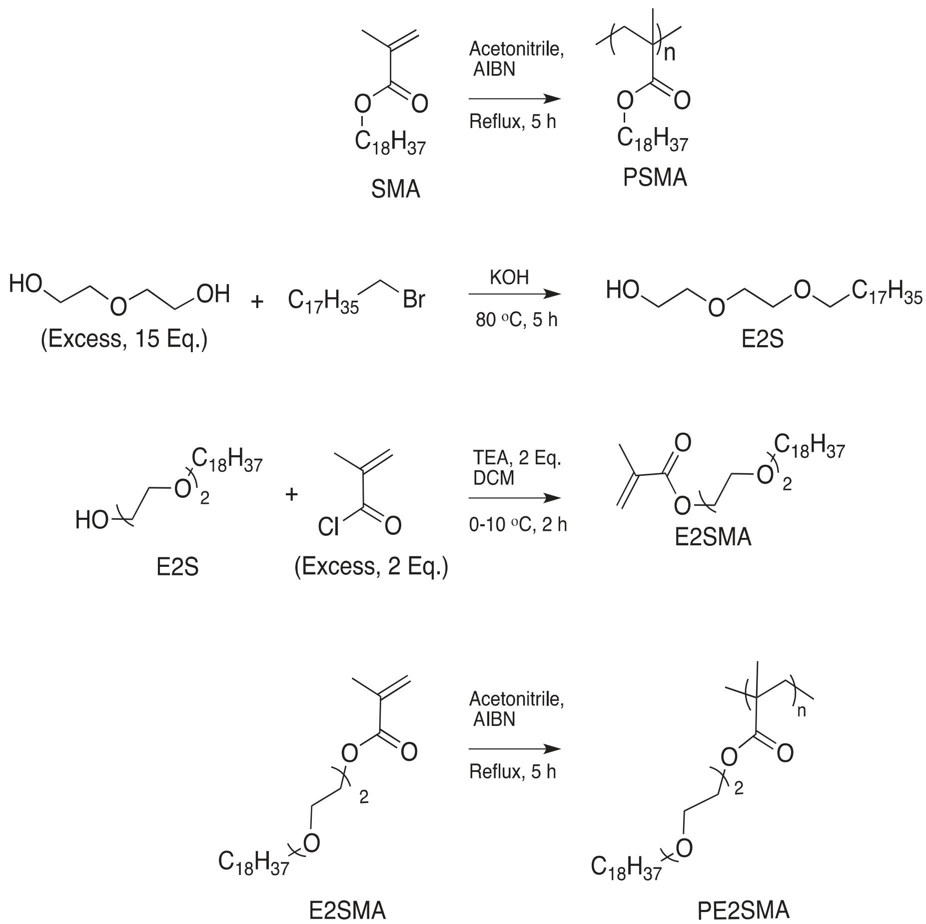

Fig. 3. Synthesis of PSMA and PE2SMA.

2. Synthesis and characterization methods

2.1. Polymer synthesis

Both poly (Octadecyl Methacrylate) (PSMA) and poly(2-(2-(Octadecyloxy) Ethoxy) Ethyl Methacrylate) (PE2SMA) were synthesized via radical-initiated polymerization as shown in Fig. 3. The syntheses are described in detail in the supplemental information. The structure of the polymers was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. Experimental details for the measurement of the thermal transitions, thermal stability and crystalline fraction can be found in the supplemental information.

2.2. Optical characterization

Optical characterization experiments were performed using a Perkin Elmer Lambda 850 UV/Vis single beam type spectrophotometer and a Thermo Scientific Nicolet iS5N FT-NIR spectrometer. Measurements were collected for the visible and NIR range, between 380 nm and 2400 nm. NIR data was collected with a resolution of 7.7 cm^{-1} and 32 scans for each measurement. The slit aperture was set to 2 nm in the visible range and in servo mode in the near-infrared range, the latter being a dynamic operation mode that varies the slit aperture as function of the optimal energy input at each wavelength. Transmittance data were acquired for both solid and melt phases using a standard compartment of 2 mm path length.

2.3. Thermal conductivity measurements

A numerical analysis of heat flow and sample temperature was performed to determine the thermal conductivity of PE2SMA and PSMA. In order to find this parameter, the stepwise DSC method designed by Merzlyakov and Schick (Merzliakov; Schick; Merzlyakov and Schick, 2001, 1999, 2001) was performed with the specific temperature-time program presented in Fig. 4. The details of the experiment are included in the supporting information. Three disks of specific diameter (~5 mm) and thickness (~200 μm) were prepared for both S-L PCM materials as well as for polystyrene(PS) and poly (methyl methacrylate) (PMMA) as reference.

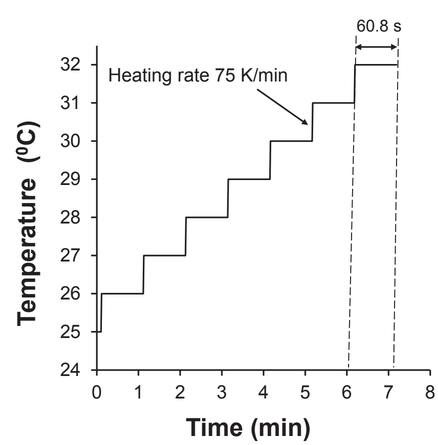

Fig. 4. Temperature-time program characterized by heating rate of 75 K/min and 60.8 s as single step period used in DSC method for determining thermal conductivities of polymer samples.

Table 1
Heat of melting as a function of spacer length and heating rate. ([a]Heating at 2 °C/min and [b]Heating at 20 °C/min). [c]thermal transition data for stearyl alcohol (S-OH) and polyethylene glycol (PEG), was included for comparison.

Compound	ΔH [J/g][a]	Peak [°C][a]	ΔH [J/g][b]	Peak [°C][b]	T dec[°C][b]
PSMA	62.0	43.1	52.2	37.7	230
PE2SMA	93.5	51.3	84.3	48.0	213
S-OH[c]	240.0	57.7	230	59	208
PEG(1400 g/mol)[c]	168.0	43.5	161.4	40.4	360

3. Results and discussion

3.1. Solid state structure and phase transitions

Table 1 summarizes the thermal properties for each polymer at two heating rates 20 °C/min and 2 °C/min. The relatively slow heating rate replicates typical temperature changes that would be typical for most heat-storing PCM applications where methacrylate-based polymers may find the most use. As seen in Table 1, both polymers exhibited similar heat of melting as a function of heating rate. As would be expected, all the melting transitions were observed at slightly higher temperatures for the 20 °C/min rate compared to 2 °C/min. Table 1 also shows a significant dependence of both the heat of melting and the melting transition maximum as a function of spacer length. As the spacer length increased from 0 atoms (PSMA) to 6 atoms (PE2SMA) the heat of melting increased from 62.0 J/g to 93.5 J/g. The heats of crystallization showed a similar trend. For comparison, the melting enthalpy of most of the reported polymeric phase change materials lies between 30–70 J/g (Fallahi et al., 2017). Polyethylene Glycol (PEG) grafted Cellulose (Li et al., 2009) and Polyethylene Glycol (PEG) grafted Polystyrene (Sar et al., 2012) have shown appreciably high crystallization enthalpy from 150 J/g to 200 J/g. However, their melting transition occurs at higher temperatures (60–70 °C), rendering them unsuitable for building applications where thermal comfort temperature is much lower. PE2SMA exhibits relatively high crystallization enthalpy at temperature closer to the thermally comfortable zone for such applications.

The thermal stability of PCMs is key for their use as materials in building temperature regulation. TGA analysis indicates that PSMA and PE2SMA are stable up to 230 °C and 213 °C, respectively, see Table 1. For our target applications, these materials will be exposed to maximum temperatures of 70 °C. Consistent with our results, in a previous study, Qiu et al. have found that microcapsules containing PSMA and n-octadecane were stable up to 230 °C and both melting point and enthalpy of melting remained constant after 1000 thermal cycles when heated between 0 °C and 50 °C (Qiu et al., 2014).

The fraction of crystalline domains present in each sample was calculated by calculating the area of the sharp reflections in the wide-angle X-ray diffraction patterns, WAXD, and comparing it to the total scattered intensity (Chung and Scott, 1973). The WAXD diffractograms are shown in Fig. 5 and the peak assignments and d-spacings are summarized in Table 2, with PEG exhibiting both higher crystalline fractions and higher heats of melting than the polymethacrylate-based systems.

The data in Fig. 5 and Table 2 indicate that the polymer with the highest heat of melting (PE2SMA) exhibited diffraction peaks that can be attributed to both ordered alkyl chains, like those present in paraffins, and ordered ethylene glycol motifs, like those present in PEG (Sirota and Herhold, 2000; Sirota and Herhold, 1999; Wentzel and Milner, 2010; Meng et al., 2013). In contrast, the polymers with the lowest heat of melting (PSMA) showed diffraction peaks ascribable only to ordered alkyl side chains (Meng et al., 2013; Ventola et al., 2002).

3.2. Optical properties

The optical properties of PSMA and PE2SMA were measured along the visible and near infra-red range. Images before and after the melting transition of both PSMA and PE2SMA are shown in Fig. 6. Fig. 7 shows the PSMA and PE2SMA transmittance between 380 nm and 2400 nm for the transparent (amorphous) and opaque (semi-crystalline) forms. The data indicates that a thermo-responsive optical contrast ratio (defined as the absorbance ratio at 500 nm between the amorphous and the semi-crystalline polymer forms) as high as 800 was observed in transmission profiles for both materials.

The variations in transmittance between PSMA and PE2SMA within the 380–460 nm range are attributed to trace color impurities in the PE2SMA. In its opaque form the pendant motifs of the polymers are in a well-ordered semi-crystalline state, which limits the transmission of visible radiation. In contrast, in the transparent form the molten phase changing motifs are randomly oriented, allowing visible light to

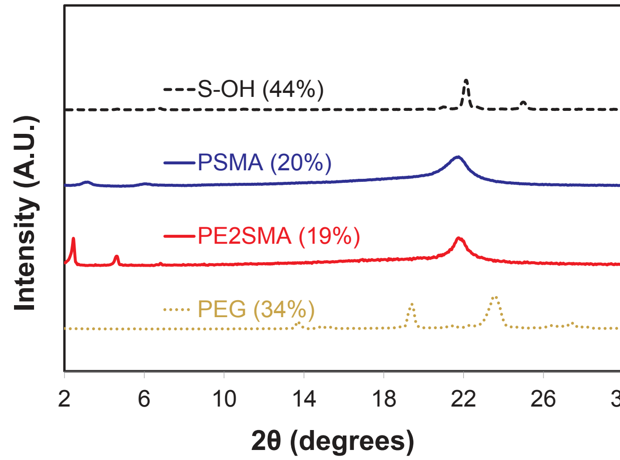

Fig. 5. WAXD patterns as a function of polymer structure (numbers in parenthesis list the crystalline fraction for each sample.

Table 2
Crystallinity of polymers determined from the WAXD patterns.

Peak Assignment	d(A)	
	PSMA	PE2SMA
Lamellar bilayer	29.33	39.39
(0 0 1) Lamellar alkane	14.92	18.05
In-plane alkyl packing		4.60
In-plane alkyl packing(200)PEG	4.20	4.19
In-plane alkyl packing		3.86
In-plane alkyl packing		3.63

Fig. 6. Opaque and transparent phases of PSMA (top) and PE2SMA (bottom).

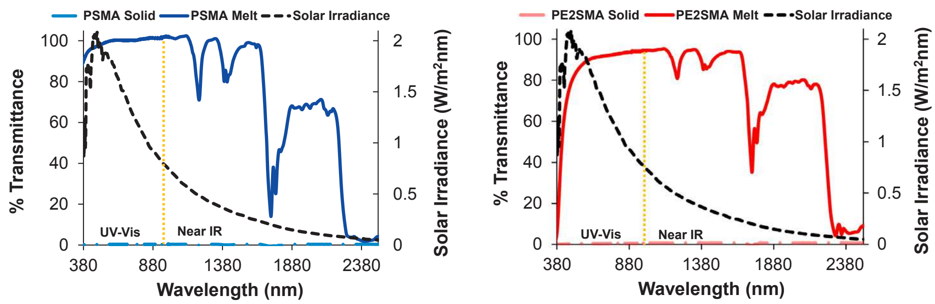

Fig. 7. PSMA(left) and PE2SMA(right) Spectral transmission for transparent and opaque forms at normal incidence. The solar irradiance spectrum as a function of wavelength was inserted in the figures for comparison.

propagate through it.

PSMA and PE2SMA exhibit the highest temperature-induced change in transmittance in the same spectral region where the solar irradiance is the most intense, see Fig. 7. This behavior makes them promising candidates to build the outer thermo-optically responsive PCM layer described in our FEM study (Guldentops et al., 2018). The photochemical stability of these PCMs is essential to their use in this type of temperature-regulating systems. A wide variety of commercially available additives acting as UV absorbers, UV screeners and UV stabilizers have been synergistically used to prevent the photo-induced chemical degradation of acrylate-based layers exposed to sunlight (Wypych, 2015; Nagai et al., 2005). These compounds can be used as additives for PSMA and PE2SMA coatings to prevent photochemical degradation from prolonged sun-light exposure.

3.3. Thermal conductivity

The rate of thermal energy charging and discharging of the phase change materials depends on their thermal conductivity. High energy charging/discharging rates can be achieved by increasing the thermal conductivity of the phase change materials by using high thermal additives, inserts or linkers (Liu et al., 2016). The measurement of thermal conductivity of the phase change materials has received less attention compared to measurements of enthalpy and melting point. Two key factors that complicate the accurate measurement of this property are the need for relatively large samples (100 g or more) and the need to consider many parameters potentially influencing the resulting values (geometry of sample, time, temperature and heat flow). The approach developed by Merzlyakov and Schick (Merzlyakov and Schick, 2001; Merzlyakov and Schick, 1999; Merzlyakov and Schick, 2001) allows the use of small samples and produces values that do not depend on as many external parameters as other methods. The thermal conductivity of most of the polymer phase change materials has been reported in the range of 0.1–0.2 W/mK (Fallahi et al., 2017). Table 3 lists the values of thermal conductivity of different materials, derived using the described DSC-based method.

The thermal conductivity experiments were performed on three different samples for all materials. The resulting thermal conductivities as a function of temperature are shown in Fig. 8 and Fig. 9 for PSMA

Table 3
Comparative thermal conductivities observed for four different materials.

Compound	Observed k [W/mK]	Expected k [W/mK]
PS	0.160–0.165[b]	0.168–0.172[b] (Merzlyakov and Schick, 2001)
PMMA	0.200–0.270[b]	0.200–0.240[b] (Hu et al., 2007)
PSMA	0.202–0.238[a]	
PE2SMA	0.303–0.330[a]	

[a] The measure is collected at 27 °C.
[b] The measure is collected at 47 °C.

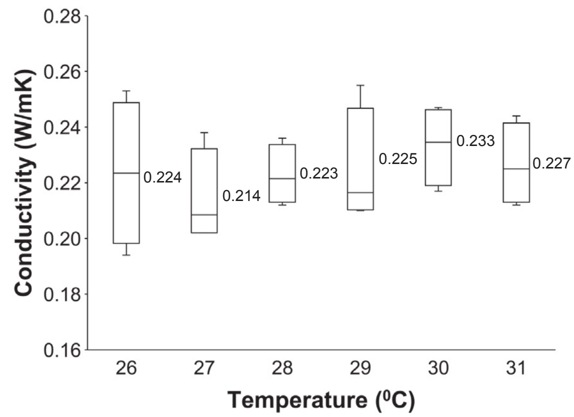

Fig. 8. Thermal conductivity of PSMA at different temperature.

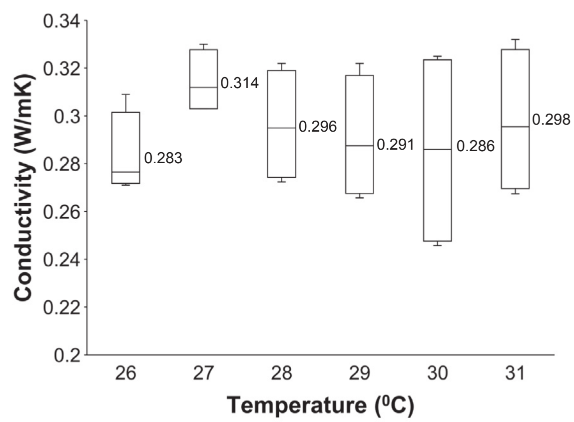

Fig. 9. Thermal conductivity of PE2SMA at different temperature.

and PE2SMA, respectively. The differences in the measured thermal conductivity between PSMA and PE2SMA are reproducible and statistically significant based on the margins of error inherent to the DSC experiments. Previous work has shown that heat transfer within polymers occurs more efficiently along covalently bonded moieties in highly oriented domains. The thermal conductivities of Polyethylene (PE) and Polypropylene (PP) have been reported to increase with increases in crystallinity (Yamanaka and Takao, 2011). Though the chemical structures of PSMA and PE2SMA differ only in the presence or absence of a diethylene glycol spacer, these led to significant differences in crystalline fractions and crystalline domain sizes. Scherrer analysis of the WAXD peaks indicated that the average crystalline domain size for PE2SMA was 1.8 times as large (8.5 nm) as those found in PSMA (4.8nm). The thermal conductivity of polyethylene oxide, with an average crystallite size of 11.2 nm, is 0.37 W/mK, which is consistent with the observation that larger crystalline domains result in higher thermal conductivities. We thus hypothesize that the relatively polar diethylene glycol spacer in PE2SMA may favor larger crystalline domain sizes, resulting in the higher thermal conductivities for PE2SMA compared to PSMA.

4. Conclusions

A series of phase changing polymeric matrices have been synthesized via thermally initiated polymerization of methacrylate-based precursors. The radiation transmittance of these films in the visible range changes reversibly as a function of temperature, exhibiting an optical contrast ratio of up to 800 for the opaque and transparent forms in the wavelength range between 380 nm and 2400 nm. The difference in crystalline fraction as a function of polymer structure followed the same qualitative trend as the one observed for the heat of melting, with higher crystalline fractions resulting in higher heats of melting. X-ray diffraction analysis indicates that the polymers with the highest heat of melting (PE2SMA) exhibit diffraction peaks that can be attributed to ordered alkyl chains and ordered ethylene glycol motifs from the diethylene glycol spacer. The thermal conductivity for these polymeric PCMs was measured using a stepwise DSC method. The differences in the measured thermal conductivity between PSMA and PE2SMA are attributed to the higher degree of crystallinity in PE2SMA due to presence of the diethylene glycol spacer in PE2SMA. The results from this work provide a straightforward materials synthesis and characterization approach that uses rationally designed polymer matrices, and is suitable for the rapid simulation-guided development of passive temperature regulation systems. Our synthetic approach can be easily adapted to produce form-stable bulk or highly porous phase change materials. Addition of up to 5% mol of glycidyl methacrylate as a comonomer produced form-stable solid-solid PCMs with comparable or higher heats of melting than those measured for PE2SMA. A Detailed description of their properties and structures will be the focus of an upcoming publication. Coupled with the results from our numerical simulations, these materials could be used to produce passive temperature-regulating building enclosures capable of significantly reducing their surface temperature increases during the summer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge financial support from the NSF Division of Civil, Mechanical and Manufacturing Innovation (CMMI) through grant# 1662903 and grant# 1662675.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solener.2019.12.064.

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