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Preparation and Characterization of High Stability Polyurea MicroPCMs Using a Two-step Method of Adding DETA by Interfacial Polymerization

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Abstract

Butyl stearate and polyurea resin polymerized via toluene-2, 4-diisocyanate (TDI) and diethylene triamine (DETA) were respectively used as the core material and the shell material in preparing MicroPCMs. The phase change properties, chemical structure, surface morphology and particle size and size distribution of microcapsules were investigated by using DSC, FTIR, SEM and Malvern laser particle size analyzer. The results show that the prepared MicroPCMs were smooth and compact. Their melting temperature and enthalpies were 23.3 °C and 79.7 J · g^{-1} respectively. The average diameter of microencapsulated PCM (MicroPCMs) is in the range of 4.5∼10.2 μm under the stirring speed of 3000∼6000 rpm. Furthermore, a two-step method of adding DETA was firstly presented, through this method, the heat stability and ethanol wash stability of the MicroPCMs has been greatly improved, and the shell of MicroPCMs prepared by the two-step method has better stability and compactness than one-step method.

Keywords: Microcapsule; Phase Change Material; Polyurea; Butyl Stearate; Interfacial Polymerization

1 Introduction

Microcapsule is a kind of small particle that contains an active agent or core material surrounded by a coating or shell [1]. Microencapsulated phase change materials (MicroPCMs) are microcapsules that contain Phase Change Materials (PCM) [2]. Due to the protection of the shell, MicroPCMs are not easily affected by the surrounding environment due to the protection of the shell, they can absorb, store and release large amounts of latent heat over a certain temperature range when experiencing a phase transition [3]. MicroPCMs can be conveniently applied in solar and nuclear heat storage systems [4], building energy saving [5], textile fibers [6], garments [7], foam plastics [8], coating and composite materials [9].

At present, Melamine Formaldehyde (MF), Urea-formaldehyde (UF), and polyurea are usually selected as shell materials for MicroPCMs [10-12]. Although there are more research achievements

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for MF and UF, and the prepared microcapsules have high strength and good heat resistance, there is a formaldehyde releasing problem, and can bring harmful effects on the environment and health. Polyurea shell on the other hand does not contain formaldehyde, and therefore has attracted the attention of more and more researches, as it can improve the preparation and use environmental characteristics in the environment. Unfortunately, there are some problems; the reaction rate between the diisocyanate and the diamine compound is quick, and its reaction control is difficult, as well as side reactions between diisocyanate and water. All these causes the instability of the phase change material content, which is from the core material of the microcapsule shell, and also causes enthalpy to be generally low. Moreover, studies show that the diisocyanate and diamine reaction in the aqueous phase can form a shell with high permeability significantly, cannot play a good protection object of the core material, and the prepared microcapsules have poor stability and compactness.

Therefore MF and UF have been widely used as wall material microencapsulated phase change material. Although polyurea shell MicroPCMs is conducive to health and environmental protection, its application has been largely restricted because of the poor stability and compactness problem. Specifically, for some areas of the stability and relatively high density of the microcapsule, its application is more limited. For example, the preparation of coated thermo-regulating textiles requires prepared MicroPCMs with a high temperature resistance, while the polyurea needs to have strong permeability, especially when heated at high temperatures (for example at 130 °C and above) in a dry state, which may be necessary for fabrics coating in the curing stages.

There are some reports about MicroPCMs containing octadecane prepared through interfacial polymerization [13-15]. However, the encapsulation effect is not satisfied due to poor intersolubility for octadecane and Toluene-2, 4-diisocyanate (TDI). To improve the intersolubility, cyclohexane is usually added. However, the improvement of solubility is limited because cyclohexane and octadecane are all non-polar materials. In addition, cyclohexane decreased the energy storage density of MicroPCMs. In this investigation butyl stearate was selected as PCM. As a polar material, it has complete miscibility with TDI and has a high latent heat, and its phase change temperature is close to that of the octadecane.

In recent years, workers in this field have paid more attention to improve the core contents, thermal stability and compactness of MicroPCMs [15-18]. In the related reports increase in reaction temperature, prolonging reaction time and higher stirring speed are all helpful to improve the stability of microPCMs but the effect is limited.

Aqueous phase reactive monomer DETA in previous studies was one-step added, while DETA was two-step added in this paper. That is, a part of DETA solution was firstly added to conduct an interfacial polymerization reaction. Then, another portion of DETA solution was added until the reaction was carried out to a certain extent, the DETA further increased to the surface of the capsule shell and internal diffusion, so that the unreacted isocyanate groups was fully reacted, and the polymerization reaction was completed. As verified by the results, the method we proposed can greatly improve heat stability and solvent stability of the microcapsules. Meanwhile, the microcapsules we prepared have good thermal storage performance, and no harmful substances were released. (i.e. formaldehyde) Furthermore, the microcapsules are environment-friendly materials, and can be used for the temperature controlling medium in many areas.