Review Article

Principles, properties and preparation of thermochromic materials

Abstract

The unique temperature-induced color changing properties of thermochromic materials make them of significant interest for applications in aerospace, anti-counterfeiting technology, construction, defense, drugs & pharmaceuticals, electronics, energy, food & agriculture, maintenance of infrastructure, materials processing & storage, military technology, optoelectronics, packaging, sensors, smart displays, textiles, thermal storage and transportation. Thermochromism occurs due to the following characteristics: (a) phase transitions in a compound (e.g. leuco dyes); (b) changes in ligand geometry or the number of solvent molecules in the coordination sphere (e.g. transition metal complex that derives its color from crystal field effects) and (c) complex factors in multicomponent mixtures. Thermochromic materials can be divided into several categories depending on their material properties and operating conditions. In recent years, numerous techniques have been used to synthesize thermochromic materials for a variety of purposes and applications. This review summarizes the various mechanisms of thermochromism, their classification, preparation and applications and discusses future development trends.

Keywords: thermal properties, polymeric materials, phase transition, materials science

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Introduction

Chromogenic materials and thermochromism

Chromogenic materials exhibit shifts in their optical behavior, usually a change in their appearance, reflectance or erasure of color, when exposed to an external stimulus. These materials can be classified according to the stimulus they respond to:

a) *Photochromic*: chemical species undergo reversible transformation between two forms that have different absorption spectra when exposed to light

b) *Thermochromic*: material undergoes change in color with change in temperature

c) *Electrochromic*: material displays persistent but reversible changes in color or opacity in response to an electrical stimulus

d) *Piezochromic*: material, usually in solid form, undergoes change in color under compression

e) *Solvatochromic*: chemical species undergoes color change due to a change in solvent polarity

f) *Carsolchromic*: material undergoes color change when exposed to an electron beam

g) *Humidochromism*: material undergoes color transformations due a change in humidity

h) *Vapochromism*: material undergoes color change in the presence of a gas or vapor

This review focuses on the thermochromic phenomenon in various chromogenic materials. In Greek, "thermos" means warm and "chroma" means color. Thermochromism refers to a change in color as a function of temperature and can be defined by an observable color change induced by a shift in molecular conformations due to a change in temperature.[1] The observed color changes are usually reversible but irreversible changes are also possible. Different materials respond to different stimuli but the mechanism for the color change

is a reversible electron or ion transfer that requires energy from an external stimulus such as to overcome a potential barrier. There are two types of thermochromism: continuous and discontinuous (Figure 1). In continuous thermochromism, a gradual color change results from the progressive shift and/or broadening of the visible absorption bands upon stress such as a change in temperature. Discontinuous thermochromism occurs when the color change is abrupt and is associated with a first- or second-order structural phase transition.[2] Thermochromic materials (TCMs) are of significant interest to researchers and manufacturers as they have the potential for many technological applications such as aerospace, functional coatings, military, printing technology, smart windows, temperature sensors etc.[3]

Figure 1 A schematic representation of thermochromism: continuous (upper) and discontinuous (lower). One has to assume that the temperature changes continuously when going from left to right.[3]

Principles of thermochromism

Solid state phase transitions

Solid-state thermochromic materials undergo semiconductor to metal transitions at a 'critical temperature', T_c.[4] The fundamental chemical principles of this phenomenon demonstrate the mechanisms of thermochromism.

Wilson and Fowler's free-electron model of the electronic configuration of solids makes the distinction between metals, semiconductors, and insulators under the assumption that electrons occupy energy bands or orbitals.[4] According to the model, semiconductors have a small forbidden energy gap between the highest filled orbital and lowest empty orbital that electrons can easily overcome as the temperature is increased and thus, semiconductors become increasingly conductive with elevated temperatures. However, the model fails to address the existence of insulating transition metal oxides despite having partially filled 3d orbitals as it does not take electron repulsion into consideration.

In 1937, Peierls suggested that the insulating behavior could be due to the strong intra-ionic Coulombic repulsion between the electrons; thermal excitation facilitates the electrons to cross the potential barrier that is needed to reach the conduction band from their low temperature localized "resting state". Wigner suggested that the electrons form a non-conducting crystalline state and Mott suggested that this crystal structure had a variable lattice constant, *b*. For large values of *b*, the material would act as an insulator while for small values of *b*, it would be metallic; thus, b_0 would be the critical value at which a transition occurs (Figure 2). As the value of b decreases, the activation energy required to form a pair of carriers also decreases; thus a discontinuous transition occurs at b_0. This is known as the "Mott transition".[4] Slater proposed a two-band model which stated that the insulating properties of the ground state in antiferromagnetic transition-metal compounds, with large values of *b*, could be explained if the d orbitals split at the Neel temperature.[4] Transition metal oxides such as Ti_2O_3, V_2O_3, VO_2, and VO, all have shifting electrical properties at high and low temperatures due to metal-to-semiconductor transitions which present as other variable properties, such as thermochromism.
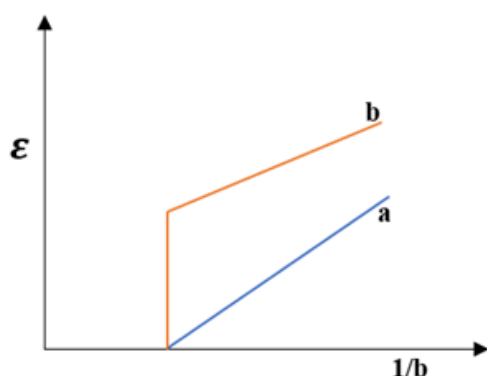

Figure 2 The change in activation energy (ε) versus reciprocal lattice constant (1/b). a- shows a continuous change, whereas b- shows a discontinuous change.[4]

Interactions between electrons are not the only way to trigger phase transitions. Change in crystal structure due to lattice distortion can also lead to the formation of a band gap between the occupied and empty orbitals which in turn, cause variable optical properties at transition temperature.[4] Rising temperatures cause the energy gap between the highest energy orbital and the lowest energy orbital to decrease almost linearly which in turn causes the distortion to disappear as the band gap approaches zero and the material becomes metallic. Phase transitions can be classified into first- or second-order reactions depending on the magnitude of the relative change in the gap with the number of excited carriers, i.e., the thermodynamic potential and its derivatives at the transition.[4] The order of the system is dependent on its energy, temperature, and entropy. As entropy increases, atoms can lower their energy to enter a more stable and ordered state which is when the phase shift occurs. In first-order transitions, this change is abrupt and discontinuous while in second-order transitions, the change is gradual and continuous, and the system enters a state of lower symmetry. These kinds of transitions are responsible for variations in color observed as thermochromic properties.

Discontinuous thermochromic phase transitions in transition metal salts

Thermochromic transition metal salts exhibit an abrupt color change also known as discontinuous thermochromism as a result of structural phase transition brought about by the associated changes in coordination geometry and/or ligand field strength.[5] High temperatures weaken the hydrogen bonding network and crystal packing forces between the molecular elements in the ligand structure, causing a shift in anion geometry. An example of this is observed in some quaternary $[CuCl_4](2-)$ (Figure 3) in which the square planar geometry of the ligand structure shifts to a less densely packed distorted or "flattened" tetrahedral configuration.[6]
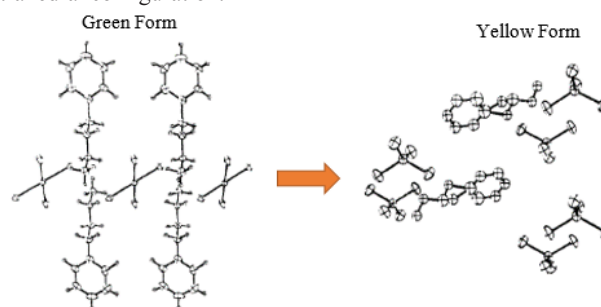
Figure 3 Phase transition of $(N-mpH)_2CuCl_4$ from square planar (left - green form) to flattened tetrahedral (right - yellow form) structure.[6]

Copper (II) and nickel (II) complexes of N, N-diethylethylenediamine display various color changes with temperature. The copper complexes change reversibly from red to violet at higher temperatures due to a temperature dependent tetragonal distortion in the copper atom environment, while the nickel complexes similarly reversibly transition from orange-yellow to bright red.[7] XRD and NMR analyses techniques were utilized to demonstrate that a decrease in the ligand field strength, due to the weakening of hydrogen bonds, resulted in a lower potential barrier for the rotation of the primary amine which in turn resulted in a structural transition.[8] Linkage isomerization of ligands are also responsible for observable color changes.

$Cu(NO_2)_2(NH_3)_2$ shows sudden color change due to the NO_2^- ligand being coordinated to the copper atom through the nitrogen atom at low temperatures, presenting as purple, and through the oxygen at temperatures above T_g, presenting as green.[9]

Molecular structural changes

Molecular structures of thermochromic materials are susceptible to temperature change which causes them to undergo a visual switching of color. Intramolecular hydrogen bonds form as a result of π-electron coupling between the acid and base centers, i.e., conjugate acid donates a proton to the conjugate base, leading to molecular structural changes.[10]

Schiff base compounds undergo thermochromism due to this phenomenon called tautomerism. For example, crystalline N-salicylidene-2- aminopyridine derivatives are Schiff base compounds that switch from the enol tautomer to the *cis*-keto tautomer as protons transfer from the oxygen atoms on -OH to the nitrogen atoms (Figure 4).[11] There is a temperature sensitive equilibrium between the two forms.[12]
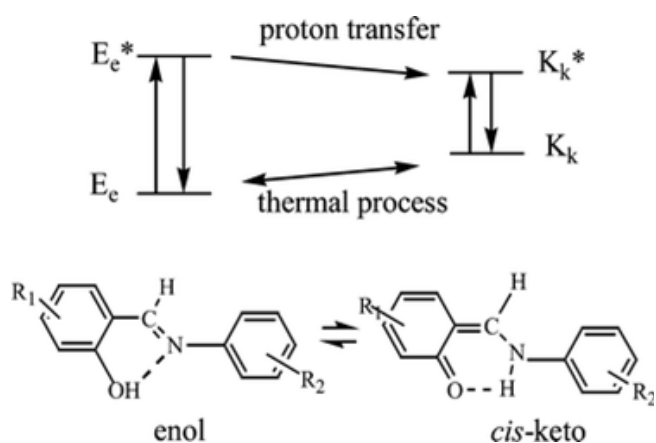
Figure 4 Energy diagram and constitutional formulas of thermochromic N-salicylideneanilines.[12]

Heat can induce an interconversion between stereoisomers of different colors. Bianthrones are known to switch between two distinct and interconvertible isomeric species, a "folded" yellow ground state "A" and a "twisted" green thermochromic state "B".[13] The B form exists in two stereoisomeric forms, B_E (higher priority groups on opposite sides of double bond) and B_Z (higher priority groups on same side).[14] Stereoisomers of a tetraphenylethene (TPE) derivative, 1,2-bis{4-[1-(6-phenoxyhexyl)-4-(1,2,3-triazol)yl]phenyl}-1,2-diphenylethene (BPHTATPE), show rich chromic effects, including Thermochromism.[15] *E*- BPHTATPE exhibits marked chromogenic effects due to its better organizability or crystallinity.[15]

Temperature changes cause structural changes in spiropyran and oxazine compounds.[16] In solution, these compounds are funereally colorless and are composed of two heterocyclic rings linked by a common tetrahedral sp3 carbon atom which enforces an orthogonal orientation between the two heterocycles.[17] At elevated temperatures, heterocyclic C–O bond cleavage occurs causing a mutual rotation of the molecular subunits around the C−C bond which in turn changes the size and dipole moment of the molecules significantly.[18] The compound forms a more planar structure which allows π-orbital overlap and shifts λ_{max} to the visible region.[18] However, the colored structure is unstable and the color stability is poor due to the high negative charge density of the oxygen atoms in the naphthalene ring.[16]

Thermochromic liquid crystals

Thermochromic liquid crystals (LCs) are complex, optically-active, thermotropic organic materials that exhibit an intermediate phase or "mesophase" between the crystalline solid and liquid phases.[19] They can be classified into various categories depending on their morphological and optical properties. The three distinct categories for thermotropic liquid crystals are Smetic, Nematic and Chiral Nematic.[19] LC molecules are usually elongated, rigid and rod-like and are called calamitic liquid crystals.[20,21] The degree and nature of the molecular ordering and orientation determines whether the material can be characterized as Smetic or Nematic. The Smetic phase is the most "solid-like" among the liquid crystal modifications due to molecular aggregates being oriented parallelly to each other in two dimensional sheets. In the Nematic phase, calamitic molecules are oriented and aligned in a spiral about a helical axis; this seeming "randomness" makes the material less symmetric and thus gives rise to anisotropic properties (Figure 5).
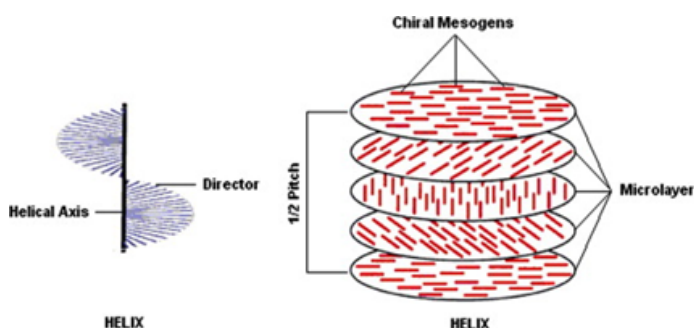
Figure 5 Helical structure in chiral-nematic or cholesteric liquid crystal.[19]

Chiral Nematic LCs are a special class of Nematic LCs that are optically active due to their molecular chirality and distinctive twisted structure.[20] The mesophase of this class of LCs can be envisioned as sheets of molecular aggregates along the helical axis with longitudinal dimensions in the order of the wavelength of visible light.[20] Each molecular sheet is skewed at an angle with respect to its adjacent sheets and this periodic structure gives rise to unique optical properties such as birefringence, chirality, circular dichroism and Bragg Scattering.[20] The degree of twist of each sheet is measured by the parameter, pitch length or "P" which is defined by the longitudinal distance between two molecular aggregate sheets of the same orientation. This length varies as a function of temperature and thus, LCs can display different colors depending on the temperature.[22,23]

LCs exhibit smetic mesophases at lower temperatures and can either reversibly transition to a crystalline solid, isotropic liquid or other mesophilic structures (nematic, cholesteric) with temperature variations.[20] There are two types of transitions:

a) N*-I transitions give a sudden color change at target temperature which can either be reverted upon cooling or give a "pseudo-irreversible" color change if alignment displacement occur.

b) N*-S transitions give a constant color change from the blue to the red end of the spectrum to black (infrared reflection) as the pitch lengthens with decrease in temperature.[23]

Cholesterol and ester derivatives of (S)-4-(2-methylbutyl)phenol are important thermochromic LCs due to the simplicity of their structures as well as their highly customizable characteristics with a wide choice of chiral branch substituents.[23]

Classification and thermochromic mechanism

Classification

Thermochromic materials can be separated into four categories: inorganic, organic, hybrid and polymeric systems such as liquid crystals. Inorganic TCMs include metal iodide, double salt, transition metal compounds, metal alloys, metal chloride, etc. and have many favorable features such as good temperature resistance, durability, light resistance and processability.[16] Organic TCMs such as spirolactones, fluorans, spiropyrans, anils, hydrazones and fulgides [24, 25] are known to have optional and adjustable colors, low discoloration temperature, high sensitivity of discoloration and low cost.[16] Macromolecular systems such as conjugated polymers like polythiophenes (PTs), polyaniline (PANI), polydiacetylene (PDA) and poly(phenylene vinylene) (PPV), have excellent processability, high corrosion resistance and are cost-competitive. Liquid crystals can be separated into three categories depending on their molecular arrangement:

nematics, smetics, and cholesterics.[22] They have good chemical stability, high thermal stability and can display different colors at different temperatures but their high chemical and UV sensitivity, along with high processability cost, limits their applications.[24]

Inorganic thermochromic materials

Inorganic thermochromic materials have a functional temperature range starting from 70°C up to 500°C, along with high thermal stability, ability to maintain chromaticity, stable crystal structure and mechanical durability for long periods, which leads to their potential applications in a variety of fields, from construction to energy efficiency.[26]

However, their fixed high transition temperature and toxic nature limit their uses in the food and biologics areas and require suitable processing measures to prevent environmental release.[26] Many inorganic salts have been used in thermochromic sensors, such as, manganese violet pigment (a mixture of manganese dioxide, ammonium dihydrogen phosphate, and phosphoric acid) applied to white cementitious material to monitor high-temperature material damage in a furnace. The pigment changes from dark violet to grayish yellow/green at temperatures above 400°C due to the evaporation of water and the liberation of ammonia from the pigment particles.[27] $CuMoO_4$ polymorphs exhibit optical contrast at the first order phase transition from a low-temperature, reddish brown γ-phase to a high-temperature green α-phase.[28] The α-phase is composed of square pyramidal $[CuO_5]$ polyhedra, elongated octahedral $[CuO_6]$ polyhedra, and $[MoO_4]$ tetrahedral; it undergoes a pseudo-reconstructive phase transition to the γ-phase which is composed of only $[CuO_6]$ and $[MoO_6]$ octahedral.[29] Cr_2O_3-Al_2O_3 pigments display a wide range of colors varying from pink → red → purple → chestnut red, depending on the Al^{3+} → Cr^{3+} substitution in the crystalline networks.[30]

Thermochromic vanadium oxide (VO_2) thin films have been used in conjunction with photocatalytic TiO_2 in the production of smart windows.[31, 32] The transmittance of VO_2 is relatively high and constant in the visible range until it is heated above its transition temperature, T_c, at which its transmittance in the infrared region decreases significantly.[31] At low temperatures, VO_2 exists in a body-centered cubic monoclinic form which consists of a tilted octahedral lattice structure with the vanadium atoms in the center. At 68°C, VO_2 undergoes a phase transition to a rutile (tetragonal/metal-like domain) structure that is highly reflective with the ability to regulate solar heat flux by responding to temperature automatically.[31,32] Varying grain size or doping VO_2 thin films with materials such as tungsten, has been shown to lower its transition temperature and improve solar heat flux.[26,34-36] Doping with species of atomic radii that is larger than the V^{4+} ion or by creating V^{5+} defects in the lattice, such as with high valence metal ions tungsten (VI), niobium (V) and titanium (IV), reduces the T_c of VO_2 to about 25°C.[39] Dopants with smaller ionic radii, such as, the low valence metal ions aluminum (III) and chromium (III), leads to increase in T_c of VO_2.[39]
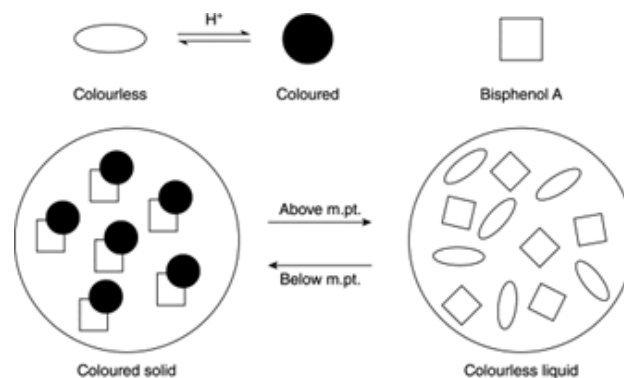
Organic thermochromic materials

Organic thermochromic materials are commonly utilized in various commercial applications such as smart packaging, security printing, textile coloring, toys and marketing,[38-42] due to their low costs and low toxicity. They are also known as leuco dyes and are usually available as a three-component system consisting of a color former, a developer and a co-solvent.[43] These systems produce a color change when the co-solvent melts leading to the destruction of the dye–developer complex, associated with a loss of color.[41,43,44] The color former is an electron donating compound such as spirolactone, fluorane or spiropyran;[41,43]

the developer is an electron acceptor (proton donor) compound such as Bisphenol A, alkyl gallates, phenols, hydroxybenzoates, and hydroxycoumarin;[43] and the co-solvents are usually long-chain alkyl alcohols, esters, or acids.[41,43] Crystal violet lactone (CVL) is one of the most studied leuco dyes (Figure 6); in the colorless form (SP or Spiropyran), the lactone ring is closed but when there is an increase in polarity in the host environment or a proton is introduced, the ring opens (MC or Merocyanine) and displays a purple color.[45-47]
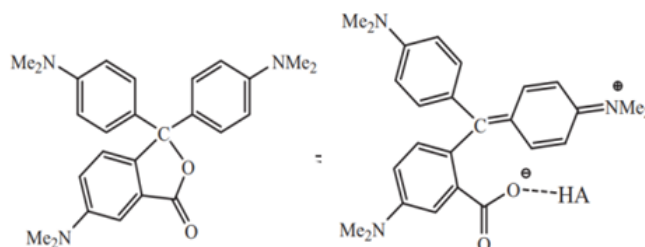
Figure 6 The ring-closing and ring-opining form of Crystal Violet Lactone (CVL). The Spiropyran (SP) form on the left and the Merocyanine (MC) form on the right, displaying blue color.[45]

Leuco dye thermochromic systems undergo reversible transformation from colored to colorless with elevated temperatures. Below the transition temperature of the solvent, the dye exists as a colored open ring protonated species that forms an insoluble complex due to the localized polar environment from the anionic developer.[49] This creates a heterogonous system. When the solvent melts with increase in temperature, the system becomes homogenous as the hydrophobic environment favors the colorless neutral ring-closed form which is soluble.[49] When the system is cooled, a phase separation occurs as the solvent solidifies and the dye-developer complex forms again (Figure 7).

Figure 7 Schematic representation of the mechanism of color change in a microencapsulated organic leuco dye thermochromic system.[49]

Organic–inorganic hybrid thermochromic materials

Organic-inorganic hybrids offer an exciting opportunity to combine the excellent electronic properties along with the structural rigidity and thermal stability of inorganic configurations with the functional and structural versatility of organic molecules.[50,51] The interactions of these materials give rise to unique and intriguing properties such as structural diversity,[52,53] tunable band gap,[54] flexibility, long diffusion length,[55] and ease of processing.[56] They have generated immense interest as a new class of functional optoelectronic materials and have been utilized in photovoltaics,[57-61] light-emitting,[62-65] lasing,[66-68] and many other applications. These materials can exhibit thermochromic behavior and it has been reported that the mechanism of thermochromism is due to lattice distortion, lattice expansion, or

ion rearrangement of their hybrid structures or a structural phase transition during exposure to changing temperatures.[69]

Metal halide hybrids such as Pb^{2+}, Sn^{2+}, Bi^{3+}, Sn^{3+}, etc. –halide, combined with organic counterions, have been extensively studied. Displacement of the nonbonding valence electron pairs around the metal centers results in the formation of acentric phases with polar or ferroelectric properties.[50] Gagor *et al.* reported the synthesis and characterization of (2-methylimidazole)BiI_4 organic-inorganic hybrid which showed significant thermochromism characteristics for direct gap semiconductors.[50] The composite continuously changes color from dark red to light orange at changes in temperature from 330 K to 150 K respectively. This behavior is primarily due to the modification of the interatomic distances between Bi-I and Bi···Bi which affects the absorption and coordination of the Bi^{3+} ion; a more asymmetric surrounding creates a broader absorption band.[50,70]

The degree of bonding between I···I intra-anionic pairs influences the electronic structure around the Fermi level as the energy gaps of the anionic chains are lower than those of the isolated ions which results in a blue shift when the dimensionality of anionic units is reduced.[50,71,72] Xiong *et al.* reported thermochromism in a ferroelectric compound, N,N′-dimethyl-1,4 diazoniabicyclo[2.2.2]octonium $CuCl4$(II), which exhibited a red shift of electronic absorption bands with an increase in temperature.[73] At room temperature (300 K), the low-dimensional flexible and variable octahedral structure of the solid crystal exhibits a yellow color and absorbs light of wavelength less than 576 nm; however, once the temperature reaches 433 K, the solid shows a red color as the absorption edge moves to 618 nm.[73] Recently, Jia *et al.* reported their studies on 1D lead-iodide hybrid, [PbI4·4-MAPY] (CP-1) (4-MAPY = pyridin-4-ylmethanamine), that exhibits reversible thermochromism from a lemon yellow to a carmine red when heated from room temperature to 420 K.[74] Single-crystal XRD analysis revealed a phase transition starting at 410 K with a complete transformation at 420 K.

Organic-inorganic hybrid perovskites (OHPs) are made up of a vast range of inorganic anions alternating with a variety of different organic cations and are one of the most extensively studied hybrid crystalline structures.[75] The energy levels of the organic and inorganic elements of the hybrid can be controlled independently which allows for the production of OHPs with different dimensionalities including zero-(0D), one- (1D), two- (2D) and three-dimensional (3D) structure at the molecular level.[76] Peng *et al.* reported on a multifunctional 2D OHP material that can be prepared into an ink and subsequently be used as a thermal sensor.[76] Differential Scanning Calorimetry (DSC) analysis showed that a phase transition occurs when the material is heated from room temperature (298 K) to 387 K. The increase in temperature results in an increase in the distance between the inorganic layers which is expressed macroscopically as a color change from yellow to dark reddish brown.[76] X-ray Diffraction (XRD) characterization, along with Tauc relation, was used to determine the change in optical band gap of the crystals which also contributed to the observed color change. Yu *et al.* reported on solid state thermochromism of an organic-inorganic hybrid molecule, [(PyCH$_2$NH$_3$)$_6$][Pb$_5$I$_{22}$]3H$_2$O .[77] A 2D motif was used to demonstrate color change from orange at room temperature to red at 80 °C (353.15 K); XRD patterns confirmed phase transition at higher temperatures with corresponding color change. Xie *et al.* reported their results on single-crystal to single-crystal (SCSC) phase transition and excitation-wavelength-dependent emission of (COOH(CH$_2$)3NH$_3$)2PbI$_4$ crystal.[78] The color of the single crystal changes from red to yellow during the phase transformation process when heated from room temperature (302 K) to 435 K.

Polymeric thermochromic materials

Polymeric thermochromic materials are increasingly being investigated due to their wide range of tunable chemical and physical properties which include structural stability, biocompatibility and ease of processing.[79] They have applications in several fields, ranging from aeronautics and aerospace design to food packaging. Thermochromic polymers can either have inherent thermo-optical properties or can be made to have such properties with the application of additives such as pigments, dyes etc.

Cholesteric and conjugated liquid crystalline polymers with chiral molecular structures form helical complexes which make them optically active. They express a Bragg's reflection type of thermoresponsive effect on exposure to visible light.[26,80] Manipulation of pitch length of these formations by varying the temperature determines their color and thus make them useful for many sensing applications. Polymeric gels and polymeric systems with microencapsulated thermochromic cholesteric LC pigments also fall under the liquid crystal category.

Conjugated polymers consist of a backbone of alternating single and double bonds with a delocalized π-electron network that contributes to their thermochromic properties.[81,82] A variety of conjugated polymers such as polythiophene, polyaniline, polypyrrole, polyphenylene, poly(phenylene ethynylene), polyacetylene, and polydiacetylene have gained enormous attention as novel functional materials due to stimulus-induced changes that take place in their electronic absorption and emission properties.[82] Polydiacetylene (PDA) has been extensively studied and is well known for its blue-to-red color transition when temperature increases above T_c; studies have suggested that as the polymer transitions from blue to red, it changes structure from a planar to a non-planar state causing a reduction of its "conjugation length".[82-85]

The conjugation length is not a precisely defined parameter, but it is usually used to denote the length of the oligomer that would absorb at the same wavelength as the polymer sample considered.[86] Other studies have suggested that this phenomenon is not related to the conjugation length but rather a change in conformation corresponding to the blue and red phases.[86] PDA has also been shown to exist as isomers of nearly equal energies that are associated with a small torsional rotation of the methyl-terminated side chain substituents which decreases the maximum absorption wavelength from blue (λ_{max} ~ 640 nm) to red (λ_{max} ~ 550 nm).[87]

Thermochromism is very pronounced in substituted poly(thiophene)s because of the temperature-induced torsions of the polymer chain that change the planar geometry of the polymer.[88] When the polymer is planar, the energy band is the widest and the band gap is the narrowest which results in the least energetic π−π* transition.[88] The band gap widens, and the conjugation lengths shorten as the polymeric geometry become less planar which results in a hypsochromic shift of the band corresponding to the π−π* transition.[88] Polythiophenes with side alkyl segments containing at least four carbon atoms display thermochromism.[89]

The mutual ordering of the side chains affects the planar-to-nonplanar conformational transition of the main conjugated backbone of the polymer.[89] Studies have shown that thermochromic behavior is dependent on the balance between electronic (connected either with red or blue shift on heating) and vibration (always connected with blue shift on heating) contributions.[89] The thermal behavior of poly(3-docosoxy-4-methylthio-phene) (PDMT) films have been investigated and it was found that each phase has differing degrees of π-π stacking and extended π-conjugation.[90]

The high temperature, disordered phase had the shortest wavelength spectra due to lowest conjugation and weak π-π stacking interactions while the low temperature annealed phase had the longest reflection spectra due to its extended π-conjugation and greatest π-π stacking.[90] The material also has a partially disordered mesophase that has an intermediate extent of conjugation and display a different color from the other states (Figure 8).[90]
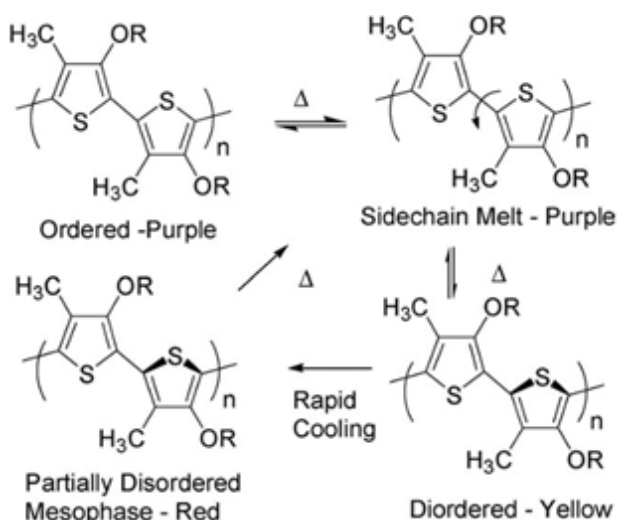
Figure 8 Proposed mechanism for the two-step thermochromic transition for poly (3-docosoxy-4-methylthiophene).[90]

Appropriately selected dopants introduced in specific host materials can drastically modify their optical, electrical, magnetic, or mechanical properties.[88] Experimental results show that plasticizing dopant anions influence the morphology of conducting polymers which in turn modify their transition temperatures.[88] If the polymer is thermochromic, this changes the temperature at which there is a visible color change.

Rannou and group investigated the effect of doping polyaniline (PANI) with diesters of 4-sulfophthalic acid and found that the system showed layered-type supramolecular organization which allowed it to exhibit two glass transition temperatures, T_{g1} and T_{g2} corresponding to the freezing of the movement of the dopant substituents and of the movements of polymer-dopant anion association, respectively.[88] At sub-T_{g1} temperatures, around 280 K, a strong thermochromic effect is observed, i.e., the material turns indigo (λ_{max} = 440 nm) due to increasing charge carrier localization indicating its insulating state.[88]

Thermochromic polymeric systems, embedded with leuco dyes, are formed by the encapsulation of a dye or pigment in a polymer envelope before being embedded into other polymeric matrices.[43] The thermochromic behavior is driven by the interactions between the three components of the system: a color former, a developer, and a co-solvent, leading to a molecular rearrangement of color formers. Phase change of the co-solvent controls the process.[91]

See both and group used Poly (lactic acid) (PLA) matrix along with the anthocyanidin dye cyanidin chloride, dodecylgallate, and the fatty acid hexadecanoic acid to make a nontoxic thermochromic polymer material that was red at 20°C and violet at 70°C.[92] Experimental results indicated that the color change, on heating, occurs at T_g and on cooling during the transformation from the mobile into the rigid amorphous phase of the glassy state.[93]

The amorphous rigid phase does not form when the concentration of the hexadecanoic acid is below the solubility limit i.e., it is completely

dissolved and thus, there is no thermochromism. Scanning electron microscopy shows that separate hexadecanoic acid rich domains exist above the solubility limit. These domains act as a nucleating agent and induce the transformation from the mobile into the rigid amorphous phase which triggers thermochromism.[93,94] In the mobile amorphous phase, the polymer-dye complexes form when multiple hydrogen bonds stabilize the anionic anhydrobase form of cyanidin chloride. During the rigid amorphous phase, the polymer backbone undergoes conformation changes which destabilize the polymer–dye complexes causing it to change into the neutral anhydrobase form (Figure 9).[93,94]
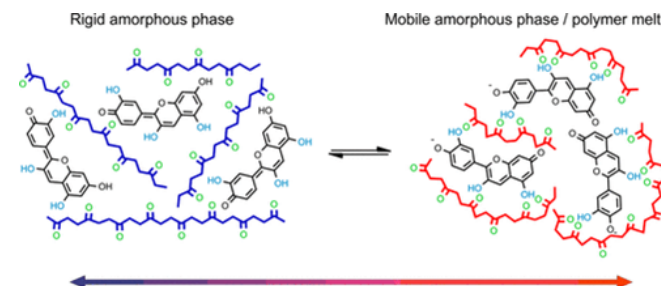
Figure 9 Scheme of the thermochromic effect and the proposed mechanism of reversible formation of PLA-dye complexes triggered by conformational changes of the polymer backbone.[94]

Methods of processing

Thermochromic materials can be characterized and synthesized in multiple ways in order to enhance their performance in various device applications. The use of characterization techniques such as thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) are important in order to understand the structural, optical, and thermal behavior exhibited by thermochromic materials. Consequently, thermochromic materials are often characterized after their synthesis. These procedures are necessary in order to increase their functionality, flexibility as well as prevent them from reacting with external environment. The general term for the technique used is Microencapsulation.[4] Microencapsulation can be divided into three methods namely chemical, physical and physiochemical methods.

Physical methods

The two main physical methods that are used to encapsulate TCMs are Spray Drying and Solvent Evaporation. Spray Drying involves the use of thermochromic and shell material in an oil water emulsion. Droplets are sprayed and drying is performed by passing a gas stream at maximum temperature. The dried particles are separated by a cyclone (dry scrubbers) and filtered. The second method is known as Solvent Evaporation. This is also done using an oil-water emulsion. However, this emulsion includes a polymer solution precursor in a volatile solvent and the thermochromic material. After the solvent evaporates, shells are formed on the thermochromic material leaving behind microcapsules that can be filtered and dried further.[26]

Physical methods of microencapsulation come with multiple advantages as they are low cost, able to produce highly efficient coating materials, and highly stable microcapsules. These methods can be scaled up in a continuous process mode. Aside from these advantages, however, they also possess some disadvantages such as the small amount produced when TCMs are processed in batches and the limited control of particle size.

Chemical methods

In the chemical microencapsulation process, shells are formed at an oil-water interface around the core. The process involves the

utilization of various polymerization and condensation techniques. In this process, the polymerization begins when the free radicals that attack the monomers are triggered during heating or a change in pH is initiated. This sort of polymerization is referred to as radical polymerization. The chemical methods of microencapsulation include in situ, interfacial suspension and emulsion polymerization.[26]

In situ polymerization

In this method, thermochromic materials are added to the solution of a surfactant to create an oil-water emulsion. A separate solution is then formed using monomers. This solution is added to the emulsion formed initially to create microcapsules. Zhu *et al.*[95] used this method to create thermochromic microcapsules with urea formaldehyde as shell material and thermochromic compounds as core material. Additionally, they loaded the microcapsules in wood coatings and discovered that the resulting materials have favorable potential in smart material fabrication applications.[95]

Interfacial polymerization

This method is used if two or more monomers can be connected to the final shell polymer or if the two monomers used are both hydrophobic and hydrophilic individually.[96] As a result, the polymerization takes place at the oil-water interface with two reactive monomers dissolved in the presence of an initiator. Cheng *et al.*[96] used this method to create a thermochromic microcapsule. They used $CoCl_2$, polyvinyl alcohol(PVA) and cyclohexane making up the oil-water interface. PVA was used as the wall material as it possesses qualities such as good film formation and high flexibility.[96] The resulting (CC/PVA-GA) microcapsules had high sensitivity, powerful solvent resistance and thermochromic ability from the loss of (bound) moisture in $[Co(H_2O)_6]^{2+}$. This enables it to have significant potential in coating and printing ink applications.[96]

Suspension polymerization

This method is ideal when both monomers and initiators are either insoluble or poorly soluble in aqueous phase solvent. Consequently, the method involves the suspension of scattered droplets containing thermochromic material, monomers and initiators in an aqueous phase with surfactants and mechanical stirring to assist the process.[96] The free radicals act as initiators and are released into the suspension to facilitate polymerization.

Emulsion polymerization

This method is used in situations where monomers are insoluble or poorly soluble in a solvent in its aqueous phase but the initiator is soluble in the aqueous phase.[95] In this case, emulsification is sustained by the addition of surfactants and mechanical stirring. As described in suspension polymerization, this method also involves scattered droplets that consist of thermochromic materials and monomers in a continuous phase with the help of surfactants. However, the initiator in the water and media solution encourages polymerization. Multiple researchers have successfully performed micro-encapsulation using this method. In a study by Ma *et al.,*[97] the process of microencapsulation for thermochromic dyes was achieved successfully by employing water-soluble monomers or polymers through an emulsion polymerization method. In this method, the thermochromic dyes were transformed into an emulsion in water, after which polymerization occurred on the outer layer in the form of tiny beads containing the thermochromic dyes. This resulted in the creation of microcapsules that effectively shielded the delicate thermochromic dyes from interacting with the components present in building coatings.

Physiochemical methods

This method like its name, combines both physical (phase separation, heating and cooling) with the chemical processes (hydrolysis, crosslinking, and condensation) to accomplish microencapsulation. This includes the following: supercritical emulsion extraction, sol-gel method, coacervation, and melt coaxial electrospinning.

Supercritical emulsion extraction

Organic solvents are extracted continuously from emulsions resulting in the formation of microspheres collected in the form of water suspension at the bottom of a counter current packed tower used in the emulsion extraction. Creating effective fabrication techniques for smart devices can be somewhat challenging. Consequently, Cricho *et al.*[98] propose the fabrication of microcapsules using this technique. These microcapsules are formed with a core of poly-lactic-co-glycolic acid (PLGA) covered by carboxybetaine-functionalized chitosan (f-chi) and loaded with MAG (Methyl Acroloyl Glycin) as well as a water-soluble fluorescein.[98]

Sol-gel processing

This is the most commonly used method of microencapsulation. This synthesis technique has advantages as it is low cost and favorable in large surface area situations. Additionally, it allows for metal dopants to be implemented with ease and can be done at relatively low processing temperatures. The method involves the hydrolysis reaction of thermochromic materials, solvent and emulsifier in a continuous phase to form a colloidal solution. Next, polycondensation of monomers is performed resulting in microcapsules after drying, sintering and curing processes. Nguyen *et al.*[99] used this process to create a sensor that is reversibly thermochromic. Cr-doped Al_2O_3 was processed using the Pechini sol-gel method and its thermochromic behavior was investigated.

The sol-gel process produced better powder at low processing temperatures than previously studied. Additionally, the Cr-doped Al_2O_3 exhibited a reversible color change from pink to gray as the temperature changed within a range of 25–600 C.[99] This reversible color change is dependent on the chromium concentration but is independent of how long the sensor is exposed to a certain temperature range. These sensors have useful applications in overheating warning and temperature monitoring of various devices including aeronautical engine components, hotplates, and furnaces.[99]

Coacervation method

The coacervation process can be classified into simple and complex methods. This classification is dependent on the number of shell materials used. The simple process involves a single shell material while the complex one requires two types of shell materials that are opposite in charge. Complex coacervation yields microcapsules with better morphology, uniform size, and better stability than simple coacervation. This method of coacervation involves the dispersion of thermochromic materials in an aqueous polymer solution to form an emulsion, and an added second aqueous polymer solution of opposing charge. Electrostatic interactions cause the shell material to be deposited on the surface of droplets. Stable microcapsules are formed by crosslinking, solvation or thermal treatment techniques.[95]

Applications of thermochromic materials

Sensors

Thermochromic materials are a major constituent of sensors, especially thermal sensors, as they change color relative to their

temperature. Polydiacetylene (PDA) is a polymer that has been used in various thermochromic sensors as it exhibits a distinct color change at a favorable range of temperatures. For example, a PDA sensor has been developed by adding a dopant which allows it to exhibit reversible thermochromism. Additionally, they can also be used in biological sensing. ThermoSpot[100] is a biosensor which is applied as a skin sticker to monitor hypothermia. This sensor changes color from green to black due to hypothermia.

Smart windows

Smart windows are windows that help to filter undesirable solar radiation. They are typically used in buildings that are designed to be more conscious of climate change.[101] Thermochromic materials are an important aspect of creating these smart windows as they facilitate energy efficiency in these buildings. They are capable of this functionality by regulating temperature during different seasons by trapping heat during the colder months and decreasing it in the warmer months. This is usually accomplished by the changing optical properties of these thermochromic materials based devices (namely reflectance and transmittance).

The thin film thermochromic material used in these applications is usually in its cold state. This implies that it reacts like a semiconductor

making it less reflective in the near infrared radiation.[102] However, this material changes its structure from monoclinic to rutile as temperature increases. This transition is known as a semiconductor to metal transition (or vice-versa) as it begins to act like a semi-metal reflecting more solar radiation in this state. This is illustrated in (Figure 10).[102]
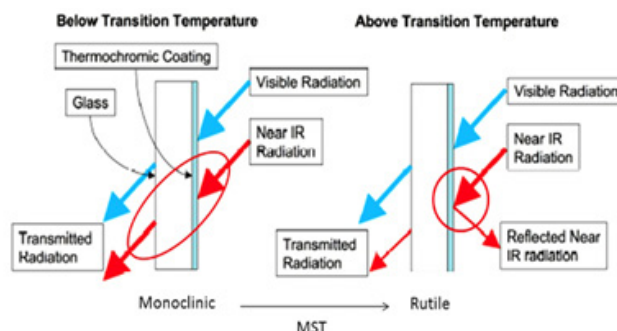
Figure 10 Schematic representation of thermochromic materials applied as an intelligent windows coating.[102]

A summary of various applications of thermochromic materials is presented in Table I.

Table I Applications of thermochromic materials

Polymer	Color change & temperature range	Mechanism	Device	Reference
Polydiacetylene (PDA)				
PDA/silica nanocomposite	Blue → Red, Reversible 47 °C	Reduction in conjugation length due to solvation stresses on PDA backbone	Temperature sensor	103
Low temp thermochromic PDA nanofibers	Blue → Red, Irreversible PCDA-Me: 28–29 °C PCDA-EGME: 21–24°C TCDA-Me: 15–18 °C TCDA-EGME: 10–12°C HCDA-Me: 7–10 °C HCDA-EGME: 2–5 °C	Thermally induced conformational distortion of PDA backbone; All-trans conformations of the alkyl groups (blue phase) are converted to some gauche forms (red phase)	Low temperature sensors for goods that require refrigeration or freezing	104
PDA vesicles with zinc(II)/ zinc oxide nanocomposites	Blue → Purple, Reversible 10–90 °C (fine-tuned by varying photopolymerization time) Purple → Red >110 °C Irreversible	Blue → Purple due to relaxation of poly(PCDA) conjugated backbone but maintains lamellar structure Purple → Red due to melting of rigid conjugated backbone which results in an amorphous phase	2D and 3D temperature sensors	105
Polythiophene				
P(PyT1-co-3DT25)	Orange → Green Reversible 25-80 °C	Increase in conjugation length of the polythiophene chain	Thermal sensors, Optoelectronic devices	106
Poly(3-alkylthiophene)	Transparent orange → translucent deep violet irreversible 80 - 10 °C	Change of polymer conformation from a rigid rod geometry at low temperatures to a random coil conformation at higher temperatures	Energy saving windows, nonlinear optoelectronic devices	107
Polylactic acid(PLA)				
PLA composite/delphinidine chloride (dye)	Green → Yellow Reversible 20-70 °C	Change occurs during the PLA dye formation as a result of a structural rearrangement of the delphindine chloride moving from a neutral phase to a anaionic phase	Biosensors and Thermal Sensors	94

Conclusion

Thermochromic materials have been studied vigorously by researchers over the years for their wide variety of applications in modernization, urbanization, and the improvement of health care systems. This review presented a discussion of thermochromism in organic, inorganic, hybrid, and polymeric materials since these are the major types of materials that exhibit thermochromism.

Additionally, these materials require investigation via synthesis and processing routes to ensure that they are more efficient and durable when used in specific applications. Microencapsulation is one of the fundamental techniques used in the improvements of thermochromic materials. The application of these materials include bio & thermal sensors, packaging and smart windows, TCMs will have even more future applications due to their tailorable properties that will allow them to be used in areas not previously considered. The increasing number of scientific breakthroughs will continue to broaden the role and scope of thermochromic materials in numerous applications that are significant to the modernization and improvement of industries today.

These include critical areas of the global economy such as defense, energy, health, manufacturing, pharmaceuticals, semiconductors, transportation, etc. As economic and environmental factors become more relevant, the high transition temperature and cost of thermochromic materials become less important, especially from the perspective of 3D-Printing and the ability to reduce their phase transition temperatures, by processes such as doping and annealing. Their non-invasive nature of conveying the desired measurement quantity, in real time, is just one of their many positive attributes.

Acknowledgments

Funding

Conflicts of interest

The authors declare that there are no conflicts of interest.

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