

Effects of Microencapsulated Phase Change Materials Granularity and Heat Treat Treatment Condition on the Structure and Performance of Polyurethane Foams

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Abstract

In this article, we study on the effect of different congregated granularities of microencapsulated n-octadecane on polyurethane foamed system, and the making of the polyurethane foams with high contents of microencapsulated n-octadecane. The results show that, when relative low granularities of microencapsulated phase change materials (MicroPCMs) are used as additives, the remnant water and formaldehyde have adverse effects on the foam, so the MicroPCMs should better be heat-treated which is helpful for removing the residual, and more uniform foam can be obtained when relative low granularities of MicroPCMs are used. The polyurethane foams with maximum contents of 28 parts of n-octadecane can be made when the polyethylene glycol-400 (PEG-400) is interfused in the foamed system to regulate the viscosity of the system. The formed foams absorb heat at about 27°C and dissipate heat at about 25°C, which heat storage is bigger than 18J/g and can be used as thermal insulation materials.

Keywords: Microencapsulated phase change materials, Polyurethane, Foam, Heat-treatment, Granularity

In the phase change process, phase change materials (PCM) can absorb and dissipate heats to control the temperature of the environment (Chaurasia, 1981, p.159). Microcapsule is the tiny “container” with the diameter of 1~1000μm, and it is the MicroPCMs which encapsulates phase change materials in the capsule wall and can realize permanent solid state of phase change materials (Xing, 2004, p.2669~2675). MicroPCMs can absorb or dissipate heats in a certain range, and the temperature is almost changeless in the process of heat absorption or heat dissipation, and this special performance has important applications in fibrous fabrics (Hittle, 2002, p.175 & Bryant, 1994 & Kim, 2002, p.1093 & Zhang, 2005, p.3729) and solar-energy (Chaurasia, 1981, p.159).

Polyurethane foam is the reactive product of isocyanate and polymer polyhydric alcohols, which applications come down to many domains (Zhu, 2005). With increasingly enhancement of people living level, the research and development of new soft polyurethane foams are more and more. If the MicroPCMs is added into the polyurethane foamed system, the foam with heat storage can be made, and this foam can store heats and regulate temperature (Bryant, 1996). Through a series of experiments, we study effects of MicroPCMs granularity and heat treat treatment condition on the structure and performance of polyurethane foams and primarily explore how to make polyurethane foams with high contents of MicroPCMs.

1. Experiment

1.1 Materials

(1) Combustion modified high resilience foam made by Jiangyin Yobo Polyurethane Co., Ltd. Specification: A group (combined polyether) YB-5181, B group (isocyanate) YB-6280. Technical data advised by the factory: quality proportion A:B=100:33, material temperature: 25±2°C, model temperature: 60±5°C, mold release time: 300~600s.

(2) Dibutyltin dilaurate (DBTL) and chemical purity made by Tianjin Chemical Reagent First Factory. PEG-400 and chemical purity made by Tianjin Tiantai Fine Chemical Co., Ltd.

1.2 The preparation of MicroPCMs

Take melamine-formaldehyde as the capsule ware, n-octadecane (imported from US. The melting point is at 28.5°C and the phase change heat is 242.4J/g) as the capsule core and adopt the in-situ polymerization method to make MicroPCMs (Zhang, 2004, p.300), and the contents of phase change materials is about 65wt%, the granule diameter of MicroPCMs is about 1~5μm. The microcapsule felts in the process of desiccation and dehydration and forms agglomeration particles,

and the diameter of agglomeration particles can achieve 1mm. Take MicroPCMs pass 80-eyes screen and make the diameter of agglomeration particles $\leq 180\mu\text{m}$.

1.3 The preparation of polyurethane foam with MicroPCMs

Mix MicroPCMs, A material, PEG-400 and DBTL according to their prescriptive quantities around intensely in the beaker, and add B material when MicroPCMs spread around in the system, and beat up quickly in 5~10s, and when the glue liquid blanches, put it in the mold, and after about 1 minute, transfer it to the oven at 60°C to foam. Release the mold when it is solidified, and so the polyurethane foam with MicroPCMs is made.

1.4 Testing and tokens

In the oven with constant temperature, respectively at 110°C, 120°C, 130°C, 140°C, 150°C and 160°C, implement heat treatment to MicroPCMs in 30 minutes, and adopt Perkin Elmer DSC-7 differential scanning calorimeter to implement heat differential analysis to the sample of polyurethane foam, and the testing range is 0~80°C, and the scanning speed is $\pm 10^\circ\text{C}/\text{min}$, and implement the protection with N₂.

Through the golden sprayed treatment to the sample of the foam, observe the cell structure of the polyurethane foam by the Quanta 200 scanning electron microscope.

Implement the test of the viscosity to A material, MicroPCMs, PEG-400 mixture by the NDJ-1 Revolving Viscosity Tester made by Shanghai Precision & Scientific Instrument Co., Ltd.

2. Results and discussions

2.1 Effects of MicroPCMs granularity on foaming

After the filling is added into the polyurethane foaming system, because the initial viscosity and surface strain of the system, the phenomena including volume shrinking, interior break, exterior break, even foam breaking and collapse will occur in the foaming process (Wu, 2005, p.5). And the capsule wall material will contain much hydroxyl group, so the MicroPCMs need to be added into the polyurethane foaming system, and dosages of various group parts, mainly including B material and organic tin activator (DBTL used in this research), need to be regulated to make better foams.

Add MicroPCMs with big granularity and without screening into the foaming system and regulate dosages of various group parts, the better foams can be made, which is show in Table 1.

After take MicroPCMs pass the 80-eyes screen (granularity $\leq 180\mu\text{m}$), foam according to the prescription of Table 1, and the result shows that foam combination and break are very serious in the foaming process and it is hard to make better foam. The reasons may include that a great lot additives such as formaldehyde, antifoam, emulsification and so on are used in the making process of MicroPCMs, and these additives stayed in finished capsules will badly influence foaming. When MicroPCMs don't pass the eyes screen, their granularities are very big, and even some parts will agglomerate, so the remnant additives absorbed on the surface are few, which has little influences to foam, and better foams can be made through the regulation of the prescription, but because some MicroPCMs agglomerations are too big (which diameter can achieve 1mm) to enter in the polyurethane foam evenly, and they will spread in the foam, which will produce limitations in the foam and decrease the performance of the polyurethane. Therefore, to improve the performance of the polyurethane foam, MicroPCMs with small granularity should fully enter into the polyurethane body. When MicroPCMs pass the 80-eyes screen, their granularities will decrease and their surface areas will increase, and the remnant additives absorbed on the surface will comparably increase, which will seriously influence foaming and induce foam combinations and foam breaks.

2.2 Effects of MicroPCMs heat treatment on foaming

Implement heat treatment to MicroPCMs screened by the 80-eyes screen under different temperatures, eliminate remnant formaldehyde and absorbed water (Zhang, 2004, p.300), reduce the diameter of agglomeration particles and regulate the prescription group parts to foam, and the results are shown in Table 2.

From Table 2, we can see that after the heat treatment to MicroPCMs screened by the 80-eyes screen, they can be made better foam materials, and the reason may be that in the process of heat treatment, the volatilizations of remnant formaldehyde and water reduce bad influences to the foaming. When MicroPCMs are treated respectively at 110°C and 120°C, the made foams have bulky apertures because the temperature of heat treatment is too low and the volatilizations of formaldehyde and water are less.

Table 3 shows the heat performance of MicroPCMs after heat treatment. When the temperature of the heat treatment is bigger than 110°C, the performance will be reduced because when the temperature of heat treatment is higher, part of MicroPCMs break and the material (n-octadecane) in the capsule core sublimes. So the condition of heat treatment should be at 130°C and in 30 minutes.

Add MicroPCMs through 80-eyes screen treated at 130°C and in 30 minutes into the polyurethane foaming system, and the foaming prescription is seen in Table 4.

When the additive quantity of MicroPCMs is bigger than 20parts, the mixture of MicroPCMs and A material presents paste state, and its system viscosity is very high, and MicroPCMs are difficult to evenly spread around in the system, and the ideal foams are difficult to be made however to regulate dosages of various group parts.

2.3 Effects of MicroPCMs granularity on the cell structure and the compressibility of polyurethane foams

Figure 1 shows TEM photos of the polyurethane foam cell structure. When MicroPCMs are added into the foaming system, the cell diameter is generally smaller than it without MicroPCMs, which is induced by the “core formation” function and accords with the rule that general added powder filling will reduce the cell diameter. The polyurethane foams made by adding MicroPCMs through 80-eyes screen into the foaming system have more even cell structure and put up good even characteristic.

2.4 Preparation research of the polyurethane foam with high content of MicroPCMs

Mix MicroPCMs (after heat treatment) with A material (the initial viscosity is 1425mPa) at room temperature, and with the increase of MicroPCMs, the viscosity will rise, which is seen in Figure 2. When additive parts of MicroPCMs are bigger than 20, the system viscosity is too high (for example, when the additive quantity of MicroPCMs is 25 parts, the mixture dynamics viscosity is 9800mPa) to make better foams.

In this experiment, we regulate the system viscosity through interfusing PEG-400 into the mixed system, and the results are shown in Table 5. When PEG-400 is mixed into the mixed system, the system viscosity will decrease and the better foam with maximum content of 28 parts of MicroPCMs can be made. When the additive quantity of MicroPCMs is 30parts, the foam shrinks seriously, because the content of vesicant in A material (combined polyether) is relative deficient, the foaming gas will reduce. Therefore, when the polyurethane foam with high content of MicroPCMs is made, the system viscosity is a very important factor, and we also can see that if the polyhydric alcohols system with low initial viscosity is used and the prescription ratio of various group parts is regulated, it can further enhance the content of MicroPCMs.

Figure 3 and Figure 4 are respectively DSC temperature rise and drop curves of polyurethane foam with different contents of MicroPCMs. The polyurethane foam without MicroPCMs has not heat adsorption and heat dissipation, and the polyurethane foam with MicroPCMs has heat adsorption and heat dissipation, and with the increase of content of MicroPCMs, its phase change heat will increase, and the measured value is smaller than the theoretical computation value perhaps because of the heat stagnation function of the polyurethane.

3. Conclusions

- (1) It needs to regulate dosages of various group parts to make better foam when adding microencapsulated n-octadecane into the polyurethane foaming system.
- (2) When the microencapsulated n-octadecane with small granularity is added, the proper heat treatment should be implemented to eliminate remnant formaldehyde and water and reduce bad influences for foaming.
- (3) The microencapsulated n-octadecane with small granularity added can enhance the equal character of the foam and make for the equality of the foam.
- (4) When the microencapsulated n-octadecane with small granularity is added, the system viscosity will increase, so the proper decrease of system viscosity can make the foam with higher content of microencapsulated n-octadecane.
- (5) The polyurethane foam with microencapsulated n-octadecane absorbs heat at about 27°C and dissipates heat at about 25°C, and the heat storage can achieve 18J/g.

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Table 1. Polyurethane foaming prescription with MicroPCMs (without screening)

A material/pphp	B material/pphp	MicroPCMs/pphp	Added DBTL /pphp	Foam
100	33	0	0	better
100	33	5	0.32	better
100	33	7	0.32	better
100	33	10	0.43	better
100	35	12	0.55	better
100	38	15	0.65	better
100	39	17	0.65	better
100	40	20	0.85	good

Note: “pphp” is the quality parts relative to 100 parts of polyhydric alcohols.

Table 2. Effects of MicroPCMs heat treatment on foaming

A material/pphp	B material/pphp	DBTL/pphp	MicroPCMs after heat treatment/pphp	Foam
100	36	0.55	15 (110°C for 30min)	bulky aperture
100	36	0.55	15 (120°C for 30min)	bulky aperture
100	36	0.55	15 (130°C for 30min)	better
100	36	0.55	15 (140°C for 30min)	better
100	36	0.55	15 (150°C for 30min)	better
100	36	0.55	15 (160°C for 30min)	better

Table 3. Heat performance of MicroPCMs after heat treatment

A material/pphp	B material/pphp	MicroPCMs/pphp	Added DBTL /pphp	Foam
100	33	0	0	better
100	33	5	0.32	better
100	33	7	0.32	better
100	33	10	0.43	better
100	35	12	0.55	better
100	38	15	0.65	better
100	39	17	0.65	better
100	40	20	0.85	good

Note: T_m represents the melt point, T_c represents the freezing point, ΔH_m represents the melt enthalpy, ΔH_c represents the crystal enthalpy, and $\Delta H_a = (\Delta H_m + \Delta H_c)/2$.

Table 4. Polyurethane foaming prescription containing MicroPCMs through 80-eyes screen

A material/pphp	B material/pphp	MicroPCMs /pphp	DBTL/pphp	Foam
100	33	0	0	better
100	33	5	0.32	better
100	33	7	0.32	better
100	33	10	0.32	better
100	34	12	0.55	better
100	36	15	0.55	better
100	38	17	0.65	better
100	38	20	0.85	better

Table 5. Foaming prescription interfused PEG

A material/pphp	PEG-400/pphp	B material/pphp	DBTL/pphp	MicroPCMs/pphp	Dynamics viscosity/ mPa	foam
92	8	36	0.55	22	6600	better
88	14	38	0.65	25	6900	better
80	20	41	0.85	28	7300	good
74	26	43	0.85	30	7600	foam shrinking

Table 6. Heat performance of polyurethane foam containing MicroPCMs

MicroPCMs/parts	Tm/°C	ΔHm/J/g	Tc/°C	ΔHc/J/g	ΔHa/J/g	ΔH/J/g
0	-	0	-	0	0	0
22	27	16	24	17	16.5	19
25	26	17	24	18	17.5	21
28	27	19	25	18	18.5	23

Note: ΔH is the theoretical computation value.

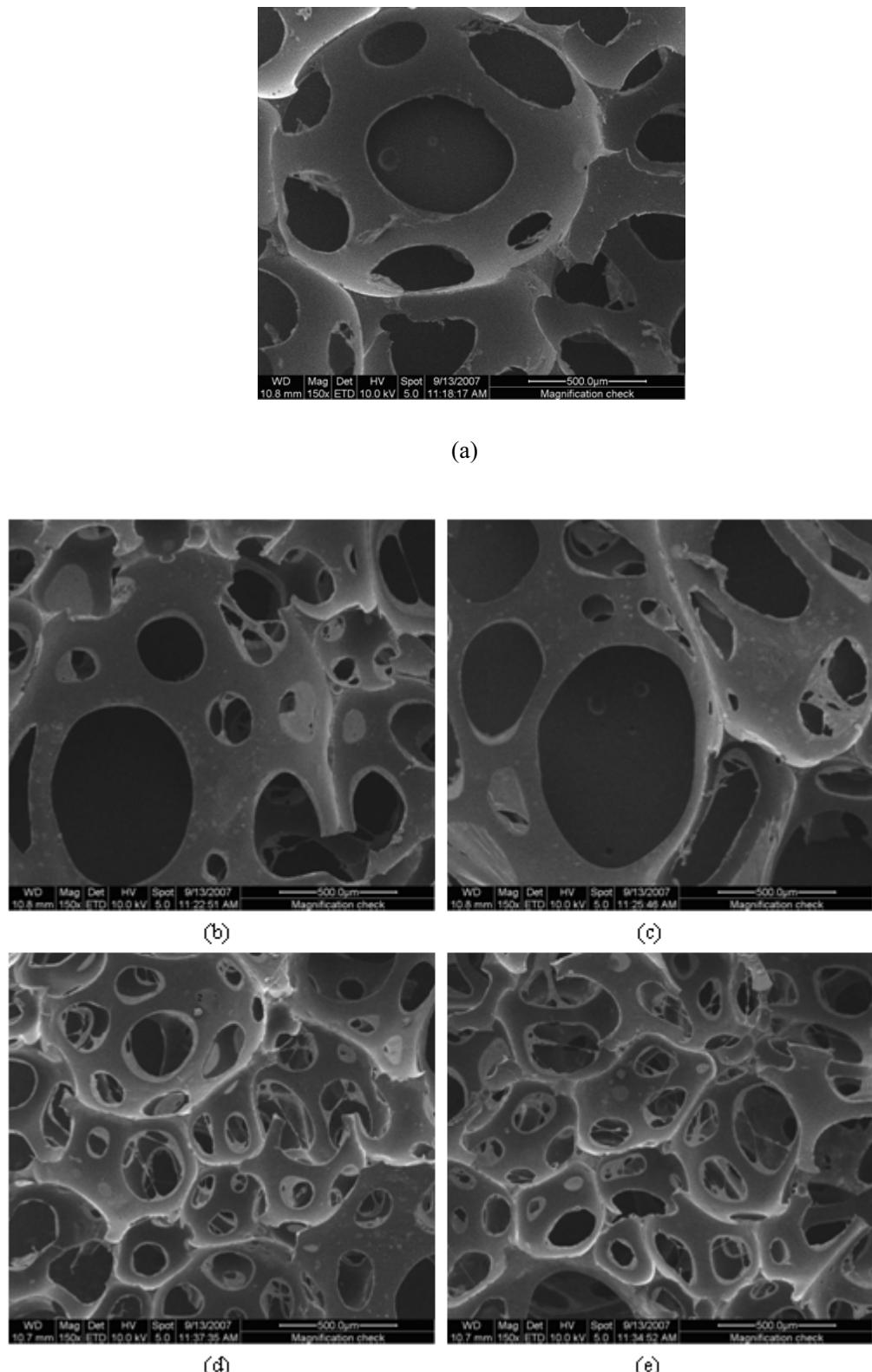


Figure 1. SEM Photos of Polyurethane Foam Cell Structure ((a) doesn't contain MicroPCMs, (b) contains 15pphp MicroPCMs without screening, (c) contains 20pphp MicroPCMs without screening, (d) contains 15pphp MicroPCMs through 80-eyes screen, (e) contains 20pphp MicroPCMs through 80-eyes screen)

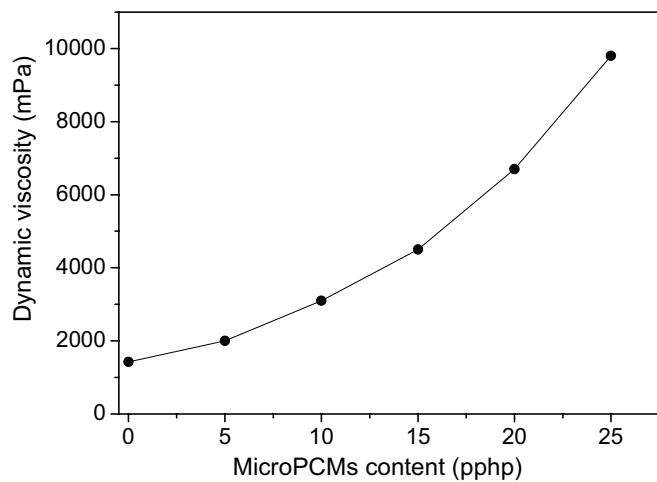


Figure 2. Mixture Dynamics Viscosity: MicroPCMs Content Curve

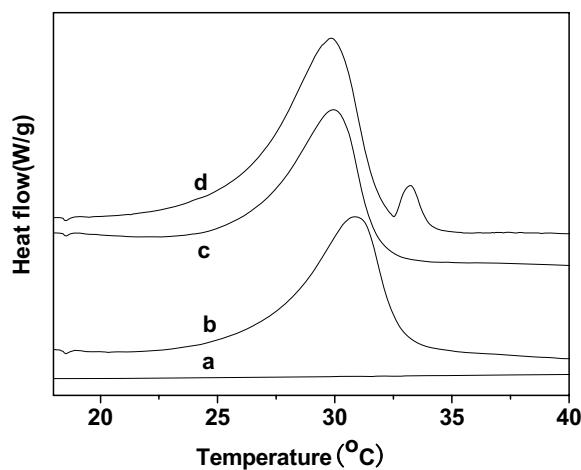


Figure 3. DSC Temperature Rise Curve of Polyurethane Foam with Different Contents of MicroPCMs
(a: 0pphp, b: 22pphp, c: 25pphp, d: 28pphp)

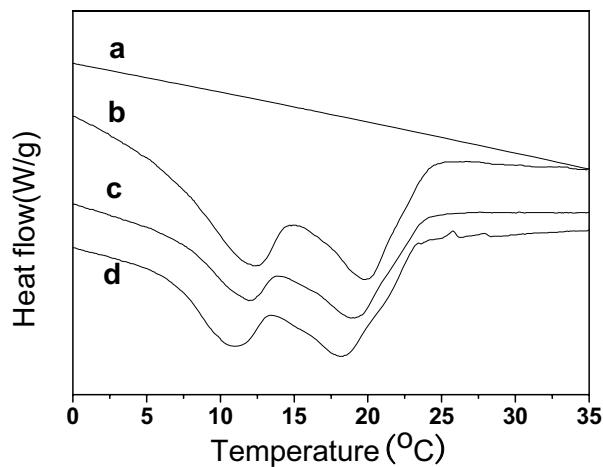


Figure 4. DSC Temperature Drop Curve of Polyurethane Foam with Different Contents of MicroPCMs
(a: 0pphp, b: 22pphp, c: 25pphp, d: 28pphp)