

# Fabrication of microencapsulated phase change materials and its application in leather

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**Abstract:** Phase change materials (PCMs) have attracted great attention from both scientific and industrial communities, which are a kind of the most important functional materials that have characteristics of absorption, storage, and releasing large amounts of latent heat over a defined temperature range while undergoing phase change. Leather containing phase change materials react immediately with the temperature changing of environment and the different areas of the body. Microencapsulation of PCMs provides a mean to solve the problem of interfacial combination with the circumstance materials. For the existing problems of microcapsules, such as coagulating and quick declination of the thermal properties of phase change materials when applied to leather, the effects of synthesis conditions of melamine-formaldehyde prepolymer on the molecular weight of prepolymer were investigated by using the software of Desgin-Expert software. The relationship between the molecular weight of prepolymer and the properties of microcapsules from the perspective of the viscosity of prepolymer were studied as well. The results showed that when the molecular weight of prepolymer was too large, part of molecules were crosslinked, which could lead to the conglutination of microcapsules and deposition of M-F prepolymer. The optimal molecular weight were obtained at pH 8.5 and 75 °C for 75min. The prepared microcapsules under optimal conditions had smooth outer surface, good disparity and complete morphology. And the leather added in such microcapsules could provide an enhanced thermal capacity which can keep the body in the comfort state.

**Key word:** phase change material; microcapsule; prepolymer; leather;

## 1 Introduction

Phase change materials (PCMs) are one of the most important functional materials that can absorb, store, and release large amounts of latent heat over a defined temperature range while undergoing phase change, and have attracted great attention from both scientific and industrial communities <sup>[1]</sup>. Microencapsulation of PCMs provides a means to solve the interfacial combination with the circumstance materials <sup>[2]</sup>. In recent years, microencapsulated Phase Change Materials (MicroPCMs) have drawn an increasing interest to provide enhanced

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thermal functionalities in a wide variety of applications just like fibers, fabrics, coatings and foam [3-8]. But there is still little information available on its application in leather.

Millions of people worldwide are exposed to various thermal environments, from which their bodies need protection. The performance requirements of protective clothing often demand the balance of widely different properties, such as thermal resistance, control of dynamic temperature and moisture in the clothing–skin microclimate. Modern leather techniques, functional leathers and artificial intelligence technologies have enabled the implementation of usable intelligent clothing [9]. Leather containing phase change materials react immediately with changes in environmental temperatures, and the temperatures in different areas of the body. When a rise in temperature occurs, the PCM microcapsules react by absorbing heat and storing this energy in the liquefied phase change materials. When the temperature falls again, the microcapsules release this stored heat energy and the phase change materials solidify again [10].

But the existing problems of microcapsules such as coagulating, sticking and coarse surface and quick declination of the thermal properties of phase change materials limited its applications in leather. So, to solve these problems was the key work of researchers. In this study, based on the problems of microcapsules mentioned above, the effects of synthesis conditions for melamine-formaldehyde (M-F) prepolymer on the molecular weight of prepolymer were investigated by using the software of Design-Expert software, as well as the relationship between the molecular weight of prepolymer with the surface morphology of microcapsules from the perspective of the viscosity of prepolymer.

## **2 Experimental**

### ***2.1 Materials***

Dodecanol (A.R.), as PCMs core, was supplied by Tianjin Kermel Chemical Reagent Co., Ltd, China. Melamine (99 wt %) and formaldehyde (37 wt% aqueous solution) were purchased from Tianjin Chemical Reagent Company, China and used as wall materials. OP-10 and sodium salt of styrene-maleic anhydride copolymer (SMA) with weight average molecular weight of 150,000 as emulsifiers was supplied by Shanghai Leather Chemical Company, China. And ethanol (95 wt %) as an extracting solvent was obtained from Tianjing Chemical Reagent Company, China. Triethanolamine (95 wt %), acetic acid (36 wt %), citric acid (98 wt %) and sodium hydroxide (A.R.) all purchased from Xi'an Chemical Regents, China, used as pH regulators. Urea (A.R.) was also obtained from Xi'an Chemical Regents.

### ***2.2 Synthesis of prepolymer***

Melamine and formaldehyde with a certain proportion were mixed with distilled water.

The mixture was stirred in the specific temperature and the pH was adjusted with triethanolamine in a fixed time. Then the melamine–formaldehyde prepolymer was obtained.

### ***2.3 Preparation of microcapsules***

Preparation of water phase: 3.5 g SMA and 0.2g NaOH mixed with 20.0 mL of distilled water were emulsified mechanically at 50 °C with a stirring rate of 2000 rpm for 2h. The emulsion was adjusted to pH 4.5 with 10.0 wt % citric acid solution.

Preparation of oil phase: An amount of OP-10 and dodecanol were mixed uniformly.

Emulsion preparation: The uniform oil phase was mixed into water phase at a stirring rate of 4000 rpm for 15 min. The white emulsion was obtained.

Microcapsule fabrication: A certain amount of prepolymer was added into the emulsion in droplets while the emulsion was stirred at a rate of 400 rpm and kept the temperature of heat preservation at 60 °C. After all the prepolymer was added into the emulsion, the mixture was continued to stir at 80 °C for 120 min. The pH of the emulsion was adjusted with 10 wt% acetic acid solution to 4.0, which terminated the polymerization. Then 1.0 g of urea was added to remove the remnant formaldehyde. The resultant microcapsules were filtered and the wet powders were dried in an oven at 100 °C for 24 h to remove the water.

### ***2.4 Viscosity measurement of melamine–formaldehyde prepolymer***

The viscosities of melamine–formaldehyde prepolymer with various synthesis conditions were measured by Ostwald's viscometer.

### ***2.5 Characterization***

FTIR spectra of melamine–formaldehyde prepolymer with different molecular weight and shell material were obtained using a spectrophotometer (BRUKER UECIOR22, wavelength 400~4000  $\text{cm}^{-1}$ ) at room temperature with the KBr sampling method.

The morphologies of the microcapsules made with different molecular weight were obtained by using a scanning electronic microscope (SEM, H600). A drop of the microcapsules dispersion was dripped on a stainless steel SEM stub and allowed air-dry. The samples were gold-coated.

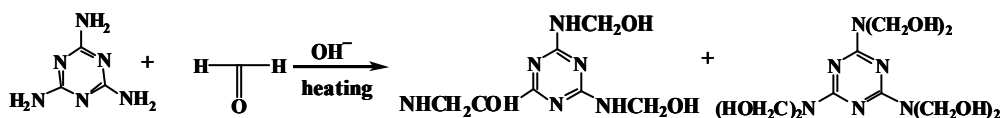
The thermal stabilities of the microcapsules made with different molecular weight were obtained by using a thermogravimetric analyzer (SDT-2960) at a scanning rate of 10 °C  $\text{min}^{-1}$  in the temperature range of 10~600 °C. The atmosphere was nitrogen.

## **3 Results and discussion**

### ***3.1 Effects of M-F prepolymer with different molecular weight on the properties of microcapsules***

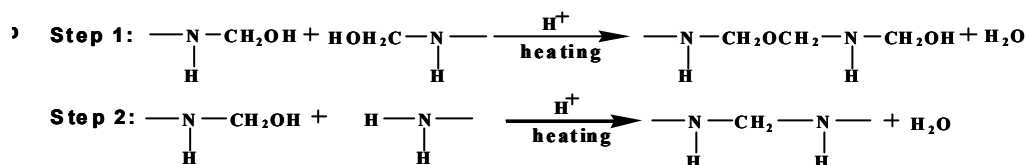
Research shows that during the initial nucleophilic addition stage, reaction between

formaldehyde and melamine molecules in basic solution leads to the formation of soluble M-F prepolymer of some forms including tri- and hexa-methylolmelamine (see Fig. 1) [11,12] .



**Fig. 1 Mechanism for the polymerization of MF prepolymer**

Through polycondensation reaction at acidic condition between methylols or between methylol and amidogen or imine group, the prepolymer was crosslinked either by ether linkage or methylene as shown in Fig. 2. The molecular weight spontaneously increased and the water-soluble continuously decreased. The product shrinked into conglomeration forming insoluble M-F three dimensional crosslinked structure [13].



**Fig. 2 Cross-linking reaction of MF prepolymer**

From here, we can see that the properties of the microcapsules have close relationships between the molecular weight and the structure of melamine–formaldehyde prepolymer. The more of straight chain structure of M-F prepolymer, the tighter of molecular range is, and then the shells of microcapsules would have smooth and compact outer surface and good flexibility [14]. A certain relation exists between the viscosity and molecular weight of macromolecule polymer. Solely from viscosity, we can't get the molecular weight of polymer. But the viscosity enlarged with the increase of the molecular weight. So in this study, we compared the molecular weight of M-F prepolymer from the perspective of the viscosity of prepolymer.

### ***3.2 Effects of Synthesis conditions for M-F prepolymer on the molecular weight of prepolymer***

**Table 1 The variables (code) and their levels**

Factor	Symbols	Level		
		-1	0	1
Time (min)	$X_1$	30	75	120
Temperature (°C)	$X_2$	60	72.5	85
pH	$X_3$	8	8.5	9

Referred to the literatures [15], time, temperature and pH of Synthesis condition were

delineated as critical variables with significant effects on the molecular weight and structure of M-F prepolymer. The effects of synthesis conditions for M-F prepolymer on the molecular weight were investigated by using a central composite design of software of Design Expert (Trial Version 7.1.1, Stat-Ease Inc., Minneapolis, Minnesota, USA). The experimental design consisted of  $2^3$  factorial points, four axial points and five replicates of the central point (Table 2). Time (min,  $X_1$ ), Temperature ( $^{\circ}\text{C}$ ,  $X_2$ ) and pH( $X_3$ ) were chosen for independent variables. The range and center point values of three independent variables were based on the results referring to the literature<sup>[15]</sup> (Table 1). The viscosity of M-F prepolymer was selected as the dependent variables for the combination of the independent variables were given in Table 2.

**Table 2 Design and results of central composite designed experiments**

Experimental No.	Level			Response $\eta/\text{mPa}\cdot\text{s}$	Water solubility
	$X_1$	$X_2$	$X_3$		
1	-1	0	1	0.586	Solvable
2	-1	-1	0	0.587	Solvable
3	-1	1	0	0.566	Solvable
4	-1	0	-1	0.575	Solvable
5	0	-1	-1	0.581	Solvable
6	0	1	-1	0.609	Deposition
7	0	-1	1	0.557	Solvable
8	0	1	1	0.580	Solvable
9	1	-1	0	0.594	Solvable
10	1	1	0	0.602	Deposition
11	1	0	1	0.583	Solvable
12	1	0	-1	0.756	Solvable
13	0	0	0	0.575	Solvable
14	0	0	0	0.575	Solvable
15	0	0	0	0.577	Solvable
16	0	0	0	0.576	Solvable
17	0	0	0	0.574	Solvable

Coefficient of determination ( $R^2$ ) is defined to be the ratio of the explained variation to the total variation and is a measurement of the degree of fitness <sup>[16]</sup>. A small value of  $R^2$  indicates a poor relevance of the dependent variables in the model. The model can fit well

with the actual data when  $R^2$  approaches unity. By analysis of variance, the  $R^2$  value of this model was determined to be 0.9098, which proved that the regression model defined well the true behavior of the system.

After removing the non-significant terms, the mathematical model representing the viscosity of M-F prepolymer as a function of the independent variables within the region under investigation was expressed by the following equation:

$$Y = 312.69 + 2.79X_1 + 2.59X_2 - 2.35X_3 + 3.81X_1X_2 - 0.51X_1X_3 - 0.61X_2X_3 + 2.84X_1^2 + 3.54X_2^2 - 0.37X_3^2$$

Where  $Y$  is the viscosity of M-F prepolymer, and  $X_1$ ,  $X_2$  and  $X_3$  are the coded variables for a time, temperature and pH of Synthesis condition, respectively.

From the regression equation coefficient, we can see that reaction time was most important influencing factor, reaction temperature secondly. While there was a positive correlation between reaction time and temperature with the viscosity of M-F prepolymer, pH was negatively correlated with the viscosity. When increasing the reaction time, the viscosity of prepolymer was improved. But when the reaction time was too long, linear molecules would polycondensed and crosslinked for further, so as to the formation of insoluble high molecular weight polymer, which decreased the viscosity of prepolymer. And when the reaction temperature was too low, melamine was difficult to dissolve in formaldehyde. The reaction rate was not quickly enough to form uniform product. Though improving the reaction temperature quickened the reaction rate, excess high reaction temperature was expected to make the formed linear molecules crosslinked for further. Moreover, M-F prepolymer was easily crosslinked under a neutral or acidic condition when the pH was extremely low. Just like the white turbid and opaque liquid of prepolymer of No.6 and 10, bulk of M-F polymer molecules were crosslinked either by ether linkage or methylene linkages forming white depositions.

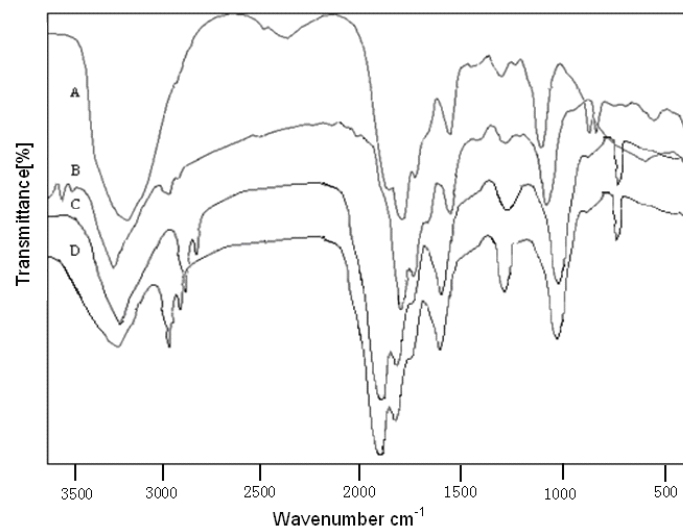
Here, we selected four different viscosities, in other words prepolymer with four different molecular weights, to prepare microencapsulated Phase Change Materials by in-situ polymerization and study the relationship between the molecular weight of prepolymer and the surface of microcapsule (table 3).

**Table 3 Synthesis conditions for prepolymer with different molecular weight**

Experimental No.	Time (min)	Temperature (°C)	pH	$\eta$ mPa·s
A (No.7)	75	60	9.0	0.557

B (No.13 )	75	72.5	8.5	0.575
C (No.11 )	120	72.5	9.0	0.583
D (No.9 )	120	60	8.5	0.594

### 2.3 FTIR Analysis of M-F prepolymer

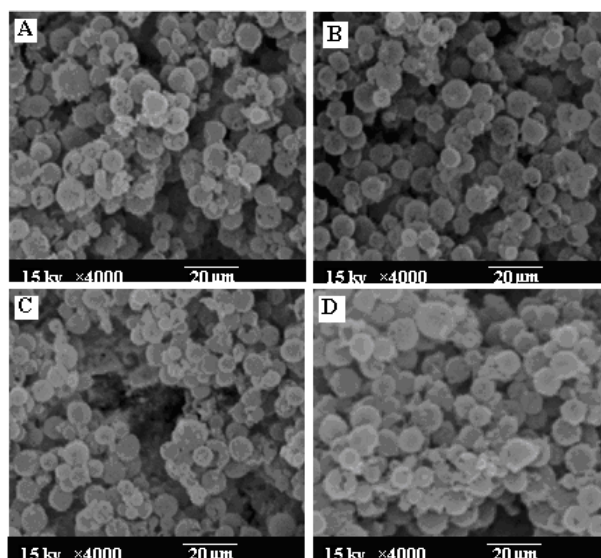


**Fig. 3 FTIR spectra of M-F prepolymer with different molecular weights**

The FTIR spectra of prepolymer with different molecular weight are displayed in Fig. 3, respectively. Based on the relationship between viscosity and molecular weight, the molecular weight successively increased with the proper order of viscosity, A、B、C and D in proper order. From Fig. 3, it can be seen that the absorptions appeared at  $3334\text{cm}^{-1}$  can be assigned to the N-H and O-H stretch of secondary amine attached to the methylene bridge of prepolymer. The peaks appeared band and strong, which were affected by the hydrogen bond of -OH. We also can see that the absorptions present a trend of remarkably falling, as the molecular weight of prepolymer increased. Because the N-H and O-H of methylolmelamine were crosslinked and converted to  $-\text{N}-\text{CH}_2-$  and  $\text{C}-\text{O}-\text{C}-$ , this resulted in the appearance of C-O-C stretching vibration absorptions at  $1160\text{ cm}^{-1}$ .

It's noted that the strong peak at  $1000\text{ cm}^{-1}$  was observed, and in other words there still had a lot of  $-\text{CH}_2\text{OH}$  in the prepolymer. This was in accordance with the fact these prepolymer were water-soluble.

### 3.4 Morphology analysis



**Fig. 4 The SEM micrographs of microcapsules synthesized by different molecular weight prepolymer.**

The SEM micrographs of microcapsules prepared by different molecular weight prepolymer were shown in Fig. 4. From the sample A to D, the molecular weight of prepolymer increased gradually. As shown in Fig. 4, the size distribution of sample A was narrow, but the surface of some microcapsules had a number of impurities and the phenomenon of flocculation. The reason maybe that the prepolymer of low viscosity was difficult to dissolve in formaldehyde liquid and the nucleophilic addition reaction was incomplete. The stable prepolymer was difficult to produce, which resulted the incomplete polycondensation in the fabrication of micrographs. The molecular chain ends contain amidogen and imine group that will ionize to possess weak positive charges in aqueous solution. Positively charged melamine–formaldehyde prepolymer, attracted by anionic carboxyl groups of the anionic emulsifier, were expected to adsorbed and fixed on the surface of negatively charged droplets of dodecanol [1].

The prepolymer of sample B have small molecular weigh and polymerization degree. The molecular chain extended freely and there was enough time for the prepolymer to bind to negative charge on the surface of the oil droplets of dodecano in the form of ionic bond. So the flocculation phenomenon of the microcapsules in sample B decreases and the globular surface becomes smoother and without any disfigurement.

The SEM micrographs of sample C and D showed the flocculation phenomenon of microcapsules with different degree. These phenomena can be explained in terms of electrostatic attractions between the negative colloids and the M-F prepolymer with positive charge by adsorption of prepolymer onto the oil droplets. The molecular weigh of their

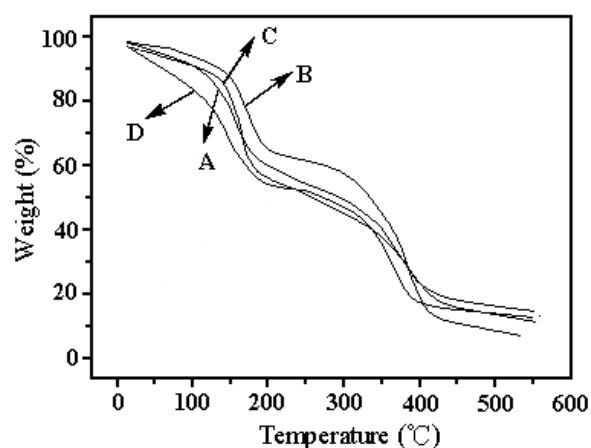


prepolymer were big relatively and the prepolymer were seriously crosslinked, which can accelerate the aggregation of the M-F prepolymer toward the surface of the core droplets. This also results in a fast deposition of the nanoparticles of the M-F prepolymer onto the surface of the microcapsules. As a result, the microcapsules are difficult to be dispersed well, resulting in their conglutination with each other and a serious agglomeration of the disfigured microcapsules occurred.

### ***3.5 Analysis of the thermal stability***

The thermal stability of microcapsules plays an important role in the leather application. Fig. 5 shows the TG curves of the microPCMs prepared by different molecular weight prepolymer. It is visible that the thermal stability of the microcapsule changed with the increase of the molecular weight of prepolymer. When the molecular weights were excessively big or small, all the TG curves of the microPCMs appeared as a descending trend. The reason can be explained by that the nucleophilic addition reaction of sample A was incomplete and owing to the forming of instable prepolymer, the polycondensation procedure was incomplete. As a result, the wall with high rigidity cracked and the capsules began to lose their weight at a lower temperature.

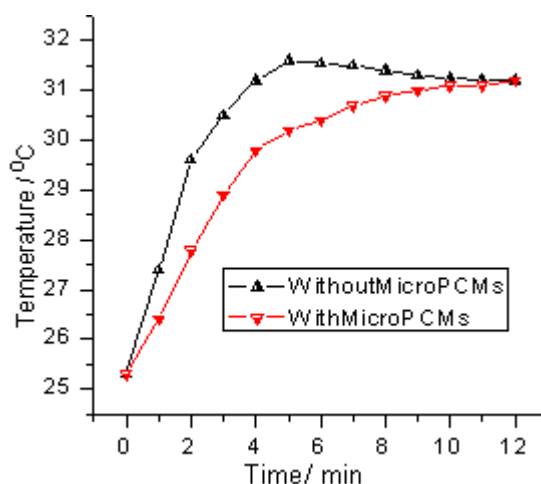
There existed a large number of methylol and amidogen or imine group in sample B. Through polycondensation reaction at acidic condition, the prepolymer was crosslinked either by ether linkage or methylene. The flexibility of walls of microcapsules improved and the intension of microcapsules increased, correspondingly, the fractured temperature of microcapsules enhanced. But the prepolymer of sample C and D were crosslinked the initial nucleophilic addition stage, inducing to the flocculation phenomenon of the microcapsules and the odd thick of walls. Owing to the inhomogenous crosslinking density, the high temperature-resistance decreased.



**Fig. 5 TG curves of microencapsules synthesized by different molecular weight prepolymer.**

### 3.6 The performance of microcapsules incorporated into the leather system

Heat loss to the environment normally takes place by convection, radiation and evaporation from the skin and by sensible and latent heat of perspiration; however, leather added with microcapsules can create a stable microclimate next to the skin in order to support the body's thermoregulatory system [17]. The tests of the thermal regulating functional performance of leather with MicroPCMs can be carried out in a climatic chamber; the temperature changes within the leather garments under conditions of rapid environmental temperature change can be measured and recorded by the thermal sensor automatically. For one such test, the test results were as represented in the Fig. 6.



**Fig. 6 Curves of temperature variation with comparison between leathers with MicroPCMs and without MicroPCMs.**

From the Fig. 6, we can see that when temperature rises due to a higher ambient temperature, the microcapsules react by absorbing heat. The PCMs in the microcapsules melt. They draw heat from their surroundings and store the surplus energy. After all the PCM becomes liquid, the temperature continually increases. In this process, the PCM acts as a thermal buffer material by releasing stored heat and provide an enhanced thermal capacity in addition to the existing passive insulation characteristic of the structure to keep the body in the comfort state [18].

## 4. Conclusion

In order to study the application of phase change materials in leather and investigate the existing problems of microcapsules in the leather application, the microcapsules containing dodecanol as a representative phase change material had been synthesized by in-situ encapsulation by polymerization of M-F precursor. The relationship between the molecular weight of prepolymer with the surface morphology and the thermal stability properties of

microcapsules from the perspective of the viscosity of prepolymer were analysed as well. The molecular weight of prepolymer is too big, which could result the conglutination of microcapsules and deposition of M-F prepolymer. The optimal molecular weight were obtained on the reaction conditions of reaction temperature 75 °C, reaction time 75min and pH 8.5. The prepared microcapsules with such conditions had smooth outer surface, good disparity and complete morphology. And the leather added with such microcapsules provided an enhanced thermal capacity in addition to the existing passive insulation characteristic of the structure to keep the body in the comfort state.

## **Acknowledgments**

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