

Preparation of Microcapsule with Property of Temperature Conditioning by Phase Transition and Its Application to Leather*

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Abstract: Micro capsule material with properties of thermal energy storing and releasing by phase transition was made from polyethyleneglycol (PEG) in some degree of polymerization as content material to store and release energy and hydrolyzate of tetracthoxysilan(TEOS) as wall material to protect contents. An ideal condition for preparing this material is N_{TEOS}: N water = 1:4 (N: number of mol), M_{PEG}: M_{TEOS} = 1:3 (M: mass of material), pH = 1, aging at 50 °C.

Performance of micro capsule in thermal energy storing and releasing as well as stability were evaluated By DSC, Fourier transform infrared spectrometer and multi-midia microscope.

Application experiment was carried out. 4% of micro capsule based on weight of leather was used, separated in water and mixed with polyurethane 9703, brushed on flesh side of leather. Thermostat Performance of leather was evaluated by following parameters with help of instrument of slab heat insulation device: CLO value, the rate of heat preservation, heat transfer coefficient and also evaluated by drawing cooling curve and heating curve when sample leather from constant temperature chamber to cool and from refrigerator to constant temperature chamber to heat with the help of far-infrared thermometer to determinate temperature without touching sample.

Comparison between sample leather in test and in control test was made. Result: Temperature of leather in test was higher or lower by 2~3 °C than leather in control test when cooling and heating leather respectively.

Keywords: PEG; TEOS; phase change materials; leather

1 Introduction

The energy and resources are becoming more and more important today, energy recycling is particularly paid more attention. Phase Change Materials (PCM), is a class cycle of Storage-release the material, when the surrounding temperature higher than its phase transition point, PCM absorbs heat on the phase transition; when the surrounding temperature is below its phase transition point, the heat is released during back Original state. However, there are a number of phase-change materials, spill as a gaseous or volatile liquid on phase transition, in order to without loss phase-change material in use of it, about 1970 people made its micro-capsules. Lane and others combine phase change micro-capsule directly with building material, find a compound material with a thermostat function. Since then, Roy and others studied the heat transfer mechanism of phase-change material in the spherical "containers" and durability in the heat cycle. Goel studied heat transfer process of phase change microcapsules suspension soliquoid in a constant flow. In China, Zhang Xingxiang, from Tianjin University of Technology prepared nano-phase-change material micro-capsule and research its heat-resistant. Wang Lixin from Hebei University of Technology, used phase-change microcapsules in the wall, prepared Compound phase-change material with self-regulated. Phase change material microencapsulation technology has been used in field of textile fibers and solar energy. At present, Research has not yet reported phase-change materials used in leather.

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Leather is a natural material of clothing, though with good insulation properties, but it is still difficult to adapt to the hot summer, in the cold winter, a fur coat is difficult to keep out the cold. In this paper, in order to expand the use of ambient temperature range of leather clothing, developed a phase-change material, adapting to put into leather into the compound of, and apply to leather, test its thermal property^[1, 2].

2 Experimental

2.1 Materials

PEG, Hydrochloric acid, TEOS, deionized water, Polyurethane PU9703. IR; TG; magnetic stirrer 85-2, electric thermostat Water pot, multi-media microscope; ultrasonic cleaning instrument, YG (B) 606D slab insulation device.

2.2 Preparation of compound phase change material

Taking PEG, TEOS, and ethanol mixed in a certain ratio, melting mixed compound completely in 60 °C water bath, stirring in speed of 20000r/min, adding bit-by-plus a certain amount of water, at last adjusting pH with hydrochloric acid. Then stirring for 0.5h in certain temperature, it was kept in the warm water for some time. Preparation of compound phase change material was effected in many factors, such as the ratio between water and TEOS, and polymerization degree of polyethylene glycol, pH and temperature of aging. In order to get good image Sol, the main factors of the preparation were analysed. After early experiments, chose L9 (34) orthogonal table, to the preparation time and optimize the energy storage density of indicators, four factors were orthogonal III level, the level of factors in Tab.1. Break up the curing compound material. Then ultrasonic scattered, and observed with the electron microscope.

Tab.1 influence factors and selected value

factor\level	1	2	3	4
$m_{\text{PEG}} : m_{\text{TEOS}}$	2:1	1:1	1:2	1:3
$n_{\text{TEOS}} : n_{\text{water}}^+$	1:2	1:4	1:6	1:8
pH	0.5	1	2	3
Aging temperture (°C)	20	30	40	50

⁺ $m_{\text{PEG}} : m_{\text{TEOS}}$:ratio between PEG and TEOS quality; $n_{\text{TEOS}} : n_{\text{water}}$: ratio between TEOS and water in molar

2.3 Testing thermal ability of compound phase change material

The thermal ability of compound phase change material was tested by TG TGA Q500, protected with N_2 , heating rate 10 °C/min. temperature is in range of 0 °C~60 °C. Phase transition point and Phase transition Enthalpy is tested by Germany's NETZSCH DSC DSC-204 analyzer, protected with liquid nitrogen, the temperature warmed up is in rate of 5 °C/min, temperature range -30 °C~60 °C.

Storage energy rate is calculated in the ratio of the unit enthalpy of the quality and the enthalpy of original material.

2.4 Compound phase-change microcapsule preparation mechanism

Tested by Fourier infrared spectrometer.

2.5 The Comprehensive factor of thermal properties of phase-change leather

2.5.1 Leather sample

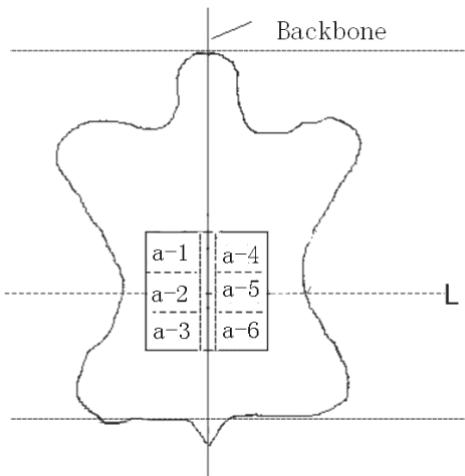


Fig.1 The leather sample

Thermal properties were affected by the leather's thickness of performance, organizational structure, fluffy, tanning method. Select six tanned leathers with smaller part-difference and same thickness. As shown in Figure 1, label as: a-1, a-2, a-3, a-4, a-5 and a-6.

2.5.2 The addition of phase-change material

Adding the phase-change material to the leather a-1, a-2, a-3, a-4, a-5 each quality are 2%, 4%, 6%, 8%, 10% of leathers; leather a-6 as the blank comparison. Some water and PU9703 were added into the phase-change materials. Making it to the liquid, scatter for 30 minutes with Ultrasound, brush liquid in the corresponding leather's meat surface, iron skin with smoothing iron, naturally dry, take into 60°C oven bake for 2h.

2.5.3 Testing of the leather thermal ability after adding phase change materials

According to the standard of GB1048-89, the sample was taken in 25cm × 25cm flat-fabric insulation instrument board. Then we tested the fine that insulation board keeping a constant temperature heated needs, to calculate the hot incubation, heat transfer coefficient and CLO value^[3].

2.6 Cooling and warming curve of the phase-change leather

Warming curve: taking the leather samples which contains different amounts of phase-change material into containing the 0°C refrigerator, attemper temperature keeping invariableness, then take out them and put in incubator of 45°C, using infrared thermometer at the same distance on the same level Test the of the sample's temperature, respectively, recorded a variety of sample's temperature T at different time intervals. Time as the abscissa ,the temperature is longitudinal coordinates, step-by-step drawing cold curve.

Cold-step curve: the temperature keeping invariableness of the leather sample containing different amounts of phase-change material in 45°C incubator, then take them into 0°C refrigerator, test warming up curve, draw Cold-step curves^[5].

3 Results and discussion

3.1 Choose the heat-retaining material

For example, there are some PEG (Tab.2) are suitable as Phase Change Material for apparel , measured the phase transition point and phase transition Enthalpy. For the different degree of polymerization of PEG, the heat- retaining capacity increase with the degree of polymerization increased, and temperature of its solid - liquid phase transition, enthalpy of phase change also increase with the

degree of polymerization increased, PEG showed good Heat storage performance. The phase transition point and phase transition Enthalpy dependent on the PEG's composition. Various parts of the body's comfortable temperature are different, for each part of the body's dress, choose different molecular weight and the ratio of PEG as a phase change materials to improve its performance thermostat will be more comfortable. In the body's comfortable temperature includes arrange, the requirements for the phase transition point is not very strict, so do not ask for much of its purity and precision, which will greatly reduce the cost of raw materials. I think for different parts of the leather products to choose a different degree of polymerization of PEG to Prepare phase-change materials, parts of the human body can adapt to the different needs of the high and low temperature.

Tab.2 Phase change temperatures and enthalpy of PEG in different Polymerization degrees

Ratio	PEG600	PEG600:PEG800=1:1	PEG800	PEG800:PEG1000=1:1	PEG1000
Phasechange temperatures (°C)	22.5 22	24.3	26.6	39.9	33.2
Phasechange enthalpy (J/g)	55.43	65.21	76.52	87.63	81.35

3.2 Testing preparation of the conditions

The main experiment characters compound material's performance According to the two indicators of gel time and energy density. Optimize the process conditions, in order to be able to get a good performance, wide application of the compound phase change materials. Tab.3 is the orthogonal experimental results.

Tab.3 Results of orthogonal design experiments

No.	n _{TEOS} : n _{water}	m _{PEG} :m _{TEOS}	pH	Aging tempreture/°C	gel time/h	energy density/%
1	2:1	2:1	0.5	20	143	59.4
2	2:1	1:1	1.0	30	66	49.7
3	2:1	1:2	2.0	40	43	33.2
4	2:1	1:3	3.0	50	175	44.2
5	4:1	2:1	1.0	40	87	58.3
6	4:1	1:1	0.5	50	12	49.6
7	4:1	1:2	3.0	20	48	32.1
8	4:1	1:3	2.0	30	183	43.1
9	6:1	2:1	2.0	50	45	59.8
10	6:1	1:1	3.0	40	23	49.7
11	6:1	1:2	0.5	30	21	33.2
12	6:1	1:3	1.0	20	177	45.1
13	8:1	2:1	3.0	30	67	59.7
14	8:1	1:1	2.0	20	46	49.3
15	8:1	1:2	1.0	50	8	31.5
16	8:1	1:3	0.5	40	182	44.6

According to the results, TEOS is in certain cases, the smaller amount of PEG , the shorter the time to

unite, but in compound phase-change material , the energy storage material is PEG, if the amount of PEG is too small, The storage energy is limited, so it will reduce the use of their properties. Water is key factors of the structure and nature of product, the more water, the more conducive to hydrolysis, but too much water has diluted the role. TEOS has high catalytic activity and hydrolysis, the room temperature is quickly; elevated temperature, you can speed up response time and enhance polycondensation advantage. In response, acid hydrolysis catalyst and process control of compound growth. Alkaline conditions are conducive to condensation, acidic conditions conducive to hydrolysis. In the high acidity, the rate of hydrolysis and condensation are both quickly; in the low acidity, rate of polycondensation are controlled by the rate of hydrolysis .The different acidity effects on the size and stability of the colloidal particle. Too high acidity will cause particles reunite, too low acidity will cause precipitation particles. As a result, the amount of acid has a direct impact on the nature of the sol [4].

According to the four factors: water and TEOS (TEOS) molar ratio, and polyethylene glycol TEOS than the quality, pH, temperature aging rate and the size of the embedded, determine the ideal conditions for the experiment $n_{\text{TEOS}}: n_{\text{water}} = 1:4$, $m_{\text{PEG}}: m_{\text{TEOS}} = 1:3$ pH = 1, aging temperature of 50 °C.

3.3 Feature of the compound phase-change material

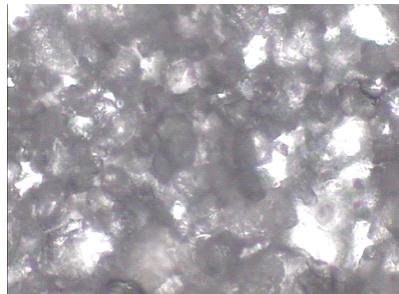


Fig.2 Prepared phase change material ($\times 400$)

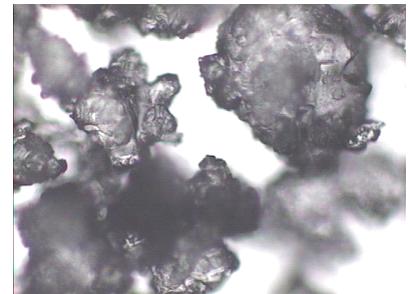


Fig.3 Prepared phase change material ($\times 1000$)

Fig.2 and Fig.3 were the prepared phase-change materials in the optical microscope to enlarge the photo 400,1000 times, from the map ,you cansee PEG and the silica prepared has generated close together, which can effectively prevent the PEG overflow from the heating liquid in the form of liquid.

3.4 Compound phase-change microcapsules' thermal performance and heat stability

This research get a degree of polymerization of PEG (PEG-A) as an example for DSC test, Figure 4, Figure 5 are DSC maps of heating and cooling of the PEG-A.

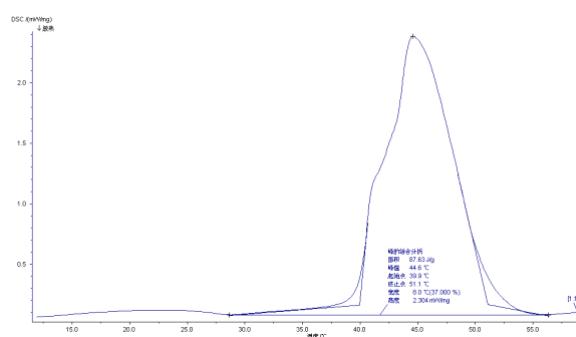


Fig.4 DSC of PEG-A in temperature rising

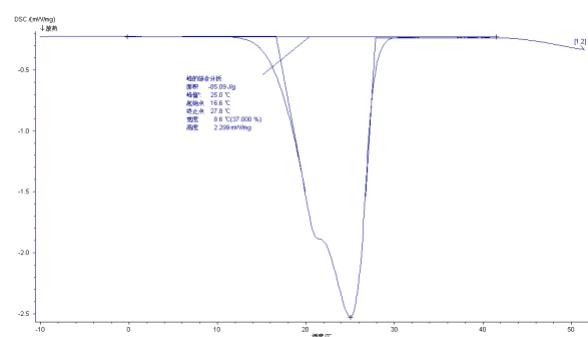


Fig.5 DSC of PEG-A in temperature

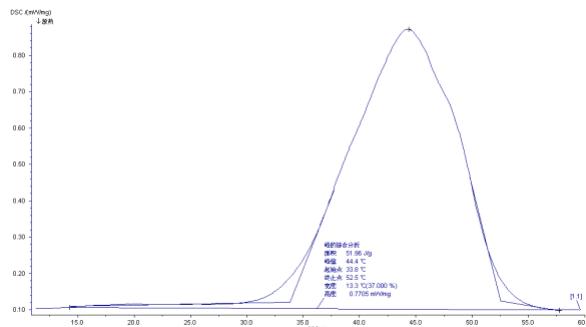


Fig.6 DSC of prepared Compound phase-change material in temperature rising

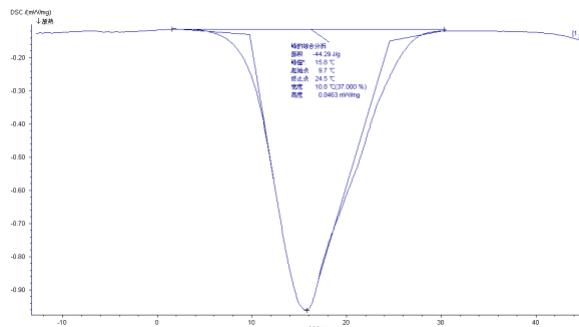


Fig. 7 DSC of prepared Compound phase-change material in temperature falling

By Fig.4, Fig.5, we know the phase transition start-up temperature of PEG-A is 39.9°C, enthalpy is 85.09J/g. at the time of cooling ,the phase transition start-up temperature is 27.8°C, enthalpy is 87.63J/g; Phase change materials made from PEG-A :the phase transition temperature is 33.8°C, enthalpy 51.96J/g, energy content is 61.1%, at the time of cooling, phase transition temperature is in the range of 22.4-9.7°C, enthalpy is 44.29J/g. This shows that the phase-change temperature range of phase-change material made of PEG-A is basic within the scope of human feeling comfortable. In addition, the preparation phase change materials also have good stability in the repeated heating and cooling 50, the phase transition start-up temperature and Enthalpy change is essentially the same. no too cool phenomenon of inorganic phase change materials. The Tg map of PEG-A and prepared phase-change material, as shown in Fig.8 and Fig.9.

Sample : JYEC

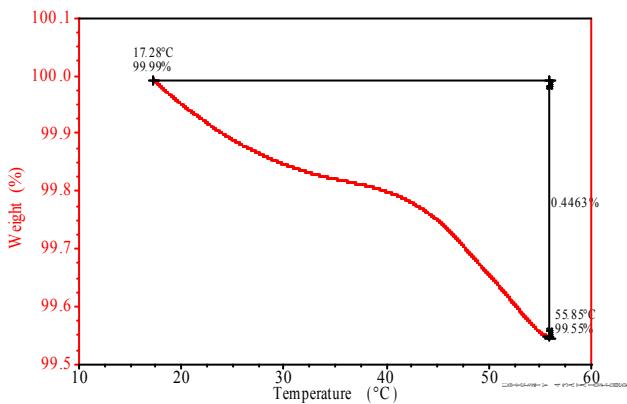


Fig.8 TG figure of PEG-A

Sample : XBWJN

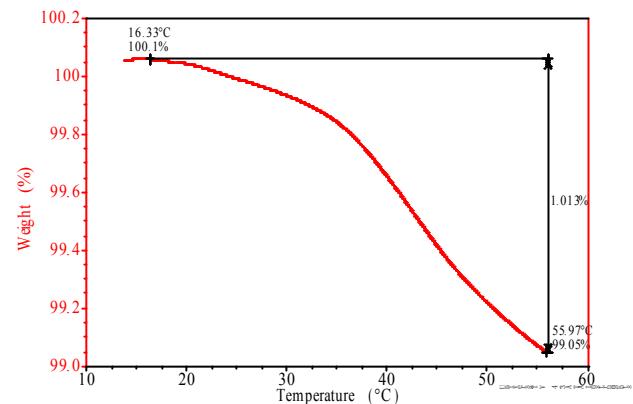


Fig.9Tg figure of made PCM

In Fig.8 and Fig.9, as we know, when temperature rise from10°C to 55°C, the PEG weight loss ratio of 0.4463%, the compound phase change materials weight loss ratio of 1.013 %. The compound change materials can be seen its heat resistance is better. Bake the compound phase transition material in temperature of 80 °C for 24h, no liquid outflow. For pure samples of PEG-A, during the hot-melt-in phase transition occurred, and the PEG / SiO₂ sample, as the network structure of the porous SiO₂ formation, as well as silicon-hydroxide and alcohol-physical cross-linking between the bond, making PEG firmly in the restrictions in SiO₂. Despite phase transition occur in the process of heating, but show different melting behavior with PEG^[5].

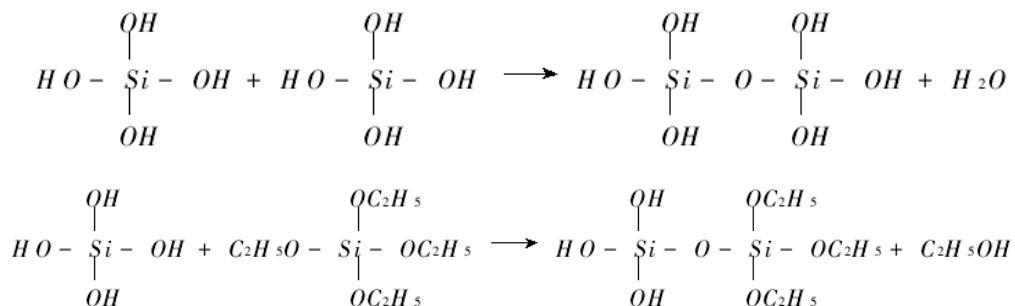
3.5 Phase-change microcapsules formation mechanism

There are three steps in hydrolysis condensation of TEOS, the reaction is as follows:

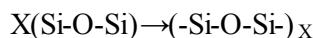
The first step: hydrolysis



The second step: condensation



The third step: polymerization



In the actual process of reaction of TEOS, the first step of hydrolysis and the second step of condensation is carried out at the same time, we say it generated a mixture of two-step sol. For the third step polymerization generated three-dimensional structure of the network called gel [6]. Test TEOS and the preparation of the phase-change materials with IR, including the spectrum as shown in Figure 8, in Figure 9. By Figure 9, curve is the infrared spectrum of TEOS. The strongest absorption peak is 1082 cm^{-1} , this is caused by the Si-O bond vibration absorption peaks. the peak at $794, 475\text{ cm}^{-1}$ is also caused by the Si-O bond vibration, peak at 1105 cm^{-1} is C-O stretching vibration of the peak in the TEOS. Hafe esterification -OH and -H on 2977 cm^{-1} bond to form hydrogen bond, the strong absorption peak emerge, peak at 2892 cm^{-1} is -CH₂- group in TEOS stretching vibration of the peak, peak at 967 cm^{-1} is a very small amount of the unesterified PEG crystallization. Figure 10 is infrared spectrum of phase change materials prepared. The strongest absorption peak of the silicon dioxide at the 1105 cm^{-1} , this is the Si-O bond vibration absorption peak. Peaks at $844, 571\text{ cm}^{-1}$ are also caused by the peaks of the Si-O bond vibration. Absorption peak at 952 cm^{-1} show the existence of three Si-OH peaks at 3425 cm^{-1} is caused by the absorption and extension of PEG intramolecular condensation -OH. 2915 cm^{-1} (-CH₂- have strong anti-symmetric stretching vibration). Infrared spectra show there is no new group generated of compound materials. We can see from the above analysis, PEG and silica compound is just the physical relationship, does not generate new material [7].

Fig.10 FT-IR of TEOS**Fig.11 FT-IR of made PCM**

3.6 Thermal properties of phase-change leather

The Tab.4 containing different amounts of phase-change materials, leather's CLO value, the rate of heat preservation, heat transfer coefficient. Use Flat-panel instrument to test the CLO value, the rate of heat preservation, heat transfer coefficient of leather, Containing different amount of phase-change material, as follows Tab.4:

Tab.4 The connection of amounts of phase-change materials contained and CLO value, the rate of heat preservation, heat transfer coefficient

amount of phase-change material	blank	2%	4%	6%	8%	10%
heat transfer coefficient/W/m ² ·°C	50.68	47.96	45.50	48.47	49.42	53.28
CLO value	0.52	0.59	0.63	0.61	0.57	0.54
rate of heat preservation /%	12.43	13.95	15.29	14.87	14.32	13.21

We can see from Tab.4, leather heat transfer coefficient increase as the phase-change material added in leather increased, when adding the volume of more than 4%, the heat transfer coefficient increased. CLO value and the rate of heat preservation are first increased and then decreased, the turning point in 4%. The data show that adding a certain amount of the phase-change material contributes to leather's heated, but if excessive, leather's heated would get lower. I think this may be due to the leather is a porous material, there are a large amount of air in the gaps, and air their own performance of heat transfer is poor, that is, the better insulation properties. Filling phase change materials, the quiescent air in the leather being squeezed out, its insulating properties will decline. And if the gap is filled, the most unique properties of leather, water vapor permeability will be lost. This is undesirable. Therefore, a more appropriate amount is 4%.

3.7 Heating curve and cooling curve

Fig.12 and Fig. 13 is heating and cooling curve of leather 4% of phase change material added and a blank form.

Fig.12 shows the leather with the phase change material and the blank form in the heat beginning ten minutes, the temperature change consistently. At phase-change point of the phase-change material (for about 32 °C), temperature of leather with phase-change material remained unchanged, while the blank sample has been heating up all along and reached basically the same as the temperature of the environment. Leather with phase change material is a clear warming down, lower than the blank sample 2 ~ 3 °C, the duration is about 30min. This is due to in the warming process, when the temperature lower than the phase-change point of phase-change material, the phase-change material has no change, leather with phase-change material and a blank sample to show the same warming of the situation. When the temperature is higher than the phase transition point, the blank sample continues to heat up. The other sample includes phase-change material, phase change material in the leather absorb heat, phase-change occurs, over time, the overall temperature of the leather remain unchanged. When all of the phase-change material turns into another phase, the temperature of leather will continue to heat up.

Fig.13 shows the blank form of sample's temperature go on cooling at a low temperature, and reach

basically the same as the temperature of the environment. The sample with phase-change material its temperature is obviously slowed down at the phase transition point (to about 22.5 °C), higher than the blank sample 2 ~ 3 °C, the duration is about 30min. This is due to in the cooling process, when the temperature drops to phase transition point, the leather with phase-change material release heat, phase change occurs, the overall temperature of the leather remain unchanged . Until all of phase change material turns into another phase, the temperature of leather will continue to cool down.

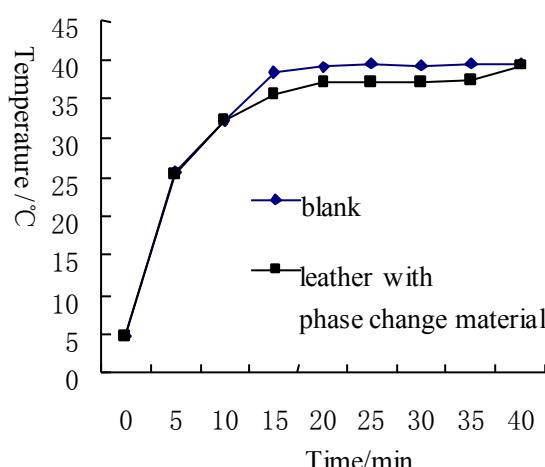


Fig.12 Heating curve

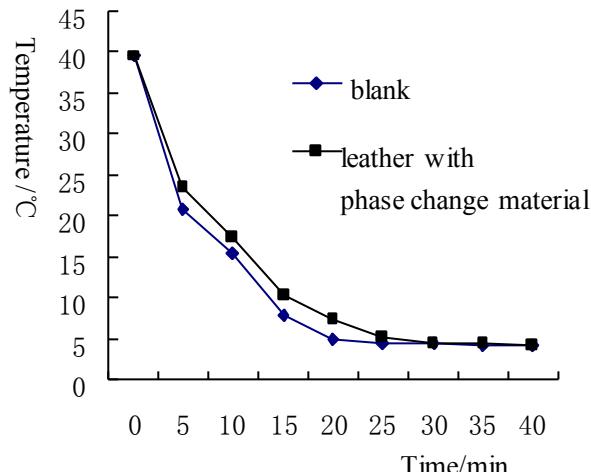


Fig.13 Cooling curve

4 Conclusions

(1) The ideal conditions for preparing Phase-change compound material is $n_{\text{TEOS}}: n_{\text{water}} = 1:4$, $m_{\text{PEG}}: m_{\text{TEOS}} = 1:3$, pH = 1, aging temperature is 50 °C. The compound phase change material's enthalpy reached 51.96J/g, energy storage density was 61.1%.

(2) The compound phase-change material has better thermal stability, silicon dioxide and PEG is a combination of physical, silica with porous media to absorb PEG, prevent PEG overflow as liquid in the process of phase transition.

(3) Brushed phase-change material 4% on leather, the heat transfer coefficient of leather is 45.50 W / m • °C, CLO value is 0.63, rate of heat preservation is 15.29 %. When the surrounding temperature is too high or too low, phase-change leather than the blank 2-3°C, lasted for about 0.5h.

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