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Preparation and Characterization of E7–PMMA Microcapsules by Solvent Evaporation

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Nematic liquid crystal E7 (core) was microencapsulated into the poly(methyl methacrylate) (PMMA, shell) via the solvent evaporation method. The morphology of microcapsules depends importantly on the initial PMMA/E7 ratio in oil phase. Solvent evaporation temperature, as well as the co-solvent, could further influence the surface morphology of microcapsules. Results of optical microscope measurements show that microcapsule shells with smooth surface are transparent. The microcapsule core loading is in accordance with the initial E7 content. The final obtained mononuclear microcapsules exhibit transparent shell, high E7 loading, and decent thermal stability.

Keywords Liquid crystal; microcapsules; morphologies; optical properties; solvent evaporation

Introduction

Polymer/liquid crystal (LC) composites, including polymer-dispersed liquid crystals (PDLC) [1–5] and polymer-stabilized liquid crystals (PSLC) [6–9], have attracted great research interests in recent years. These composites are applied in the displays due to the advantages such as polarizer free, alignment-layer free, short response time, and facile preparation. However, the conventional devices prepared by phase separation methods [1–12], for instance polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS), and solvent-induced phase separation (SIPS), still have unsolved issues such as the low contrast and the high driving voltage. Smaller droplets of LC in the PDLC result in haze [13], and broad size distributions of LC in the PDLC lead to a high threshold and driving voltage [14, 15].

Microencapsulation through emulsion has been employed to control the size and size distribution of LC droplets in the polymer matrix. It is reported that PDLCs from 3–4 μm monodispersed LC microcapsules have outstanding electro-optical performance [14]. Moreover, the LC materials confined in microcapsules become pressure insensitive, and thus become the feasible candidates for subsequent coating by many conventional methods [16].

In the past few years, LC/polymer microcapsules were prepared mainly by solute co-diffusion method/diffusion-controlled swelling method [13, 15, 17–20], coacervation phase separation [21], and PIPS [22]. Unfortunately, the LC loadings in these microcapsules are

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usually low. The LC amount anchored in the polymer matrix determines the switching behavior of the composite systems [23, 24]. The outstanding contrast ratio, low threshold, and driving voltage for a PDLC can be achieved with higher content of LC in the polymer matrix. Thus, preparing LC microcapsules with high core loading is quite significant.

Solvent evaporation is a simply way to prepare microcapsules with solid or liquid cores. It is usually applied to obtain microcapsules with high core loadings for its controlled phase separation [25, 26]. Here in this study, we introduce this method to prepare microcapsules with LC cores and high core loadings.

In this paper, poly(methyl methacrylate) (PMMA)/E7 microcapsules were prepared by emulsion and solvent evaporation method. We investigated the surface morphologies of polymer shells and inner core shapes. Core material loadings, shell thickness, optical, and thermal properties of the microcapsules were also compared and discussed.

Experimental

Materials

PMMA ($M_w = 5.0 \times 10^4$–1.0×10^5 g/mol, refractive index 1.49) was purchased from Taiwan Chimei Company. Nematic LC E7 ($T_{NI} = 59^\circ$C, $n_e = 1.72$, $n_o = 1.51$) was obtained from Shijiazhuang Chengzhi Yonghua Display Material Company. Poly(vinyl alcohol) (PVA, $M_w = 8.8 \times 10^4$ to 9.2×10^4 g/mol, 88% hydrolyzed, Tianjin Keruisi Reagent Company) was used as emulsifier. Poly(vinyl pyrrolidone) (PVP, $M_w = 4.0 \times 10^4$ g/mol, Keruisi) and distilled deionized water were used as received. Organic solvents such as dichloromethane (DMC, Guangfu Chemicals), acetone (Guangfu Chemicals), ethyl acetate (North Tianyi Chemicals), and ethanol (Guangfu Chemicals) were reagent grades and used without further purification.

Preparation of PMMA/E7 Microcapsules

Microcapsule shell PMMA (0.15 g) and core E7 (1.00 g) were first dissolved in a mixed organic solvent of 8.5 mL DMC and 1.5 mL ethyl acetate. Then the solution was added into 40 mL 2 wt% PVA aqueous solution in drops at 20°C while stirring at 1500 rpm. The stirring rate was kept at 1500 rpm for 20 min, and then reduced to 300 rpm to form an Oil/Water (O/W) emulsion. Afterwards another 40 mL of 2 wt% PVA aqueous solution was added to dilute the emulsion. This emulsion was then heated up to 35°C within 20 min. The organic solvents were removed by evaporation under atmospheric pressure for about 10 h. The obtained microcapsules were repeatedly washed with deionized water via decantation, and then concentrated.

Characterizations of Microcapsules

Microcapsule morphologies were examined by scanning electron microscope (SEM, S4800, JP-Hitachi Ltd.). To observe inner structures, fractured microcapsules were obtained by scraping microcapsules on a glass plate or cutting microcapsules embedded in PVP. To determine microcapsule sizes and size distributions, about 600 microcapsules were selected randomly and analyzed by SEM. The optical properties of microcapsules were investigated by using an optical microscope (Lv-UEPI, JP-Nikon) and a stereo microscope (SMZ1500, JP-Nikon). Thermal analysis was carried out on differential scanning calorimetry (DSC,

Diamond, US-Perkin Elmer) to determine the phase transition point of E7 cores. Samples sealed in aluminium pans were heated in a nitrogen flow from 20°C to 100°C at 10°C/min.

To determine the core loadings, about 0.5 g dry microcapsules were extracted by superfluous ethanol. The residual solid was collected, dried, and weighted. The E7 loading in microcapsules ($C_c\%$) was calculated by Eq. (1), where W_p is the weight of residual solid and W_t is the weight of dry microcapsules.

$$C_c\% = 1 - W_p/W_t \tag{1}$$

Results and Discussion

The Morphology of Microcapsules

SEM images of microcapsules with different PMMA/E7 ratios are shown in Fig. 1. PMMA/E7 ratio significantly influences the microcapsule morphology, involving in both of the surface morphology and inner structure.

As shown in Figs. 1(A)–(E), the surface morphology of microcapsules became smoother with the decrease of PMMA/E7 ratio. This is caused by the reduced shell thickness at a lower PMMA content in the matrix, facilitating the solvent removal [27]. Fig. 1(E) indicates that microcapsule with fold surface was obtained at a much lower ratio (PMMA/E7 as 0.10 g/g). It is most likely due to the thin shell that is not strong enough to withstand the SEM sample preparation conditions, leading to the collapse of microcapsules. High PMMA/E7 ratio produces multi-core microcapsules, while lower ratio is inclined to form mononuclear microcapsules. The phase volume effect [22], the influence of the E7-rich phase volume fraction, is responsible for the phenomena we observed. At a high PMMA/E7 ratio (0.40 g/g), the phase volume fraction of E7 is relatively low, which benefits the swelling and dissolution properties of PMMA in E7–DMC solution (E7–PMMA compatibility). Thus E7 was separated into more fine domains from the PMMA phase. As a result, multi-core microcapsules were prepared [see Fig. 1(a)]. At a medium PMMA/E7 ratio (0.25 g/g), the compatibility of E7 and PMMA decreases, resulting in a descent of E7 domain numbers [see Fig. 1(b)]. At a very low ratio (<0.20 g/g), mononuclear microcapsules were obtained [see Figs. 1(c)–(e)].

Interestingly, as the PMMA/E7 ratio is 0.20 g/g, a special type of microcapsules was obtained. The sample has nonspherical core/shell structure [see Fig. 1(c)] and partial coarse and partial smooth surface [see Fig. 1(c)]. "Acorn" two-phase particles, the oil droplets having PMMA-rich phase and E7-rich phase, were also observed in this preparation procedure (see Fig. 2). Obviously, there is a transformation of two-phase particles from "acorn" type to final core/shell structure. This is caused by the different diffusion coefficients of the three phases [28] during phase separating, including continue phase (aqueous phase), polymer shell phase (PMMA), and core materials phase (E7). Therefore, the formation of earlier "acorn" two-phase particles causes the uneven shell thickness of the final microcapsules. As a result, coarse surface is formed at the thick shell parts, while the surface of thin shell is smooth.

The solvent evaporation temperature would also influence the morphologies of microcapsules. As shown in Fig. 3, microcapsule surface became smoother as the solvent evaporation temperature increased from 30°C to 60°C. In the study of Li et al. [29] and Jeyanthi et al. [30], hollow microcapsules with porous shells were obtained while increasing the temperature to remove the solvent. The formation of coarse surface was attributed to the fast

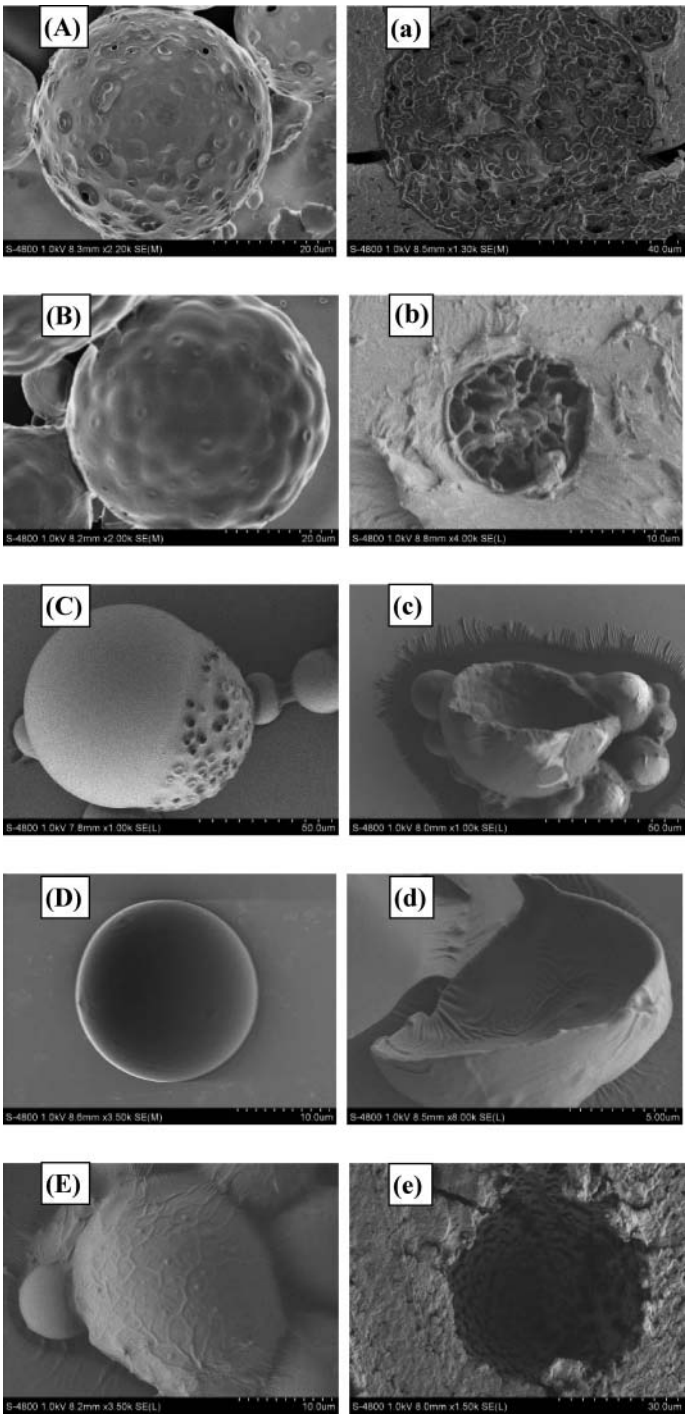

Figure 1. SEM images of microcapsules prepared with different PMMA/E7 ratios (g/g): (A, a) 0.40, (B, b) 0.25, (C, c) 0.20, (D, d) 0.15, (E, e) 0.10. Images of (a), (b), and (e) were fractured microcapsules embedded in PVP coating.

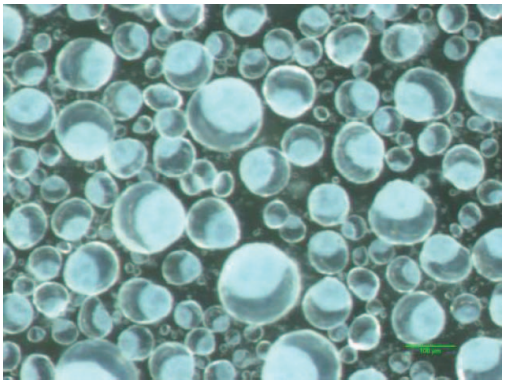

Figure 2. Stereo microscope image of two-phase particles formed in phase separation stage with the PMMA/E7 ratio of 0.20 g/g.

removal of solvent during the evaporation process. Here in this study, our results were inconsistent with the above report. It is probably due to the decrease of E7 viscosity at higher temperature, facilitating the polymer phase migration and solvent evaporation. However, a broad particle size distribution was found once the temperature was beyond the boiling point of solvent at a given pressure. It is highly possible that solvent bubbles forming at a high temperature could destroy the emulsified droplets.

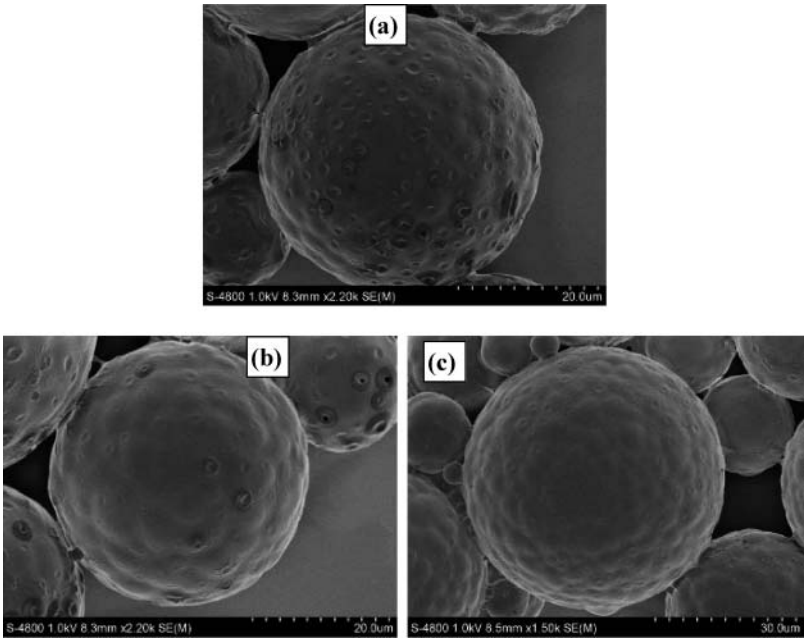

Figure 3. SEM images of microcapsules prepared with the PMMA/E7 ratio of 0.25 g/g, and by removing the solvent at (a) 30°C, (b) 35°C, and (c) 60°C.

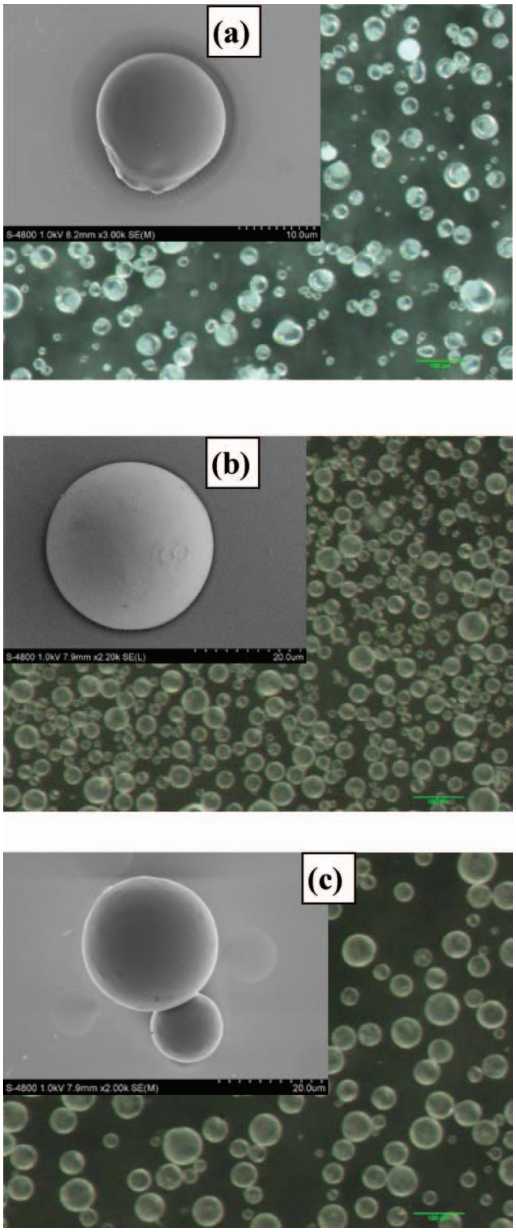

Figure 4. Stereo microscope and SEM images of microcapsules produced from pre-emulsions with the PMMA/E7 ratio of 0.15 g/g and various co-solvents in DMC: (a) non-co-solvent; (b) 15% ethyl acetate; (c) 15% acetone.

In addition, smoother surfaces were observed for microcapsules obtained with the presence of co-solvent such as acetone [see Fig. 4(b)] or ethyl acetate [see Fig. 4(c)] in comparison to those without co-solvent [see Fig. 4(a)]. This can be deduced that the addition of these co-solvents would change the diffusion coefficients of the three phases, avoiding the formation of "acorn" two-phase particles in the beginning.

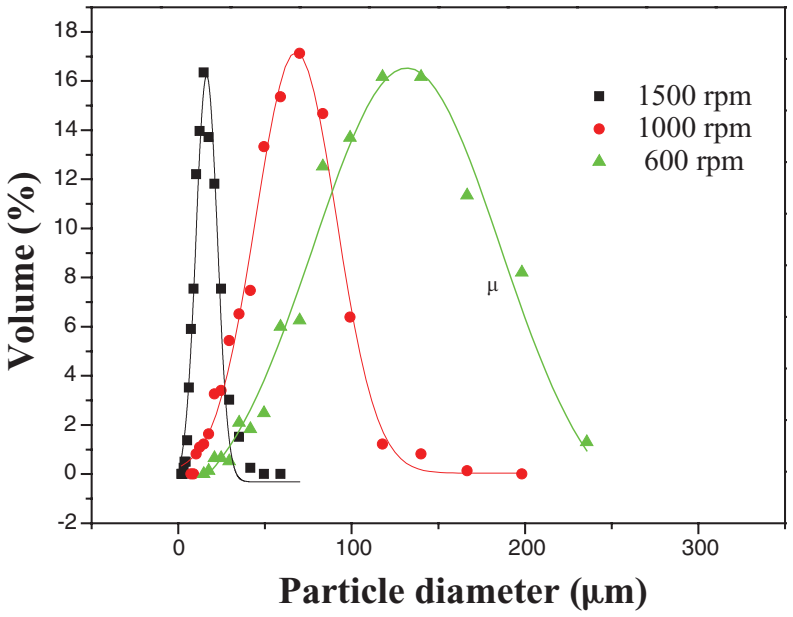

Figure 5. Particle size distributions of microcapsules prepared with the PMMA/E7 ratio of 0.15 g/g. The emulsification agitation rates are (■) 1500, (●) 1000, and (▲) 600 rpm.

Particle Diameters and Size Distributions

Through the method of solvent evaporation, microcapsules from several to hundreds microns could be prepared significantly depending on the preparation conditions. Figure 5 shows the diameters and size distributions of microcapsules prepared at different emulsification agitation rates with the PMMA/E7 ratio of 0.15 g/g. It is clearly shown that the size and size distribution of microcapsules could be obviously reduced by increasing the agitation rate. The average diameters of the samples prepared with present agitation rates of 600, 1000, and 1500 rpm were 132.60, 68.38, and 16.87 μm, respectively.

Optical Properties

PMMA/E7 microcapsules with different surface morphologies were observed by stereo microscope. As shown in Fig. 6, microcapsules with smooth surface have transparent shells, whereas coarse surface makes the shells opaque. Specially, the shells with partial coarse surface are partial opaque and partial transparent.

As stated previously, lowering the PMMA/E7 ratio and increasing solvent evaporation temperature, as well as using acetone or ethyl acetate as co-solvent, can produce a smoother surface, which brings higher chance for the existence of transparent microcapsules. Mononuclear microcapsules with transparent shells can be easily obtained by using acetone or ethyl acetate as the co-solvent during the preparation, and the solvent evaporation temperature is recommended to be 35°C for PMMA/E7 ratio between 0.10 g/g and 0.15 g/g.

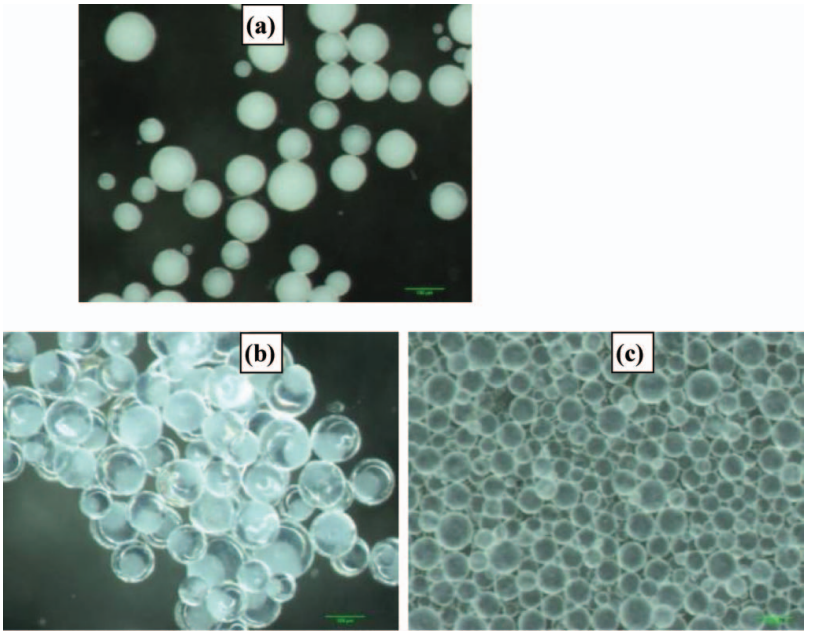

Figure 6. Stereo microscope images of microcapsules observed with (a) coarse surface, (b) partial coarse surface, and (c) smooth surface.

E7 Loading in Microcapsules

Herein, microcapsules with 65–91 wt% E7 loading were prepared (see Table 1). An extremely good agreement was clearly found between the final E7 loadings of microcapsules (C_c%) and the initial E7 contents in the matrix except for Sample 1. The E7 loading of Sample 1 is less than the initial E7 content, it is probably due to the loss of E7 through the holes in their surface during drying. Obviously, as the initial E7 content was 90.91 wt%

Table 1. Core loadings in microcapsules measured by extracting

Samples	Morphology		Initial E7 content[a] (%)	C_c%[b] (%)
	Surface	Inner structure		
1	Coarse (holes)	Multi-core	71.43	65.08
2	Coarse	Multi-core	80.00	79.88
3	Coarse/smooth	Core/shell	83.33	83.37
4	Smooth	Core/shell	86.96	87.02
5	Wrinkled[c]	Core/shell	90.91	90.89

[a]The weight ratio of initial E7 amount to the total adding amount of E7 and PMMA.
[b]E7 loading in microcapsules calculated by Eq. (1).
[c]The microcapsules were observed to have transparent shells. The wrinkles on their surface might be formed during drying when the shell was so thin that the spherical microcapsules collapsed.

(corresponding to the PMMA/E7 ratio of 0.10 g/g), the core loading of mononuclear microcapsules with transparent shell could be achieved as high as 90.89 wt%.

Shell Thickness of Microcapsules

On the basis of the conservation of volume, for a core/shell microcapsule with homogenous shell thickness, the ratio of the volume occupied by the shell (V_s) to the total microcapsule volume (V_t) is interpreted as $\Phi_p = (V_s/V_t)$. The r represents microcapsule radius, and thus the shell thickness t can be calculated by the following equation:

$$t = [1 - (1 - \Phi_p)^{1/3}]r. \tag{2}$$

And the radius of E7 droplet (R) confined in the microcapsule can be expressed as

$$R = r - t = (1 - \Phi_p)^{1/3}r. \tag{3}$$

Since there is an extremely good agreement between the measured E7 loading in microcapsules and the initial LC content in the matrix, it is reasonable to estimate V_s to be the volume of PMMA initially added in the matrix and V_t to be the whole volume of E7 and PMMA initially added in the matrix. So Φ_p is a controllable given value for certain preparation condition. Thus, the shell thickness (t) and E7 droplet size (R) can be predicted. For the fractured microcapsule shown in Fig. 7, its shell thickness was about 210 nm by direct measuring, which agrees well with the value of 211 nm predicted from Eq. (2).

Thermal Analysis

DSC analysis was employed to determine the phase transition temperature of E7 cores. In this study, mononuclear microcapsules with high E7 loadings and different average sizes were studied. As shown in Fig. 8, the transition temperature of each sample was about 59°C. It was reported that the phase transition point for nanoscale E7 droplets would

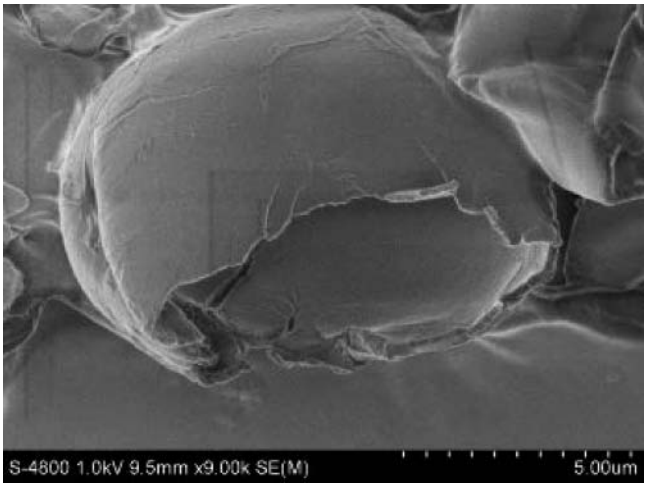

Figure 7. SEM image of fractured microcapsule prepared with the PMMA/E7 ratio of 0.15 g/g ($\Phi_p = 0.112$). Microcapsule radius is 5.440 ± 0.010 μm and its shell thickness is 210.0 ± 1.0 nm.

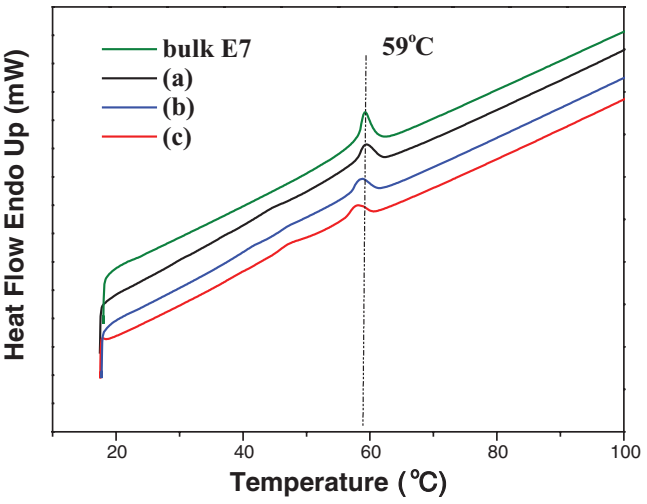

Figure 8. DSC curve of mononuclear PMMA/E7 microcapsules in comparison with bulk E7. Core loadings and average sizes of the samples are (a) 87 wt%, 53.94 μm; (b) 89 wt%, 24.02 μm; and (c) 91 wt%, 7.48 μm.

decrease significantly in comparison with its corresponding bulk materials [31]. However, our results indicated that when E7 was encapsulated by PMMA as micron size droplets, its phase transition point has no substantial changes for all the samples we analyzed. Therefore, the microencapsulated products can be applied at the same temperature environment as that of LC core materials.

Conclusions

Microcapsules with E7 cores and PMMA shells could be prepared conveniently by solvent evaporation method. The morphology of the microcapsules depends strongly on the initial PMMA/E7 ratio in the oil phase. At a high ratio (>0.25 g/g), microcapsules with multi-core structure and coarse surface can be obtained. Medium ratio (≈0.20 g/g) brings about the core/shell microcapsules with partial coarse surface. The low ratio (<0.15 g/g) produces mononuclear microcapsules with smooth surface. Increasing solvent evaporation temperature, as well as using acetone or ethyl acetate as co-solvent, would be favorable to prepare microcapsules with smoother surface. Furthermore, E7 loading in microcapsules is easy to be controlled by the initial addition amount. This is especially advantageous when preparing microcapsules with a high core loading. Due to the control of material compositions and shapes with ease, the shell thickness of microcapsules could be precisely predicted. Specifically, thermal stable PMMA/E7 microcapsules with mononuclear structure, transparent shell, and high E7 loading (90.89 wt%) were prepared, showing great potential for the application within display devices.

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