

Preparation and characterization of a series of thiourea derivatives as phase change materials for thermal energy storage

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Received: 02.08.2010

A series of solid-liquid phase change materials, thiourea derivatives, were prepared via condensation of thiourea with the respective carboxyl chlorides (lauroyl chloride, myristoyl chloride, and palmitoyl chloride) and were then characterized by using FT-IR, ¹H-NMR, differential scanning calorimetry (DSC), and thermogravimetric (TG) analysis. The thiourea derivatives (1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea) were structurally symmetric and had long alkyl groups to crystallize. Thermal analysis by DSC and spectroscopic investigation by FT-IR spectroscopy were performed on the samples before and after thermal cycling tests to determine thermal reliability. The maximum latent heats of melting and freezing of the thiourea derivatives were found to be 114.6 and -110.0 J/g for 1,3-didodecanoyl thiourea, 119.5 and -122.4 J/g for 1,3-ditetradecanoyl thiourea, and 148.8 and -142.7 J/g for 1,3-dihexadecanoyl thiourea after accelerated thermal cycling. A TG instrument was used to determine the starting point of degradation in the thiourea derivatives; it was found that the thiourea derivatives degraded at sufficiently higher temperatures than the expected utility temperatures.

Key Words: Thiourea, phase change materials, thermal properties

Introduction

Thiourea, having a considerably wide range of applications, is a functional organic compound similar to urea, except that the oxygen atom is replaced by a sulfur atom. The properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen. Thus, thiourea is a versatile reagent

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in organic synthesis. It is produced and consumed by the thousands of tons throughout the world every year.¹ The main application of thiourea is in textile processing.² Moreover, thiourea reduces peroxides to the corresponding diols.³ The reaction produces an unstable epidioxide as an intermediate, which can only be identified at -100 °C. Epidioxide is similar to epoxide except for 2 oxygen atoms. This intermediate is reduced to diol by thiourea. Thiourea is also used in the reductive work-up of ozonolysis to give carbonyl compounds.⁴ Another effective reagent for this reaction is dimethyl sulfide, but it is highly volatile and has an obnoxious odor, whereas thiourea is odorless and conveniently nonvolatile due to its polarity. In addition, thiourea is commonly employed as a source of sulfide, e.g. for converting alkyl halides to thiols. Such reactions go on through the intermediacy of isothiuronium salts.⁵ The reaction capitalizes on the high nucleophilicity of the sulfur center and the hydrolytic instability of the isothiuronium salt. Thioureas are also used as building blocks for pyrimidine derivatives. Thus, thioureas condense with β -dicarbonyl compounds.⁶ The amino group on the thiourea initially condenses with a carbonyl, followed by cyclization and tautomerization. Desulfurization delivers the pyrimidine. Similarly, aminothiazoles can be synthesized by the reaction of alpha-halo ketones and thiourea.⁷ Recently, thiourea was also used for increasing technologies for plasma membrane proteomics⁸ and for direct enantioselective aldol reactions catalyzed by a proline-thiourea host-guest complex.^{9,10} The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions, and some N-substituted-N'-carbonyl thioureas have been used in commercial fungicides. 11,12 N, Ndialkyl-N'-benzoylthioureas have been found to be useful ligands for the potential determination of traces of transition metals by means of normal phase chromatography.¹³ More significantly, these reagents have been shown to selectively extract several of the platinum group metals in the form of remarkably stable neutral metal chelates. 14 N, N-dialkyl-N'-benzovlthiourea derivatives with such properties and their metal complexes were synthesized and their thermal behaviors were examined.^{15–18}

Thermal energy storage materials can store thermal energy in the form of sensible heat and latent heat. The use of latent heat storage by phase change materials (PCMs) has received considerable interest over the past decades.¹⁹ Various materials (paraffins, fatty acids, polyethers, salt hydrates, etc.) and their mixtures have been studied for latent heat storage applications.²⁰ PCMs have many applications in solar energy storage. waste heat recovery, smart air-conditioned buildings, temperature-adaptable greenhouses, electric appliances with thermostatic regulators, energy-storing kitchen utensils, insulating clothing, and so on. The advantages of PCMs in heat storage systems are their high latent heat of fusion per unit of mass, energy storage and release at a nearly uniform temperature, small volume change for heat storage systems, and reasonable heat losses from the system during the charging and discharging of heat.^{21,22} Fatty acids are PCMs with considerable heat storage density and cheap prices.²³ However, their thermal stability is poor and they sublimate during heating. They also have a bad odor. To overcome these drawbacks and to obtain PCMs with desirable performances, a number of fatty acid derivatives with high phase change heat storage capacities have been synthesized previously. $^{24-28}$ In our previous works, we produced esters, amides, and ureas to investigate their thermal energy storage properties, and our studies in different materials are ongoing. The aim of the present study was to produce solid-liquid PCMs based on thiourea derivatives. Amides are good ligands for metals and the thiourea derivatives produced here could be further improved for energy storage properties by phase changing. The structural characterization of the thiourea derivatives produced by reacting thiourea with fatty acid acyl chlorides was performed using FT-IR and ¹H-NMR spectroscopy devices. In order to investigate the thermal properties, a differential scanning

calorimetry (DSC) instrument was used. The thermal endurance of the materials was determined using a thermogravimetric (TG) analysis instrument.

Experimental

Materials

Thiourea, sulfurous oxychloride $(SOCl_2)$, and carbon tetrachloride were all obtained from Merck and used without further purification. Lauric, myristic, and palmitic acids were also obtained from Merck and were purified to remove trace water.

Synthesis of 1,3-dialkyloyl thioureas

Lauric, myristic, and palmitic acids were converted to their acyl chlorides in the presence of sulfurous oxychloride. Each of the fatty acid chlorides was then reacted with thiourea by the dropwise addition of the corresponding acyl chloride to a stoichiometric amount of thiourea (molar ratio of thiourea to acyl chloride, 1:2), mixing thoroughly. The procedure was the same as in the synthesis of 1,3-dialkyloyl ureas.²⁹ Its reaction path is given in Figure 1.



Figure 1. Synthetic scheme for thiourea derivatives (X: 10, 12, and 14).

FT-IR spectroscopy investigation of the compounds was performed on KBr disks at a sample-to-KBr ratio of 1:20 using a JASCO 430 FT-IR spectrophotometer (JASCO, Japan), while ¹H-NMR spectra in CDCl₃ were recorded with an NMR device (AVANCE III, 400 MHz, Bruker, USA) with trimethylsilane as an internal reference standard.

Thermal analysis of 1,3-dialkyloyl thioureas

Thermal properties of thiourea derivatives, such as the melting and crystallization points and latent heats, were measured using a DSC instrument (DSC 131, Setaram, France). The analyses were carried out at a heating rate of 5 $^{\circ}$ C/min under a constant stream of argon at a flow rate of 60 mL/min. Reproducibility was tested by conducting 3 measurements.

The thermal reliability of 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea was tested by heating a series of samples above the melting point 3000 times and cooling in a thermal cycling instrument (BIOER-TC-25/H, Bioer Technology, China) using the experimental procedure from our

previous work.³⁰ The changes in chemical structures and thermal properties of the thiourea derivatives after the thermal cycling test were investigated by FT-IR and DSC spectroscopy measurements.

The thermal endurance of the 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea compounds was investigated with a TG analysis instrument (TGA7, PerkinElmer, USA), which was calibrated with calcium oxalate. From each of the thiourea derivatives, 10-mg samples were used for the measurements. The experiments were performed at a temperature range of 30-800 °C with a heating rate of 10 °C/min under a static air atmosphere.

Results and discussion

FT-IR spectroscopy analysis is one of most widely used techniques to prove synthesis and possible interactions in organic compounds. FT-IR investigation is applied to thiourea derivatives for the determination of molecular structure and to prove structural stability at the end of accelerated thermal cycling. Figure 2 shows the FT-IR spectrum of lauric acid as a sample of used fatty acids (a), the FT-IR spectra of 1,3-didodecanoyl thiourea before thermal cycling (b), and of 1,3-didodecanoyl thiourea after thermal cycling (c). In Figure 2, there are hydroxyl absorption peaks between 3410 and 3550 cm⁻¹, which disappear in the synthesized products. Carboxylic acid in fatty acids also forms a broad carbonyl band due to hydrogen bonding interactions between the ester oxygen and acid hydrogen. The carbonyl peak shifts slightly and forms a single peak in the thiourea samples. Carbonyl peaks observed at around 1698 cm⁻¹ in the fatty acids' spectra were observed at 1703, 1698, and



Figure 2. FT-IR spectra of lauric acid (a), 1,3-didodecanoyl thiourea before thermal cycling (b), and 1,3-didodecanoyl thiourea after thermal cycling (c), respectively.

 1695 cm^{-1} for 1,3-didodecanoyl thiourea (a), 1,3-ditetra decanoyl thiourea (b), and 1,3-dihexa decanoyl thiourea (c), respectively.

In a mide structures, there are 2 resonances, so the NH stretching peak is observed to be very soft. The carbonyl peak at around 1700 cm⁻¹ in the synthesized compounds overlapped with the NH peak observed at around 1610 cm⁻¹. The amide formation was also evidenced with an amide bending vibration at around 1500 cm⁻¹.

Symmetric and asymmetric stretching peaks of $-CH_2$ - and CH_3 between 2800 and 3000 cm⁻¹ are characteristic for both the fatty acids used and the thiourea compounds. These peaks deepened when the number of C atoms increased.

The thiourea compounds were treated with heat before FT-IR measurements; in other words, they were melted and solidified at least one time. Comparing the standard spectra of thiourea derivatives to the spectra of



Figure 3. ¹H-NMR spectra of the thiourea derivatives.

thiourea derivatives after thermal cycling, it was found that there was no considerable alteration in the spectra except for the CO_2 absorption peak at 2300 cm⁻¹. CO_2 could easily be absorbed by organic compounds from the air.

¹H-NMR study

The ¹H-NMR spectra of the thiourea derivatives are shown in Figure 3, and the characteristic groups and the peaks belonging to those groups are noted with small letters. It is seen that the CH_2 peak intensities increased in the order of 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea. The peaks all corresponded to chemical groups showing the high purity of the compounds. Upon considering the integral values, it can be seen that the most intense peaks, at around 1.2 ppm, were due to CH_2 groups with integral values of 2 more hydrogen atoms than calculated, which can be explained by overlapping NH hydrogens in that region. On the other hand, the OH hydrogen appearing after 10 ppm in the NMR spectra of fatty acids disappeared in the synthesized compounds.

Thermal properties

As seen from the phase change enthalpy and melting temperature values and curves of the thiourea derivatives in the Table and Figure 4, the phase change temperature of the thiourea derivatives increased with the increasing C number in the paraffinic sides. The melting enthalpy values of the PCMs before thermal cycling were measured as 116.3, 122.5, and 153.6 J/g for 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3dihexadecanoyl thiourea at the temperatures of 40.2, 44.7, and 51.7 °C, respectively. The crystallization enthalpies were -112.4, -126.7, and -150.6 J/g for 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea at the temperatures of 42.5, 47.4, and 52.0 °C, respectively. After thermal cycling, the melting enthalpy values of the PCMs were measured as 114.6, 119.5, and 148.8 J/g for 1,3-didodecanoyl thiourea, 1,3-ditetradecanoyl thiourea, and 1,3-dihexadecanoyl thiourea at the temperatures of 42.5, 49.3, and 56.7 °C, respectively, and the crystallization enthalpies were measured as -110.0, -122.4, and -142.7 J/g for 1,3-didodecanovl thiourea, 1,3-ditetradecanovl thiourea, and 1,3-dihexadecanovl thiourea at the temperatures of 43.9, 49.2, and 54.1 °C, respectively. Among the thiourea derivatives, 1,3-dihexadecanoyl thiourea showed the maximum change in the temperatures and enthalpies of melting and crystallization, at 2.6 °C and 6.1 J/g and within the percentages of 4.6% and 4.1% after thermal cycling, respectively. Single endothermic and exothermic peaks showing the purity of the compounds were observed for each of the thiourea derivatives during the heating and cooling periods, respectively. In addition, the resulting thiourea derivatives had a proper phase change temperature over the range of 40.2-56.7 °C.

The thermal energy storage performance of the thiourea derivatives is caused by the fact that the different integrities of the crystals need different amounts of energy to transform from the solid to the liquid state.^{25,26} The integrity of the crystalline thiourea derivatives increased in succession with the increasing number of C atoms due to the effect of the C–C chain length on crystallization. As a result, most of the prepared thiourea derivatives, with proper melting temperatures and excellent heat storage densities, can meet the practical demand of PCMs to store or release energy.

PCMs	Thermal energy storage properties			
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	T_m (°C)	$\Delta H_m (J/g)$	T_f (°C)	$\Delta H_f (J/g)$
Uncycled dodecanoic acid ³⁰	42.1	190.1	42.2	-194.2
Uncycled ditetradecanoic acid ³⁰	52.4	210.7	52.5	-212.7
Uncycled dihexadecanoic acid ³⁰	60.5	221.4	59.9	-226.6
1,3-didodecanoyl thiourea	40.2	116.3	42.5	-112.4
1,3-didodecanoyl thiourea after 3000 cycles	42.5	114.6	43.9	-110.0
1,3-ditetradecanoyl thiourea	44.7	122.5	47.4	-126.7
1,3-ditetradecanoyl thiourea after 3000 cycles	49.3	119.5	49.2	-122.4
1,3-dihexadecanoyl thiourea	51.7	153.6	52.0	-150.6
1,3-dihexadecanoyl thiourea after 3000 cycles	56.7	148.8	54.1	-142.7

Table. The thermal properties of the fatty acids and thiourea derivatives before and after thermal cycling.



Figure 4. The phase change enthalpy and melting temperature curves of thiourea derivatives.

Figure 5 shows TG analysis curves of the thiourea derivatives belonging to homologous compounds correspondingly. They were consistent in inherent properties and started to degrade above 170 °C by 2-step decomposition reactions. As is seen from the derivative TG analysis curves in Figure 5, the maximum rates of degradation were at different temperatures and the second degradation step was indefinite. The onset points for the starting point of the first degradation steps for 1,3-dodecanoylthiourea, 1,3-tetradecanoylthiourea, and 1,3-hexadecanoylthiourea were at 198, 220, and 228 °C, respectively.



Figure 5. TGA curves of 1,3-dodecanoylthiourea (a), 1,3-tetradecanoylthiourea (b), and 1,3-hexadecanoylthiourea (c).

Conclusion

A series of thiourea derivatives were prepared by condensation of fatty acid acyl chlorides with thiourea, and their chemical structures were confirmed by FT-IR and ¹H-NMR investigations. With the increasing C atoms in the carboxylic counterpart, the phase change temperature and enthalpy of the thiourea derivatives increased.

Accelerated thermal cycling of the thiourea derivatives revealed the structural consistency and thermal durability of the prepared products. In addition, the thermal stability of the compounds was tested by a TG analysis device; it was found that the thiourea derivatives degraded in 2 distinguishable steps at considerably higher temperatures than ambient temperature.

The thiourea derivatives, with proper melting temperatures and considerable heat storage densities, have extensive potential in solar space heating and air conditioning systems, more so than most of the literature materials. The resultant compounds furthermore have no acid hydrogens to cause corrosion or ligand properties to be improved for thermal conductivity, i.e. the response time during utility. In this respect, further studies are ongoing.

Acknowledgement

The authors are pleased to acknowledge the financial support provided by the Gaziosmanpaşa University Scientific Research Committee (Project No: 2008/31).

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