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Development of Phase Change Materials for Refrigerated Transportation of Fruits and Vegetables

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Abstract. Phase change materials (PCMS) are getting used more and more popularly in heating and refrigeration because of their environment friendliness and economic benefits. In this paper, research and development of organic phase change materials and inorganic-organic PCMS are reviewed. The advantages and disadvantages of PCMs are analyzed. The phase change cold storage composite material is developed. This composite material is composed of organic and inorganic matter. Its properties include melting point (-4.8℃) and phase change fusion latent heat are studied. The Differential Scanning Calorimeter (DSC) is used to determine the properties. The results show that the material is of good thermal performance. It can be used in refrigerated transport for almost fruits and vegetables. The amount of PCMs B-type needed is calculated for a 20 feet cold hold-over plate refrigerator car. Calculations indicate this kind of refrigerator car is suitable for not more than 36 hours transport for some pre-cooled fruits or vegetables. The paper points out that the performance characteristics, theoretical model of heat transfer, phase transition mechanism and composite technology should be focused on, and organic composite phase change cold storage material is an important developing direction in the future.

Introduction

The post-harvest losses of fruits and vegetables in the process of circulation in developing countries is very serious. As an indispensable link in cold chain logistics system, cold chain transport is an important means to keep agricultural products fresh and safe in displacement of time and space, and provide ideal cold chain environment to reduce chemical changes and biological changes, physical changes and other factors impact on the loss of perishable goods. Highway is the main way of refrigerated transport (Liu and Xie, 2009), the traditional mechanical refrigeration transport vehicle goes through a lot of diesel oil or gasoline, running cost and goods damage rate is high, temperature inside is not stable. Compared with the traditional mechanical refrigerator car, cold hold-over plate refrigerated vehicles which utilize cold storage technology to keep temperature suitable have many advantages like low cost, low energy consumption, good environmental protection, etc. (Guo, 2014).

High temperature is the key factor result in loss of fruit and vegetables in the process of transportation. A study found that vitamin C and other nutrients of some vegetables such as spinach will be reduced 90% after stay in 30 °C for 24 hours (Li et al, 2009). Phase change cold storage material is charged and solidified, then absorb heat conducted from outside to keep the suitable temperature in operation process (Saito, 2002). So, appropriate cold storage material is the most critical points. Solid-liquid phase change materials like crystalline hydrated salt and organic matter has been studied in recent years. Although crystalline hydrated salt has the advantages of larger phase change latent heat, high coefficient thermal conductivity and phase transition, but it if of lower price and small volume change while phase changing. It's easy to be cooled in the process of practical application. The degree of over-cooled will be reduced by adding nucleating agent, but it needs prevent precipitation of nucleating agent, phase separation of crystal salt hydrate will appear at the same time (Li, 2010).

Zhang (2013) uses the cooling curve of PCM to draw the phase diagram and found the eutectic melting point of lauric acid-caprylic acid, the mass ratio of PCM is 21:79. The differential scanning calorimetry (DSC) curve shows that the PCM melting temperature is 7.0□ and the latent heat is 130. 8kJ/kg. The charging and discharging performance of the material was tested for 40 times. The DSC curve shows that at the 40th testing times, the PCM melting temperature is 7.73□, latent heat is 134.0kJ/kg. It is of good steady performance for cycling and suitable to be low-temperature phase change materials for fresh refrigeration industry. A kind of eutectic composite phase change cold storage material which was made up of caprylic acid and tetradecy alcohol has been prepared by experimental method by Yang (2013). The initial melting temperature of the material was 6.9□, the phase change latent heat was 151 kJ/kg. After 200 times circulations of solidification and melting as well as heat release characteristic tests, the stability of material was found very good. The thermal conductivity was improved greatly after added mass fraction of 6% of graphite. As a kind of new material, it can be used to transport some fruits and vegetables which are suggested transporting above 10□ during hot seasons. A new phase change material which was formed by three different materials was prepared (Li, 2009). The temperature and the latent heat of this material were measured by the DSC was -15℃ and 174.1kJ/kg. The component of this material were propanetriol, sodium acetate and water, all of them were cheap and easy to get, so the new material can he used in the filed of refrigerator and cryogenic transportation greatly.

Material Selection

PCM not only requires some good thermodynamic, dynamic and chemical properties, but also feasibility and economic performance. According to the different condition of refrigeration, cold storage material is supposed to possess the characteristics of appropriate transformation temperature, higher latent heat and good heat conduction performance. At the same time, the phenomenon of dissolution should not occur in the process of transformation, so the chemical composition of the phase-transition medium will remain stable. And the phase transition must be reversible, non-over cold, stable and safe.

The main work of this research is to develop the cold storage material that its phase transition temperature is about -4~-6℃ in order to obtain the ambient temperature of 0~6℃ for almost fruits and vegetables refrigerated transportation. Suitable melting temperature and higher latent heat should be take considered when select the cold storage materials. On the basis of two condition, the material should be low corrosive, cheap, readily available, non-toxic and no environment pollution. Based on the consultation of the LAN’s Handbook of chemistry, ammonium chloride from inorganic substances and glycerol from organic substances are selected. The composite PCM is mixed by ammonium chloride and glycerol. Through experiment, the thermal physical parameter of the new material is obtained. Table 1 shows some freezing point of glycerol solution.

Table 1. The freezing point of glycerol solution.

mass fraction (%)	10	20	30	40	50	60	70	80
melting point (℃)	-1.6	-4.8	-9.5	-15.4	-23	-34.7	-38	-20.8

DSC Test

The thermal parameters of the phase change materials are the key to the choice of the actual phase change materials, Its testing method has not been related to national and international standards. At present, differential thermal analysis, differential scanning calorimeter and modulated differential scanning calorimeter are widely used.

In this experiment, heat flow type DSC with liquid nitrogen cooling and indium as reference material for calibration is used. Protection gas is 99.99% purity nitrogen, flow rate of purge gas is

20ml/min, flow rate of protection gas is 60ml/min, temperature rise range is -60℃~200℃, temperature rise rate is 5K/min. Prepare a series of glycerol solution with different concentrations which start at 10%, and increases by 10%. According to the results, 20% glycerol solution is suitable for fruits and vegetables transportation. The results of the mixture experiment are shown in figure 1-3 and table 2.

Table 2. Thermal physical properties of mixtures.

composition of mixture	mass(mg)	melting point(℃)	latent heat(J/g)
A	8.9	-4.6	191
B	9.3	-4.8	214.3
C	9.6	-5.7	178.3

Note: A, B, C, representing mixture in different proportion of ammonium chloride and glycerol solution respectively.

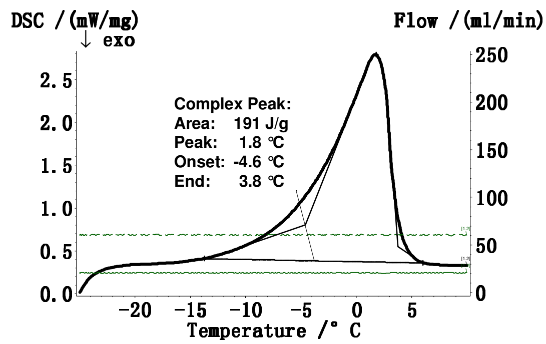

Figure 1. The DSC curve of mixture A in phase change process.

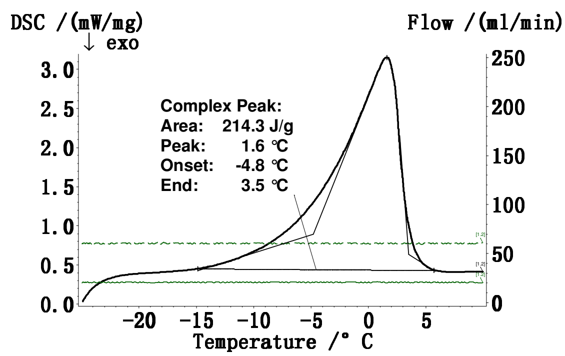

Figure 2. The DSC curve of mixture B in phase change process.

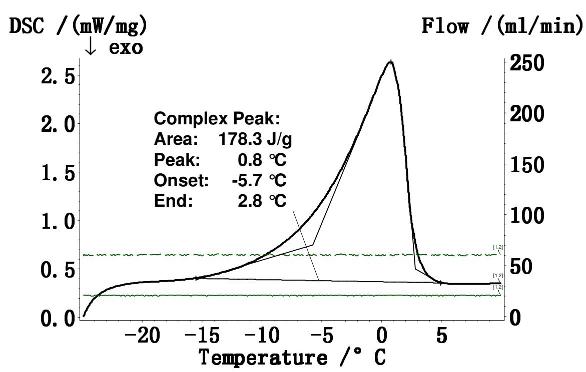

Figure 3. The DSC curve of mixture C in phase change process.

From figure 1~3, the melting point of mixture A,B ,C are all feasible, but the phase change latent heat of mixture B is the highest, i.e., 214.3J/g, Considering phase change temperature and phase change latent heat, the mixture B is the most suitable mixture for refrigerated transportation of fruits and vegetables.

Heat Capacity and Density

Heat Capacity

Specific heat is the heat capacity per unit mass of the material. For phase change materials, it should be of a larger specific heat capacity. The heat capacity can be tested by direct method and indirect method with DSC.

The results of heat capacity will be more accurate by indirect test method. But this study roughly estimate the specific heat capacity of the PCM by simple direct method because of the limitation of resources. From the DSC curves of sample endothermic or exothermic rate in figure1~3, the heat flow rate is proportional to the sample of instantaneous heat capacity. The heat capacity (C_p) can be obtained directly by the formula 1and 2. It is calculated out as 4.68J/(g· K).

$$\frac{dH}{dt} = mC_p\frac{dT}{dt} \tag{1}$$

$$C_p = \frac{dH}{dt} \times \frac{1}{m} \times \frac{1}{dT/dt} = \frac{y}{\beta} \tag{2}$$

Density

Weighing cylinder again after dropping 1ml to pre-weighed cylinder with a dropper by electronic balance 5 times, the average value of density is obtained, i.e,1.08g/ml.

Application and Conclusions

Application

According to ATP (the Agreement on the International Carriage of Perishable Foodstuffs and on the Special Equipment to be used for Carriage) and China SB/T 10728- 2012 (Technical requirements for perishable food cold chain--Fruit and vegetable), the B-type PCMs can be used for refrigerated transport of almost leafy vegetables, cauliflowers, fungus, and non-tropical fruits which need a storage temperature within 0-6℃.

Taking a 20 feet refrigerator car with cold hold-over plate which filled fully with solution of B-type PCMs as an example. Assume that the car is loaded with 8 tons pear or broccoli which are pre-cooled to about 3~5℃. In the course of transport, the average outdoor temperature is 25℃, the temperature inside of the car and pear or broccoli keeps between 0~5℃. Three circumstances of transport are considered, one is in urban distribution (last for about 12hrs), and another is in long distance transport (last for about 48 and 72 hrs). Therefore, the cooling-load (Q) and the quantity (G, V) of B-type PCMs needed can be calculated (Table 3, Figure 4). The 20 feet refrigerator car with cold hold-over plate is shown in figure 5.

From table3, the amount of B-type needed in pear transport in 48 hours is 602Kg and 700Kg in broccoli transport in 36 hours respectively, so it is easy to reach in the actual application because of the light weight of PCMs needed. But in 3 day’s long distance transport, 903Kg or 1368Kg of PCMs will be needed and exceed the maximum weight 740Kg. It will need extra plate. This will take up about 11% or 17% of cargo weight. They are not economical. So, this kind of refrigerator car is suitable for not more than 48 hours transport for pre-cooled pear or 36 hours transport for pre-cooled broccoli.

Table 3. Cooling load and quantity of PCMs.

Goods	time（h）	total Q (KJ)	G (Kg)	V（m^3）
Pear	12	33758	158	0.146
	36	98179	459	0.425
	48	128845	602	0.557
	72	193266	903	0.836
Broccoli	12	50326	235	0.218
	36	147883	691	0.64
	48	195117	911	0.844
	72	292674	1368	1.266

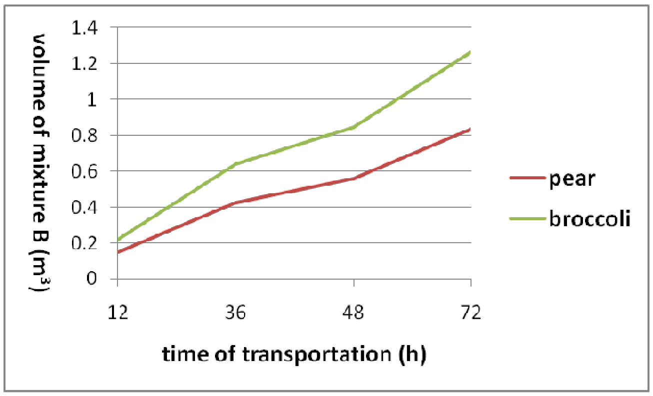

Figure 4. The volume calculation of mixture B in pear and broccoli transportation.

Figure 5. The concept sample of 20 feet refrigerator car with cold-hold plate.

Conclusions

(1) A kind of PCMs (type B) which is fit to fruits and vegetables is developed in this study, its melting point is -4.8, and its heat latent is 214.3J/g.

(2) A refrigerator car with cold hold-over plate which is filled with the PCMs (type B) is used for simulating calculation. This kind of refrigerator car is suitable for an about 36 hours transport for pre-cooled fruits and vegetables.

Development Trend and Prospect

Application prospect of phase change materials is very broad in peak load shifting (Qureshi et al, 2011), solar energy utilization, air conditioning energy saving (Castell et al, 2010) and refrigerated transport and so on(Sharma et al, 2009). Although domestic and foreign scholars have made great progress in the research of organic matter and organic- inorganic composite phase change materials, due to the limited characteristics of organic phase change materials, there is still a long distance away from the large-scale practical application. The key research directions of phase change cold storage materials are:

(1) Screen out the low price of raw materials, develop environment-friendly and stabile phase change cold storage materials, reduce toxic gas released in the operation.

(2) Organic-inorganic composite phase change materials can overcome the shortcomings of single organic or inorganic phase change cold storage materials, but the mechanism of its phase change is still not clear. In future, the research should focus on the study of organic- inorganic phase change cold storage materials, and find out the mechanism of its phase change, provide the basis for the preparation of the excellent performance.

(3) The organic matter in solid and liquid state has low thermal conductivity, and its viscosity in liquid is larger. So the heat transfer ability of pure organic matter is very poor. At present, add a good heat conductor and preparation of composite materials is the more effective method to improve the thermal conductivity. But the heat transfer capability is not limited to the heat conduction coefficient. It should establish a heat transfer theoretical model for the application of phase change materials.

(4) In the process of developing composite phase change materials, different composite technologies have a negligible effect on the performance of the composite. So it is one of directions to explore good performance composite phase change materials through the study on compound mechanism.

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