Thermal property prediction and measurement of organic phase change materials in the liquid phase near the melting point ☆

William E. O'Connor, Ronald Warzoha, Rebecca Weigand, Amy S. Fleischer, Aaron P. Wemhoff *

Department of Mechanical Engineering, Villanova University, 800 Lancaster Ave., Villanova, PA 19085, USA

HIGHLIGHTS

- Liquid-phase thermal properties for five phase change materials were estimated.
- Various liquid phase and phase transition thermal properties were measured.
- The thermal diffusivity was found using a best path to prediction approach.
- The thermal diffusivity predictive method shows 15% agreement for organic PCMs.

ARTICLE INFO

ABSTRACT

Organic phase change materials (PCMs) are a popular choice for many thermal energy storage applications including solar energy, building envelope thermal barriers, and passive cooling of portable electronics. Since the extent of phase change during a heating or cooling process is dependent upon rapid thermal penetration into the PCM, accurate knowledge of the thermal diffusivity of the PCM in both solid and liquid phases is crucial. This study addresses the existing gaps in information for liquid-phase PCM properties by examining an approach that determines the best path to prediction (BPP) for the thermal diffusivity of both alkanes and unsaturated acids. Knowledge of the BPP will enable researchers to explore the influence of PCM molecular structure on bulk thermophysical properties, thereby allowing the fabrication of optimized PCMs.

The BPP method determines which of the tens of thousands of combinations of 22 different available theoretical techniques provides best agreement with thermal diffusivity values based on reported or measured density, heat capacity, and thermal conductivity for each of five PCMs (heneicosane, tricosane, tetracosane, oleic acid, and linoleic acid) in the liquid phase near the melting point. Separate BPPs were calibrated for alkanes based on heneicosane and tetracosane, and for the unsaturated acids. The alkane and unsaturated acid BPPs were then tested on a variety of similar materials, showing agreement with reported/measured thermal diffusivity within ~15% for all materials. The alkane BPP was then applied to find that increasing the length of alkane chains decreases the PCM thermal diffusivity, showing how the determination of the BPP can be used to aid in the prediction of how the molecular structure of organic PCMs influences PCM performance in energy storage applications.

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1. Introduction

Organic phase change materials (PCMs) have been proposed as a viable energy storage mechanism through solid–liquid phase change at the melting point temperature. This energy storage could have significant applications in solar energy [1–7], building envelope thermal barriers [8–16], and passive cooling of portable electronics [17–19]. Since the extent of phase change during a heating or cooling process is dependent upon the amount of thermal penetration into the PCM, the thermal diffusivity of the PCM is an important thermophysical property for the viability of the material in an energy storage application.

The thermal diffusivity, α_{th}, is defined as

$$\alpha_{th} = \frac{\lambda}{\rho c_p} \tag{1}$$

where λ is thermal conductivity, ρ is mass density, and c_P is the mass-based heat capacity. Data regarding some of the solid and

Nomenclature

a_i, d_i	group contribution parameters, dimensionless
a_P	Peng–Robinson fluid model intermolecular potential parameter, J m^3
a_R	Redlich–Kwong fluid model intermolecular potential parameter, J m^3 K$^{0.5}$
a_S	Soave–Redlich–Kwong fluid model intermolecular potential parameter, J m^3
a_V	Van der Waals fluid model intermolecular potential parameter, J m^3
b_P	Peng–Robinson fluid model equivalent molecular volume, m^3
b_R	Redlich–Kwong fluid model equivalent molecular volume, m^3
b_S	Soave–Redlich–Kwong fluid model equivalent molecular volume, m^3
b_V	Van der Waals fluid model equivalent molecular volume, m^3
c_p	mass-based heat capacity, J/(kg K)
C_{pl}	molar heat capacity, J/(mol K)
$c_{p,st}$	mass-based heat capacity of sapphire sample, J/(kg K)
D_s	difference in heat flow between empty reference pan and sample of interest, mW
D_{st}	difference in heat flow between empty reference pan and sapphire sample, mW
E	reference calorimetric sensitivity, dimensionless
f, α	fluid model-dependent parameters, dimensionless
g	temperature ramp rate, °C/min
H	system enthalpy, J
h	Planck's constant, J s
k_B	Boltzmann's constant, J/K
M	molecular mass, kg/kmol
m_i	melting enthalpy group contribution parameter, dimensionless
M_j	occurrence of group j in a molecule, dimensionless
N	number of molecules in a system, dimensionless
N_{atoms}	number of atoms, dimensionless
N_A	Avogadro's number, kmol^{-1}
n_i	occurrence of group i in a molecule, dimensionless
N_k	occurrence of group k in a molecule, dimensionless
pck	critical pressure group contribution parameter, dimensionless
tck	critical temperature group contribution parameter, dimensionless
$tfp1k$	first-order melting temperature group contribution parameter, dimensionless
$tfp2j$	second-order melting temperature group contribution parameter, dimensionless
P	pressure, Pa
P_c	critical pressure, Pa
P_o	atmospheric pressure, Pa
P_r	reduced pressure, dimensionless
P_{rb}	reduced boiling point pressure, dimensionless
Q	canonical partition function, dimensionless
R	ideal gas constant, J/(kmol K)
T	temperature, K
T_b	boiling point temperature, K
T_c	critical temperature, K
T_m	melting point temperature, K
T_{rb}	reduced boiling point temperature, dimensionless
U	system internal energy, J
V_s	saturated liquid molar volume, cm^3/mol
W	weight for second-order groups (= 0 for 1st order, = 1 for 2nd order), dimensionless
W_s	weight of sample of interest, mg
W_{st}	weight of sapphire sample, mg
Z	critical compressibility factor, dimensionless
α_{th}	thermal diffusivity, m^2/s
ΔH_f	latent heat of fusion, J/kg
ΔH_m	total enthalpy of melting, J/mol
ΔS_m	total entropy of melting, J/(mol K)
ε	molecular eccentricity, dimensionless
$\theta_{rot,m}$	rotational temperature, K
λ	thermal conductivity, W/(m K)
λ_f^*	reduced thermal conductivity correction term, dimensionless
λ_m^*	reduced thermal conductivity of a monatomic liquid, dimensionless
ξ	number of molecular degrees of freedom, dimensionless
ρ	mass density, kg/m^3
σ	molecular symmetry, dimensionless
τ	molecular flexibility, dimensionless
ω	acentric factor, dimensionless

liquid phase properties of organic PCMs on the right-hand side of Eq. (1) are readily available [20,21], but gaps exist in available data. Furthermore, the gaps in liquid-phase properties cannot be filled by equivalent solid phase properties since the shifted molecular arrangement between solid and liquid phases could have a dramatic influence on the thermophysical properties in the following ways through a loss of a molecular lattice structure:

- The lattice configuration contains a strong influence on the scattering mechanisms in phonon behavior in thermal conduction.
- Losing the lattice structure adjusts the available effective degrees of freedom of the molecules, thereby altering the specific heat.
- A loss in lattice structure affects the molecular packing arrangement, influencing the material density.

Furthermore, a PCM ideally exists in its liquid phase during one half of a heating/cooling cycle, and therefore an accurate model of the thermal response of the PCM should apply the liquid phase thermal properties, especially during a freezing process. However, many investigators have either ignored thermal gradients within the PCM [9] or assumed that the solid and liquid properties are equivalent in numerical investigations [10,12,22]. Therefore, this study aims at determining accurate predictive techniques of liquid phase thermophysical properties for two principal classes of organic PCMs: alkanes and unsaturated (fatty) acids.

This study is intended to supplement the large body of work on PCM enhancement using nanoscale inclusions. Several studies [23–27] investigated the impact of adding highly-conducting nanoscale inclusions into a base organic PCM. In general, researchers have found that these composites contain significant conductivity enhancement (in general >100% enhancement for >1 wt% filler) but with a sacrifice in the latent enthalpy of fusion (∼7–15% reduction for typical loading values). Fan et al. [26] compared different fillers and found that graphene nanoplatelets and short cylindrical inclusions (e.g., carbon nanotubes) provide better conductivity enhancement than long inclusions. The limiting factor in PCM nano-composite performance is the combination of thermal properties associated with the base PCM, and therefore improving the thermal properties of the base PCM – the focus of this effort – will lead to more effective PCM nano-composites.

A number of theoretical techniques exist to determine various properties of liquids including critical temperature (T_c), critical