Synthesis of poly(urea–formaldehyde) encapsulated dibutyltin dilaurate through the self-catalysis of core materials

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Abstract: Polymeric microcapsules (MCs) filled with catalyst can be controlled to release the catalyst to initiate the polymerization reaction. In the present work, poly(urea–formaldehyde) (PUF) MCs filled with DBTDL (PUF/DBTDL MCs) were prepared using urea (U) and formaldehyde (F) as the wall shell materials by in situ polymerization. The U–F resins could easily polymerize in the presence of the core material DBTDL to produce PUF polymers, then they deposited on the surface of the DBTDL droplets, forming PUF/DBTDL MCs. The decomposition temperature (T_d) at 5 % weight loss of PUF/DBTDL MCs was about 245 °C. The application of PUF/DBTDL MCs to cyanate ester resins preliminarily showed the reaction control capability of the MCs due to the slow release of DBTDL through the wall shell.

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Key words: Microcapsule, Catalyst, Properties, Diffusion-controlled reaction, Characterization

1. Introduction

Organotin compounds can be widely used as catalysts to initiate the polymerization process of thermoset resins such as epoxy resins [1], polyester [2], cyanate ester resins [3, 4] and polyurethane [5]. The most commonly used organotin compound is dibutyltin dilaurate (DBTDL), which is exceptionally versatile and effective for polymerization [2–4, 6, 7]. However, because of the high catalytic activity, even small additions of DBTDL can lead to sharp increase in reaction rates, in some cases leading to un-controlled reaction and difficult processability. References have been reported that polymeric microcapsules (MCs) containing catalysts can be designed to control the releasing of catalyst in response to environmental conditions such as humidity [8], temperature [9], electric field [10], light [11, 12] and ultrasound [13], so MCs used as catalyst controllers for the chemical reaction have gradually attracted more attentions from researchers. For example, Deyrai et al. [14] reported that polycarbonate microparticles filled with DBTDL could release DBTDL to control the ethylene-co-vinyl acetate (EVA) crosslinking reaction. Vallance et al. [15] stated that the encapsulated catalyst controlled the polymerization of a cyclic polycarbonate oligomer composition at elevated temperature. Kim [16] illustrated that the addition of microencapsulated latent catalyst could cure epoxy resins, lower cure conversion rate and obtain a good shelf-life for epoxy resin. Cho et al. [17] demonstrated that the polyurethane microcapsules containing DBTDL embedded in a vinyl ester matrix were broken by mechanical damage and released DBTDL to initiate the polymerization between hydroxyl end-functionalized polydimethylsiloxane (HOPDMS) and

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polydiethoxysiloxane (PDES). Obviously, the encapsulated catalyst offers a safer and effective solution to control the polymerization reaction as well as enhances the shelf-life to accommodate process time for polymer composites.

In this work, the microencapsulated DBTDL has been designed and studied. PUF was selected as the wall shell to encapsulate DBTDL due to its wide acceptance as the wall shell [18–23]. Although PUF MCs can be easily synthesized in situ technique in water, the heating, acid or alkali fluids must be carefully controlled to obtain the satisfied structures and properties of PUF MCs, and the PUF MCs synthesis process is a multistep control system [18–23]. In the present study, PUF microcapsules filled with DBTDL catalyst were synthesized in water through a selfcatalysis of DBTDL core material method. Because DBTDL is slightly soluble in water (<0.1 g/100 mL at 20 °C), and the dissolved DBTDL dissociates to form carboxylic acid [24], which catalyzes the polymerization of urea (U)–formaldehyde (F) resins at room temperature, the complex process of the MCs can be simplified for the lack of heating and external acids. The synthesized PUF/DBTDL MCs were investigated using confocal Raman spectroscopy, scanning electron microscopy (SEM), optical microscopy (OM), laser scanning confocal microscopy (LSCM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to determine chemical structure, morphology, size distribution, and thermal stability. The PUF/DBTDL MCs were applied to cyanate ester resins to demonstrate the proof of the diffusion-controlled reactions.

2. Experimental

2.1Materials

Urea (U) and 37 wt% formaldehyde (F) were selected as shell materials, which are bought from Tianjin Chemical Plant, China. Sodium dodecylbenzenesulfonate (SDBS, 99 % purity) used as the emulsifier and triethanolamine (TEA) were bought from Tianjin Chemical Reagents Factory, China. Analytical grade dibutyltin dilaurate (DBTDL, density: 1.066 g/mL at 25 °C; thermal decomposition >250 °C; molecular weight: 631.65; water solubility:<0.1 g/100 mL at 20 °C) was used asreceived condition and provided by Tianjin Damao Chemical Reagents Factory. Industrial grade bisphenol A dicyanate ester resins (BADCy, molecular weight 278) with 98 % purity were obtained from Zhejiang Shangyu Shengda Biochemical Co. Ltd, China.

2.2Preparation of MCs

(1) At room temperature (20–25 °C), U (10.0 g, 0.167 mol), F (7.4 g, 0.246 mol) and deionized water (30.0 g, 1.667 mol) were mixed in a 500 mL three-neck round-bottomed flask that connected to a reflux condenser and equipped with a mechanical stirrer. After the U dissolved, the pH of solution was adjusted to 8–9 with TEA at 60–70 °C for 1 h to produce the U–F prepolymer solution.

(2) Under agitation, 100 mL of 0.5 wt% aqueous solution of SDBS was added to the prepolymer solution, DBTDL (60.0 g, 0.095 mol) was added to form an oil–water (O/W) emulsion. After

3 h, the reaction was complete. The suspension of MCs was rinsed with deionized water and acetone, filtered, and air-dried for 24 h. The yield of MCs was 65.6 g.

2.3Raman spectroscopy

Raman spectroscopy and Raman imaging of the MCs were performed at room temperature using a micro-confocal Raman spectrometer (Horiba JY-HR800) equipped with a piezo-scanner and high-NA objectives. Circularly polarized laser light (CrystaLaser, λ = 532 nm) was focused on the surface or the center of samples with a diffraction-limited spot size (≈λ/2). The center of MCs was determined by moving the laser light probe based on the pre-calculated distance (MCs' radius) from the outer surface of MCs. An avalanche photodiode detector (APD) was used to record high resolution Raman images. Figure 1 shows the crosssectional view of MCs.

2.4Confocal laser scanning microscopy

The structures of PUF/DBTDL MCs were examined in the reflection and transmission mode using the 488 nm line of an air-cooled argon laser of a confocal laser scanning microscope (CLSM, Leica TCS SP2, Leica Microsystems GmbH, Germany). For imaging purpose, a dispersion of dry MCs in water was prepared. Under these conditions, the shell wall could be clearly distinguished from the background.

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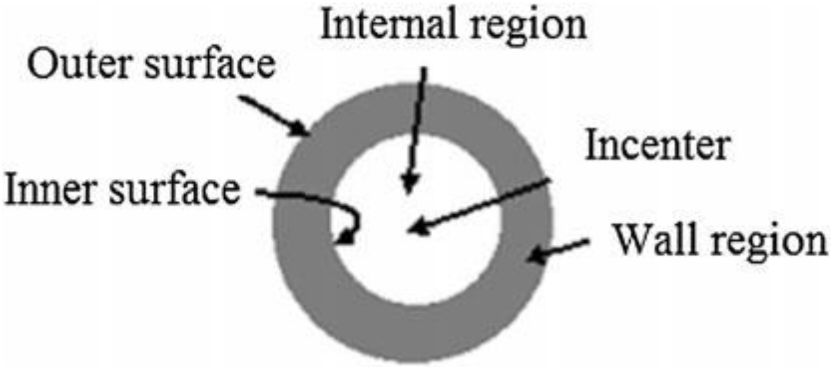

Figure 1: *Cross-sectional view of MCs*

2.5Scanning electron microscopy

The surface morphologies of PUF/DBTDL MCs were observed using a scanning electron microscope (SEM, S-4700).

2.6Light microscopy

The morphologies of samples were observed using light microscope (LM, SMZ-B2, Chongqing Aote Optics Instrument Co., Ltd).

2.7Size analysis

The size analysis of PUF/DBTDL MCs was performed using a laser particle size analyzer (OMEC LS800).

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2.8 Thermal analysis

Differential scanning calorimetry (DSC, 2910 MDSC, TA Instruments) was performed at a heating rate of 10 °C/min in a nitrogen atmosphere. Thermogravimetric analysis (TGA Q50, TA Instruments) was performed at a heating rate of 10 °C/min in a nitrogen atmosphere.

2.9 Measurement of pH

The pH of the solvent solutions was measured using a pH-Potentiometer (ZD-2, Shanghai Precision and Scientific Instrument Co. Ltd.).

2.10 Determination of MCs core content

The DBTDL core content was extracted using acetone as solvent. The MCs samples were initially ground and washed with acetone at room temperature, then the residual PUF shell materials were placed for dry. Based on the initial weight of intact MCs (W_{MCs}) and the weight of the residual MCs shell walls (W_{UF}), the DBTDL core content (W_{core}) of the MCs was calculated using Eq. (1).

$$W_{\text{core}} = \left(1 - \frac{W_{\text{UF}}}{W_{\text{MCs}}}\right) \times 100\,\% \tag{1}$$

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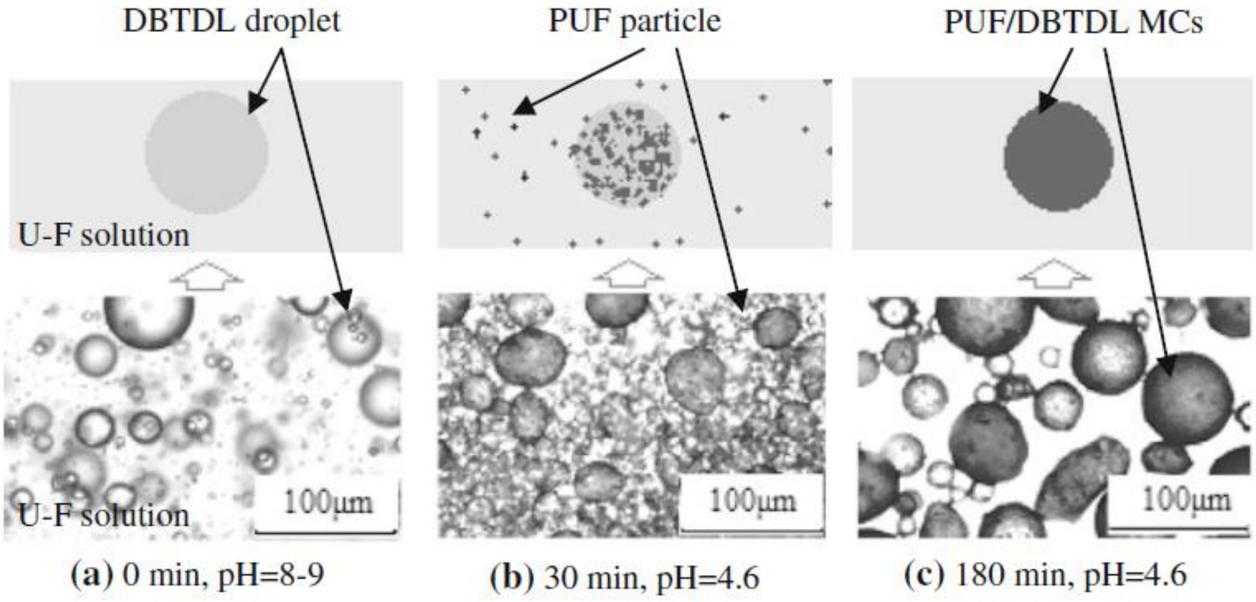
3. Results and discussion

3.1Microencapsulation process

Figure 2 shows the process for encapsulating DBTDL droplets at room temperature. Figure 3 shows the chemical structures of DBTDL, U, F and PUF [25]. When DBTDL is poured into the prepolymer solution of U–F resins, DBTDL droplets can form while constant stirring as shown in Fig. 2a. Because DBTDL is slightly soluble in water, a trace amount of DBTDL dissolves in water and dissociates to form carboxylic acid [24], which initiates the condensation reaction of the U–F resins at the interfaces between DBTDL droplets and U–F resins. The cross-linked PUF polymer aggregates/particles deposit on the surface of DBTDL droplets, forming PUF/DBTDL MCs as shown in Fig. 2b. As the processing time increases, more PUF polymer aggregates/particles deposit on the surface of DBTDL droplets, increasing the thickness of the shell wall. After 3 h, the reaction is complete and the MCs can be separated easily from the solution (Fig. 2c). Figure 4 shows the size distribution of PUF/DBTDL MCs. The mean diameter of MCs is about 76 lm, and the size distribution is asymmetric. In this study, the DBTDL core content of PUF/DBTDL MCs is approximately 88 %. Figure 5 shows the solution pH value over time after DBTDL addition. During the microencapsulating process, the solution pH value decreases from 9 to 4.6, indicating that DBTDL in water solution generates acid. However, once DBTDL droplet is encapsulated and the wall shell is well formed, the DBTDL core material is isolated from the water solution, arresting the hydrolysis of DBTDL and stabilizing the solution pH.



(a) 0 min, pH=8-9 (b) 30 min, pH=4.6 (c) 180 min, pH=4.6

Figure 2: The process for encapsulating DBTDL droplets at room temperature

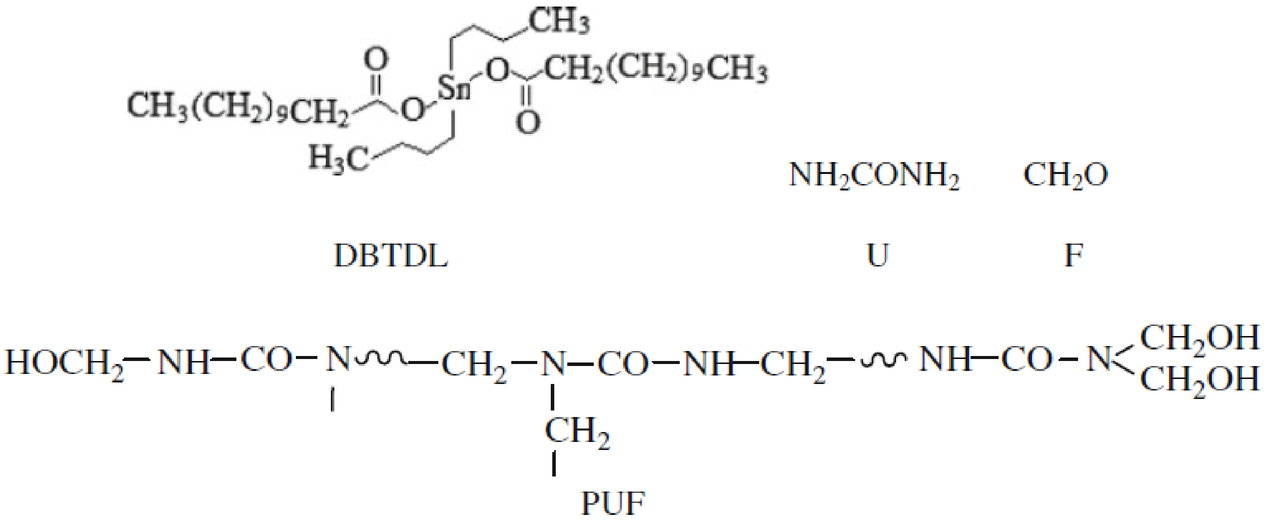


***Figure 3:** The chemical structures of DBTDL, U, F and PUF*

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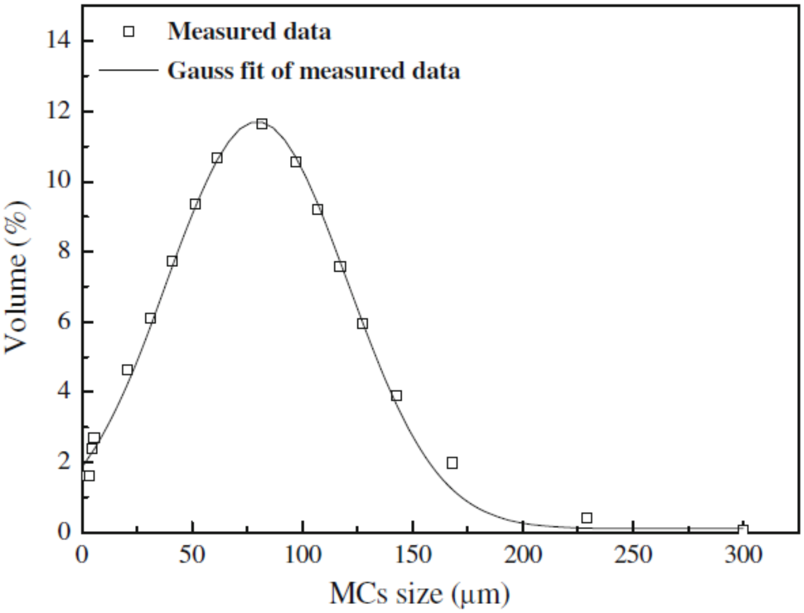
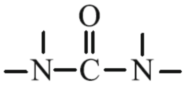


Figure 4: *The size distribution of PUF/DBTDL MCs*

3.2Chemical structure of MCs

Raman spectroscopy was employed to determine the structure of PUF/DBTDL MCs and confirms that DBTDL was encapsulated. Figure 6 shows the spectra of PUF, DBTDL, the outer surface and the central ingredient of the PUF/DBTDL MCs. The PUF spectrum exhibits the –NH– and –OH vibration peaks at 3,707–3,050 cm^{-1} and the  $-\overset{|}{N}-\overset{\overset{O}{\|}}{C}-\overset{|}{N}-$ vibration peaks at 1,649 and 1,544 cm^{-1}. The DBTDL spectrum contains strong absorbance peaks of –CH3 and –CH2– at ~2,852 to 2,954 cm^{-1},

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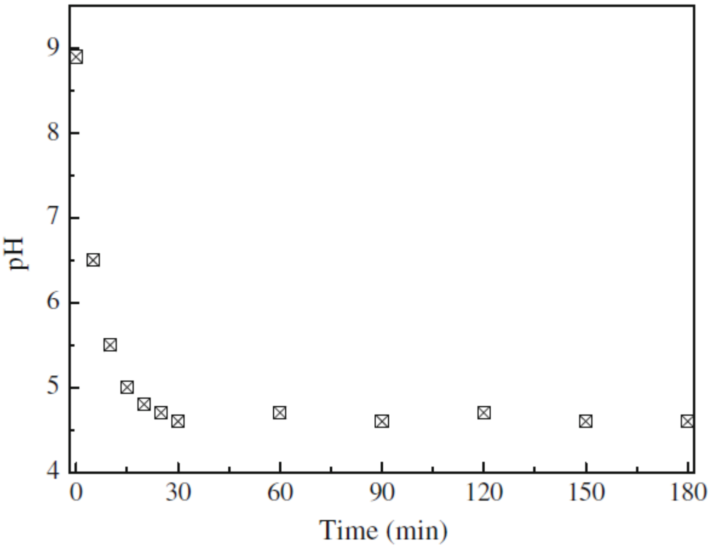

Figure 5: *The pH value of solution over time after DBTDL addition*

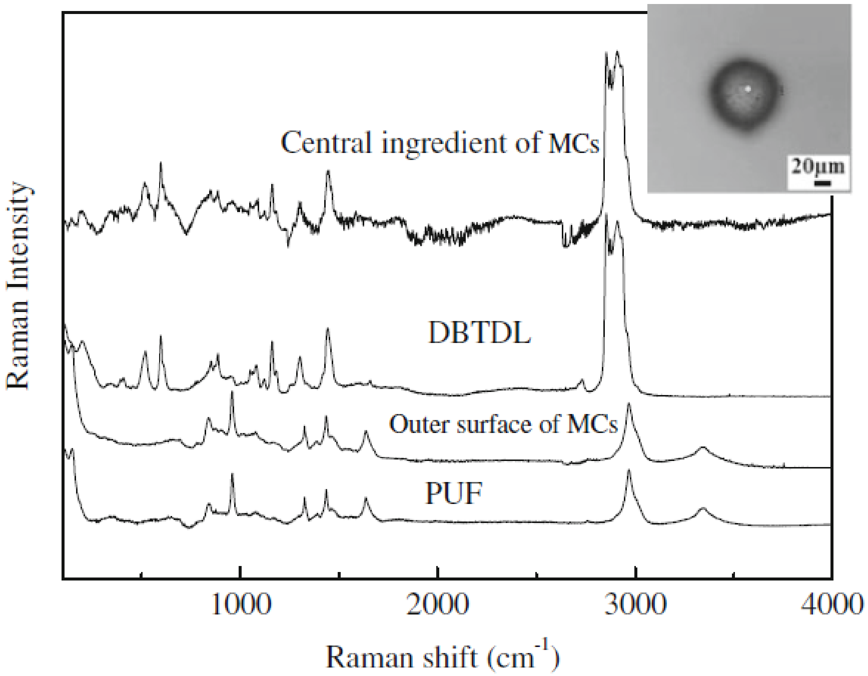

Figure 6: *Raman spectra of PUF, DBTDL, the outer surface and the central ingredient of PUF/DBTDL MCs*

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and the Sn–O absorbance peak at 1,603 cm^{-1}. Using the characteristic peaks of PUF and DBTDL as references, spectra from the outer surface and the centre of PUF/DBTDL MCs reveal that MCs surface contains the characteristic peaks of PUF, while the core of the MCs shows the characteristic peaks of DBTDL. The comparisons indicate that DBTDL is encapsulated with PUF.

Figure 7 shows LSCM images of PUF/DBTDL MCs in transmission and reflection modes. The white ring areas (Fig. 7b) represent the wall shells that encapsulate the DBTDL core material. The shell walls are thin relative to the core.

3.3The thermal stability of PUF/DBTDL MCs

Figure 8 shows DSC curves of PUF, DBTDL and PUF/DBTDL MCs. DSC curve of PUF shows three obvious endothermic peaks at 193, 250 and 275 °C, and they are caused by the several successive thermal degradation steps of PUF [26]. The DSC curve of DBTDL demonstrates an endothermic peak at about 253 °C, and this is caused by the decomposition of DBTDL. As the decomposition reactions for PUF and DBTDL take place at the same temperature (about 250 °C), the endothermic peak on the DSC curve of PUF/DBTDL MCs is attributed to the thermal decomposition of both PUF and DBTDL. However, the PUF decomposition peaks at 193 and 275°C cannot be observed on the DSC curve of PUF/DBTDL MCs because of the lower weight ratio of PUF to DBTDL and the chemical protection from DBTDL [27].

Figure 9 shows TGA curves of PUF, DBTDL and PUF/DBTDL MCs. The weight loss of PUF is due to the removal of entrapped residual water, the elimination of free formaldehyde at lower temperature (<125 °C) and the decomposition of PUF at higher temperatures (>125 °C). The

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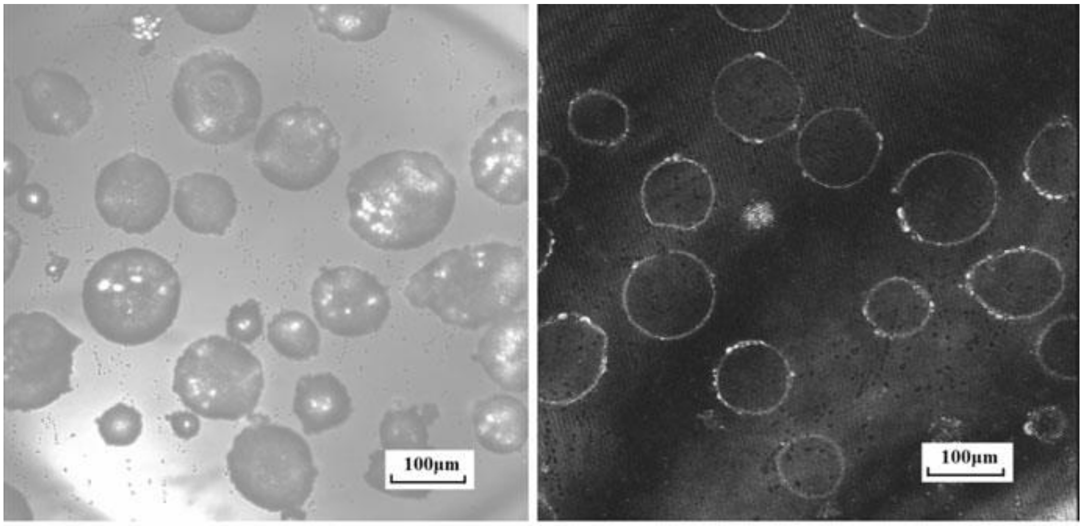
decomposition temperature (T_d) at 5 % weight loss of PUF happens at 121 °C and the maximum thermal decomposition rate of PUF occurs in the range of 250–350 °C. The T_d of DBTDL is 240°C and the temperature of maximum thermal decomposition rate is 250–400 °C. For PUF/DBTDL MCs, the T_d is 245 °C, and the maximum thermal decomposition rate occurs in the temperature range of 250–350 °C that is caused by decomposition of both PUF and DBTDL.



(a) Transmission mode **(b)** Reflection mode

Figure 7: *LSCM images of PUF/DBTDL MCs*

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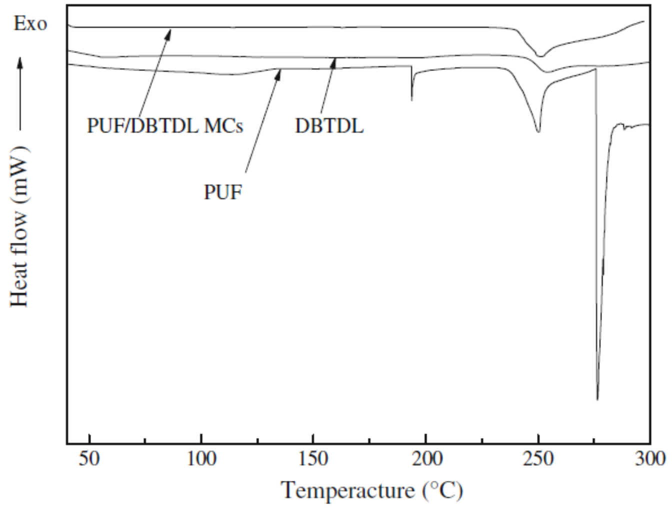


Figure 8: *DSC curves of PUF, DBTDL and PUF/DBTDL MCs*

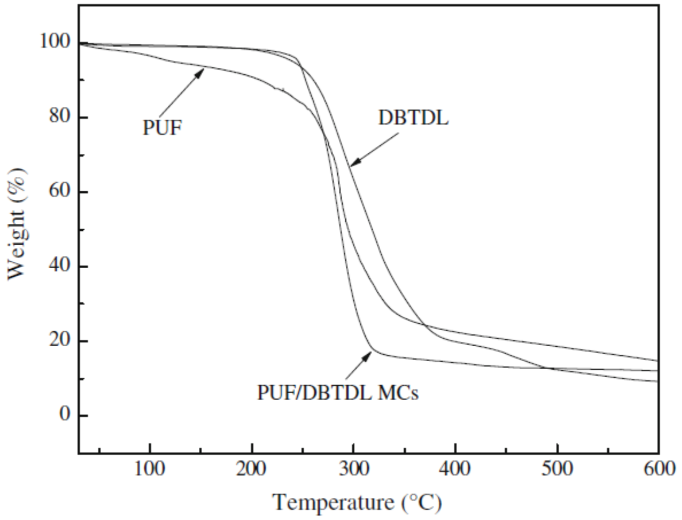
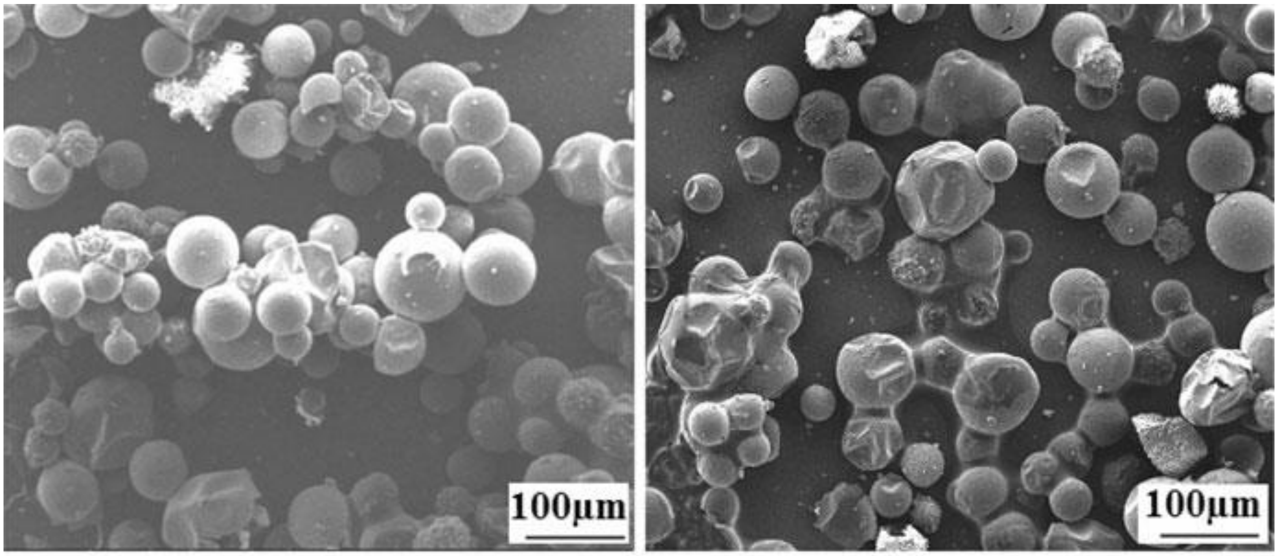
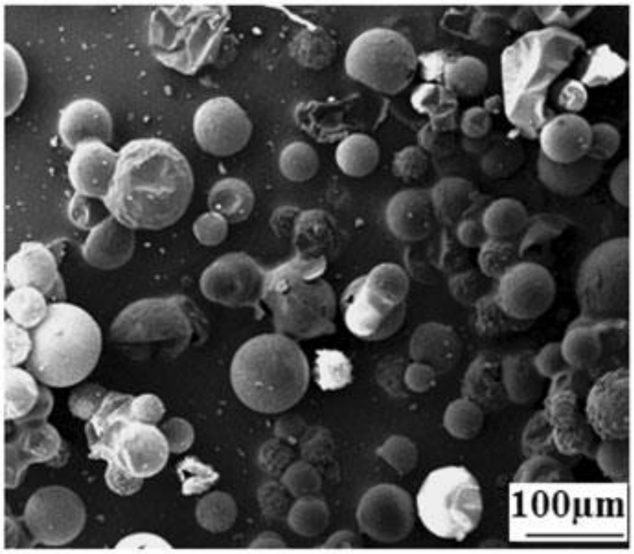


Figure 9: *TGA curves of PUF, DBTDL and PUF/DBTDL MCs*

Figure 10 shows SEM images of PUF/DBTDL MCs treated at 200 °C for 1 and 2 h, respectively. Although some slight dimples and shrinkages can be observed on the surface of the MCs, the MCs can maintain a relative spherical shape after heated at 200 °C for 1 and 2 h, respectively. The shape distortions of the MCs are attributed to the diffusion of core materials, the non-elastic thermal expansion and the contraction during the heating and cooling process [28]. Some coherent MCs appear as shown in Fig. 10c, further supporting the assertion of the diffusion of the core materials during heating.



(a) Fresh MCs (b) 200 °C/1h



(c) 200 °C/2h

Figure 10: *SEM images of PUF/DBTDL MCs after heated at 200 C for 1 and 2 h*

3.4 Application of MCs to cyanate ester resins

In this study, bisphenol A dicyanate ester resins (BADCy) were selected as the reactive resin to illustrate that PUF/DBTDL MCs were capable of catalyzing and controlling the curing temperature of polymer. Normally, catalyst solutions, catalyst derivatives or as-received catalysts can be used to catalyze the polymerization reactions of cyanate ester resins [3, 4, 29, 30], and the concentrations of the catalyst are always 0.001–0.08 % per 100 g cyanate ester. Figure 11 shows DSC curves of BADCy systems with and without DBTDL catalyst, and a series of prototype formulations of BADCy/MCs system. Note that the two systems BADCy/0.11 wt% DBTDL and BADCy/0.125 wt% MCs contain equivalent amounts of DBTDL, affording opportunity for comparison. For all formulations, the endothermic peaks at ~83 °C correspond to the melting of BADCy, while the exothermic peaks above 100 °C correspond to the polymerization of BADCy. The exothermic reaction peak of the pure BADCy occurs at 311 °C, while the addition of 0.11 wt% DBTDL catalyst lowers it to 165 °C. For

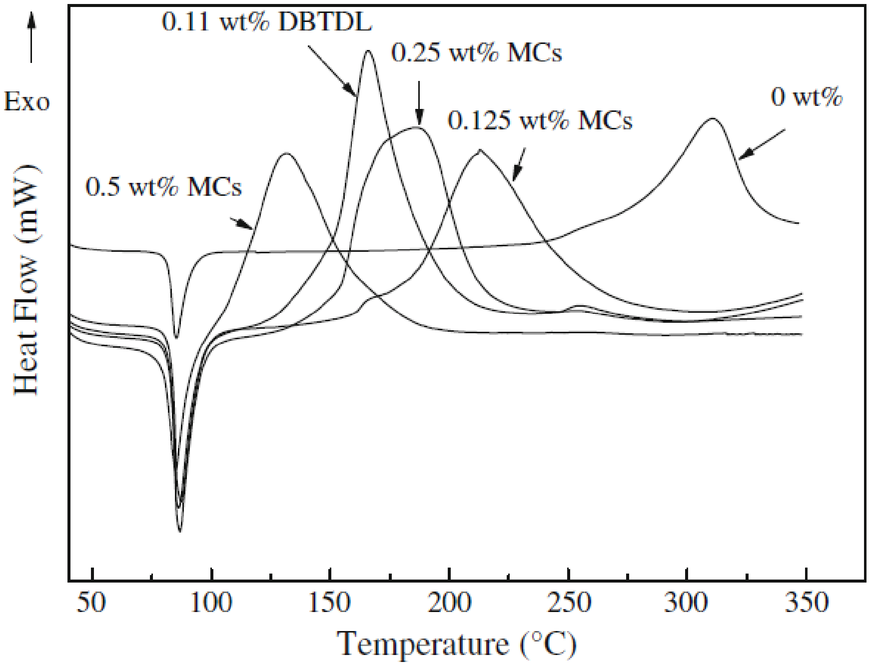


Figure 11: *DSC curves of BADCy systems with and without DBTDL catalyst, and BADCy/MCs systems*

prototype BADCy/MCs formulation containing 0.125 wt% MCs, the polymerization temperature is 220 °C, which is substantially different from the polymerization temperature of ‘‘standard’’ BADCy/0.11 wt% DBTDL. Moreover, the reaction peak width (FWHM) of BADCy/0.125 wt% MCs is 53 % broader than that of BADCy/0.11 wt% DBTDL. The reason is that the DBTDL catalyst is gradually released across the shell walls under the heating condition. The addition of 0.25 and 0.5 wt% MCs can reduce the exothermic peak temperature of the pure BADCy to 181 and 123 °C, respectively. Obviously, simply varying the content of the encapsulated DBTDL can effectively control the reaction temperature of BADCy and afford greater flexibility in process design, which are important for the manufacture of polymer composites.

4. Conclusions

PUF/DBTDL MCs were successfully synthesized through the self-catalysis of DBTDL core materials because the acid generated by hydrolysis of DBTDL in water led to the polymerization of U–F resins. The PUF/DBTDL MCs exhibited good thermal stability up to ~245 °C. The DBTDL catalyst could be released from PUF/DBTDL MCs by heating. The utility of the MCs was explored by formulating prototype BADCy blends, demonstrating that PUF/DBTDL MCs had the ability to adjust the polymerization temperature by varying the content of MCs under heat conditions. The ability of PUF/DBTDL MCs to adjust the polymerization temperature is expected to expand the other similar resins.

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