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Discoloration mechanism, structures and recent applications of thermochromic materials via different methods: A review

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ABSTRACT

Thermochromic material is a kind of smart material whose color will vary as the result of the phase transition caused by the temperature change. The characteristics of thermochromic materials are the memory functions to the temperature, having great potential applications in aerospace, military, anti-counterfeiting technology, construction and other fields. In recent years, many kinds of thermochromic materials have been prepared by different methods and their discoloration mechanisms are various according to published literatures. In this paper, the classification, discoloration mechanism, preparation methods, application fields and development trend of thermochromic materials are reviewed.

1. Introduction

Functional materials have occupied more than 85% in the field of new materials, which is the hot spot in the development of high technology. Since the 1970s, thermochromic compounds, a new type of functional materials with unique color change, have attracted the attentions of many scientists [1–3]. Thermochromic material contains discoloration substances and other auxiliary components, which is also called temperature sensitive material. The color can vary with the change of temperature in a certain temperature range, because the visible absorption spectrum of discoloration compounds or mixtures can be changed when heated or cooled [4,5].

Thermochromic material has two types: irreversible and reversible discoloration. As shown in Fig. 1, there are everal forms of discoloration [6]. Thermochromic discoloration often accompanies with photochromic reaction to enrich the functionality and intelligence of materials [7–9]. The applications of thermochromic material have been explored in many fields, such as aerospace, military, smart windows, printing technology, textile, architectural coatings and so on [10–15]. Some thermochromic materials can be used in the toys for children and anti-counterfeiting technology, but there are few researches concerned with food packaging. When people pay more attentions to the food safety, thermochromic materials will have a huge potential application in the field of food packaging.

2. Classification and discoloration mechanism of thermochromic materials

2.1. Classification

Thermochromic materials can be divided into inorganic, organic and liquid crystal types. Inorganic thermochromic materials mainly include metal iodide, double salt, transition metal compounds, metal alloys, metal chloride, et al., having advantages of good temperature resistance, durability, light resistance and processability [16]. Organic thermochromic materials occupying most quantities and species contain spiropyrans, fluoranthene, triarylmethane, ethylene with substituents and organic complexes [17], having advantages of optional and adjustable colors, low discoloration temperature, high sensitivity of discoloration and low cost. Therefore, organic thermochromic materials show significant advantages compared with other kinds of thermochromic materials, which have get much more attentions [18,19]. Liquid crystal can be divided into smectic, nematic and cholesteric types according to molecular arrangement, which has the advantages of good stability and high thermal sensitivity, but its application is limited because of its chemical sensitivity and high cost [20].

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2.2.2.2. Mechanism

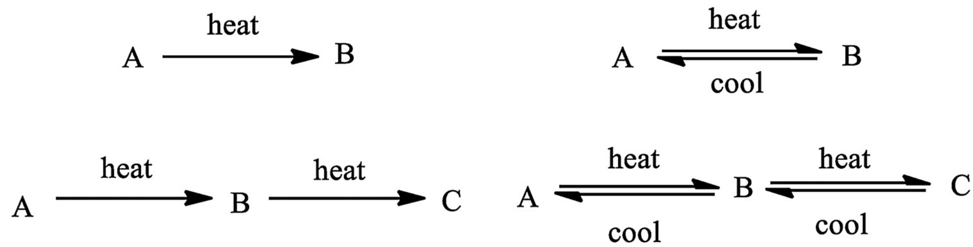

Fig. 1. Forms of the discoloration for thermochromic materials. (A, B and C denote different colors).

Table 1
Components and effects of organic reversible thermochromic materials [21].

Component	Sort	Effect
Electron donor	Triaryl and their phthalides, fluoran, indole phthalide, spiro-pyran, et al.	decide the color
electron acceptor	Phenols, sulfonic acids, carboxylic acids, et al.	decide the color chroma
Eolvent compounds	Alcohols, esters, et al.	decide the discoloration temperature

2.2. Discoloration mechanism

2.2.1. Organic reversible thermochromic materials

2.2.1.1. Intermolecular electron transfer. Such thermochromic materials are generally composed of electron donor, electron acceptor and solvent compounds. The compositions and roles of each part are shown in Table 1 [21]. In general, the oxidation-reduction potential of the electron donor is relatively close to that of the electron acceptor, and electron transfer occurs between them resulting in the molecular structure change of the electron donor when the temperature changes. The direction of the reduction reaction depends on the temperature, resulting in the change of system color [16]. A typical electron transfer process is shown in Fig. 2 (a).

A new electron donating-accepting inorganic-organic hybrid, $[Hpyz]_2[Ag_2\ I_4]\cdot H_2O$ ($Hpyz^+$ = monoprotonated pyrazinium), has been constructed by Hao [22]. Pyrazinium iodoargentate exhibits versatile photo- and thermo-chromism due to the reversible hydration-dehydration, as well as subsequent intermolecular electron transfer and changes of intermolecular charge transfer state.

2.2.1.2. Structural changes in the molecules. Some thermochromic materials themselves appear discoloration phenomenon when the temperature rises, because the molecular structures of such materials are susceptible to temperature change [23].

2.2.1.2.1. Intramolecular proton transfer. When the temperature rises, the protons in the molecules are transferred and the molecular structure of the material changes, resulting in the reversible thermochromic phenomenon. The discoloration of Schiff base compounds is based on this mechanism. For example (as shown in Fig. 2(b)), salicylaldehyde acetaminide is a kind of Schiff base containing –O—H and can form the intramolecular hydrogen bond. When the temperature increases, protons are rapidly transferred from the oxygen atoms to the nitrogen atoms, the enol type of salicylaldehyde acetaminide turns into the cis-form ketone and the color changes reversibly.

2.2.1.2.2. Dimensional structure change. Molecular dynamics simulation researches have shown that polythiophene containing alkyl segments are easily changed from planar to stereo structure with the temperature increasing [24,25]. The polythiophene conjugate repeating unit containing the five-membered heterocyclic ring is coplanar at a lower temperature. When the temperature rises, the C-S bond is distorted and the conjugate repeating unit changes from the planar structure to the spatial structure (as shown in Fig. 2(c)). The optical absorption of polythiophene will have a blue shift due to the increase of the molecule band gap.

2.2.1.3. Crystal transition. Crystal transformation is a common discoloration mechanism for inorganic thermochromic materials. However, many organic thermochromic materials also follow this mechanism. The related research has shown that the π-π interaction of 2,3-bis(phenyle-thenyl)-5,6-dicyanopyrazine crystal can be enhanced by increasing the temperature, the lattice contraction and discoloration will appear [26]. When the temperature reaches to 174.5 °C, the compound has a reversible change from yellow to red.

2.2.1.4. Ring opening of molecule. The discoloration of spiropyran and oxazine compounds is due to the breakage of C—O in molecules and the formation of the conjugate system with the temperature rising. However, the negative charge density of the oxygen atoms in the naphthalene ring is very high after opening the rings of the compounds, the structure is unstable and the color stability is poor. The discoloration mechanism of spiropyrane is shown in Fig. 2(d).

In addition, the discoloration of organic materials is also related to electron spin state, pH value and other factors [20]. Some researchers have prepared transparent spin-crosslinked composite films which are in a high-speed spin state and colorless at 27 °C. When the temperature decreases, this film becomes purple. The discoloration system consists of acid-base indicator such as phenol red, phenolphthalein and other weak acids (fatty acids) providing the protons. When heated to a certain temperature, the carboxyl protons are activated and can react with the affinity substance, resulting in the gain and loss of proton. When cooled, the proton in the carboxyl and the color of the material will recover.

2.2.2. Inorganic reversible thermochromic materials

The factors of the discoloration for inorganic thermochromic materials mainly refer to the changes of crystal lattice, ligand geometry and crystal water. The discoloration of the inorganic oxide is related to the change of the crystal structure, while the inorganic complex is related to the coordination structure or hydration degree. Common inorganic thermochromic materials and their discoloration principles are shown in Table 2 [16].

2.2.2.1. Mechanism of crystal transformation. Most metal ion compounds are influenced by the crystal transition and can show the discoloration. Some discoloration materials in the crystalline state will generate the lattice displacement when heated, resulting in the change of crystal form. After returning to the room temperature, the original crystal form and the color are restored in time [18]. Such as Cu_2HgI_4 and Ag_2HgI_4, their crystal forms are positive tetrahedral structure at low temperature, and then become cubic structure when heated. The dependence of the two crystal structures on the temperature can make the compound change its color [27].

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