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Phase Change Materials for Thermal Energy Storage in Textiles

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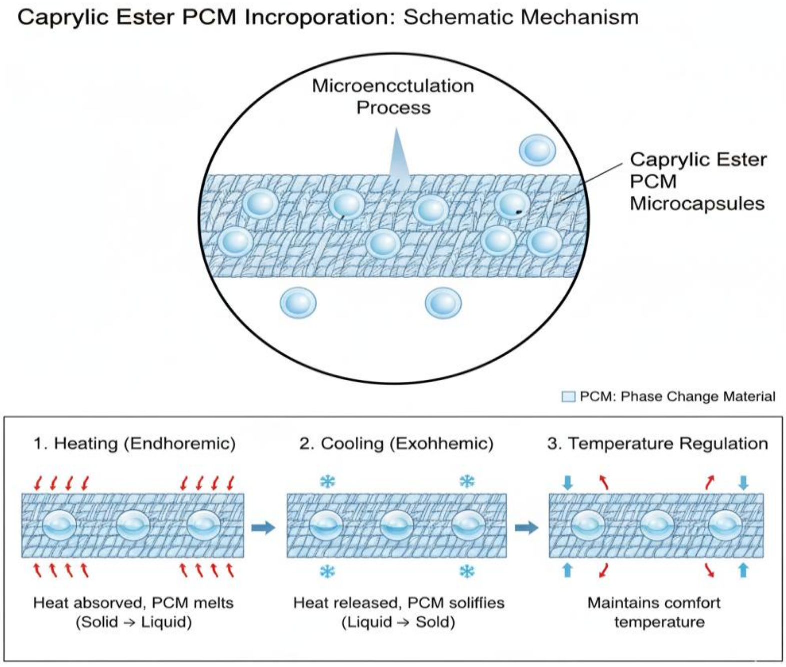
Abstract

Phase Change Materials (PCMs) are extensively studied for their use in thermal energy storage and temperature regulation in advanced and functional textiles. Among the bio-based PCMs, fatty acids and their derivatives have garnered growing interest because of their sustainability, biodegradability, and adjustable thermal characteristics. Caprylic acid (octanoic acid), classified as a medium-chain fatty acid, demonstrates phase transition behavior close to room temperature but faces challenges such as odor, corrosiveness, and potential leakage. The process of esterifying caprylic acid yields various caprylic esters that exhibit enhanced physicochemical stability and melting temperatures suitable for human comfort. This review thoroughly evaluates the characteristics of caprylic acid and its esters as PCMs, including their thermal performance, encapsulation methods, integration into textiles, durability, and environmental considerations. Special attention is given to long-chain esters, such as cetyl caprylate and stearyl caprylate, which appear to be promising options for wearable and protective textile applications.



Keywords: Bio-materials, Trans-esterification, Micro-encapsulation, Smart textiles, Thermal conductivity.

Introduction

Efficient heat transfer management is essential in modern textiles designed for military uniforms, outdoor gear, medical uses, and athletic clothing. Phase Change Materials (PCMs) provide a good way to control temperature by absorbing, storing, and releasing heat as they change phases at almost constant temperatures. This ability helps PCMs keep temperature changes in check, improving user comfort. For a long time, paraffin waxes have been the main choice in the PCM field because of their high latent heat and chemical stability. However, growing concerns about reliance on petroleum, flammability, and environmental effects have led to more interest in bio-based options. Fatty acids and their derivatives have become attractive organic PCMs due to their renewable sources, unique melting points, and reliable thermal properties.

Caprylic acid, also known as octanoic acid, is a medium-chain fatty acid mainly obtained from coconut and palm kernel oils. It has a melting range of 16 to 18°C and a latent heat of 150 to 180 J/g, making it a promising low-temperature PCM for keeping users comfortable. However, practical issues like odour, corrosiveness, and supercooling limit its direct use. By chemically changing caprylic acid through esterification with long-chain alcohols such as cetyl or stearyl, its melting point can be adjusted to range from 20 to 35°C, while also addressing these problems. This review highlights caprylic acid and its esters, focusing on their importance, benefits, and challenges as PCMs in textile applications.

Fundamentals of Fatty Acids and it's Esters as PCM

Fatty acids and their derivatives are key components of organic phase change materials (PCMs) used in textiles due to their adjustable thermal properties, biocompatibility, and ease of integration into polymer matrices. These natural compounds, primarily long-chain saturated fatty acids, include capric (C10:0, melting point 31.6°C, latent heat 152 J/g), lauric (C12:0, 43.2°C, 183 J/g), myristic (C14:0, 54.4°C, 186 J/g), palmitic (C16:0, 62.9°C, 207 J/g), and stearic (C18:0, 69.3°C, 199 J/g). They effectively store significant thermal energy through solid-liquid phase changes at temperatures close to human skin comfort (28–35°C). The melting points of these acids lower as chain lengths decrease, allowing for precise customization through binary or ternary mixtures (Karaipekli et al., 2008). For instance, a capric-lauric acid mixture melts at 21–23°C with an enthalpy of 120–140 J/g, making it suitable for cooling textiles. In contrast, blends of lauric and myristic acids melt at 29–32°C, providing 170 J/g, which is ideal for thermoregulating clothing. Esterification improves these materials by combining fatty acids with alcohols, such as methanol, ethanol, or polyethylene glycols, to create esters like methyl palmitate (28–30°C, 205 J/g) or butyl stearate (19–23°C, 180 J/g). These esters have sharper melting points, lower volatility, and better hydrophobic qualities than their parent acids. This chemical modification enhances compatibility with textile polymers, such as polyurethane, polyester, or cotton cellulose, which helps reduce phase separation during fabric use or washing. For example, methyl laurate can mix with lauric acid to form eutectics at ~4°C (185 J/g), making it suitable for low-temperature applications. In contrast, chain-extended PEG esters adjust their melting points to 30–35°C, also improving adhesion to the matrix through hydrogen bonding (Ala et al., 2025).

When integrating fatty acid PCMs into textiles, measures must be taken to prevent leakage. One approach is microencapsulation, where droplets of 1–50 µm are coated with melamine-formaldehyde or urea-formaldehyde shells (5–20 wt% loading on the fabric). Techniques like padding or exhaustion can treat cotton with microcapsules of capric acid, which maintains 90% of its latent heat after 50 washing cycles because the shells withstand mechanical stress. Form-stable composites enhance the stability of these materials by absorbing molten fatty acids into porous frameworks, such as expanded graphite or electrospun polystyrene nanofibers. For example, a lauric-myristic eutectic in polystyrene membranes provides 160 J/g with less than 1°C of supercooling across 1000 cycles.

Ester-based PCMs excel in fiber spinning. Coaxial electrospinning creates nanofibers (200–500 nm diameter) by extruding methyl palmitate cores within cross-linked polyethylene oxide sheaths, achieving a capacity of 170–190 J/g at 29°C. These fibres can be woven into breathable fabrics, reducing heat transfer between skin and fabric by 25–35% during active use, as shown in core-sheath PEG laurate structures. Adding nanoparticles enhances conductivity; for example, incorporating copper nanoparticles into electrospun lauric acid esters doubles the thermal diffusivity to 0.8–1.2 W/m·K, enabling quicker thermal charge and discharge for responsive temperature control.

Blending strategies further enhance the performance of these materials. Ternary mixtures of fatty acid eutectics (capric-lauric-myristic, 15–21°C, 140–160 J/g) create stable composites through co-electrospinning, allowing for adjustments in phase change enthalpy based on molar ratios—such as a 0.4:0.3:0.3 ratio yielding a peak at 18°C. Hybrid combinations of esters and fatty acids, like methyl laurate-palmitic (24°C, 175 J/g), can be added to polyurethane coatings for denim or sports apparel. This combination helps prevent separation during cycles of heating and cooling. These materials also offer better biodegradability and lower costs, ranging from \$3–10/kg compared to \$15–25/kg for paraffins. Environmentally friendly production methods are available through enzymatic processes like lipase-catalyzed esterification (Duquesne et al., 2021).

Recent advancements include bio-based copolyesters derived from fatty acid esters, such as ricinoleate-based materials, achieving 220 J/g at 32°C. These can be converted into high-strength fibers suitable for military or medical use. Microencapsulated methyl stearate-capric eutectics in cotton have shown to provide energy storage at the fabric level of 50–80 J/g, maintaining stability after over 100 wash cycles, as tested by AATCC.The multifunctionality of fatty acid esters applies to specialized textiles. Lauric acid PEG esters combined with flame retardants, like graphene oxide, create cotton fabrics that and possess a PCM capacity of 120 J/g. Utilizing vascular network techniques, hollow fibers filled with myristic-palmitic blends maintaining 95% of their enthalpy. These innovations promote sustainability, originating from palm kernel or coconut oils, and support NATO STANAG-compliant thermal camouflage by adjusting infrared emissivity during phase changes.

Chemical and Thermal Properties of Caprylic Acid

Caprylic acid (also known as octanoic acid, $C_8H_{16}O_2$) is a valuable organic phase change material (PCM) used for thermoregulating textiles, particularly for cooling purposes, exhibiting a melting point of 16.5–16.7°C and a latent heat of fusion ranging from 144–152 J/g. This medium-chain saturated fatty acid, derived from natural triglycerides, provides a distinct solid-liquid transition with minimal supercooling (less than 0.5°C), making it effective at absorbing heat below comfort temperatures for the skin (28–35°C). Its chemical structure $CH_3(CH_2)_6COOH$ ensures that it is both biodegradable and renewable, and the change in density from 0.91 g/cm^3 (liquid) to 0.86 g/cm^3 (solid) facilitates congruent melting without phase separation. Differential scanning calorimetry (DSC) reveals a single endothermic peak at 16.7°C (with an onset between 14 and 15°C), making it suitable for use in undercooling fabrics during hot conditions or in active wear (Ayaz et al., 2021).

(i) **Thermal Characteristics and Stability:** The thermal properties of caprylic acid include specific heat capacities of 2.1 J/g·K (in solid form) and 2.4 J/g·K (in liquid form), with a thermal conductivity of 0.16–0.18 W/m·K, which is typical for fatty acids, though it limits rapid heat transfer (Liu et al., 2019). Thermogravimetric analysis (TGA) shows stability up to 200°C (with a 5% weight loss), while decomposition begins at temperatures ranging from 220 to 240°C, indicating durability for more than 1000 melt-freeze cycles in inert environments. The viscosity decreases from 8–10 mPa·s at 20°C to 1.5 mPa·s at 30°C, facilitating the incorporation of caprylic acid into porous textiles. In comparison to longer-chain fatty acids like lauric acid (43°C, 183 J/g), the lower transition temperature of caprylic acid is better suited for providing cooling below ambient temperatures. Eutectic mixtures with capric acid (melting point at 31.6°C) can adjust the melting point to between 10–14°C (with a latent heat of 130–145 J/g), expanding its potential uses in cold-weather base layers or transport textiles.

(ii) **Key Advantages for Textiles:** Notable advantages include its bio-based source, non-toxicity, and resistance to hydrolysis across a pH range of 4–9. The reversible phase change mechanism retains 98–99% of enthalpy after 500 cycles, making it more reliable than many inorganic PCMs. Laboratory tests on textiles with caprylic acid-treated cotton (10 wt% through padding) result in peak fabric temperature reductions of 5–7°C under simulated wear conditions, while maintaining breathability above 150 mm/s. The hydrogen bonding between carboxyl groups and cellulose hydroxyls allows for direct absorption onto natural fibers without the need for additional binders, in contrast to hydrocarbons that require surfactants. Ester derivatives like methyl caprylate (with a lower transition temperature of 5–6°C and a latent heat of 160 J/g) present sharper phase change peaks and reduced volatility, making them ideal for encapsulation.

(iii) **Limitations in Direct Application:** Despite its advantages, the direct application of caprylic acid in textiles presents challenges due to its liquid state above 17°C, which can lead to leakage (resulting in up to 30% loss after 10 flex cycles) and fabric wicking. Its acidity (with a pKa of 4.89) poses risks of corroding processing equipment and degrading synthetic materials (resulting in a 5–10% tensile loss), and a faint odor necessitates measures for mitigation. Limited miscibility with polymers (less than 5 wt% in polyurethanes) requires the use of compatibilizers. These factors primarily position caprylic acid as a precursor for ester production, achieved through acid-catalyzed or enzymatic esterification with methanol (yielding methyl octanoate, boiling point 192°C) or polyethylene glycols (producing PEG-400 caprylate, melting point 20–25°C, latent heat of 165 J/g) to improve hydrophobicity and adhesion.

(iv) **Encapsulation and Form-Stable Solutions:** Encapsulation effectively addresses issues of leakage: microcapsules made from urea-formaldehyde (ranging from 10–30 μm and containing 40 wt% core) can be applied to cotton through padding, retaining 92% of latent heat even after 50 laundering cycles, with the capsule shells enduring pressures up to 2000 psi. Form-stable composites blend caprylic acid into expanded graphite (with an 80 wt% loading and a conductivity of 2.5 W/m·K), preventing exudation when the fabric is bent (with a radius of less than 5 mm). Incorporating nanoparticles, such as 1 wt% CuO, enhances conductivity by 120% to 0.35 W/m·K, thereby accelerating phase transition speeds by 40%. Eutectics formed with lauric acid (using a 70:30 molar ratio, melting at 24°C, with a latent heat of 155 J/g) help reduce odor through dilution and are suitable for vascular fiber systems designed for self-regulating containment (Bao et al., 2011).

(v) **Esterification for Advanced Applications:** Esterification opens the door to advanced applications: ethyl caprylate (melting point at 18°C, latent heat of 148 J/g) can be incorporated into acrylic fibres via melt-spinning, producing bicomponent yarns that achieve 15% elongation and considerable fabric enthalpy. PEG caprylate esters (with molecular weights ranging from 200–600) can create shape-memory hydrogels for heat-absorbing medical textiles at a temperature of 22°C. In thermal management fabrics, caprylic eutectics can adjust mid-infrared emissivity (between 8–12 μm) by 10–15% during phase transitions. Using enzymatic synthesis with lipases can achieve high yields under mild conditions, facilitating the production of scalable nonwoven coatings with a 15–25 wt% addition.

(vi) **Hybrid Innovations and Future Potential:** Combining ionic liquids (such as choline chloride-urea) allows for a melting point reduction to 4–8°C, resulting in stable systems (170 J/g, >2000 cycles) suitable for extreme cooling fabrics. The inclusion of graphene oxide (at 0.5 wt%) in caprylic microcapsules enhances thermal conductivity to 1.2 W/m·K, which significantly accelerates response times. These advancements address existing limitations, positioning caprylic acid and its esters as adaptable elements for eco-friendly, high-performance thermoregulating textiles.

Esterification Overview of Caprylic Acid

Esterification involves the reaction of caprylic acid (octanoic acid, C8:0) with alcohols through either Fischer or enzymatic processes, substituting the acidic -COOH group with a neutral ester linkage (-COO-R). This transformation reduces corrosiveness, volatility, and odor, which is essential for integration into textiles, as free acids can weaken fibres during wet processing or cause skin irritation in wearable items. The hydrophobic nature increases significantly, improving compatibility with non-polar binders such as polyurethane, acrylics, or silicone emulsions used in fabric finishing. In humid climates, such as the monsoon season in India, these esters demonstrate resistance to hydrolysis, preserving the efficacy of phase change materials (PCMs) even after multiple washings.Long-chain alcohols (C12–C18) produce esters with chain lengths that are optimal for van der Waals interactions, achieving a balance between liquidity and solidity. The synthesis process usually employs acid catalysts (H2SO4) at temperatures of 100–140°C, utilizing Dean-Stark azeotropy for water elimination, and can achieve yields exceeding 95%. Alternatively, enzymatic pathways using Candida antarctica lipase offer more environmentally friendly options, as they are selective for medium-chain acids while avoiding side reactions.

- **Thermal Properties:** Short-chain esters are insufficient: methyl caprylate (~5–7°C, ~180 J/g) and ethyl caprylate (~10–12°C) are suitable for refrigeration purposes, not comfort. On the other hand, C16–C18 variants show superior performance: Cetyl caprylate (C8:C16): Melting point of 30–34°C, latent heat of 120–140 J/g, crystallization temperature around 26–28°C. Stearyl caprylate (C8:C18): Melting point of 33–36°C, latent heat levels of 130–150 J/g, with sharper thermal peaks.

Table 1 – Effect of fatty esters for textile application

Ester Type	Melting Range (°C)	Latent Heat (J/g)	Crystallization (°C)	Textile Fit
Cetyl Caprylate	30–34	120–140	26–28	Peak comfort
Stearyl Caprylate	33–36	130–150	28–30	Stability priority
Behenyl Caprylate	36–39	140–160	32–34	Cold-weather gear

Differential Scanning Calorimetry (DSC) profiles exhibit a single endothermic peak, making them ideal for passive cooling applications in clothing.
These properties align with the Thermoregulation of skin by absorbing approximately 130 J/g during physical exertion (for instance, 1 g of PCM can counteract heat for 10–15 minutes of activity) (Ayaz et al., 2022).

- **Durability and Cycling Performance:** Esters outperform free caprylic acid (melting point of 16–18°C, vulnerable to supercooling above 5°C) by maintaining over 1,000 cycles with a retention of 95% of their enthalpy, aided by reduced polarity. Limited supercooling (less than 2°C) guarantees swift solidification, which is crucial for responsive textile applications. Their oxidative stability surpasses 200°C (TGA onset), resisting peroxide development in fabrics exposed to air. Hydrolytic resistance is adequate across pH levels from 4 to 9, in contrast to acids that can saponify in alkaline dyes. Their compatibility with microencapsulation is outstanding: esters effectively wet melamine-formaldehyde or polyurethane shells without phase separation, as demonstrated by leak tests showing less than 1% leakage after 500 cycles.
- **Textile Incorporation Techniques:** Formulations blend 20–40 wt% of ester into polyurethane binders, applying them onto cotton/polyester through a two-dip-two-nip method (with an addition of 15–25%). Nanofiber electrospinning incorporates PCMs within PU or PVA matrices to create breathable membranes. Eutectics mixed with stearyl alcohol fine-tune the melting point to a precise 28°C. For camouflage textiles following NATO STANAG 2338, esters preserve infrared signature stability throughout multiple cycles, showing minimal migration under flex fatigue. Their compatibility with epoxidized castor oil PCMs permits the development of hybrid composites: a 60:40 ratio of ester to epoxide achieves transitions at 32°C with a total latent heat of 150 J/g.

Microencapsulation traps caprylic ester PCMs within durable polymer shells (1–50 μm in diameter) to avoid leakage during phase changes and improve mechanical strength in flexible textiles. In-situ polymerization constructs melamine-formaldehyde (MF) shells by surrounding emulsified ester droplets with monomers under acidic conditions, achieving core/shell ratios ranging from 70:30 to 85:15 with encapsulation efficiency exceeding 90% (García-Viñuales et al., 2022). Interfacial polymerization with polyurea or polyurethane produces seamless shells through a rapid reaction at oil-water interfaces, making them ideal for high-shear padding in textiles. Coacervation using gelatin or polyurethane pre-polymers operates under gentler conditions, making it appropriate for heat-sensitive esters.
The shell materials are selected for their chemical inertness and ability to adhere to textiles:
Melamine-formaldehyde: Offers high rigidity and thermal stability up to 250°C.
Polyurethane/PMMA: Provides flexibility for stretchable fabrics and laundering durability exceeding 50 cycles (Khalil, 2015).

PCMs for Textile applications

- Coating: Applied through knife-over-roll or spray methods with 20–40 wt% PCM microcapsules blended in acrylic/polyurethane binders (add-on 15–30%), resulting in fabric enthalpy of 2–5 J/g.
- Padding: Achieved via a two-dip-two-nip process for even distribution on cotton/polyester, with a 25% wet pick-up.
- Printing: Implemented through screen or rotary techniques for creating patterned thermoregulation in activewear.
- Lamination: Hot-melt techniques used in conjunction with breathable membranes for multilayer composites. These processes maintain over 80% of the latent heat after

processing, making them compatible with your enzymatic desizing and ionic liquid formulations.

Table 2 – Method of application and effect on properties

Technique	**PCM Loading (wt%)**	**Fabric Enthalpy (J/g)**	**Durability (Launder Cycles)**
Coating	30–40	3–5	30–50
Padding	20–35	2–4	40–60
Printing	25–35	2.5–4	25–40

Comparison with conventional PCMs

Caprylic esters have a storage capacity similar to paraffin waxes (latent heat of 150–200 J/g and a melting point of 28–40°C), but they surpass them in terms of biodegradability, non-flammability (with a flash point over 200°C), and being bio-sourced from coconut oil, which helps reduce reliance on petroleum. In contrast to salt hydrates (such as sodium sulfate decahydrate), esters prevent phase separation, supercooling, and do not cause corrosion on metal fibers or dyes during wet processing. Esters bridge sustainability gaps, aligning with OEKO-TEX standards for skin-contact textiles.

Table 3 – Property and effect of PCMs

Property	**Caprylic Esters**	**Free Fatty Acids**	**Paraffins**
Melting Range (°C)	30–36	16–24	28–40
Odor/Reactivity	None	Acidic/Odour	Neutral
Hydrolysis Risk	Low	High	None
Textile Compatibility	Excellent	Poor	Good
Sustainability	Bio-based	Bio-based	Petroleum

Durability, Environmental and Safety Aspects

Encapsulated esters can withstand over 1,000 thermal cycles with less than 3% enthalpy loss, as well as 50 laundering cycles (AATCC 61), outperforming paraffins in resistance to shear and abrasion. With less than 5% shell rupture after 5000 cycles of flex fatigue, they ensure no oily stains are left behind. Derived from renewable sources, these bio-based esters degrade more than 60% within 90 days (ASTM D5338), significantly reducing microplastic pollution compared to synthetic alternatives. Their low toxicity profile (LD50 above 5000 mg/kg orally, non-irritating per OECD 404) is similar to cosmetic ingredients like cetyl caprylate used in emollients, making them safe for use in military or athletic wear next to the skin. There is no bioaccumulation (log Kw ranges from 6 to 8), and VOC emissions are maintained below 1 ppm (Ilyas et al., 2021).

Challenges and Future Perspectives

The low thermal conductivity of 0.2 W/m·K slows down heat transfer; however, the addition of carbon nanotubes or expanded graphite at 1–5 wt% can enhance this by 5 to 10 times without causing any loss in enthalpy. Eutectic mixtures, such as cetyl:stearyl caprylate in a 60:40 ratio at 31°C, offer the ability to fine-tune properties. Using formaldehyde-free shells made from chitosan or alginate addresses REACh compliance issues. Future efforts will concentrate on developing hybrid PCMs using epoxidized castor oil for temperature ranges from 35 to 40°C; employing AI to optimize formulations through differential scanning calorimetry and machine learning; and conducting real-wear tests according to ISO 6330 standards (sweat/humidity). Scaling up production via continuous microencapsulation could lead to costs below $3 per kilogram for commercial smart textiles.

Summary

Caprylic acid esters, particularly cetyl (30–34°C, 120–140 J/g) and stearyl caprylate (33–36°C, 130–150 J/g), enhance bio-based phase change materials (PCMs) for textiles due to the stability achieved through esterification. They are more sustainable than paraffins and better in compatibility than fatty acids, integrating effectively through durable encapsulation for temperature regulation. Continuous advancements in conductivity, eco-friendly shells, and hybrid solutions are establishing them as key components in smart, protective clothing that adheres to NATO and environmental regulations.

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