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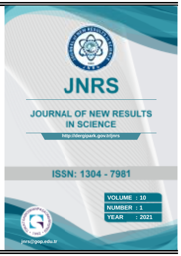

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Recent applications of microencapsulated phase change materials

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Electrospinning method

Abstract — This study aims to inform about the up-to-date knowledge on the applications of microencapsulated phase change materials (MEPCMs). The most recent applications of MEPCMs are in the fields of thermotropic, thermochromic and electrospinning, which can be considered as smart systems. MEPCMs serve as protector materials for those unresistant against thermal environmental conditions. The common treatment of them is thermal storage. They serve other or hybrid properties after functionalization. Especially in solar energy systems, thermotropic materials are an important technology for overheating protection. Applications of reversible thermochromic microcapsules are extensively applied in many ways: sinks, coatings of smart materials, cement, textiles, luminescent thermosensors, and colour indicators. Nanofibers obtained by electrospinning method have many uses such as cosmetic applications, tissue engineering, filtration applications, agricultural applications, nanosensors, biomedical tools, protective clothing, reinforced composite making, controlled active substance release and will serve shortly responding thermal systems to environmental changes due to extended surface area and body structure due to fiber formation.

Subject Classification (2020):

1. Introduction

Storage of low or high heat energy temporarily for later use is defined as thermal energy storage. This feature acts as a transition between the energy need and the use of energy [1]. There are three types of heat storage methods: latent heat, sensible heat, and chemical reaction heat. Among the different thermal energy storage techniques, one of the most effective thermal energy storage methods is latent heat storage due to its high energy storage capacity. Latent heat is defined as the heat stored or emitted during phase change [2-6]. Substances that can absorb and store heat during the transition from one phase to another, i.e., during the phase change process, and on the contrary, can dissipate this stored heat in the case of phase change are known as phase changing substances (PCM) [3,4]. Phase changing substances transition from one phase to another within a certain temperature range [5]. Substances show four types of phase changes: solid-liquid, liquid-gas, solid-gas and solid-solid phase change [7-9]. PCM's temperatures are constant during melting and freezing/crystallization. With this feature, PCMs

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absorb more heat than other materials [10-12]. During the phase change, its temperature remains constant until the phase changing substance melts or solidifies [13-15].

The fact that they absorb a large amount of latent heat and emit this latent heat during melting and solidification processes without a significant temperature change causes phase changing substances to be in great demand as a heat storage source. The latent heat energy that occurs during the solid-liquid phase change is much higher than the energy (sensible heat) generated during the cooling/heating of the substance [4-6]. PCMs with different melting temperatures are used in various fields for thermal energy storage. For example, they are used in building materials, textile products, transportation and storage of temperature-sensitive materials (medical products, food, etc.), cooling of electronic devices, active and passive heating and cooling systems [16]. Classification of PCMs used for thermal energy storage is given in Figure 1.

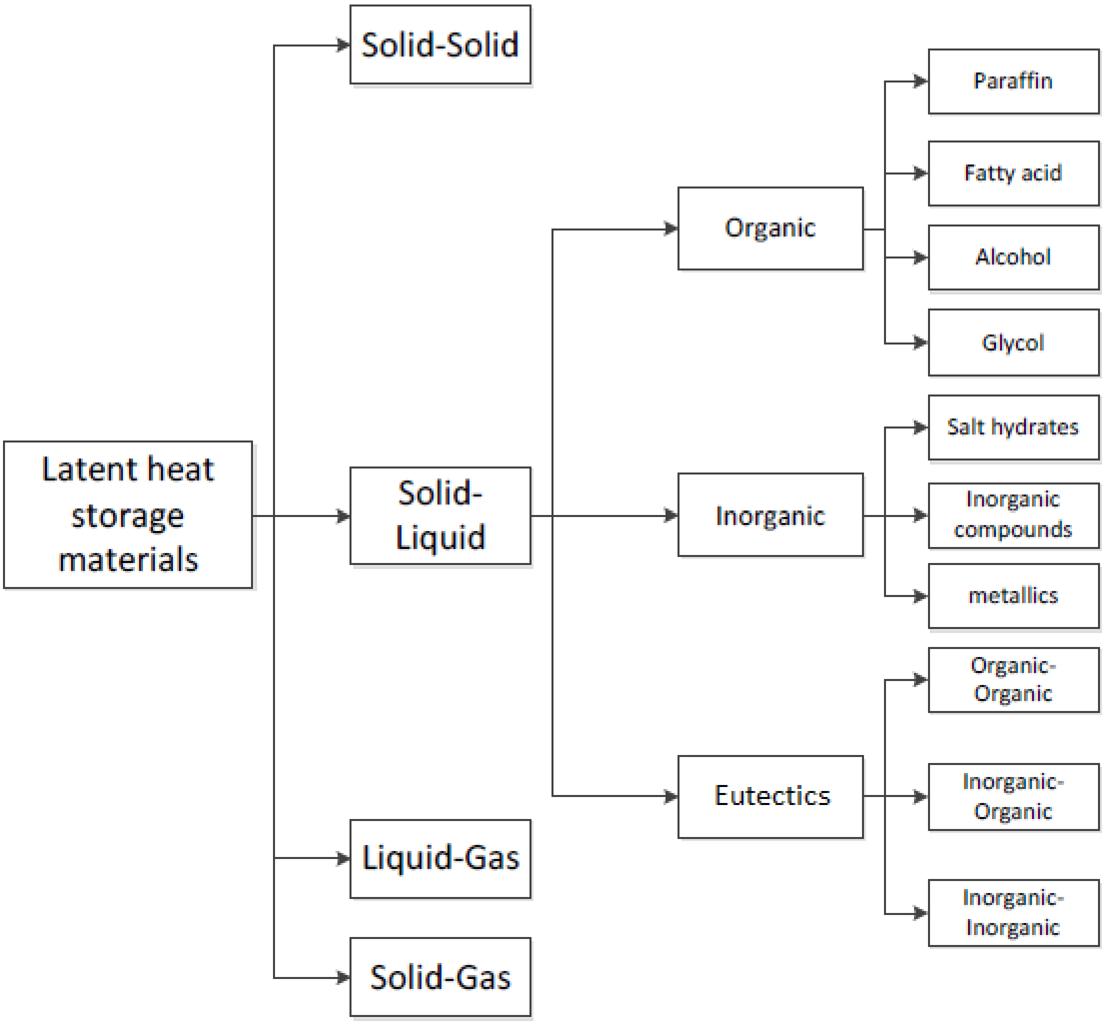

Figure 1. Classification of PCMs used for thermal energy storage [6]

Some basic parameters such as phase change temperature, phase change enthalpy, solid and liquid heat capacity and thermal conductivity should be considered while selecting PCM. Substances that have phase change in the range of 0-120 °C are candidates for use as PCM. These are grouped as organic, inorganic, and mixtures and also divided into subgroups within themselves [17]. Solid-liquid organic PCM species can leak into their environment during the heat storage process if applied directly to the material without encapsulation. Most organic PCMs are flammable, posing a serious potential fire hazard, in addition to having low thermal conductivity and poor thermal response. However, most inorganic PCMs are corrosive, which can cause irreversible damage to storage containers [10]. Such problems can be overcome using microencapsulated phase change materials (MEPCMs) or nanocapsulated phase change material (NEPCM) with different encapsulation technology. As shown in Figure 2, a typical structure of MEPCM or NEPCM consists of core and shell layers that can be classified as mononuclear, polynuclear, or matrix type [6]. The thermophysical properties of some paraffin are as in Table 1. Also, the thermophysical properties of some eutectic PCMs are given in Table 2.

Table1. Thermophysical properties of some paraffin [6]

Name	Chemical Formula	T_m (°C)	H (kj/kg)	k (W/mK)	ρ (kg/m^3)	Cp (kj/kg)
n-Dodecane	$C_{12}H_{26}$	-12	216	0.21 (s), 0.21 (l)	750	n.a.
n-Tridecane	$C_{13}H_{28}$	-6	n.a.	n.a.	756	n.a.
n-Tetradecane	$C_{14}H_{30}$	4.5-5.6	231	n.a.	771	n.a.
n-Pentadecane	$C_{15}H_{32}$	10	207	0.17	768	n.a.
n-Hexadecane	$C_{16}H_{34}$	18.2	238	0.21 (s)	774	n.a.
n-Heptadecane	$C_{17}H_{36}$	22	215	n.a.	778	n.a.
n-Octadecane	$C_{18}H_{38}$	28.2	245	0.35 (s), 0.149 (l)	814 (s), 775 (l)	2.14 (s), 2.66 (l)
n-Nonadecane	$C_{19}H_{40}$	31.9	222	0.21 (s)	912 (s), 769(l)	n.a.
n-Eicosane	$C_{20}H_{42}$	37	247	n.a.	n.a.	n.a.
n-Heneicosane	$C_{21}H_{44}$	41	215	n.a.	n.a.	n.a.
n-Docosane	$C_{22}H_{46}$	44	249	n.a.	n.a.	n.a.
n-Tricosane	$C_{23}H_{48}$	47	234	n.a.	n.a.	n.a.
n-Tetracosane	$C_{24}H_{50}$	51	255	n.a.	n.a.	n.a.
n-Pentacosane	$C_{25}H_{52}$	54	238	n.a.	n.a.	n.a.

Table 2. Thermophysical properties of some eutectic PCMs [6]

Name	Composition $(wt.\%)$	T_m (°C)	H (kj/kg)
Diethylene glycol	n.a.	-10	247
Tetradecane+octadecane	n.a.	-4.02	227.52
Water+polyacrylamide	n.a.	0	295
Tetradecane+docosane	n.a.	1.5-5.6	234.33
Tetradecane+hexadecane	91.67+8.33	1.7	156.2
Tetradecane+geneicosane	n.a.	3.54-5.56	200.28
$Na_2SO_4+NaCl+KCl+H_2O$	31+13+16+40	4	234
Tetrahidrofurano (THF)	n.a.	5	280
Pentadecane+heneicosane	n.a.	6.23-7.21	128.25
Pentadecane+docosane	n.a.	7.6-8.99	214.83
Pentadecane+octadecane	n.a.	8.5-9.0	271.93
$Na_2SO_4+NaCl+KCl+H_2O$	32+14+12+42	11	n.a.
$C_5H_5C_6H_5+(C_6H_5)_2O$	26.5+73.5	12	97.9
Triethylolethane+water+urea	38.5+31.5+30	13.4	160

(Cp: Specific heat (kJ / kg), H: Latent heat (kJ / kg), k: Thermal conductivity (W / m • K), T_m: Melting temperature (°C), ρ: Density (kg / m^3).

Microcapsules are nano, micro or macro-sized particles produced by placing an active ingredient in a polymeric wall structure as the core material. Phase-changing microcapsules are microcapsules containing PCM as the core material. By microencapsulation, the PCM in the liquid phase can be packed in micro size, and the permanence in the structure can be ensured [18]. Microcapsules can be single-core, multi-core and matrix-shaped structures. The compatibility of core-wall materials is also essential. Also, the morphology of microcapsules can be a smooth, symmetrical shape, depending on the chemicals used and the production methods, or they can be porous and rough. A schematic representation of the microcapsule morphology is given in Figure 2.

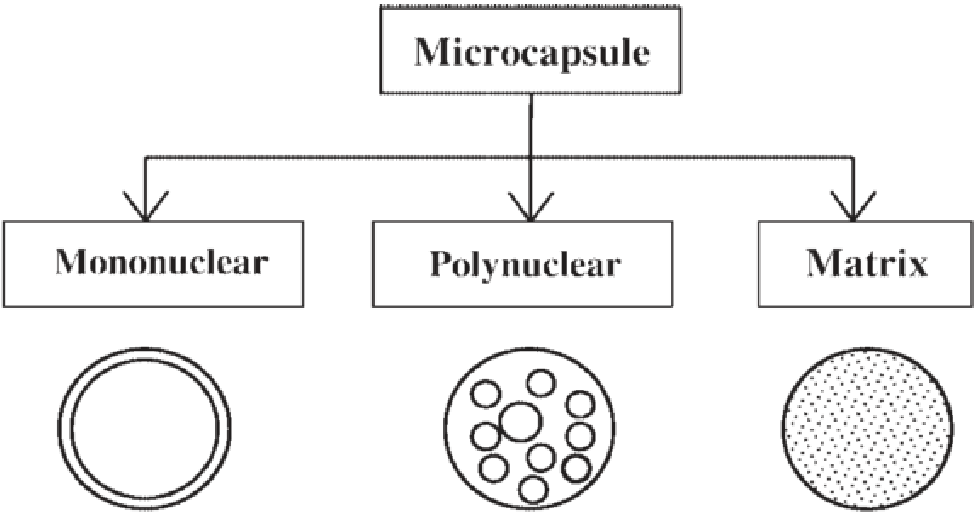

Figure 2. Structure of MEPCMs and NEPCMs[17]

The working principle of MEPCM is given in Figure 3.

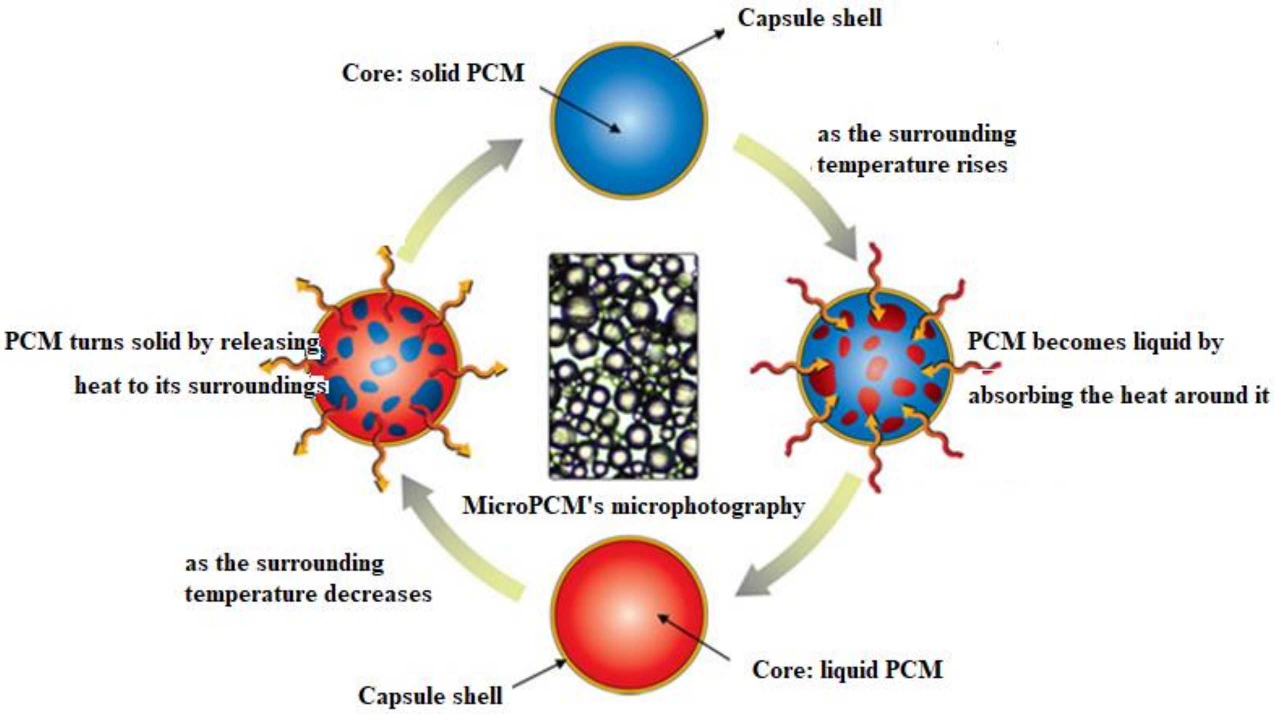

Figure 3. Working principle of a MEPCM in an energy storage system [19]

Commonly used microcapsule production techniques are as follows.

Chemical Process	**Mechanical Process**
Interface Polymerization	Spray Drying Method
Emulsion Polymerization	Cool-Drying Method
Micel Polymerization	Hot Melt Microencapsulation
Radical Chain Polymerization	Centrifuge Method
Polycondensation Polymerization	Rotational Suspension Separation
In-Situ Polymerization	Fluid Bed Method
Phase Separation Method (Coacervation) 1. Simple Coacervation 2. Complex Coacervation	
Supercritical Fluid Method	
Molecular Encapsulation Method	

With the advancement of technology, the demand for micro/nano-sized materials increases day by day. Microcapsules take their place in almost every aspect of our lives. Issues related to MEPCMs [20-23] with excellent latent thermal energy storage capacity [24- 28] have been extensively investigated in recent years. It has made significant progress in fundamental research MEPCMs, solar-thermal conversion systems [29], thermal energy storage, and the like. Also, significant progress has been made in some areas, such as encapsulated autonomous healing materials, drug delivery, photochromic materials and reversible thermochromic materials, thermotropic materials, and nanofiber production [30].

2. Thermochromic systems

Applications of reversible thermochromic microcapsules are extensively applied in areas such as inks [31], coatings of smart materials [32], cement, textiles [33], luminescent thermosensors [34] and colour indicators [35]. Recently, luminescent dye or leuco dye-based thermochromic (TC) systems [36] have been chosen as core materials for fabricating the temperature-sensitive thermochromic microcapsule [30, 37]. Chromic materials can respond to external stimuli such as light, temperature, humidity, pH change, and electric and magnetic fields [38-41]. Thermochromism is defined as the reversible change in the component's colour with temperature [40, 41]. Reversible thermochromic are technically direct or indirect systems. Direct thermochromic systems show colour change with direct heat. Unlike direct systems, the colour change in indirect thermochromic systems depends on the change in the ambient temperature. Examples of direct thermochromic systems are stereoisomerism, liquid crystals and molecular rearrangements [42-45]. Indirect thermochromic systems themselves do not show chromism; they require a combination of a leuko dye, a developer and a solvent in certain proportions. Therefore, these systems can be named multicomponent systems [46]. Organic thermochromic materials have many advantages, such as regulating colour change according to temperature and regulating the variety of colour changes and therefore have become the main research focus in recent years [38-41]. Thermochromic materials have broadly important application areas such as security printing, plastic tape thermometers, food packaging, medical thermography, non-destructive testing of engineering products, electronic circuitry systems [45], the pharmaceutical industry and the limited range textile industry. In multicomponent systems, reversible colour change at a certain temperature from one colour to another or colourless to colour depends on a developer's interaction in an environment created by a colour generator (a leuco dye) and a co-solvent. The solvent creates a phase change medium for the three-component thermochromic system. The melting and crystallization points of the solvent determine the system's colour change temperatures [42,46]. Alcohols, hydrocarbons, esters, ethers, ketones, and fatty acids are examples of solvents for thermochromic composites [43-50]. The colour improver is a weak acid that acts as proton donors to create the coloured state of the leuco dye components. The most commonly used improvers are bisphenol-A, gallates and phenols. Leuco dyes are electron donors such as spirolactone, spiropyrans or fluoranes, the most common of which is the crystalline purple lactone (CVL) dye. In the three-component thermochromic system, leuco dye and developer interact with each other at low temperature. In that case, the lactone ring opens up and the system gives a strong colour in the solid phase. When the temperature rises, the system is colourless due to the closed lactone ringin the liquid phase [40, 41, 46-48, 51, 52]. Thermochromic systems show lower enthalpy since they consist of phase change agent, dye and dye auxiliary chemical. The dissolved dye and dye auxiliary chemical cause the phase change temperature to decrease due to the cryoscopic effect. This is a typical situation for thermochromic systems, and the decrease in enthalpy is a disadvantage. In contrast, the decrease in the phase change temperature is a significant advantage since the operating temperature can be adjusted. Figure 4 shows the formation process of thermochromic microencapsulated phase change materials (TC-MEPCM) prepared by the in-situ polymerization method. In Figure 5, a nanocapsule drawing with a thermochromic energy storage feature is given.

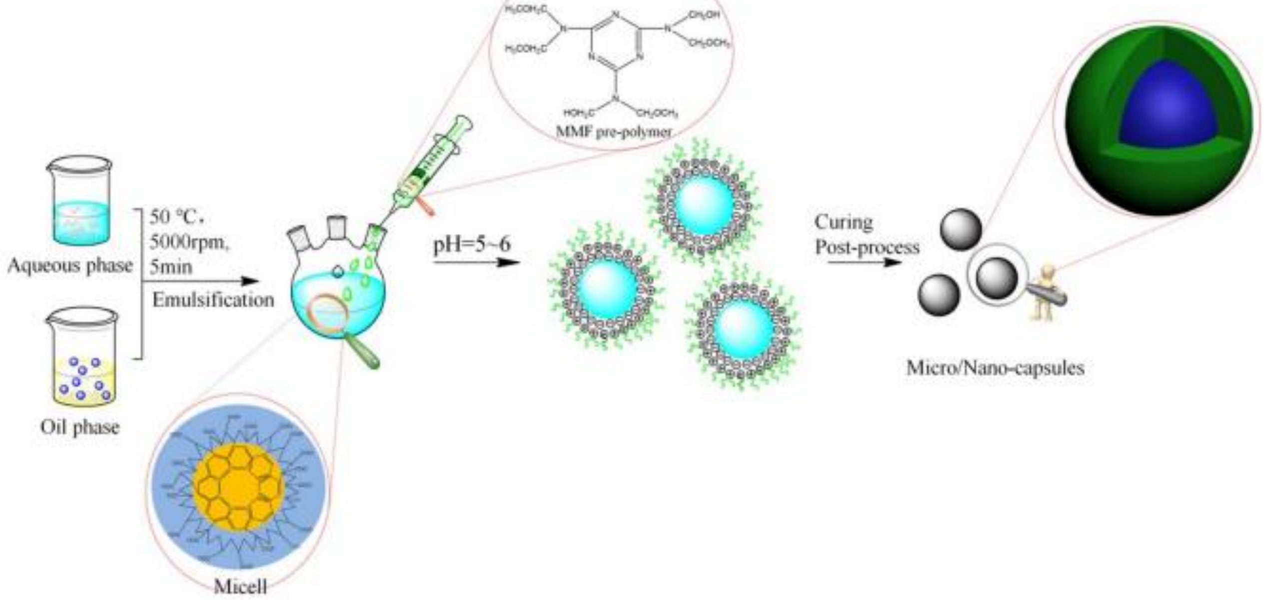

Figure 4. Formation process of TC-MEPCMs [30]

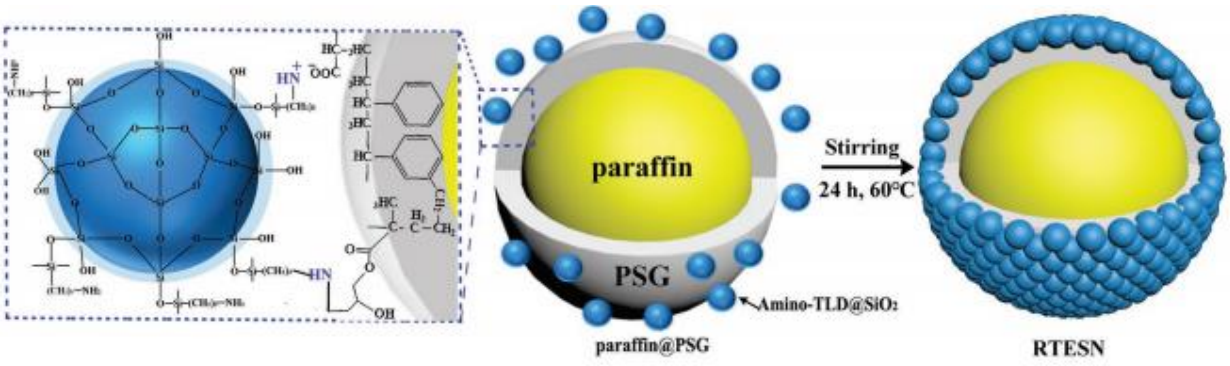

Figure 5. Raspberry-shaped nanocapsule drawing with thermochromic energy storage property [53]

3. Thermotropic systems

Chromogenic materials are perfectly suited for solar control glass applications [54-56]. Scientists and engineers have turned to develop new electrochromic, thermochromic and thermotropic materials for potential technical applications. Usually, conventional non-modifiable protective solar films combine reflection and absorption of infrared and UV rays, resulting in a noticeable temperature drop during the summer months [57]. In contrast, thermochromic and thermotropic systems can be compared in their impact on the energy efficiency of buildings. Here, thermotropic materials that act based on reflective effects appear to be more advantageous. Reflection partially prevents sunlight from entering the building and windows and facade elements and is, therefore, more advantageous compared to thermochromic systems. Thermochromic systems come to the fore in applications where a permanent appearance is needed from the inside out. Thermotropic systems exhibit light scattering feature depending on temperature change. If increased scatter is associated with significant backscatter due to temperature rise, the materials are suitable for an application in solar control. This area investigated thermotropic effects of phase separation, an isotropic and an anisotropic (liquid-crystalline) phase transition and areas between the case and the matrix of a refractive index caused by extremely different temperature dependence [58]. Fixed-area (TSFD) thermotropic systems change their light transmission from transparent to light scatter when they reversibly reach a certain threshold temperature. [59, 60]. Due to their autonomous temperature-triggered mode of operation, they are superior to actively operated shading devices which can be more prone to component malfunction [61]. Thus, TSFD can provide efficient overheating protection for buildings and solar thermal collectors [62, 63]. Thermotropic overheating protection is an important technology, especially for installing solar collectors made of cost-effective plastics [63, 64]. TSFD consists of at least two components: a matrix material and a thermotropic additive as the minor component finely dispersed in it. Both components exhibit similar refractive indices at temperatures below the threshold temperature. As a result, incoming solar radiation is not scattered, and the TSFD appears transparent [65]. Schematic sections of a thermotropic transparent outer insulation and coating (TEIF) system are given in Figure 6.

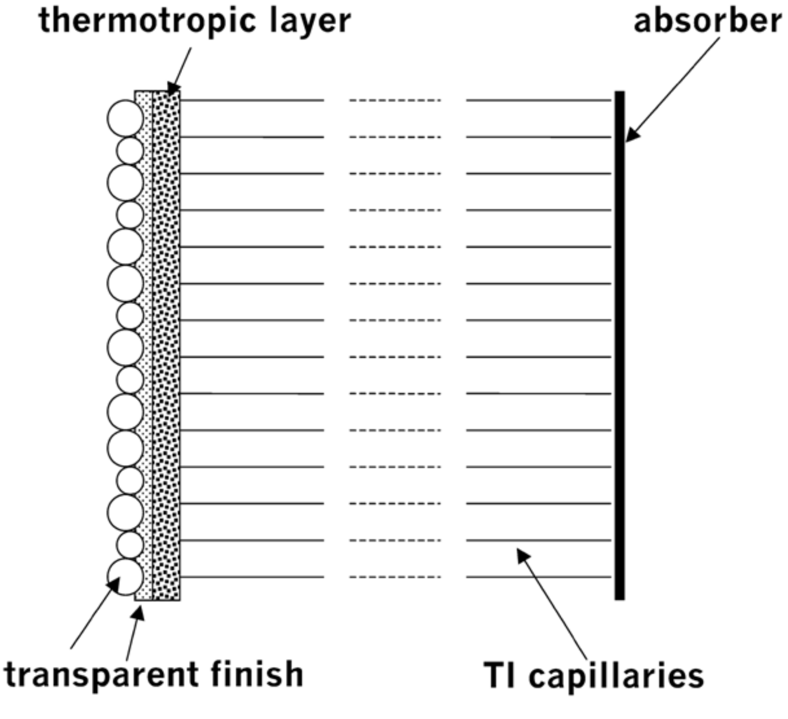

Figure 6. Schematic cross-sectional representation of a thermotropic transparent outer insulation and coating (TEIF) system [66]

4. Electrospinned MEPCMs

The electrospinning process [67-70] produces superfine fibers with diameters ranging from 10 mm to 10 nm by forcing a polymer melt or a solution through a spinneret with an electric field and then pulling the formed filaments as they solidify or coagulate. Due to the ease with which nanometer-sized fibers can be produced from a range of natural and synthetic polymers, they have received much attention in technology recently [71]. Nanofibers have a diameter of less than 1μm, and they are filamentous structures whose lengths are considerably higher than their diameters. Polymeric nanofibers can be produced by different techniques such as drawing, mould synthesis, phase separation, self-assembly and electrospinning [72]. Among these methods, the electrospinning method has many advantages such as high encapsulation efficiency, ease of application, high loading capacity, the ability to work with synthetic and natural polymers, obtaining fibers in sizes ranging from a few nanometers to micrometers, obtaining mechanically durable and flexible fibers, no need for purification because one type of fiber is obtained, two or three-dimensional fiber production, obtaining very long fibers from a few centimeters to meter dimensions and low-cost method.

In addition to these advantages, the disadvantage of the method can be considered the unstable jet formation, the fact that many parameters significantly affect the fiber formation and structure [73]. Nanofibers have a high molecular orientation. Due to their small size, they have fewer structural defects and thus have very well mechanical properties. Due to the small diameter, they have high surface/volume ratios or surface/ mass ratios, so they have high surface areas. The fact that nanofibers form structures with a large surface area increases their capacity to retain or emit functional groups, ions and a wide variety of nano-level particles [74]. Nanofibers obtained by the electrospinning method have many uses such as cosmetic applications, tissue engineering, filtration applications, agricultural applications, nanosensors, biomedical tools, protective clothing, reinforced composite making, controlled active substance release [75]. One of the alternative applications is to transform microcapsules into nanofibers with the electrospinning method to increase their applicability in different areas by expanding their surface area. This method, known as electrospinning, is a method developed to produce nanofibers from polymer solutions and is one of the easiest methods applied to form polymer-based nanofibers. This method makes it possible to create nanofibers with various morphological properties in a controlled manner with polymer solutions within the electric field generated by high voltage. The schematic representation of the electrospinning system is given in Figure 7.

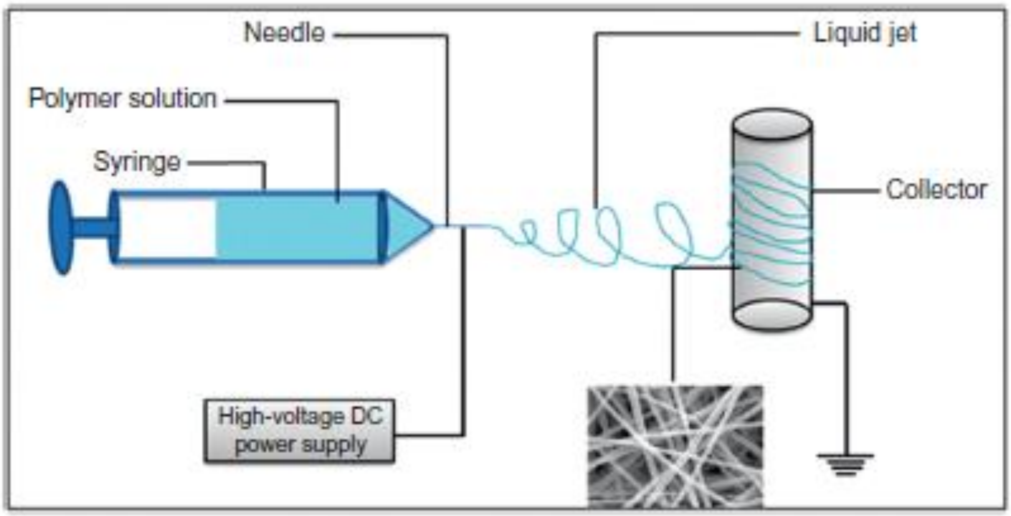

Figure 7. Schematic representation of the electrospinning system [75]

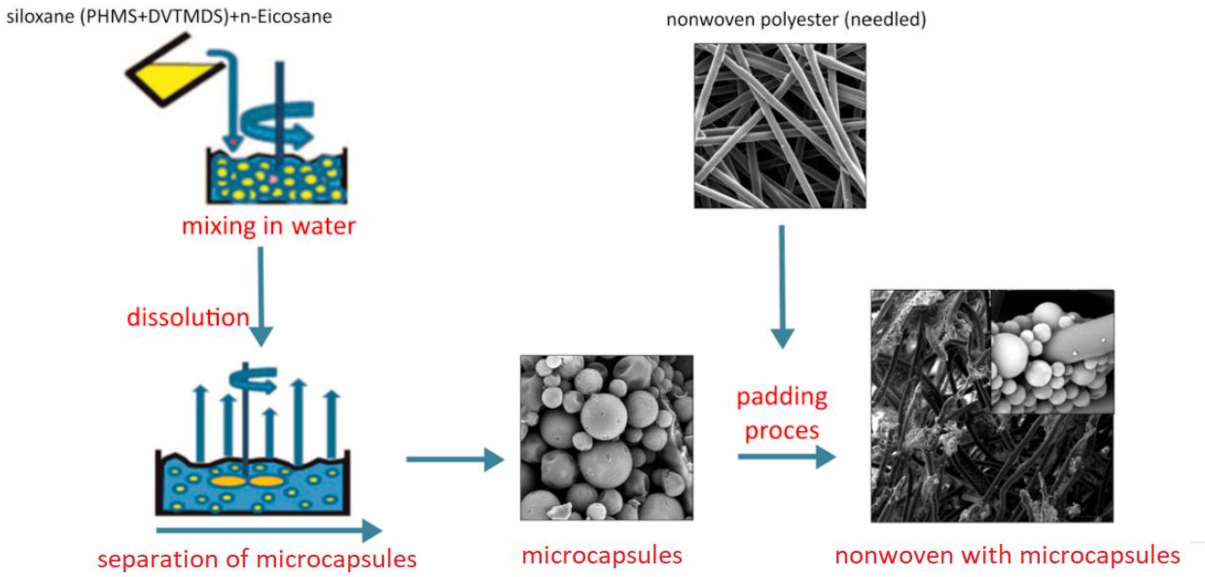

Figure 8. Schematic representation of the microencapsulated nanofiber production [76]

5. Conclusion

Microencapsulated phase change materials (MEPCMs) were first used in applications such as buildings and textiles with direct doping methods for heating and air conditioning. For this purpose, they are used for coating purposes in the interior of buildings by adding to plaster, as well as bonded to textile fiber cross-sections or surfaces. After a while, they have also been validated for different purposes, such as thermotropic systems, thermochromic and sensor materials, and electrospinning fabrics. Especially in solar energy systems, thermotropic materials are an important technology for overheating protection. Thermotropic systems are also used as a heating component in hybrid systems, benefiting from the greenhouse effect. Applications of reversible thermochromic microcapsules are extensively applied in many areas such as inks, coatings of smart materials, cement, textiles, luminescent thermosensors and colour indicators. Nanofibers obtained by the electrospinning method have many uses, such as cosmetic applications, tissue engineering, filtration applications, agricultural applications, nanosensors, biomedical devices, protective clothing, reinforced composite production, controlled active substance release. In the present study, it is aimed to summarize the innovations and applications of MEPCMs. It is thought that these materials will take place as an important group in the smart materials class in the next period. It is estimated that the usage areas will develop by adding new ones every day.

Author Contributions

Ruhan Altun Anayurt: Conceptualization, investigation, writing original draft, review and editing.
Cemil Alkan: Investigation, writing original draft, review and editing, supervision.

Conflicts of Interest

The authors declare that they have no known competing commercial interests or personal relationships that could have influenced the work reported in this paper.

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