Review on research and application of phase change materials in cold storage refrigerator

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Abstract. Phase change material energy storage technology can effectively improve energy efficiency and alleviate environmental deterioration. Therefore, it is widely used in cold chain equipment such as cold storage refrigerators. In this paper, the low-temperature phase change materials (T_m<10°C) for refrigerators were reviewed, and the advantages, disadvantages and research of each phase change material were analyzed and compared. In addition, this paper reviews the effect of microcapsule technology on the properties of low-temperature phase change materials, and introduces the application of cold storage refrigerator in food and pharmaceutical cold chain. Finally, the research direction of cold storage refrigerator is prospected and the key problems to be solved are put forward.

1. Introduction

Cold chain logistics is a kind of logistics system, which usually refers to frozen and refrigerated goods such as food, medicine or biological products, in the production, transportation, sale and consumption of each link before, always maintained at the optimal refrigeration temperature, at the same time to reduce loss and maintain quality as the goal [1, 2]. In China, a large amount of food is not guaranteed by the cold chain every year, which leads to food decay, with a loss rate of more than 20%, causing serious waste of energy and resources [3, 4]. Phase change material energy storage technology can store and release a large amount of heat energy reversibly, which is a technology that can effectively alleviate environmental deterioration and energy shortage [5]. Low-temperature phase change materials (melting temperature below 10°C) are widely used in cold chain transportation equipment such as cold storage refrigerators due to the high latent heat and constant phase change temperature. According to the cold chain transportation demand at different temperatures, the effective utilization of energy can be realized by configuring suitable phase change materials. At present, the refrigeration forms used in the refrigerator are mainly divided into mechanical and cold storage. The refrigerators with mechanical refrigeration system have the following characteristics: high equipment cost and maintenance, high energy consumption, noise and low economic benefit [2, 6]. The cold storage refrigerators with phase change materials have the characteristics of high loading efficiency, basically no noise, using night
power, low cost and flexibility [7-9], which can solve the ‘first mile’, ‘last mile’ and multiple small batch distribution problems in cold chain transportation [10, 11].

In this paper, the classification and research of low-temperature phase change materials, the influence of microcapsule technology on the performance of phase change materials, and the application of cold storage refrigerators in food and pharmaceutical cold chains are described. The research priorities of cold storage refrigerators in the future are summarized and prospected, aiming to further optimize the cold storage refrigerators and improve the cold chain transportation technology in China.

2. Low-temperature phase change materials

There are three ways of thermal energy storage, namely sensible heat method [12], latent heat method [13, 14] and chemical heat storage method [15]. Due to the phase change of materials at the melting point, the latent heat energy storage has a high energy storage capacity and a small change of working temperature. Therefore, in a specific temperature range, the latent heat energy storage method of phase change materials is better [16, 17]. For example, for the storage and transportation of temperature-sensitive products (certain food, pharmaceutical or biological products, etc.), the use of phase change materials can basically maintain them at a constant temperature [18]. As shown in Figure 1, low-temperature phase change materials can be divided into inorganic, organic and composite types. Moreover, ideal phase change materials should have the properties in Table 1.

Table 1. Properties of ideal phase change materials [13, 19-21].

| Classification   | Properties                                      |
|------------------|-------------------------------------------------|
| Physical         | Small volume change, low steam pressure, high density and phase balance |
| Chemical         | Good chemical stability, non-corrosive, non-toxic and non-flammable |
| Thermal performance | High thermal conductivity, suitable phase change temperature, high latent heat and high specific heat capacity |
| Kinetic          | No or low undercooling and high crystallization rate |
| Economic         | Rich resources, easy access, low cost, recyclable and non-polluting |

Figure 1. Classification of phase change materials [3, 19, 22].

2.1. Inorganic phase change materials

Inorganic phase change materials mainly include metal alloys, inorganic compounds and salt hydrates [19]. The physical parameters of common inorganic low-temperature phase change materials are shown in Table 2. Most metal alloys are limited in the field of low temperature energy storage due to their high melting point [23]. Inorganic compounds usually refer to compounds without carbon and some carbon oxides. Because most inorganic compounds have small latent heat and are harmful to human body, they
are difficult to be widely used in cold storage systems. The cheapest and most common inorganic compound is ice, which has the advantages of high latent heat, constant phase change temperature, high specific heat and environmental protection [24]. Salt hydrate has a certain application prospect in the field of low temperature. Its general chemical formula is \( AB \cdot n(H_2O) \), where \( n \) represents the number of water molecules, and \( AB \) represents metal carbonates, sulfites, phosphates, acetates or chlorides [25]. The phase transformation process of salt hydrate is mainly dehydration and hydration, which can be described by equation (1)(2). In the process of dehydration or melting of salt hydrated, part or all of the crystal water will be lost [13]. Salt hydrate is an ideal inorganic low-temperature phase change material with high latent heat and thermal conductivity, small volume change, high availability and low cost. However, it has the disadvantages of low specific heat, easy corrosion, undercooling, inconsistent melting and phase separation [26].

\[
AB \cdot nH_2O \leftrightarrow AB \cdot mH_2O + (n-m)H_2O \tag{1}
\]

\[
AB \cdot nH_2O \leftrightarrow AB + nH_2O \tag{2}
\]

Munyalo et al. [27, 28] prepared two low-temperature phase change materials by adding 0.2wt.% - 1wt.% magnesium oxide (MgO) and 0.2wt.% - 1wt.% multi-walled carbon nanotubes (MWCNT) in \( BaCl_2 \cdot 2H_2O \) solution. It was found that the addition of MgO and MWCNT decreased the undercooling and increased the stability. Lang et al. [29] prepared a new type of low-temperature phase change material composed of three kinds of salt hydrates. It was found that sodium alginate as thickener could change the melting temperature and latent heat. Moreover, NaF, \( Na_2B_4O_7 \cdot 10H_2O \) and nano activated carbon were effective nucleating agents to reduce undercooling. In view of some shortcomings of salt hydrates, table 3 lists the corresponding improvement measures.

Table 2. Physical parameters of some inorganic phase change materials (\( T_m \leq 10^\circ C \)) [23, 30].

| Name                  | Chemical formula | Type              | Melting temperature \( T_m / ^\circ C \) | Latent heat \( H / kJ/kg \) | Thermal conductivity \( k / W/(m\cdot K) \) |
|-----------------------|------------------|-------------------|------------------------------------------|----------------------------|---------------------------------------------|
| Zinc chloride trihydrate | ZnCl₂·3H₂O       | Salt hydrate      | 10                                       | −                         | −                                           |
| Lithium chlorate trihydrate | LiClO₃·3H₂O     | Salt hydrate      | 8                                        | 253                       | −                                           |
| Antimony chloride    | SbCl₃            | Inorganic compound| 4                                        | 33                        | −                                           |
| Deuterium oxide      | D₂O              | Inorganic compound| 3.7                                      | 318                       | 0.595                                       |
| Phosphorus oxychloride | POCl₃           | Inorganic compound| 1                                        | 85                        | −                                           |
| Water                | H₂O              | Inorganic compound| 0                                        | 333                       | 0.598                                       |

Table 3. Improvement measures of salt hydrates.

| Shortcomings                  | Improvement measures                                      | Reference |
|-------------------------------|-----------------------------------------------------------|------------|
| Inconsistency melting         | Reduce separation through encapsulation of phase change materials | [31, 32]  |
|                               | Solid salt suspension by adding thickener                  | [33]       |
|                               | Add extra water so that molten crystals do not produce supersaturated solutions | [34]       |
|                               | Modify the chemical composition of the system to achieve consistency | [35]       |
| Supercooling caused by poor nucleation | Add nucleating agent                                      | [19]       |
| Phase separation              | Add relevant chemicals to increase solubility              | [36]       |
| Corrosion                     | Use corrosion-resistant materials                           | [37]       |
2.2. Organic phase change materials
Organic phase change materials mainly include paraffin and non-paraffin [19, 38]. Common organic phase change materials are shown in Table 4. Paraffin is a saturated hydrocarbon material with wax-like consistency at room temperature, and its main component is alkanes (expressed by CnH2n+2, n is the content of alkanes). Paraffin has the advantages of harmless, reliable, inexpensive and non-corrosive, but its thermal conductivity is lower than that of non-organic phase change materials, which leads to the decrease of energy storage rate [20]. The available organic non-paraffin phase change materials mainly include fatty acids (chemical formula is CH3(CH2)nCOOH), which have good chemical stability, corrosion resistance and nontoxic properties [20, 22, 39].

The thermal conductivity of organic phase change materials can be effectively improved by adding nanomaterials, expanded graphite or carbon fibers [40, 41]. Zhou et al. [42] prepared binary organic phase change materials of n-octanoic acid-tetradecane (mass ratio 49:51) with melting temperature of 1.0°C and latent heat of 191.8kJ/kg by low eutectic method, and found that this material can be used in the field of low temperature energy storage. At the same time, in order to find a low-temperature material suitable for cold storage at 2~3°C, decanoic acid-palmitic acid-expanded graphite phase change material was prepared [43]. Using n-octanoic acid-decanoic acid (71:29) and 8% expanded graphite as the substrate, Li et al. [44] prepared a phase change material with melting temperature and latent heat of 0.9°C and 112.7kJ/kg, respectively, which was suitable for pharmaceutical cold chain.

Table 4. Physical parameters of common organic phase change materials (Tm<10°C) [23, 30, 45].

| Name          | Chemical formula | Type       | Tm / °C | H / kJ/kg | Relative molecular mass |
|---------------|------------------|------------|---------|-----------|-------------------------|
| Dimethyl adipate         | C12H14O4         | Non-paraffin | 9.7     | 164.6     | 174.2                  |
| n-Pentadecane         | C13H32           | Paraffin   | 168     | 212.4     |                         |
| Formic acid          | CH2O2            | Non-paraffin | 7.8     | 247       | 46.0                   |
| n-Tetradecane        | C4H10            | Paraffin   | 227     | 198.4     |                         |
| n-Tridecane          | C14H22           | Paraffin   | 6       | 184.4     |                         |
| Triethylene glycol   | C4H4O4           | Non-paraffin | 7       | 247       | 150.2                  |
| n-Dodecane           | C12H26           | Paraffin   | 9.5     | 216.2     | 170.3                  |
| n-Undecane           | C11H22           | Paraffin   | 25.5    | 141.9     | 156.3                  |
| n-Decane             | C10H22           | Paraffin   | 29.6    | 201.8     | 142.3                  |
| n-Nonane             | C9H20            | Paraffin   | 53.5    | 120.6     | 128.3                  |

2.3. Composite phase change materials
Single inorganic and organic phase change materials have many defects, which are difficult to be widely used in the field of low-temperature energy storage. The suitable composite method can be used to prepare low-temperature phase change materials with suitable melting temperature and excellent performance. Eutectic phase change material is a type of composite low-temperature phase change material, which is usually a crystallization mixture formed by melting and freezing of two or more low melting point components in the crystallization process. According to the component types, it can be divided into inorganic eutectic, organic eutectic and inorganic-organic eutectic phase change materials [19, 30]. Table 5 lists some low-temperature eutectic phase change materials.

Eutectic salt solution is a main type of inorganic eutectic phase change material. Eutectic salt solution is widely studied in freezing cold chain with temperature below 0°C. Xie et al. [46] studied the ternary eutectic solution composed of K2HPO4·3H2O, NaH2PO4·2H2O and Na2S2O3·5H2O, and prepared low-temperature phase change materials with melting temperature of −5.30°C and latent heat of 161.8kJ/kg by impregnation method and modified expanded graphite adsorption. They had low supercooling and good thermal stability, and had broad application prospects in the preservation and transportation of frozen food and household refrigeration. In view of the transportation of meat and ice cream products, Liu et al. [47] proposed a cold storage device combined with phase change materials, and developed a low-cost binary eutectic phase change cold storage material with a melting point of −26.7°C. The cold storage device is more energy-saving than the traditional mechanical refrigeration system. Cong et al. [48] prepared NaCl-NaNO3, NaCl-Na2SO4 and NaCl-KCl solutions and their phase transition temperatures were −27, −21 and −23°C, respectively, which were suitable for freezing applications in cold chain. At the same time, it was found that the melting heat of ternary eutectic salt solution was
affected by the base solution, additives and eutectic ratio. Although eutectic salt solution is widely used in low-temperature environments such as freezing cold chain, its corrosion problem cannot be ignored [37]. Advanced encapsulation technology and corrosion resistant materials are worthy of further study.

Table 5. Common low-temperature eutectic phase change materials (Tm<0°C).

| Component | Tm / °C | H / kJ/kg | Reference |
|-----------|---------|-----------|-----------|
| 6.49wt.%KsSO4 + H2O | −1.55 | 26.88(kJ/mol) | [18] |
| C10H16COOK-KCl (85.72:14.28) | −2.8 | 254.6 | [49] |
| 0.19wt.%NaOH + H2O | −2.8 | 265.98 | [45] |
| Tetradecane + Octadecane | −4.02 | 227.52 | [18] |
| Calcium lactate + NH4Cl (50:50) | −4.3 | 265.2 | [50] |
| 90wt.%NaCl + H2O | −5 | 289 | [51] |
| 0.272wt.%ZnSO4 + H2O | −6.5 | 235.75 | [45] |
| 0.225wt.%BaCl2 + H2O | −7.8 | 246.44 | [45] |
| Zein + Dodecane (70:30) | −10 | 34.5 | [52] |
| 0.195wt.%KCl + H2O | −10.7 | 253.18 | [45] |
| CH3OH + CH3COONOa + H2O (1:01:08) | −14 | 172 | [53] |
| 0.35wt.%Ca(NO3)2·3H2O + H2O | −16 | 199.35 | [45] |
| 0.195wt.%NaCl + H2O | −16 | 248.44 | [45] |
| ClimesIC-18 (NaNO3 + H2O) | −18 | 306 | [54] |
| 0.397wt.%Na2CO3 + H2O | −18.5 | 187.75 | [45] |
| 18%NaCl + 5%SAP + 0.03%diatomite + H2O | −18.98 | 120.6 | [55] |
| TMP + NH4Cl + H2O + TiO2 + PAAS | −19.9 | 246.8 | [56] |
| 0.224wt.%NaCl + H2O | −21.2 | 228.14 | [45] |
| 30.5wt.%Al(NO3)3 + H2O | −30.6 | 131 | [18] |
| MgCl2 + MWCNTs + H2O | −34.54 | 146.9 | [57] |
| 0.36wt.%CuCl2 + H2O | −40 | 166.17 | [45] |
| 0.298wt.%CaCl2 + H2O | −55 | 155.52 | [45] |
| 0.51wt.%ZnCl2 + H2O | −62 | 116.84 | [45] |

3. Microencapsulation of low-temperature phase change materials

Microencapsulation of low-temperature phase change materials is to encapsulate one or several low-temperature phase change materials by physical, chemical or physical-chemical methods to form micron-sized core-shell capsules (diameter 1-1000μm) [18]. The physical methods include air suspension coating, spray drying, solvent evaporation and electrostatic precipitation. Chemical methods include suspension polymerization, interfacial polymerization, emulsion polymerization, in situ polymerization and suspension crosslinking. Physical-chemical methods include condensation, ionic gel and sol-gel [58, 59]. As shown in Figure 2, different types of core-shell capsules can be obtained according to the physical and chemical properties of the core material, the composition of the core and shell, and different microcapsule technologies. Microcapsule low-temperature phase change materials have small size, which is conducive to solving the problems of supercooling, phase separation, leakage and corrosion of traditional phase change materials [60, 61]. In addition, the microencapsulated low-temperature phase change material has the cycle availability, which can be processed into various polymer products and further extend the cold chain terminal. It is an excellent cold storage material for short-distance refrigerated transportation [62].

In recent years, many scholars have studied the low-temperature microcapsule phase change materials. Zhao et al. [62] synthesized non-crosslinked copolymer shells by in-situ suspension copolymerization of harmless styrene and methyl methacrylate, and successfully encapsulated n-dodecane, n-tridecane and n-tetradecane by microphase separation. Thus, three recyclable microencapsulated low-temperature phase change materials (LTPCMs) were obtained: n-do-LTPCM, n-tri-LTPCM and n-tetra-LTPCM. At the same time, it was found that n-tetra-LTPCM-65 had good cold release performance, which could meet the needs of short-term refrigerated transportation of food,
medicine or biological products. Fang et al. [63] prepared microencapsulated phase change materials with calcium carbonate as shell and tetradecane as core by using sodium dodecyl sulfate and alkylphenol polyoxyethylene ether as mixed templates. The optimal mass ratio of core to shell was 50:50, and the microencapsulation efficiency was 25.86%. Due to its good thermal stability, it has great application potential in cold storage. However, its microencapsulation efficiency is low, and it is difficult to mass production. At the same time, its thermal conductivity is very high, which is not conducive to the cryopreservation of temperature-sensitive food, medicine or biological products. Fu et al. [64] prepared a new composite phase change cold storage slurry by dispersing tetradecane@polystyrene-silica (Tet@PS-SiO₂) phase change material into the base fluid. The results showed that the melting latent heat of the synthesized capsule was 83.38J/g and a regular spherical core-shell structure, and had good mechanical stability and thermal stability. Therefore, Tet@PS-SiO₂ slurry was a fluid that could be used for cold energy storage. However, it did not further study the thermal buffer capacity (i.e., holding time). In order to solve the leakage problem of dodecane (T_m=−9.6°C) in the use process, Chen et al. [65] infiltrated it into the hydrophobic fumed silica to prepare a stable molding dodecane/hydrophobic fumed silica phase change material. After cold storage experiments and software simulation, it was found that it has high enthalpy, good thermal stability and cycle performance, and is a good cold storage material. Pérez-Masiá et al. [52] developed a new type of food packaging material, which used electrospinning technology to coat corn protein with dodecyl whose phase transition temperature is −10°C; But the packaging technology is complex and expensive, it is difficult to achieve large-scale industrial production.

From the above research, it can be seen that the research of low-temperature microcapsule phase change material core mainly focuses on paraffin with low phase change temperature. Moreover, most scholars have studied the low-temperature microencapsulated phase change materials with temperature above 0°C, while there are relatively few studies on the phase change temperature below 0°C. However, the microencapsulated phase change materials within this temperature range are exactly required for some food, medicine or biological products.

![Figure 2. Morphology of different types of microcapsule [58].](image)

4. Application of cold storage refrigerator in cold chain

The packaging forms of low-temperature phase change materials used in cold storage refrigerators mainly include: cold storage plate, cold storage bag and cold storage box, as shown in Figure 3. The cold storage plate has the advantages of long service life and large cooling capacity. The cooling process is completed by releasing the cooling capacity stored in the eutectic salt solution after freezing [66]. At
the end of food and pharmaceutical cold chain, cold storage bags are often combined with temperature control incubators to achieve the purpose of cold preservation. Cold storage boxes are often used for the preservation and transportation of some drugs like vaccines. The existing research on cold storage refrigerator mainly focuses on low-temperature phase change materials, while the actual effects of cold storage plates and cold storage bags used in cold storage refrigerators in food and pharmaceutical cold chain, such as the quality change of fresh food, the change of nutritional quality, the cold storage effect of drugs and the temperature fluctuation in the refrigerator are relatively few.

Figure 3. Cold storage plate, cold storage bag and cold storage box [3, 18].

4.1. Cold storage refrigerators for food cold chain transportation
For perishable foods, including fruits, vegetables, dairy products and fish products, it is necessary to maintain cold storage or freezing state throughout the cold chain. If the cold chain breaks occur, the perishable food cannot be stored in the required temperature range, which will stimulate the growth of pathogens and spoilage microorganisms, so that the products cannot be eaten [67]. Table 6 lists the optimal storage temperature of various foods in refrigerated transportation.

Table 6. Optimum storage and transportation temperature of various foods.

| Temperature area                      | Temperature | Food category                                      |
|---------------------------------------|-------------|---------------------------------------------------|
| Fruit and vegetable preservation area  | 2 ~ 8°C     | Apples, pears, citrus, grapes and other fruits    |
|                                       |             | Fresh vegetables such as cabbage, celery, tomato and carrot |
|                                       |             | Eggs, beer, drinks and other foods                |
| Meat and fish preservation area        | 0 ~ 2°C     | Fresh fish or pork, beef, chicken and other fresh meat |
| Water temperature cold storage area    | −2 ~ −3°C   | Cheese, milk, etc.                                |
| Micro-frozen cold storage area         | −3 ~ −5°C   | Some aquatic products, butter, sausage, etc.      |
| Soft freezing area                     | −6 ~ −8°C   | Seafood, unfrozen meat, etc.                      |
| Mild freezing area                     | −10 ~ −14°C | Frozen fruits and vegetables and some frozen meat products |
| Rapid freezing zone                    | below −18°C | Ice cream, frozen fish and some frozen meat products |

Figure 4. Incubator structure and layout of cold storage plate.

With the improvement of people’s quality of life, more and more attention has been paid to the texture and flavor of food. How to maintain a stable and sufficient low temperature in the process of product storage and distribution is one of the most difficult challenges for fresh food [68]. In order to meet the needs of cold storage and preservation of different fruits and vegetables, Xu et al. [69] developed a multi-temperature storage and preservation incubator combined with vacuum insulation technology. Two kinds of phase change materials were used: n-octanoic acid-butyric acid (T_m = 7.1°C) and potassium sorbate-water (T_m = −2.5°C). The incubator structure and the layout of the cold storage plate are shown in Figure 4. At the same time, the software was used to simulate the temperature field in the incubator.
The results showed that the middle temperature zone and low temperature zone of the incubator could maintain low temperature for 13 and 14h at 7 ~ 9°C and −2 ~ 0°C, respectively. Moreover, these phase change materials had stable thermal properties and were environmentally friendly, and had great application potential in the cold chain of fruits and vegetables. Tang et al. [70] used pure water, 18.8% NaCl, 46.3% C2H6O and 29% CaCl2 solution to make cold storage bags in the insulation box, and used no cold storage bags as control to simulate the short-distance transportation of tuna meat in summer. The sensory indicators, core temperature, thiobarbituric acid value, texture and other related physical and chemical indicators of tuna meat were determined. The results showed that the insulation box with 18.8% NaCl could maintain the quality of tuna meat and keep it frozen for 2h, which was suitable for short-distance terminal transportation. The insulation box with 46.3% C2H6O is not suitable for the distribution of tuna meat due to its short refrigeration time and high cost; The tuna meat can be maintained at −40°C for 2.5h in a 29% CaCl2 insulation box, and the center temperature is only −20.74°C after 5h of freezing transportation, which can well maintain the quality of tuna meat. Table 7 summarizes the research on other low-temperature phase change materials suitable for food cold chain.

Table 7. Low-temperature phase change materials for food cold chain refrigerators.

| Components | Tm ℃ | H kJ/kg | Performance evaluation | Actual application effect | Reference |
|------------|-------|---------|------------------------|--------------------------|-----------|
| 75.5% Na2SO4·10H2O | 6.4 | 141 | Good thermal stability, basically no undercooling and phase separation | The insulation box constructed with phase change materials and vacuum insulation board has high feasibility and excellent refrigeration characteristics, which is suitable for fruit and vegetable cold chain. | [4] |
| 12.5% PAAS | | | | | |
| 0.25% Deionized water | | | | | |
| 3% Borax | | | | | |
| 16% / 4% NH4Cl / KCl | −35.54 | 146.9 | High latent heat and thermal conductivity, low undercooling and good thermal stability | It is suitable for low temperature environments such as special cold chain and cold storage plate refrigerator. | [57] |
| CaCl2-Ca(OH)2-Xanthan | | | | | |
| 1wt.% MWCNT | | | | | |
| 1% Sodium polyacrylate | 0.294 | 334.4 | No undercooling, high thermal conductivity | Using the phase change material and vacuum insulation board to build a low temperature refrigerated transport box can keep the quality of yogurt 87h. | [73] |
| 0.1% MWCNT | | | | | |
| H2O | | | | | |

The cold storage refrigerator with excellent phase change materials can maintain the quality of food for a long time. Therefore, for different foods, phase change materials with high latent heat value, good thermal stability, no supercooling and phase separation, nontoxic and tasteless, and good thermal conductivity should be selected, so as to achieve the best cold preservation effect of food.

4.2. Cold storage refrigerators for Pharmaceutical cold chain transportation

In the medical cold chain, cold storage refrigerator also has a wide range of applications. For different medical supplies, phase change materials with appropriate phase change temperature are selected and combined with the insulation box to achieve the purpose of refrigerated transportation. Table 8 lists the optimal storage temperature of some biological products.

Table 8. Optimal storage temperature for some biological products.

| Type | Storage temperature |
|------|---------------------|
| Insulin, general vaccines, etc. | 2~8°C |
| Fresh frozen plasma and cold precipitation | below ~ 20 ℃ |
| Whole blood and red blood cells | 2~6°C |
| Ebola vaccine, mRNA COVID-19 vaccine, etc. (before dilution) | -60 °C -80 °C or lower |
| Biological cells, tissues or organs | -80 °C or lower |

Vaccine is a special biological product, which is very sensitive to the change of external temperature. The recommended temperature range of most ordinary vaccines is 2 ~ 8 °C. If the storage temperature exceeds this range, its biological activity will be reduced or even completely destroyed [74, 75]. Yin et al. [76] developed a cold storage incubator for vaccine transportation. The external insulation material of the incubator is extruded polystyrene plate with low thermal conductivity. The paraffin / SiO2 aerogel composite cold plate is placed in the innermost of the incubator, and the phase transition temperature is between 3 ~ 6°C. Zhao et al. [3] developed a low-temperature phase change material with dodecanol,
tetradecane and expanded graphite as substrates and a phase transition temperature of 4.3°C. At the same time, a new type of cold storage box incubator suitable for the transportation of inactivated vaccines has been developed, and users can monitor the temperature of the vaccine in real time through the mobile phone. The cooling capacity is released and transferred more evenly between the tubes, so as to realize the efficient use of the cooling capacity. However, with the emergence of nucleic acid vaccines, a new type of vaccines, unprecedented challenges have been posed to the refrigeration and transportation technology of vaccines. The COVID-19 nucleic acid vaccine produced by Pfizer/Biotech Co. Ltd. needs to be stored at −60 ~ −80°C before dilution. The traditional cold storage refrigerator is difficult to meet such storage requirements. At this time, dry ice / liquid nitrogen is needed for temporary storage or ultra-low temperature refrigerator is used [77]. In order to study the effect of blood containers using phase change materials on the quality of red blood cell transportation in plateau areas, Yi et al. [78] developed a powerless blood incubator using phase change materials, as shown in Figure 5. The phase change material is tetradecane, and its melting temperature is 4.5 ~ 5.6°C. After long-distance transportation of red blood cells in the plateau region, the hemoglobin content and blood biochemical indexes still meet the national standards, indicating that the use of with phase change materials can promote the storage and transportation of red blood cells in high altitude areas.

As a short-range cold chain transport equipment, cold storage refrigerator has a unique advantage in the pharmaceutical cold chain, which can further expand the cold chain terminal, especially when the power is out of supply or in areas where medical resources are scarce.

![Figure 5. Structure and appearance of phase change material blood incubator.](image)

5. Conclusion
The paper reviewed the classification and related research of low-temperature phase change materials, the influence of microcapsule technology on phase change materials and the application of cold storage refrigerators in food and Pharmaceutical cold chain. In the future, the following aspects should be focused on in the research of cold storage refrigerators:

- For inorganic phase change materials, the development of nucleating agents and high thermal conductivity and quality thickeners closer to the lattice parameters of the target material is the future direction. Adding nanomaterials, graphite powder or carbon fiber, etc. can effectively improve the thermal conductivity of organic phase change materials. The future focus is on its mechanism research, thermal performance optimization and other new technologies. For composite phase change materials, we should focus on the study of the composite mechanism, and explore the preparation of safe and environmentally friendly materials with excellent thermal conductivity.

- In the synthesis process of low temperature microcapsule phase change material, it is necessary to abandon harmful substances such as formaldehyde and melamine, simplify complex preparation process, reduce production cost and improve production safety and reliability. At the same time, in the future, the cushioning effect of low temperature microcapsule phase change material (i.e., the holding time) should be further tested to determine its cushioning
ability. For some food and medical products refrigerated or frozen, phase change temperature below 0 °C low temperature microcapsule phase change material research is the future focus.

- For food, medicine or biological products, the most suitable phase change material should be selected according to its characteristics and temperature zone through many experiments. The development of ultra-low temperature phase change materials with excellent performance and the optimization design of refrigerator structure are one of the future research priorities. In addition to the development of low-temperature phase change materials, the actual effects of cold storage plates and cold storage bags used in cold storage refrigerators in food and Pharmaceutical cold chains should be further studied, such as the quality change of fresh food, the change of nutritional quality, the cold storage effect of drugs or biological products, and the temperature fluctuation in cold storage refrigerators. At the same time, the multi-temperature distribution logistics technology is also worthy of attention. In view of the storage temperature zones of different food, medicine or biological products, simultaneous distribution of different products can be realized, which can improve the efficiency of cold chain transportation, enhance economic benefits and save energy.

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