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Construction of intelligent bio-PCM Matrix for Cotton Fabrics to Improve Thermal Comfortability and Human Protection



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<u>In Loving Memory of Late Professor Doctor ""Mohamed Refaat Hussein Mahran""</u>

Abstract

PCMs are commonly used in thermal energy storage systems for solar engineering, building materials, spacecraft, and textile industries, particularly smart and technical textiles. Researchers are interested in the numerous organic and inorganic PCMs that have a broad range of melting and solidifying temperatures due to their potential uses in various industries. This review describes PCM, its working principle with textiles, and the applications of PCM-incorporated textiles.

Keywords: PCM-incorporated textiles, Thermal Comfortability and Human Protection

1. Introduction

Protection from harsh environmental conditions has long been a crucial requirement for textile products. As a result, the primary reason for the ongoing need for protective textile goods is the growing focus on reducing industrial hazards and assuring workers' health, safety, and protection[1]. Smart textiles are functionalized textiles having some incorporated components within the textile structure that allow the textile to feel or respond to the environment, such as intense heat, severe cold, magnetic, nuclear radiations, electrical, chemical, and so on[2].

All materials absorb heat via their structure throughout the heating process as the temperature rises. During the cooling process, the stored heat will be released into the environment[3]. Many years ago, researchers discovered a novel method for incorporating phase change materials (PCMs) into textile materials to increase their thermal performance. Phase-change materials can change state when exposed to a specific temperature range. These materials absorb energy while phase change occurs during the heating process; otherwise, this energy can be transmitted to the environment in the phase change range via a reverse cooling process[4, 5].

Textiles incorporating phase change materials react instantly to temperature changes in the environment and different parts of the body. When temperatures rise, the PCM responds by absorbing heat and storing it in the liquid phase transition materials. When the temperature falls, the microcapsules release the stored heat energy, causing the phase-change materials to solidify once again[5]. This review describes PCM, its working principle with textiles, and the applications of PCMincorporated textiles.

2. Cotton fabrics

Cellulose, the most prevalent polymer in nature, can be found in the purest form in cotton fibers. Cotton is a linear cellulose polymer, and the repeating unit is cellobiose (**Error! Reference source not found.**), which is composed of two glucose units. Cotton is made up of roughly 65-70% crystalline and 35-30% amorphous regions[6]. Cotton has several advantageous characteristics. as it is breathable, comfy, and long-lasting, which make it useful in the textile industry.

3. Protective textiles

Protective textiles are a type of technical textile that is utilized primarily for its performance or functional properties[7]. A fundamental necessity for textile products has always been protection from extreme environmental conditions. so that, the main

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reason for the continuous need for protective textile products is the growing focus on reducing occupational dangers and ensuring the health, safety, and protection of the workers[8].



Figure 1: chemical structure of the cellulose

Many different types of personal protective garments are made to meet specific end-use requirements. protective textiles can be categorized based on their end-use purposes, such as thermal (cold) protection, radiation protection, flame protection, chemical protection, electrical protection, and biological protection[9].

In a protective clothing system, the interaction between clothes and the human body creates an environment that impacts human comfort, and it also serves as a barrier to protect the body from environmental hazards. In summary, the protective apparel has three functions[10]:

- Protection: protect humans from environmental risks and that is the major aim of protective textiles.
- Comfortability: give human comfort, such as thermal comfort.
- Mobility: preserve the wearer's ease of mobility while they do certain tasks. so that the person can carry out their activity without difficulty.

A fourth need for protective clothing is the garment's durability since the clothing system must retain the three major functions under certain circumstances.

 Durability: the capacity of the clothes system to sustain the three fundamental functions (protection, comfort, and mobility) under diverse environmental circumstances.

Protective textiles are intended for usage in certain areas to shield people from specific environmental threats. Environmental dangers are usually classified based on their properties. Some examples are shown below[10, 11]:

- Thermal hazards: flame, heat, etc.
- Chemical risks: alkali, acids, oil, toxic chemicals, erosive chemicals, etc.
- Biological and biochemical risks: virus, bacterial, etc.
- Electrical risks: high current electricity, electrical spark, high voltage, etc.

3.1. Smart textiles for protection

As the need for occupational safety and health in the workplace increases, workers in numerous industrial sectors must wear protective apparel[12, 13]. Smart textiles can be used to protect people from severe conditions because Smart textiles are fabrics that can recognize and respond to environmental circumstances or stimuli, originating from mechanical, thermal, chemical, electrical, or other sources[14, 15]. Smart textiles can sense and respond to humans and their surroundings[16].

Textile products that can work differently from a conventional textile and are capable of performing a specific purpose are considered smart textiles. Some examples of smart textiles are fabrics that can regulate body temperature, fabrics that can release moisturizer or medicine into the skin, and textiles that may reduce muscle vibration during physical activity. There are also simple, aesthetically pleasing uses for smart textiles, such as those that can change color, light up in patterns, or show images and video[**17-33**].

3.2. Classification of Smart Textiles

Smart textiles can be classified according to their performance into 3 types: [21, 22, 24, 27, 34-41]

3.2.1. Passive smart textiles

The first generations of smart textiles give extra features in a passive mode, i.e., regardless of environmental change. For example, a highly insulating coat would maintain insulation to the same degree Regardless of the outside temperature. UV-protecting clothing, anti-static fibers, antimicrobial textiles, and waterproof fabrics are typical examples of passive smart textiles[12, 17, 42, 43].

3.2.2. Active smart textiles

Active smart textiles are the second generation of smart textiles that can sense, react, and alter their function in response to changes in either the external environment or the human body. Phase change materials, heat-sensitive dyes, and shape memory materials are examples of active smart textiles [12, 17, 42].

3.2.3. Ultra smart textiles

Ultra smart textiles are the third generation of smart textiles that can respond to their surroundings and adapt to different circumstances. An ultra-smart or intelligent textile is essentially made up of a unit that acts similarly to a brain, with cognition, reasoning, and activation capabilities. Wearable computers and spacesuits are two examples of ultrasmart materials. However, ultra-smart textiles are still in their infancy and require more research[12, 16, 17].

3.3. Phase Change Materials for Thermoregulation

The human body is a thermoregulatory system. The body continuously produces heat, CO₂, and water through the metabolism of food and muscular movement. The rate at which thermal energy is released from the body is typically regulated by blood vessel dilatation temperature. The most suitable temperature for the human body is regarded to be 37 degrees Celsius[44], and a variation of ±4.5 degrees Celsius may cause thermal discomfort to humanoids; hence, a balance between heat discharge and heat generation must be maintained. Though skin adjusts to changes in ambient temperature most of the time, abnormal temperature changes can be fatal because they can lead to horripilation, excessive sweating, nasal secretions, and other maintaining symptoms related to thermoregulation[45].

Hence, fundamental ideas in textile engineering are being used to design new textile products that can sense and respond to external stimuli coming from the environment or the human body. As a result, thermoregulated smart textiles using Phase Change Material (PCM) have been produced, providing thermal protection.

Phase Change Material (PCM) was produced through the challenge of coping with the extreme temperature changes in space. Outlast Technologies, Inc., located in Colorado, obtained an exclusive license to the PCM technology in 1991, to revolutionize outdoor apparel. After creating a prototype and introducing the idea to the textile sector, outlast introduced its first commercial product (gloves and shoes) in 1997. [4].

Phase change materials are a type of heat storage material. These heat storage materials are divided into two categories: sensible heat storage materials and latent heat storage materials [46]. When heat contributes to the temperature change of the heated substance, it is known as sensible heat. When heat is transmitted to an object, the object's temperature rises. When heat is released from an object, its temperature decreases [4, 46, 47]. An example of This is a glass of water that is heated by the sun.

When the sun shines on the glass, the water's energy increases, and the water molecules become more energetic, and the temperature of the water increases. Sensible heat is the term for this. In contrast, latent heat is heat that is sensed by a change in the material's state rather than a temperature change (change of phase). During the phase transition process, The temperature of the substance does not vary [4, 46, 47]. An example of this is a glass of ice cubes placed in direct sunlight, the ice will begin to heat up sensibly. When the ice reaches its phase transition temperature (0°C), it begins to melt. If you measure the temperature of the ice as it melts, you will notice that it will remain at 0°C until all of the ice has melted. This is because when a PCM, such as ice, changes phase, the temperature remains constant until all of the material has melted. Figure 2 depicts the difference between sensible and latent heat.



Figure 2: The difference between sensible heat and latent heat.

As previously noted, sensible heat is defined as heat that helps the heated material's temperature change. Furthermore, the transferred heat (H) is proportional to the temperature change (T), with the following relationship:

$$H \alpha \Delta T \implies H \alpha (T_f - T_i)$$
 Equation 1

where Tf denotes the final temperature and Ti denotes the starting temperature. (C) is the proportionality constant, known as "the heat capacity." The heat capacity is the amount of heat required to increase the temperature of a substance or material by one degree in units of energy per degree.

$$H = C \left(T_f - T_i \right)$$
Equation 2

The quantity of heat required to change the substance's temperature by one degree for every unit of mass is known as specific heat, or specific heat capacity (CP). As a result, it is an intense variable with a unit of energy per mass per degree. therefore, it can be computed using the following equation:

$$H = m C_p \Delta T$$
 Equation 3

where m is the material mass, ΔT is the heatinduced temperature change, and CP is the materialspecific heat.

Latent heat is heat that is not perceived by temperature changes but is instead sensed by changes in the material's phase. The temperature of the substance remains constant during the phase change. Furthermore, the following equation may be used to determine latent heat:

$$H = m L_p$$

where Lp is the phase-change material's specific latent heat (melting, crystallization, or condensation process).

Equation 4

The following equation may be used to compute the specific heat of any unknown material using standard specific heat values of sapphire (alumina, Al2O3):

$$C_{P \ Sample} = \frac{H_{Sample}}{H_{Alu \min a}} \times \frac{m_{Alu \min a}}{m_{Sample}} \times C_{P_{Alu \min a}}$$
Equation 5

Sapphire (Al2O3) is used for the determination of the heat capacity as a calibrant.

The following equation can be used to obtain the specific heat values Cp of this alumina:

 $C_n(T) = \alpha + \beta T + \delta T^2 + \varepsilon T^3 + \eta T^4 + \lambda T^5 + \varphi T^6 + \gamma T^7$ Equation 6

3.4. Working principle of phase change materials (PCMs)

Material exists in four states: solid, liquid, gas, and plasma. The process by which a substance changes from one state to another is known as phase change. There are four types of phase changes: (a) solid to liquid (b) liquid to gas (c) solid to gas and (d) solid to solid. The most often used latent heat storage material, PCM, which can transform from solid to liquid or liquid to solid state, is excellent for the manufacture of heat-storage and thermoregulated fabrics and garments[5].

Phase Change Materials (PCM) can store and release huge quantities of energy, this energy is known as latent heat. Phase-change materials (PCM) are utilized to store latent heat. The storage of latent heat or thermal regulation is dependent on the transition of the (PCM) from one phase to another. As shown in Figure 3, When such a substance is heated to its melting point, it absorbs heat during the transition from solid to liquid state and releases heat upon returning to the solid state[17, 48-50]. This phenomenon is attributed to the breakage of chemical bonds in the molecules of PCMs as the temperature rises, resulting in the melting of the material by storing heat energy, which is then released when the temperature falls during reverse cooling (crystallization process) restoring the chemical bond[51].



Figure 3: Schematic representation of the phase change process

When comparing the heat absorbed during the melting of a phase change material (PCM) to that absorbed during a conventional heating process, a PCM melts and absorbs a significantly larger quantity of heat. For example, a paraffin-PCM absorbs around 200 kilojoules per kilogram during the melting process. If a fabric absorbed the same amount of heat, its temperature would rise by 200 K. The heat absorbed by the paraffin during the melting process is released into the surrounding environment during a cooling process that begins at the crystallization temperature of the PCM. When the heat storage capabilities of textiles and PCM are compared, it is clear that applied paraffin-PCM to textiles may significantly increase their heat storage capacities/4, 52].

3.5. Properties of phase change materials

To be able to choose a good PCM, and successfully design a storage application, the properties of the material have to be known[53]. The most prominent properties are as follows.

3.5.1. Melting temperature: Tm

It is the primary factor for choosing a product since it must be suitable for the purpose. It is quite simple to determine using differential calorimetric analysis. However, it might vary by a few degrees depending on the origin or purity (and the nature of the impurities) of the components. There are two of fusion: "congruent" fusion forms and "incongruent" fusion. When the substance reaches the melting temperature, the liquid and solid phases present are in equilibrium and have the same composition. The state reversibly changes in this case. As a result, all of the energy held during completely melting is released during crystallization, increasing the material's resistance over the cycles. In most cases, this form of fusion occurs in pure substances[54].

The melting can be incongruous. In this situation, two phases are generated first, one liquid and one solid, and eventually, a liquid phase is obtained. In general, the material decomposes into liquid and crystals at temperatures lower than its melting point. During the cooling process, a two-phase mixture containing a solid compound of a different composition than the specified compound is formed. The starting material progressively changes over the cycles, all the more swiftly since fluctuations in density might cause phase segregation, which exacerbates the degradation problem. [54].

3.5.2. The crystallization temperature/ supercooling phenomena

The temperature of crystallization is not always the same as the temperature of the liquid-to-solid transition. There can occasionally be a little delay in the kinetics of crystallization, which depends on both nucleation processes and the material's crystal development. This phenomenon, also known as supercooling, occurs when a substance momentarily persists in a liquid form at a temperature below its crystallization point[**54**].

3.5.3. The enthalpy of phase change (ΔH)

The enthalpy of fusion is the amount of energy absorbed by the substance during the solid/liquid transition. By fully releasing this energy, the liquid/solid transition is achieved. These enthalpies may be established experimentally using typical differential scanning calorimetry analysis[53].

Figure 4 schematically depicts a typical differential scanning calorimetry (DSC) heating thermogram for PCM melting. The PCM absorbs a substantial amount of latent heat from the surrounding environment during this phase change. To use its latent heat of fusion to absorb, store, and release heat or cold during such phase changes, PCM may be repeatedly converted between the solid and liquid phases. Figure 4 illustrates this PCM phase transition phenomena. The shaded region represents the latent heat (J/g)[5, 55].



Figure 4: Scheme of DSC heating of phase change material

3.5.4. Thermophysical characteristics of PCMs

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- Melting temperature stays within the specified working range.
- A high latent heat of fusion per unit volume leads to a reduced container capacity required to carry a given amount of energy.
- A high specific heat capacity for improved sensible heat storage.
- High thermal conductivity in both liquid and solid phases to help in the charging and discharging of energy from the storage system.
- To reduce the confinement problem, a slight volume change during phase transformation and low vapor pressure at working temperature are utilized.
- Consistent melting of the phase change material to retain the storage capacity of the substance throughout each freezing/melting cycle.

3.5.5. Kinetic characteristics of PCMs

- To avoid liquid phase supercooling, a high nucleation rate is required.
- Rapid crystal growth for the system to meet the heat recovery need from the storage system.

3.5.6. Chemical characteristics of PCMs

- A reversible freeze/melt cycle.
- There is no degradation after a substantial number of freeze/melt cycles.
- For safety, choose non-toxic, non-flammable, and non-explosive materials.

3.6. Classification of phase change materials

PCMs are classified into three types based on their chemical composition: organic PCMs, inorganic PCMs, and eutectics PCMs as shown in Figure 5[56].



Figure 5: Classification of phase change materials.

3.6.1. Organic PCMs

Organic PCMs are acceptable for their various applications because they provide a broad range of melting temperatures. Their melting temperature is determined by the number of carbon atoms in their chemical structure. They are often harmless, inexpensive, and have a big supply of basic materials[52]. Organic PCMs are chemically stable, non-reactive, and can withstand sub-cooling[5, 57]. Organic PCMs include paraffins[58], polyethylene glycol[59], and fatty acids[60].

3.6.1.1. Paraffin waxes

Paraffin waxes are saturated alkanes having the chemical formula C_nH_{2n+2} , where n is the number of carbon atoms in the molecules. The structure of paraffin wax is often linear, cyclic, or branched. [61]. The melting temperature of solid paraffin waxes is between 30 to 80 degrees Celsius and rises with the number of carbon atoms in alkanes increase. The latent heat of fusion of paraffin waxes can range from 150 to 280 kJ/kg. The presence of C-H and C-C bonds in paraffin waxes results in significant thermal energy absorbed during the melting phase and released during the solidification process, resulting in a high latent heat of fusion[62].

paraffin wax has gained great interest in thermal energy storage Because of its strong thermal physical features, such as a reasonable melting temperature, high latent heat energy, low supercooling, and consistent chemical and thermal performance[63]. Some examples of paraffin waxes are:

arc.
n-tetradecane (n = 14),
n-pentadecane (n = 15),
n-hexadecane (n = 16),
n-heptadecane (n = 17),
n-octadecane (n = 18),
n-nonadecane (n = 19),
n-eicosane (n = 20),
n-heneicosane (n = 21),
n-docosane (n = 22),
n-trikozane (n = 23),
n-tetracosane (n = 24),
n-pentacosane (n = 25),
n-hexacosane (n = 26),
n-heptacosane (n = 27),
n-octacosane (n = 28),
n-nonacosane $(n = 29)$ and
n-triacontane (n = 30)[62, 63].

3.6.1.2. polyethylene glycol

Polyethylene glycols (PEGs), commonly known as poly(oxyethylene) are used as PCM in textile applications. Another kind of non-paraffin organic PCM is polyethylene glycol. They are made up of linear oxyethylene (-O-CH2-CH2-) with hydroxyl (-OH) terminal groups. PEG's phase transition temperature can be adjusted by adjusting the molecular weight. PEG has a molecular weight ranging from 200 to 20,000. With increasing molecular weight, PEG's melting temperature and latent heat rise. However, the latent heat of PEG with a molecular weight of more than 10,000 reduces because the crystallinity of PEG is reduced by the long molecular chains[5, 64]. The development of the crystalline phase is influenced by the molecular weight of PEG; higher-molecularweight PEGs have a greater inclination to form crystalline phases due to decreased segmental mobility and more convenient geometrical alignment[5]. Table 1 shows the thermal properties of PEGs [64].

Many researchers have investigated PEGs as PCMs in a variety of thermal storage applications due to their desirable properties, such as acceptable melting temperature intervals, high heat of fusion, low vapor pressure when melted, stability in thermal and chemical environments, biodegradability, non-flammability, non-corrosiveness, nontoxicity, and reasonable price[65-67].

Table 1. Thermal properties of PEG

Samples	T _{on} (°C)	<i>Т</i> _р (°С)	T _{end} (°C)	$\Delta H_{\rm m}$ (J g ⁻¹)
PEG1000	19.0	45.6	76.7	78.6
PEG1500	33.5	57.3	87.8	150.1
PEG2000	42.0	63.0	90.9	163.1
PEG4000	45.6	64.7	93.9	172.0
PEG6000	46.9	66.7	94.9	175.0
PEG8000	47.6	67.7	97.2	177.2
PEG10000	50.3	69.7	99.5	191. 0
PEG20000	51.0	67.7	95.8	180.5

Note: Ton, onset phase change temperature; Tend, end phase change temperature; Tp, peak of phase change temperature; Δ Hm, melting latent heat.

3.6.1.3. Fatty Acids

Among the organic PCMs, fatty acids have piqued the interest of several researchers as promising materials. Plant- and animal-based fats and oils can be hydrolyzed to produce fatty acids. The hydrolyzed fats and oils are purified and separated[**52**]. In PCM applications, fatty acids are recognized to be a renewable source with characteristics comparable to paraffin waxes[**68**]. Fatty acids have the chemical formula $CH_3(CH_2)_{2n}COOH$ and are carboxylic acids with a lengthy hydrocarbon chain and a terminal carboxyl group. Because fatty acids are frequently found as esters in oil and fats, there is an abundance of them available worldwide. Fatty acids are typically composed of an even number of carbon atoms (4 to 28). The fatty acids commonly used as PCMs are capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, and arachidic acid. Fatty acids have melting values ranging from 30 to 74 C and latent heat ranging from 140 to 208 J/g. They exhibit PCM features that are desirable, such as congruent melting, high stability, biodegradability, and nontoxicity[**64**, **69**].

3.6.2. Inorganic PCM

Inorganic PCMs are divided into salt hydrates, metals, and alloys[70]. In general, as compared to organic PCMs, inorganic compounds have double the latent heat storage capacity per unit volume[64].

3.6.2.1. Salt Hydrates

Salt hydrates, the most significant class of PCMs at low and medium temperatures, have been thoroughly studied for possible uses in latent heat thermal energy storage due to their high latent heat per unit volume, comparatively high thermal conductivity, and minimal volume variation during the phase change process. The typical formula for salt hydrates is AB. nH₂O and they are composed of inorganic salts and water. Water and inorganic salts are linked by chemical bonds that can be destroyed or restored at different temperatures. Equation (7) explains that the phase change process of salt hydrates is essentially a dehydration/hydration process. When the temperature rises over the melting point, the salt hydrates absorb heat and dehydrate all or part of the water[64, 71].

AB. nH_2O AB + nH2O Equation (7)

3.6.2.2. Metals and Alloys

Metals and alloys have strong thermal conductivities and a high heat storage density per volume. Furthermore, metals and alloys have high melting points that are often greater than 300 degrees Celsius. As a result, metals and alloys successfully minimize the issues and are extremely competitive with other PCMs for high-temperature thermal energy storage[64, 72].

3.6.2.3. Eutectics

Eutectics are classified into three types based on their constituent materials: organic PCMs with organic PCMs, inorganic PCMs with inorganic PCMs, and organic PCMs with inorganic PCMs. The preparation of Eutectic PCMs aims to improve thermal stability by avoiding leakage during the phase transition, improve thermal energy storage efficiency by improving thermal conductivity, and modify the PCM working situation by adjusting the supercooling degree and phase transition temperature[**62**].

4. Incorporation of PCMs into textile

PCMs that change phases at temperatures just above and below human skin temperature are suitable for use in textiles. This intriguing characteristic of PCMs might be used to create allseason protective fabrics. Fiber and fabric with PCMs can store the heat body that creates and then release it back, as it needs. Because the phase change process is dynamic, the materials are continually changing from one condition to another based on the amount of physical activity of the body and the outside temperature. some of the processes for PCMs' incorporation into the textile are coating, lamination, spinning, and printing techniques [5].

4.1. coating method

To coat PCM onto textile material, they are first dispersed and wetted in a water solution including an anti-foaming agent, a dispersion, a surfactant, and a polymer combination, after which the coating is applied to the textile substrate. Polymers such as acrylic **[73]** and Polyurethane-based macromolecules are commonly used in the production of phase-changing fabrics **[74]**. Pad-dry-cure, knifeover-roll, knife-over-air, transfer, and dip coating are all methods for coating PCMs onto fabric.

4.2. Lamination

PCMs are inserted into thin films of the polymeric substrate before being applied to the inner side of the fabric via the lamination process to promote thermo-physiological wearing comfort of textile garments[5, 75]. In the lamination approach, water-blown polyurethane foam is mixed with 20-60% PCM capsules before being applied to the fabric via the lamination process, where the water is removed from the system by drying[75].

4.3. Spinning

The spinning approach is one of the most extensively used ways for integrating PCMs in fabric, in which variable concentrations of PCMs are mixed with various liquid polymers or polymer solutions and spun using various processes such as dry, melt, or electrospinning. in general, instead of using melt spinning, which can lead to microcapsule breakdown at higher temperatures or PCM aggregating under dry powder form, solvent spinning is typically used to incorporate microcapsule PCM into fibers.



Figure 6: advantage and disadvantages of organic, inorganic, and eutectics PCMs

Simultaneously, the spinning of fibers and PCM improves the protection of capsulated PCM with dual walls, where the first wall is the capsule wall and the second wall is the fiber itself. The main benefits of phase-changing spun fiber are that no further modification is required in subsequent processing (knitting and weaving) and after the treatment stage (finishing, drying, printing), as well as good durability of PCM capsule demonstrating no adverse effect on softness, touch, drape, and color of final clothing material[**76**].



Figure 7: lamination process

4.4. Printing

The printing procedure has the advantage of giving control over the coating area on the fabrics. Alicja Nejman et al. covered PET fabrics with MPCMs using printing, coating, and padding processes. It was revealed that the printing process has the highest melting enthalpy of the PCM-incorporated fabrics while having the lowest air permeability[77].

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6. Conflict of interest

The authors have no conflict of interest

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