



# Novel polyphenylene oxide microcapsules filled with epoxy resins

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**Abstract:** Novel polyphenylene oxide (PPO) microcapsules filled with epoxy resins (PPOMCs) were synthesized by *in situ* polymerization technology with 2, 6-dimethyl phenol as shell materials and diglycidyl ether of bisphenol A epoxy resins as core materials. The structures and morphologies of PPOMCs were characterized using Fourier-transform infrared spectroscopy, micro-confocal Raman microscope, laser scanning confocal microscopy, scanning electron microscopy and optical microscopy, respectively. The thermal properties of PPOMCs were investigated using differential scanning calorimetry and thermogravimetric analysis. The influences of different processing parameters such as the weight ratio of shell material to core material, kind of surfactant and reaction temperature on the morphologies and sizes of PPOMCs were investigated. Preliminary investigation on application of PPOMCs to thermosetting resins 4,4'-bismaleimidodiphenylmethane/O,O'-diallylbisphenol A (BMI/BA) system was conducted. Results indicate that PPOMCs can be

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synthesized successfully. The sizes and surface morphologies of PPOMCs may be significantly affected by different processing parameters. PPOMCs can be well prepared at about 30°C, and they depend strongly on the kind of surfactant and the weight ratio of shell material to core material. PPOMCs basically exhibit high thermal stability when the temperature is below 258°C. The addition of PPOMCs can improve the mechanical properties and maintain the thermal properties of BMI/BA system. The released core materials from PPOMCs may repair the matrix cracks through the polymerization of epoxy resins initiated by curing agent.

Key words: polymerization; morphology; thermal properties; microencapsulation; epoxy resin

## 1. Introduction

Because the microencapsulation technologies can be used to store different solids or liquids and protect the encapsulated ingredients from environmental influences, microcapsules have been used for many different applications including food industries,[1] medicines,[2] electronic inks,[3] catalysts,[4] flame retardant,[5,6] etc. In recent years, the new application of microcapsules to polymer composites has been developed. Researchers report that polymeric microcapsules can impart multiple functions into polymer composites, such as self-healing and toughening. For example, poly(urea-formaldehyde) (PUF) microcapsules filled with healing agents such as dicyclopentadiene (DCPD)[7-10] and epoxy resins[11-13] can be embedded in epoxy composites to repair cracks in the matrix and toughen the composites. The addition of PUF microcapsules filled with DCPD can heal the microcracks within block copolymers (polystyrene block-polybutadiene

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block-polystyrene).[14] In our group, PUF microcapsules filled with epoxy resins have also been used to enhance the mechanical properties of bismaleimide composites.[15] For practical use, polymeric microcapsules with high thermal stability are needed for polymer composites fabricated at high temperature. According to prior work,[16, 17] epoxy resins show higher thermal decomposition temperatures compared to DCPD and thus have potential as microcapsule core materials for high-temperature polymer composites. However, PUF has relatively low thermal stability, and thus when the processing temperature is above 200°C, chain scission may occur, and extensive fragmentation occurs above 300°C.[18] Because PUF microcapsules filled with epoxy resins cannot withstand temperatures >200°C, they have adversely affect the thermal and mechanical properties of polymer composites.

Polyphenylene oxide (PPO) resins exhibit high toughness, high dimensional stability, good flame retardation, low moisture uptake, high glass transition temperature ( $T_g = 210^\circ\text{C}$ ), thermal degradation temperature (about 350°C) and excellent electrical insulation.[19-21] They can be easily prepared by the oxidative polymerization of 2, 6-dimethyl phenol (DMP) at room temperature using organic or inorganic solvents in the presence of a copper-amine-complex catalyst under oxygen.[22-24] Additionally, PPO can be easily separated from water due to its insolubility. Because of these characteristics, PPO meets most of the requirements for synthesizing microcapsules with high thermal stability and microencapsulating ingredients in water at room temperature.

In this study, DMP was adopted as a shell material to prepare PPO microcapsules filled with epoxy resins (PPOMCs). The chemical structures, morphologies, sizes and thermal stability of synthesized microcapsules were characterized by Fourier-transform infrared (FTIR) spectrometry, micro-

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confocal Raman microscopy, scanning electron microscopy (SEM), laser scanning confocal microscopy (LSCM), optical microscopy (OM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The preliminary application of PPOMCs to 4,4'-bismaleimidodiphenylmethane/O,O'-diallylbisphenol A (BMI/BA) was discussed.

## 2. Experiments

### 2.1 Materials

DMP (analytical grade) used as shell material was purchased from Rising Chemical Co. Ltd, China. Diglycidyl ether of bisphenol A (DGEBA, epoxide equivalent weight: 196 g/mol) epoxy resin used as core material was purchased from Wuxi Resin Plant, China. Surfactants sodium dodecylbenzene sulfonate (SDBS, 99% purity), sodium dodecyl sulphate (SDS, 99% purity) and gelatin (99% purity) used as the emulsifiers were purchased from Tianjin Chemical Regents Factory, China. Chemical pure cuprous chloride (CuCl) was obtained from Shanghai Guanghua Technology Co., Ltd, China. Chemical pure ethylenediamine (EDA) was obtained from Shanghai Sunheat Chemicals Co., Ltd, China. The desired amount of CuCl and EDA was dissolved in water to prepare the Cu-EDA complex. BMI was purchased from Xibei Chemical Institute, China. O,O'-diallylbisphenol A (BA) was provided by Sichuan Jiangyou Chemical Factory, China. 4,4'-diaminodiphenyl sulfone (DDS) was purchased from Shanghai Jiacheng Chemical Co. Ltd, China.

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## 2.2 Preparation of microcapsules

At room temperature, DMP and deionized water were mixed in a 500-ml three-neck round-bottom flask connected to a reflux condenser and equipped with a mechanical stirrer, and the pH of mixture system was adjusted to about 13 with sodium hydroxide aqueous solution. When DMP was dissolved into water, 100 ml of surfactant aqueous solution and a slow stream of DGEBA were added to the solution to form oil in water emulsion under agitation (430 rpm), stirring for 20–30 min, the reactor was brought to the desired temperature (30–50°C), and the mixture was vigorously stirred under oxygen, subsequently a small amount of catalyst Cu-EDA complex was added. After about 3–4 h, the reaction was ended. The obtained suspension of PPOMCs was rinsed with deionized water and acetone, filtrated and air-dried for 24 h. Table 1 gives the processing parameters for synthesizing PPOMCs.

**Table 1:** The processing parameters for synthesizing PPOMCs

Sample No.	Temperature (°C)	Kind of surfactant	Weight ratio of DMP to DGEBA	Core content ( $W_{vcorei}$ ) of PPOMCs (wt%)	Relative content of epoxy group (%)	Yield (%)
1	30	1.0wt%SDBS	1:0.8	43	96	88
2	30	1.0wt%SDBS	1:1.2	56	98	93
3	30	1.0wt%SDBS	1:1.8	61	97	90
4	30	1.0wt%SDS	1:1.2	56	96	87
5	30	1.0wt%gelatin	1:1.2	56	97	86
6	40	1.0wt%SDBS	1:1.2	32	96	52
7	50	1.0wt%SDBS	1:1.2	20	96	39

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### 2.3 Preparation of BMI/BA/PPOMCs system

The weight ratio of BMI and BA was fixed as 1:1 throughout the work in this paper. BMI/BA/PPOMCs systems were prepared by casting method. The mixture of BMI and BA was heated to 130°C and then kept at the temperature for about 60 min with stirring. PPOMCs and BMI/BA were blended quickly and thoroughly, and then the mixture was poured into a mould. After degassed at 120°C for 1h, BMI/BA/PPOMCs systems were cured following the schedule: 120°C/1h + 150°C/2h + 180°C/2h + 200°C/2h.

In order to prove the reactivity of epoxy resins in PPOMCs, 10wt% DDS was added to the above mentioned mixture of BMI/BA and PPOMCs to prepare BMI/BA/PPOMCs/DDS system. Here, DDS was used to initiate the reaction of epoxy resins released from fractured microcapsules under heat condition. BMI/BA/PPOMCs/DDS system was also cured following the schedule: 120°C/1h + 150°C/2h + 180°C/2h + 200°C/2 h.

### 2.4 Characterization

Fourier-transform infrared (FTIR) spectra were performed using a FTIR spectrometer (NICOLET 5700) to identify the chemical structure of the specimen, which was prepared by grinding the sample with a potassium bromide.

Raman spectrometry was performed using micro-confocal Raman microscope (HR800, Horiba Yvon Co., France) to detect the structures of microcapsules at different site. The Raman spectrum

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of internal ingredient of PPOMCs was obtained by focusing the laser toward the central point of microcapsule.

The structure and morphology of the microcapsules were characterized using confocal laser scanning microscope (Leica TCS SP2, Leica Microsystems GmbH, Germany). As a control, microcapsules were investigated in the transmission mode at 488-nm line of air-cooled argon laser. Under these conditions, the wall shell as black area clearly distinguished from the background. 3D reconstruction software was also applied to analyze the structure of microcapsule.

The surface morphology of microcapsule was observed using scanning electron microscope (SEM, S-4700), optical microscope (OM, SMZ-B2, Chongqing Aote Optics Instrument Co., Ltd, China).

Size distribution of microcapsule suspensions was analyzed using Malvern MasterSizer 2000 particle size analyzer.

DSC measurement was performed using a TA calorimeter (2910 MDSC, TA) at a heating rate of 10°C/min in a nitrogen atmosphere.

TGA was done by using a thermogravimetric instrument (TGA, Q50, TA) at a heating rate of 10°C/min in a nitrogen atmosphere.

The flexural strength was measured according to GB 2570–95 on a testing machine (ZMF1250), and the impact strength was performed according to GB 2571–95 on testing machine (XCL-40). At least ten specimens for each system were tested.

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## 2.5 Determination of core content of PPOMCs

The core content of PPOMCs was determined by extracting method, and acetone was used as extracting solvent. First, the microcapsule samples were grinded with a pestle in a mortar at room temperature, and then the crushed or fractured microcapsules were collected and washed with acetone several times, drying at room temperature. Knowing the initial weight of intact microcapsules ( $W_{0PPOMCs_i}$ ) and the weight of residual wall shell ( $W_{PPO_i}$ ) of microcapsules, the wall shell content ( $W_{VPPO_i}$ ) and core content ( $W_{Vcore_i}$ ) of microcapsule can be calculated according to eqns ((1)) and ((2)).

$$W_{VPPO_i} = \frac{W_{PPO_i}}{W_{0PPOMCs_i}} \times 100\% \quad (1)$$

$$W_{Vcore_i} = 1 - W_{VPPO_i} \quad (2)$$

## 2.6 Determination of content of epoxy group

Quantitative estimation of characteristic group can be obtained by FTIR using internal standards. During the microencapsulation process, the phenyl ring cannot be affected by the media, and its band may be selected as reference band. The relative content of epoxy group of PPOMCs can be evaluated according to eqn ((3)).

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$$W_{\text{epoxy group}} = \frac{S_{\text{epoxy group}}/S_{\text{Ph}}}{S_{0 \text{ epoxy group}}/S_{0 \text{ Ph}}} \times 100\% \quad (3)$$

where  $W_{\text{epoxy group}}$  is the relative content of epoxy group of microcapsule sample.  $S_{\text{epoxy group}}$  and  $S_{\text{Ph}}$  are the integral areas of characteristic peaks of epoxy group at about  $910 \text{ cm}^{-1}$  and phenyl ring at about  $1510 \text{ cm}^{-1}$  of microcapsule sample, respectively.  $S_{0 \text{ epoxy group}}$  and  $S_{0 \text{ Ph}}$  are the integral areas of characteristic peaks of epoxy group at about  $910 \text{ cm}^{-1}$  and phenyl ring at about  $1510 \text{ cm}^{-1}$  of DGEBA.

### 3. Results and Discussion

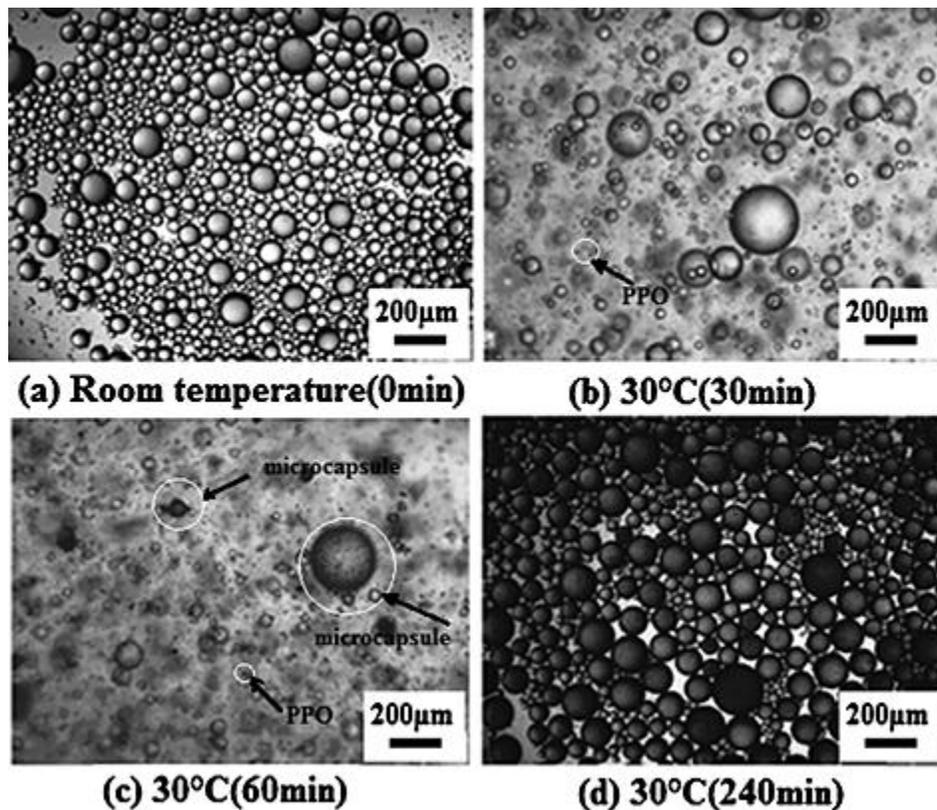
#### 3.1 Microencapsulation process

The microencapsulation process of core material of PPOMCs (sample No.2) is monitored by OM. Figure 1 shows OM images along with the temperature during the microencapsulation process. At room temperature, DGEBA core materials are slowly added to the prepared DMP solution under agitation, they can form small DGEBA droplets in the solution as shown in Fig. 1(a). As the temperature is gradually raised up to  $30^\circ\text{C}$ , the solution becomes emulsion with the increase of reaction time owing to the formation of PPO polymers as shown in Fig. 1(b), which results from the oxidative polymerization of DMP.[24] PPO polymers cannot dissolve in water, they may deposit on the surface of DGEBA droplets. Owing to PPO polymer with different molecular weight, only some large high molecular weight PPO particles can be observed, and they are indicated by small

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gray or dark particles in Fig. 1(b). As the processing reaction time further increases, more PPO particles can form and deposit on the surface of DGEBA droplets, many high molecular weight PPO particles represented by small gray or dark particles in Fig. 1(c) can be observed. Also, some microcapsules can be observed due to the deposition of some PPO materials on DGEBA droplets as shown in Fig. 1(c). After 240 min, the wall shell of microcapsule becomes thick owing to the further reaction of DMP and the deposition of PPO particles at the core-water interface, the resultant PPOMCs can be obviously observed as shown in Fig. 1(d).



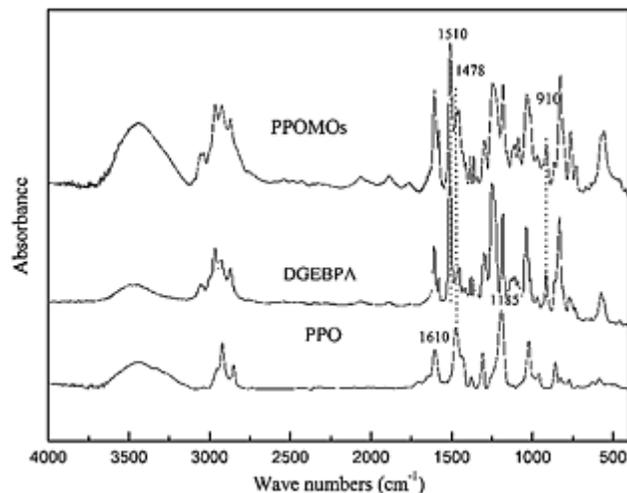
*Figure 1: mages along with the temperature during the microencapsulation process.*

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### 3.2 Chemical structures and morphologies of PPOMCs

Figure 2 shows FTIR spectra of PPOMCs (sample No.2), PPO wall shell and DGEBA. The absorption peaks at  $1610\text{ cm}^{-1}$  and  $1478\text{ cm}^{-1}$  in FTIR curve of PPO belong to the stretching vibration of phenyl ring (Ph), and the peak at  $1185\text{ cm}^{-1}$  is attributed to the stretching vibration of Ph–O bond. In the case of DGEBA, the absorption peak at  $910\text{ cm}^{-1}$  belongs to epoxy group, and the peak at  $1510\text{ cm}^{-1}$  is attributed to the vibration of phenyl ring. Compared with the PPO and DGEBA, the synthesized PPOMCs contain the structural units of PPO and DGEBA owing to the obvious absorption strengths at  $1610\text{ cm}^{-1}$ ,  $1478\text{ cm}^{-1}$ ,  $910\text{ cm}^{-1}$  and  $1510\text{ cm}^{-1}$  in their FTIR curve, indicating that DGEBA may be microencapsulated by PPO wall shell.



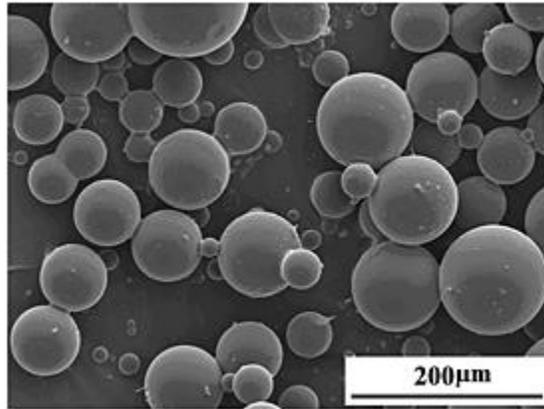
**Figure 2:** FTIR spectra of PPOMCs (sample No.2), PPO wall shell and DGEBA.

Figure 3 shows SEM image of PPOMCs (sample No.2). The microcapsules are spherical. Figure 4(a) shows LSCM image of PPOMCs in transmission mode, and Fig. 4(b) shows the 3D image obtained by analyzing the wall shell of PPOMCs using the reconstruction software. The black rings represent

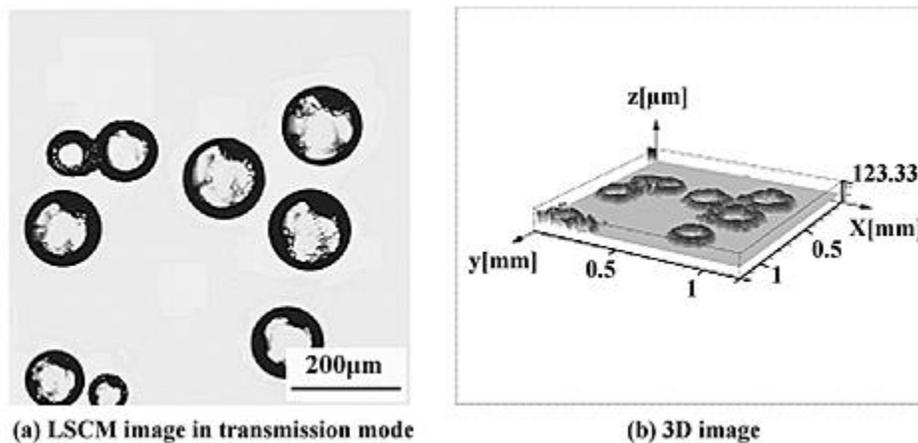
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PPO wall shells, and areas within the rings represent the core material DGEBA, indicating that DGEBA can be microencapsulated by PPO.



*Figure 3: SEM image of PPOMCs (sample No.2).*



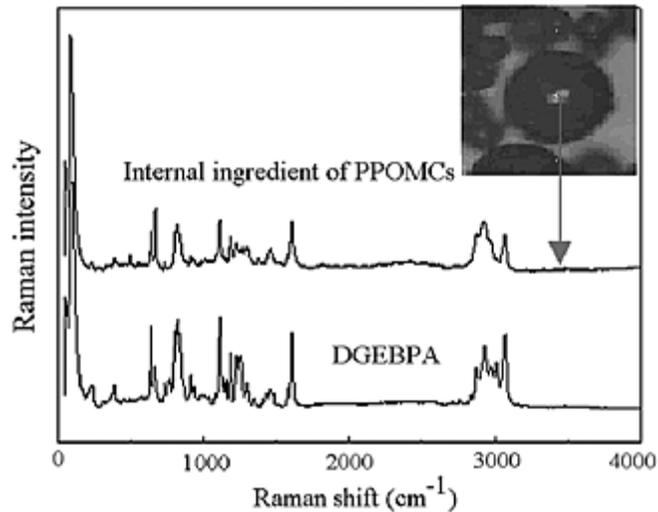
*Figure 4: LSCM image of PPOMCs (sample No.2).*

Raman spectrometry was also used to detect the internal structure of PPOMCs. Figure 5 shows a Raman spectrum of DGEBA and the internal ingredient of the microcapsule. The peak at  $1610\text{ cm}^{-1}$  is attributed to phenyl, and the peak at about  $1260\text{ cm}^{-1}$  belongs to an epoxy group. The Raman

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shift of the internal ingredient of the microcapsule shows no change compared with DGEBPA, indicating that DGEBPA was encapsulated.



**Figure 5:** Raman spectrum of DGEBPA and the internal ingredient of PPOMCs (sample No.2).

During the microencapsulation process of DGEBPA, epoxy groups are affected by the basic solution, and a reaction between hydroxyl groups in DMP and epoxy groups may arise. In addition, a trace amount of Cu-EDA complex catalyst present in PPOMCs may initiate the reaction of DGEBPA, causing decomposition.[16, 17] Thus, the content of epoxy groups must be considered to ensure the application potential of PPOMCs. The relative content of epoxy groups in PPOMCs (sample No.2) calculated according to eqn ((3)) and Fig. 2 is about 98%. The relative content of epoxy group in other PPOMCs samples is about 96–97% as listed in Table 1, indicating that the effect of media on epoxy groups during the microencapsulation process is negligible. Because the reaction system is heterogeneous,[25] the concentration DMP of Cu-EDA complex catalyst in solution system may be diluted, and consequently the reaction rate of DGEBPA is decreased

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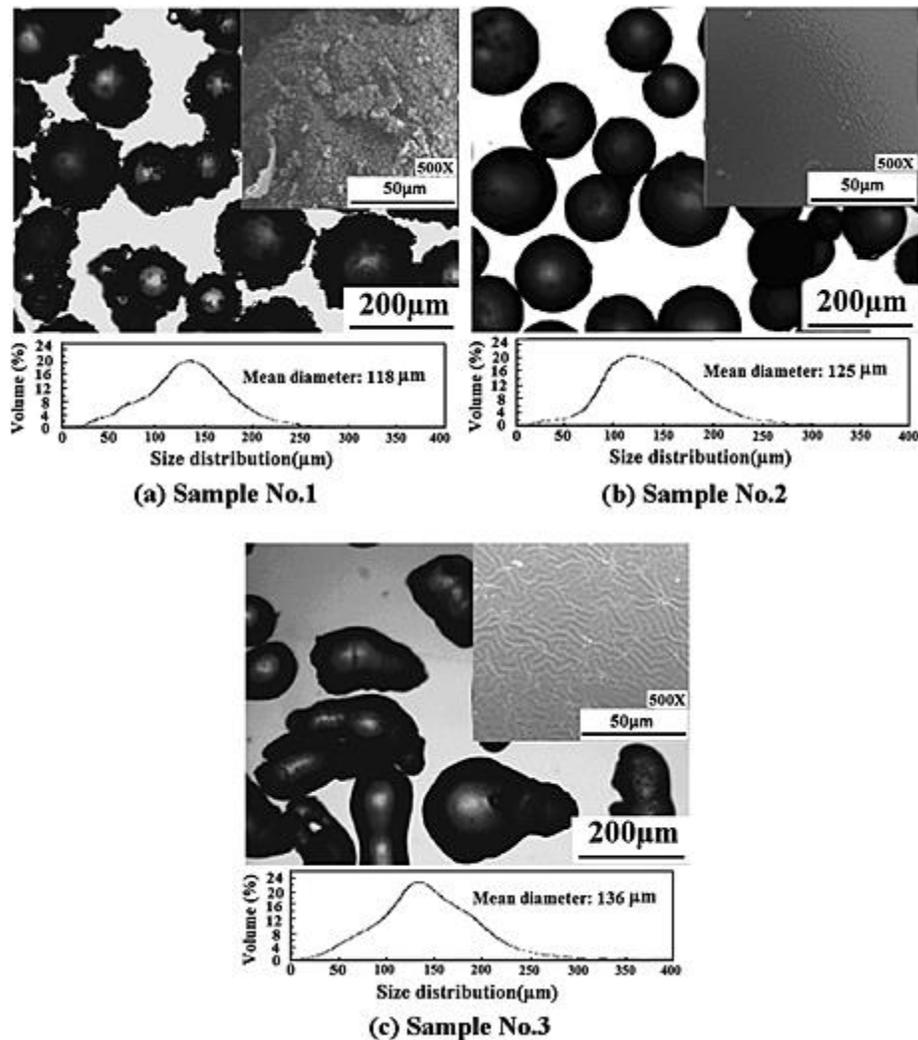


significantly.[26] Additionally, because the reaction takes place at the interphase between DGEBA and DMP (or Cu-EDA complex), quantitative relationship between reactants and products in the chemical reaction cannot be calculated according to stoichiometry,[27, 28] and the epoxy group content can remain roughly constant.

### 3.3 Effects of different weight ratio of DMP to DGEBA on PPOMCs

Figure 6 shows OM and SEM images of PPOMCs prepared with different weight ratios of DMP to DGEBA along with size distribution curves (sample No.1–sample No.3). The microcapsule surfaces become smoother with increasing DGEBA. This behavior can be explained by the fact that increasing core material can reduce the deposition of PPO particles on each core material droplet, and thereby reduce the collision probability of PPO particles. Smaller amounts of DGEBA produce spherical microcapsules (sample No.1–sample No.2), whereas larger amounts of DGEBA cause microcapsules with irregular shapes (sample No.3). The phenomena is attributed to the larger amounts of core materials forming larger emulsion droplets, which under agitation conditions readily deform owing to turbulent shear force. Figure 6 also shows the wide range of microcapsule sizes. The mean microcapsule diameters for samples No.1–No.3 are 118  $\mu\text{m}$ , 125  $\mu\text{m}$  and 136  $\mu\text{m}$ , respectively. Thus, the mean diameters of PPOMCs increase with increasing amounts of core material, because the larger core droplets result in larger PPOMCs.

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*Figure 6: OM and SEM images of surfaces of PPOMCs along with size distribution curves (sample No.1–sample No.3).*

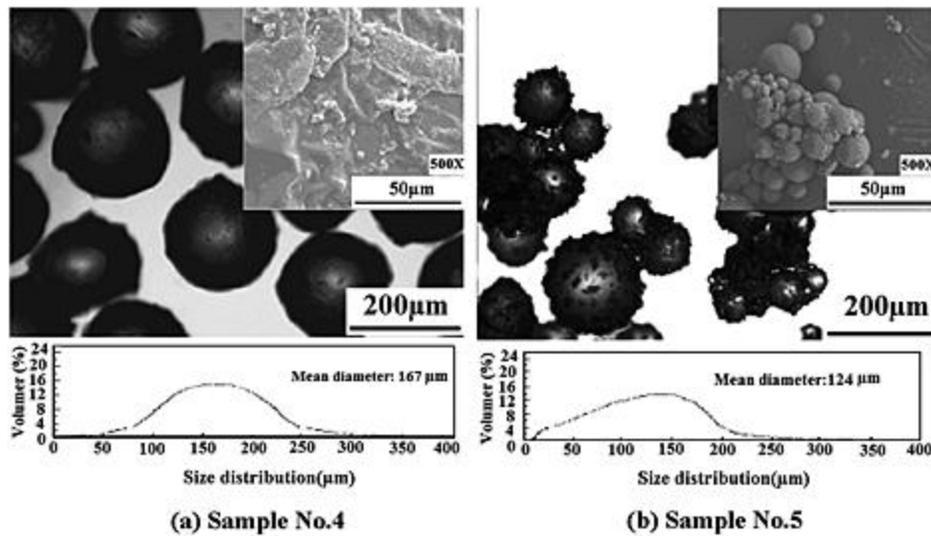
### 3.4 Effects of kind of surfactant on PPOMCs

The effects of surfactants SDS, SDBS and gelatin on morphologies and sizes of PPOMCs (No.2, No.4 and No.5) are shown in Fig. 6(b) and Fig. 7. The surface morphology of sample No.4 is rougher than that of sample No.2. This phenomenon can be explained by the fact that SDS and SDBS are

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anionic surfactants, although SDS shows higher hydrophile-lipophile balance values compared to SDBS. When the surfactant concentration is held constant, the emulsion system containing SDS can become unstable and undergo blistering. This may lead to the erratic deposition of PPO wall shell materials and cause roughening and corrugation of the surface, as shown in Fig. 7(a). Gelatin is a carbohydrate polymer, and its melting point is 24–28°C. When the system temperature is about 30°C, the addition of gelatin may increase emulsion viscosity, causing microcapsules to form aggregates, as shown in Fig. 7(b). In addition, because of the increased emulsion viscosity, some aggregates of PPO may form and attach to PPOMC surfaces. The mean diameters of microcapsule samples No.2, No.4 and No.5 are 125 μm, 167 μm and 124 μm, respectively, indicating that the kind of surfactant may influence the size distributions of PPOMCs.



**Figure 7:** OM and SEM images of surfaces of PPOMCs along with size distribution curves (sample No.4 and No.5).

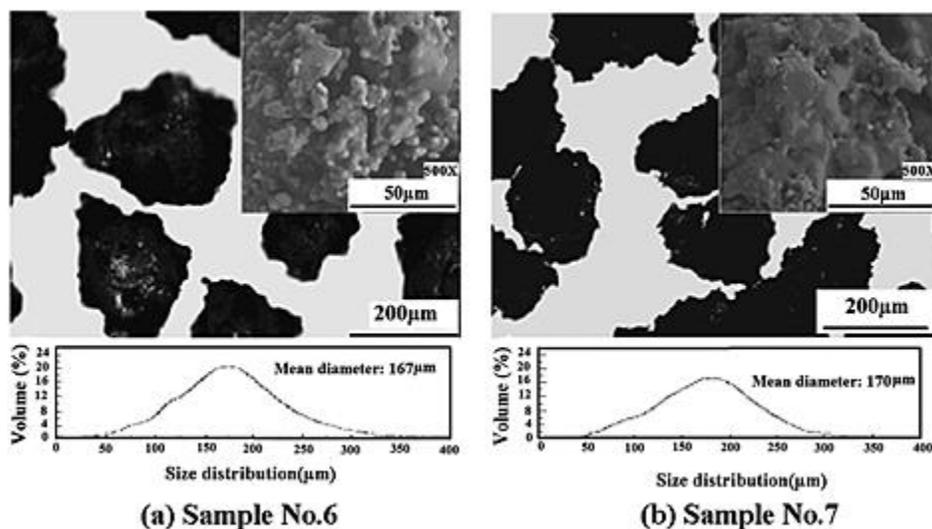
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### 3.5 Effects of reaction temperature on PPOMCs

The influence of reaction temperature on the morphologies and sizes of PPOMCs (sample No.2, sample No.6 and sample No.7) is shown in Fig. 6(b) and Fig. 8. The reaction temperature is varied from 30°C to 50°C. When the reaction temperature is above 30°C, the shapes of PPOMCs gradually become irregular, and the surfaces of PPOMCs become rough. Raising temperature can increase the polymerization reaction rate of DMP[29] and the deposition rate of PPO particles on each core droplet, forming rougher surface and irregular microcapsules. Because of this, the mean microcapsule diameters of samples No.6 and No.7 prepared at higher reaction temperature are larger than that of microcapsule sample No.2, as shown in Fig. 8. Owing to the higher polymerization reaction rate of DMP at higher temperature, PPO particles may not quickly and completely encapsulate all core material droplets, especially for larger droplets, resulting in lower yields of microcapsules (sample No.6 and sample No.7), as listed in Table 1. In addition, the redundant PPO particles and wall shell fragments from unencapsulated microcapsules may deposit on microcapsule surfaces, increasing the wall shell thickness and reducing the core material content of microcapsules.

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**Figure 8:** OM and SEM images of surfaces of PPOMCs along with size distribution curves (sample No.6 and No.7).

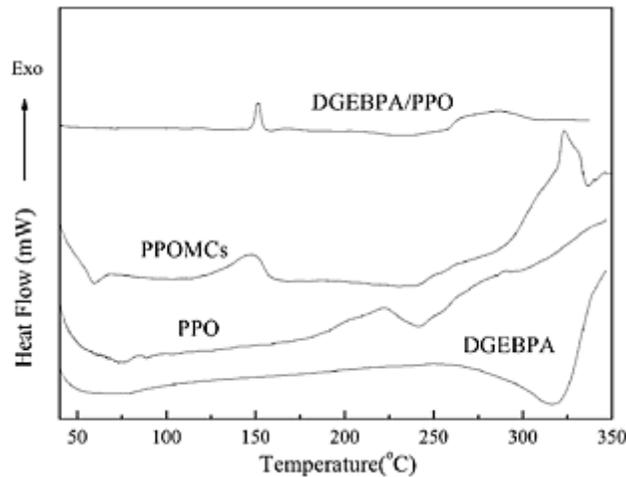
### 3.6 Thermal stability of PPOMCs

Figure 9 shows DSC curves of DGEBA, PPO, PPOMCs (sample No.2) and DGEBA/PPO system. The endothermic peak at 320°C in the DSC curve of DGEBA is attributed to the decomposition of DGEBA. The endothermic peak temperature at 240°C in the DSC curve of PPO is the melting point. The endothermic peak at 150°C in the DSC curve of DGEBA/PPO system arises from the polymerization of DGEBA initiated by the phenolic hydroxyl and Cu-EDA complex existing in PPO, and the endothermic peak above 250°C is attributed to further polymerization of DGEBA. For PPOMCs, a weak endothermic peak and two exothermic peaks can be observed in the DSC curve. The first endothermic peak at 60°C is caused by evaporation of water and other small molecules existing in PPOMCs. The first exothermic peak at 150°C is caused by the polymerization of DGEBA initiated by PPOMCs, which contains a trace amount of phenolic hydroxyl and Cu-

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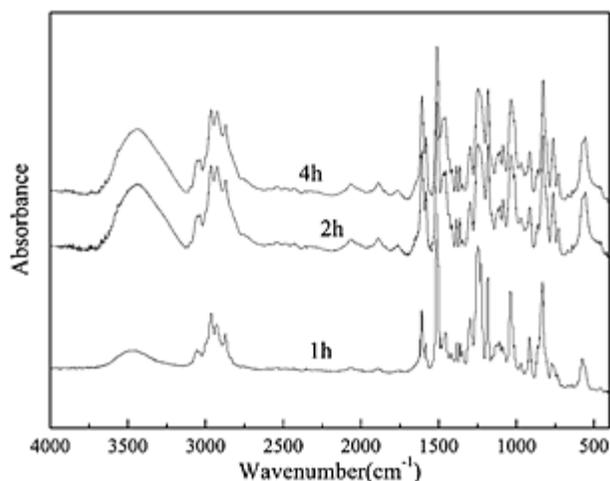
EDA complex, and the second exothermic peak at 320°C is caused by further polymerization of DGEBA. Because the endothermic and exothermic reactions may occur concurrently for DGEBA/PPO and PPOMCs at high temperature ( $\geq 250^\circ\text{C}$ ), the peaks may overlap, and the resultant exothermic peak may be diminished.



**Figure 9:** DSC curves of DGEBA, PPO wall shell, PPOMCs (sample No.2) and DGEBA/PPO system.

To ensure the practicality of PPOMCs after treatment at 150°C, the contents of epoxy group in PPOMCs (sample No.2) were evaluated by FTIR (Fig. 10) using internal standards after treatment at 150°C for 1, 2 and 4h, respectively. According to eqn ((3)), the calculated relative content of epoxy groups are 96%, 95% and 95%, respectively, indicating only slight consumption of epoxy groups and demonstrating the viability of PPOMCs.

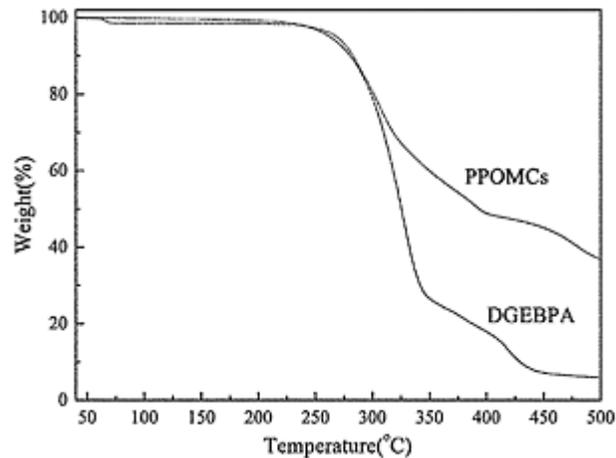
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**Figure 10:** FTIR of PPOMCs (sample No.2) treated at 150°C for 1, 2 and 4h.

Figure 11 shows TGA curves of DGEBA and PPOMCs (sample No.2). For DGEBA, the weight loss in the range of 250–500°C is attributed to the decomposition of DGEBA. In the case of PPOMCs, the weight loss at about 60°C is mainly due to the removal of entrapped residual water and other small molecules, and the weight loss at higher temperature (>250°C) is mainly due to the decomposition of DGEBA and the cross-linked polymer resulting from the polymerization reaction of DGEBA. Additionally, the thermal decomposition of PPO wall shell may cause the weight loss of PPOMCs. When temperature is above 250°C, PPOMCs show smaller thermal degradation rate compared with DGEBA, the reason is the polymerization of a part of DGEBA. The temperature of 5 wt% weight loss percentage ( $T_d$ ) for PPOMCs is about 258°C, which is 50°C higher than  $T_d$  of PUF containing epoxy resins.[30]

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*Figure 11: TGA curves of DGEBA and PPOMCs (sample No.2).*

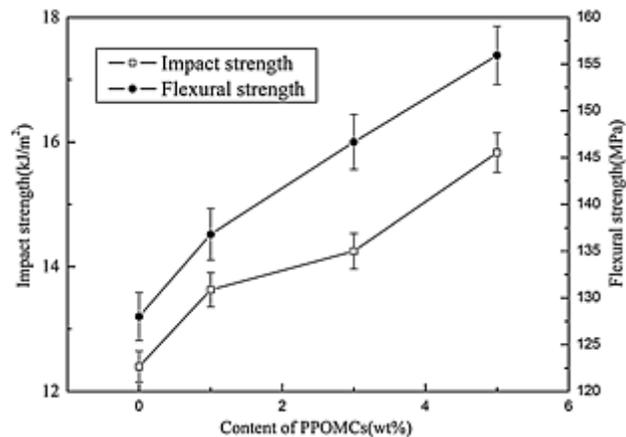
### 3.7 Application of PPOMCs to BMI/BA

In order to show the potential application of PPOMCs, 1wt%, 3wt% and 5wt% PPOMCs (Sample No.2) are embedded in high-performance thermosetting BMI/BA resin system. Figure 12 shows the mechanical properties of BMI/BA/PPOMCs systems. In this study, the addition of PPOMCs can improve the impact strength and flexural strength of cured BMI/BA. When the content of PPOMCs is 5wt%, the impact strength and flexural strength of BMI/BA/PPOMCs are about 27% and 18% higher than that of BMI/BA system. The improved mechanical properties of BMI/BA/PPOMCs can be explained by the following reasons: First, according to reference,[31] PPOMCs can be considered to be visco-elastic (mainly elastic) at smaller deformations and plastic at a larger deformation, they may act as fillers to reduce the stress of resin matrix during the curing process. Second, PPOMCs may act as points of the stress concentration under triaxial stress conditions generating shear yielding or microcracking in matrix. Third, during the microcrack propagating, crack pinning or blunting

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effects of PPOMCs,[32] the debonding of PPOMCs from matrix and the cavitations of PPOMCs can absorb more energy, thus stabilizing the crack.



**Figure 12:** The mechanical strength of BMI/BA/PPOMCs systems.

Table 2 lists the degradation temperature ( $T_{di}$ ) at different weight loss percentages and the temperature of maximum degradation rate ( $T_{max}$ ) of BMI/BA with different PPOMC content (0wt%, 1wt%, 3wt% and 5wt%), as determined by TGA.  $T_{d1}$ ,  $T_{d2}$ ,  $T_{d3}$  and  $T_{d4}$  represent 5wt%, 10wt%, 15wt% and 20wt% weight loss temperatures, respectively. The introduction of 1–5wt% PPOMCs basically maintains the  $T_{di}$  and  $T_{max}$  of cured BMI/BA, which derives from the inherent thermal stability of PPOMCs.

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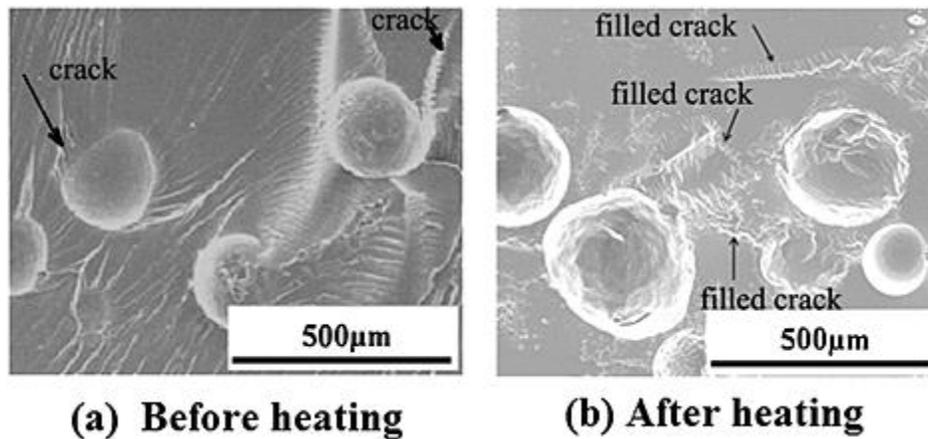


**Table 2:**  $T_{d1}^a$  and  $T_{max}^b$  of BMI/BA/PPOMCs systems

	$T_{d1}$ (°C)	$T_{d2}$ (°C)	$T_{d3}$ (°C)	$T_{d4}$ (°C)	$T_{max}$ (°C)
BMI/BA	382	391	412	423	443
BMI/BA/1%PPOMCs	385	390	409	422	443
BMI/BA/3%PPOMCs	386	392	410	423	443
BMI/BA/5%PPOMCs	384	388	412	417	443
a. $T_{d1}$ , $T_{d2}$ , $T_{d3}$ and $T_{d4}$ represent 5wt%, 10wt%, 15wt% and 20wt% weight loss temperature, respectively. b. $T_{max}$ represents the temperature of maximum degradation rate.					

To demonstrate the reactivity of epoxy resin in the microcapsules, the cured BMI/BA system with 10wt% PPOMCs and 5wt% DDS was first fractured, then heated at 130°C/1h + 200°C/1h. Figure 13 shows SEM images of the fractured BMI/BA system with PPOMCs and DDS before and after heating. Obvious cracks can be observed in matrix before heating (Fig. 13(a)), and the matrix cracks are filled after heat treatment (Fig. 13(b)). The reason is the fact that the viscosity of core materials becomes lower during heating, the damaged PPOMCs can release core materials into the cracks. The core materials can polymerize when contacting the curing agent DDS under heating condition, and the polymerized core materials may bond crack faces and heal matrix cracks, demonstrating the reactivity of the epoxy in the microcapsules.

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*Figure 13: SEM images of the fractured BMI/BA system with PPOMCs and DDS before and after heating.*

#### 4. Conclusions

In this study, PPOMCs were synthesized with DMP shells and DGEBPA cores. The surface morphology of PPOMCs can be altered by adjusting by the weight ratio of DMP to DGEBPA, by addition of surfactant, and by reaction temperature. Superior results were obtained for sample No.2, the processing parameters for which were as follows: the 1:1.2 weight ratio of DMP to DGEBPA, SDBS surfactant and reaction temperature of 30°C. During the microencapsulation process, epoxy resins were only slightly affected by the surrounding media, and the epoxy group content in PPOMCs was preserved. PPOMCs exhibited excellent thermal stability up to about 258°C, indicating that the prepared PPOMCs are candidates for high-temperature applications. Application of appropriately designed PPOMCs to BMI may improve mechanical properties, maintain thermal stability and enable healing of matrix cracks.

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