Preparation of Crosslinked Poly(lactic acid-co-glycidyl methacrylate) Microspheres by Phase Inversion Emulsification

Kamonchanok Thananukul [a], Atitsa Petchsuk [b], Wilairat Supmak [b], Preeyaporn Chaiyasat [c], Amorn Chaiyasat [c] and Pakorn Opaprakasit* [a]

[a] School of Bio-Chemical Engineering and Technology, Sirindhorn International Institute of Technology (SIIT), Thammasat University, Pathum Thani 12121, Thailand.

[b] National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency, Pathum Thani 12120, Thailand.

[c] Department of Chemistry, Faculty of Science and Technology, Rajamangala University of Technology Thanyaburi, Pathum Thani 12110, Thailand.

* Author for correspondence; e-mail: pakorn@siit.tu.ac.th

ABSTRACT

Biodegradable/biocompatible microspheres have been prepared from poly(lactic acid-*co*-glycidyl methacrylate), P(LA-*co*-GMA), copolymers by a phase inversion emulsification (PIE) process. As the copolymer contains unsaturated functional groups, this can be crosslinked by employing thermo-curing reaction. Effects of co-surfactant concentrations and the aqueous phase addition rate on efficiency of the particle formation are evaluated. The addition of sodium dodecyl sulfate (SDS) co-surfactant at slow rates leads to narrow size distribution and higher stability of the microspheres, due to formation of effective structures of polyvinyl alcohol (PVA) surfactant and SDS at the oil/aqueous interface. The resulting microspheres are spherical shape with rough wrinkled surface morphology and bimodal particles size distribution at 1 and 10 μm. Curable behavior of the microspheres are also investigated. The semi-crystalline particles consist of network structure with high gel content of 50%, as the crosslinking efficiency is promoted by mixing the copolymers and the initiator homogeneously in droplets covered by the surfactant molecules. These microspheres with tunable properties can be applied in many fields, especially in cosmetic and biomedical applications.

Keywords: microspheres, phase inversion emulsification, crosslink, polylactic acid, glycidyl methacrylate

1. INTRODUCTION

Polymeric materials in a form of microsphere have attracted vast interests for industrial use in various applications, including cosmetic and personal care products, pharmaceutical products, drug delivery carriers, insecticides, paints and textile products [1, 2]. Microspheres with core-shell structure provide special function in protecting active

agents inside the core from degradation or early contact with targets, which allows sustained release behavior. These materials can be prepared from either synthetic or natural polymers. However, the majority of synthetic microspheres imposes adverse effects to the environment, due to their non-degradable nature which leads to waste accumulation and contamination of the ecosystem.

Polylactic acid (PLA) is one of the widely used degradable polymers, as this is produced from 100% renewable resources, such as corn, sugar beets, or rice. PLA is rigid thermoplastic that can be either in semi-crystalline or amorphous forms [3]. The material possesses remarkable properties, including good mechanical properties, biocompatibility, biodegradability, and non-toxicity. Nevertheless, some of its properties require further improvements for specific applications, such as biodegradability rate, flexibility, mechanical properties, thermal properties, hydrophilicity, and lack of specific functional groups. These shortcomings can be improved by copolymerization with other monomers, for example, poly(lactic-*co*-glycolic acid) (PLGA) [4], poly(lactic acid-*co*-ethylene glycol) block copolymers (PLA-*co*-PEG) [5], poly(lactic acid-*co*-[-caprolactone) (PLA-*co*-PCL) [6], and poly(lactic acid-*co*-glycidyl methacrylate) (PLA-*co*-GMA) [7]. Among these, P(LA-*co*-GMA) is very interesting, as this copolymer is degradable, but exhibits curable property due to methacrylate units. [7, 8].

Various techniques have been developed in preparation of polymeric microspheres, for example suspension, emulsion, coacervation, and spray drying [9]. In this regard, ability to control size and size distribution of the resulting microspheres is important for commercial production. Microspheres prepared from typical suspension polymerization usually show broad particle size distribution. Recently, a phase inversion emulsification (PIE) technique has been widely used in fabrication of polymeric microsphere for use as cosmetic products and biomedical materials. This process consumes low amount of energy for generation of particles with narrow particle size distribution (PSD). During the process, there is a formation of two phases of emulsions, consisting of water-in-oil (W/O) and oil-in-water (O/W). In early stage, the W/O emulsion is formed. A water phase is then continuously added into the system, until the content of water is higher than the oil phase, the W/O emulsion is irreversibly converted to an O/W phase [10, 11]. The major advantage of this technique is a decrease of oil droplet coalescence, as the use of surfactant/co-surfactant combination enhances the adsorption onto the oil-water interface. Therefore, the obtained particles show narrow PSD.

In this work, P(LA-*co*-GMA) copolymers, which contains methacrylate functional as an active site for further crosslinking reactions, is employed in the preparation of microspheres by employing an PIE method. Effects of co-surfactant concentrations and addition rate of the aqueous phase on particle size and PSD of the resulting microspheres are investigated. Surface morphology, particle size and shape, and gel content of the obtained particles are characterized. The materials have high potential for use in various fields, especially in cosmetic and biomedical applications.

2. MATERIALS AND METHODS
2.1 Materials

Poly(lactic acid-*co*-glycidyl methacrylate), P(LA-*co*-GMA) copolymer was synthesized in this laboratory, using *L*-lactide (LA) and

glycidyl methacrylate (GMA) at an LA/GMA molar feed ratio of 90/10 [7]. The molecular weight of synthesized P(LA-co-GMA) copolymer was 7,500 g/mol. Their chemical structure were shown in Figure 1. Benzoyl peroxide (BPO) initiator (Acros, 75%) was purified by recrystallization in ethanol before use. Poly(vinyl alcohol) (PVA) (Aldrich, 87-90% hydrolyzed, M_w=30,000-70,000) and sodium dodecyl sulfate (SDS) (Carlo, ≥99%) surfactants were used as received. Chloroform solvent was purchased from LabScan.
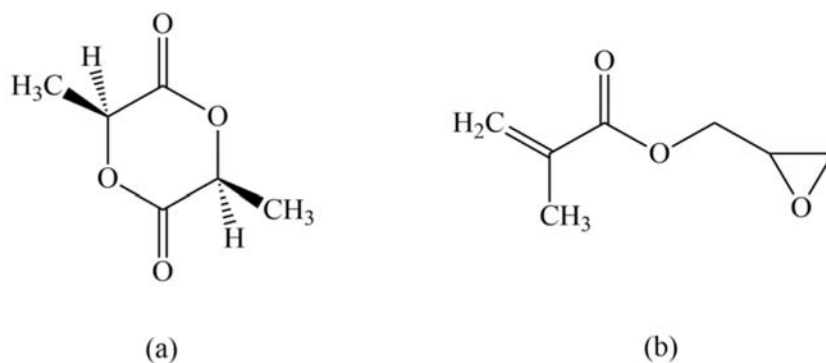

Figure 1. Chemical structures of (a) L-lactide (LA) and (b) glycidyl methacrylate (GMA).

2.2 Experimental Methods
2.2.1 Preparation of icrospheres by PIE

Crosslinked P(LA-co-GMA) microspheres were prepared by a phase inversion emulsification (PIE) method. Essentially, the copolymer, BPO (4 wt% of copolymer), and PVA were dissolved in chloroform solvent. The copolymer droplets were initially formed by dropwise addition of the aqueous phase, containing SDS as co-surfactant, into the system. The immiscible phases were homogeneously mixed using a mechanical stirrer at 500 rpm. After completion of the aqueous phase addition, the reaction temperature was raised to 80 °C and kept for 2 h. Thermal curing reaction of the methacrylate groups in the copolymer's structure leads to a formation of microspheres. The resulting emulsion was then placed in a fume hood at room temperature for overnight to evaporate the remaining solvent. The precipitated microspheres were collected by centrifugation at 40,000 rpm for 20 min. Residual surfactants were washed by re-suspending in deionized water and centrifugation for 2 times. Microsphere powders were finally obtained after incubation in a hot air oven at 50 °C for 24 h. The overall preparation conditions, including the co-surfactant concentrations and aqueous phase addition rates, are optimized, as detailed in Table 1.

1. Effect of co-surfactant concentrations

The presence SDS as a co-surfactant in the system enhances the stabilizing efficiency of PVA surfactant to generate uniform particles with narrow size distribution. Effect of the SDS content on the particle forming efficiency was investigated by varying its concentration from 0, 5, 8 and 12%w/v. The experiments were conducted by gradually dropping the aqueous phase into the oil phase at a constant rate of 2 mL/min.

2. Effect of aqueous phase additional rates

The aqueous phase addition rate affects diffusion time of solvent molecules to form oil-water interface. In these experiments,

SDS solution with a constant concentration of 12% w/v was gradually dropping into the oil phase. The addition rates were varied at 2, 4 and 8 mL/min.

Table 1. Summary on preparation conditions of P(LA-*co*-GMA) microspheres.

Formulation code	Components						Aqueous phase addition rate (mL/min)
	PLA-*co*-GMA (g)	BPO (g)	PVA (g)	Chloroform (mL)	SDS (%w/v)	Water (mL)	
Effect of co-surfactant concentrations							
0% SDS	5.0	0.2	2.0	15	-	50	2
5% SDS	5.0	0.2	2.0	15	5	50	2
8% SDS	5.0	0.2	2.0	15	8	50	2
12% SDS	5.0	0.2	2.0	15	12	50	2
Effect of aqueous phase additional rates							
AR2	5.0	0.2	2.0	15	12	50	2
AR4	5.0	0.2	2.0	15	12	50	4
AR8	5.0	0.2	2.0	15	12	50	8

2.2.2 Preparation of microspheres by suspension crosslinking

In addition, the corresponding microspheres were also prepared by a different technique, the suspension crosslinking method, for comparison with those from the PIE method at the same optimal conditions. Essentially, the copolymer, BPO and PVA were dissolved in chloroform and used as an oil phase. The aqueous phase was, then, poured into the oil phase under magnetic stirring at 500 rpm at 80 °C for 2 h. The obtained microspheres were filtered and washed by deionized water. Finally, the powder was dried in a hot air oven at 50 °C for 24 h.

2.3 Characterizations
2.3.1 Particle size analysis

Average particle diameters and size distributions of the P(LA-*co*-GMA) microspheres were measured by laser light scattering (Mastersizer 2000, Malvern). The instrument offers a broad measuring range at 0.2-2,000 μm. Each sample was measured in triplicate and average values were reported.

2.3.2 Morphological observation

Morphology of microspheres was examined by a polarized optical microscope (ZEISS) and a Scanning Electron Microscope (SEM) (JSM-5410LV and JSM-7800F, JEOL). SEM images were acquired after gold sputtering at an acceleration voltage of 15 kV. To observe core-shell structure, cross-sectional sample was prepared by breaking the microspheres with sonication while being immersed in liquid nitrogen.

2.3.3 FTIR analysis

Chemical structures and functional groups of the curable microspheres were evaluated by using Fourier Transform Infrared (FTIR) spectroscopy in an Attenuated Total Reflection (ATR) mode (Nicolet iS5, Thermo Scientific). Each spectra was acquired by accumulation of 32 scans at a resolution of 2 cm^{-1}.

2.3.4 Gel content

The degree of crosslinking of the microspheres was determined by measuring their gel contents, employing a Soxhlet extraction. The dried microspheres were weighed before extraction by THF at 100 °C for 24 h. After that, the remaining solid samples were dried in a vacuum oven at 50 °C for 48 h, in which their weights were re-measured. The gel content of microspheres was calculated using Equation (1).

$$\%\text{Gel content} = \frac{W_{rd}}{W_{d}} \times 100 \qquad (1)$$

where W_{d} is the initial weight of microspheres
W_{rd} is the dried weight after extraction

2.3.5 Thermal properties

Thermal properties of the samples were investigated by using Differential Scanning Calorimeter (DSC) (822^e; Mettler Toledo) with a nitrogen flow rate of 60 mL/min. The samples (10 mg) were sealed in an aluminum crucible and heated from -20 to 200 °C at a scanning rate of 20 °C/min. Two heating cycles were performed and a holding time of 5 minutes was employed between each run.

3. RESULTS AND DISCUSSION
3.1 Preparation of Crosslinked Microspheres

P(LA-*co*-GMA) microspheres are prepared by employing an PIE method. This method obtains narrow particle size distribution (PSD) microspheres. Effect of co-surfactant content and addition rate of the aqueous phase on structures and property of the microspheres are studied.

1. Effect of co-surfactant concentrations

The presence of co-surfactant is an important factor for enhancing formation of particles with smaller sizes and narrow size distribution. The combination of two (co)surfactants improve colloidal stability of microspheres without high stirring speed. Therefore, anionic co-surfactant SDS is employed in the aqueous phase. Optical micrographs of the resulting microspheres obtained at different SDS concentrations are shown in Figure 2. It is clearly seen that the application of SDS leads to a decrease in size of the particles and a prevention of particles aggregation. Results on particle size distribution of the resulting microspheres with different surfactant concentrations are displayed in Figure 3. Without SDS, particles with an average size of 132 mm and a broad size distribution were obtained. The application of SDS leads to a decrease in the particle size. The degree of size reduction depends on the SDS concentrations, in which average dimeters of 36, 22, and 11 μm were obtained from SDS concentrations of 5, 8, and 12%, respectively. This is because in a single surfactant system, large segments of PVA are located at the oil/aqueous interface. Addition of SDS promotes hydrophilic character of PVA backbone, and hence decreases the interfacial tension to cover the polymer droplets and prevent coalescence [12, 13]. However, a bimodal size distribution pattern is observed when SDS contents of 8 and 12% are applied. This suggests aggregation formation in these reactions. Also, as PLA-*co*-GMA copolymer is semi-crystalline in nature, it is likely that the particles might form lamellar structure in part of larger particles size.
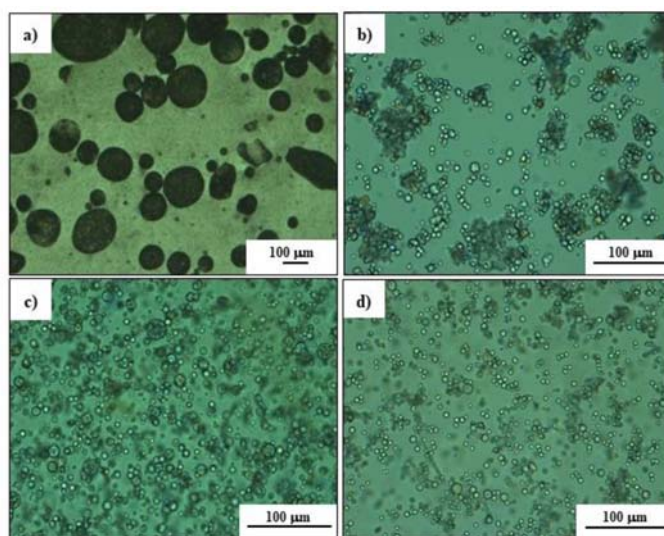
Figure 2. Optical micrographs of P(LA-*co*-GMA) microspheres prepared at different SDS concentrations: (a) 0% SDS, (b) 5% SDS, (c) 8% SDS, and (d) 12% SDS.
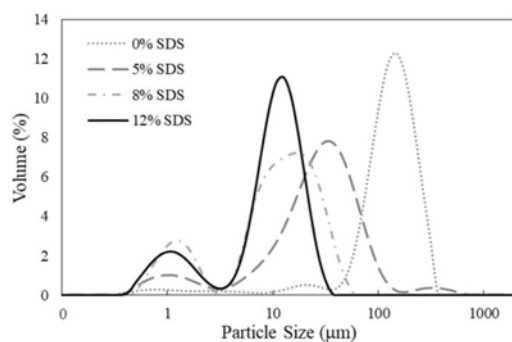

Figure 3. Particle size distribution of microspheres prepared at different co-surfactant concentrations.

2. Effect of aqueous phase addition rates

Figure 4 illustrates the corresponding results on microspheres prepared at various addition rates of the aqueous phase. Bimodal size distribution is observed in all conditions. The change in the addition rate affects sizes of the larger fraction, i.e., average diameter of 2nd mode PSD decreases from 17 to 11 µm when the addition rate is decreased from 8 to 2 mL/min. In contrast, average size of the smaller fraction remains constant at around 1 µm. This is likely because when the addition rate is slower, PVA has enough time to diffuse and form layer structures at the oil/aqueous interface of the polymer droplets [14, 15]. The low addition rate also enables the mixture to retain its low viscosity, which in turn, promotes smaller-sized droplets formation during the phase inversion step [14, 16].
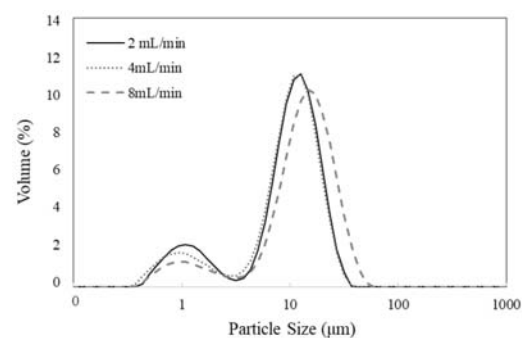

Figure 4. Particle size distribution of microspheres prepared at different addition rates of the aqueous phase.

3.2 Formation of Microspheres and Mechanisms

The *in situ* crosslinking of P(LA-*co*-GMA) microspheres was initiated by a thermal-curing agent, benzoyl peroxide (BPO). At the decomposition temperature of the initiator,

BPO decomposes to form free radical (I→2R•). The active species react with alkene groups in the copolymer chains, leading to formation of covalent network. The reaction is summarized in Figure 5.
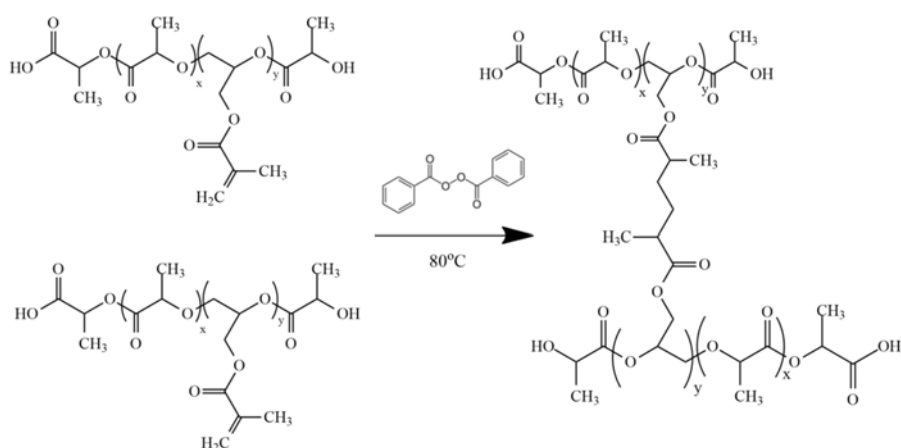

Figure 5. Proposed crosslinking reaction of P(LA-*co*-GMA) copolymer.

The crosslinked reaction is confirmed by ATR-FTIR spectroscopy, as shown in Figure 6. FTIR spectrum of neat copolymer shows characteristic bands at 1760 and 1720 cm⁻¹, corresponding to the stretching mode of C=O groups of PLA and GMA, respectively. The presence of characteristic modes at 1637 and 815 cm⁻¹ are due to the C=C stretching of GMA. After the

formation of the crosslinked network, the bands of GMA, both at 1637 and 815 cm⁻¹, disappear. Moreover, the C=O stretching mode of GMA at 1720 cm⁻¹ are slightly broader, and overlap with the C=O stretching band of PLA [7]. This confirms the formation of crosslinked structures in P(LA-*co*-GMA) microspheres.
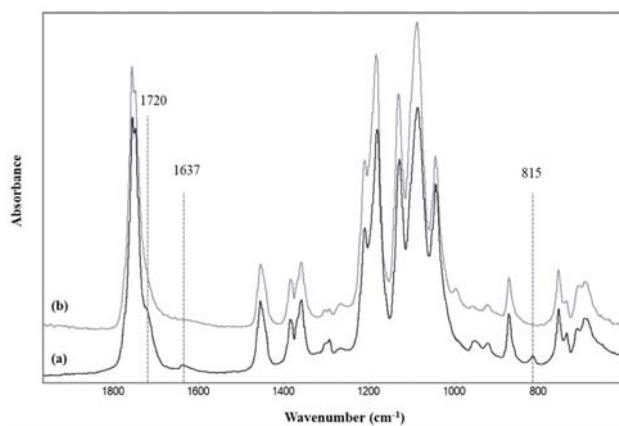

Figure 6. ATR-FTIR spectra of neat P(LA-*co*-GMA) copolymer (a) and P(LA-*co*-GMA) crosslinked microspheres (b).

3.3 Curing Behavior and Properties of Microspheres

From the preliminary results, optimum conditions for preparation of microspheres by a PIE technique are 12 %w/v SDS concentration and 2 mL/min aqueous phase addition rate. Therefore, efficiency of this process is compared with that of a traditional suspension crosslink technique, in terms of chemical and physical properties of the resulting microspheres, by employing these optimum conditions.

Figure 7 shows SEM images of the microspheres prepared by PIE and suspension crosslinking methods. Both techniques produce particles with regular spherical shape, whose particles sizes are in good agreement with the results on particle size distribution. Particles with 2 distinct groups of sizes are clearly observed. The microspheres prepared by the PIE method display rough wrinkled surface morphology (Figure 7a and 7a′), reflecting the presence of lamellar crystalline structures [17]. In contrast, the corresponding particles prepared by the suspension crosslinking procedure show relatively smoother outer surface (Figure 7b and 7b′). The particle size and size distributions of the microspheres were measured by Mastersizer particle size analysis. Particles size of the suspension crosslinked microspheres is slightly larger than that of the PIE microspheres, as summarized in Table 2. This suggests that the gradually drop of the aqueous phase into the oil phase in the PIE method leads to a complete coverage of polymer droplets by micelle formation of the surfactant molecules. At the phase inversion step, the surfactant/ co-surfactant effectively stabilizes particle formation and prevent reversible combination of the droplets [18]. The suspension technique, coalescence and breakup of polymer droplets dynamically occur during the second stage of reaction. Particles size of the resulting microspheres, therefore, is bigger [12]. The PSD of both samples shown quite similar values because the presence of bimodal distribution curve.
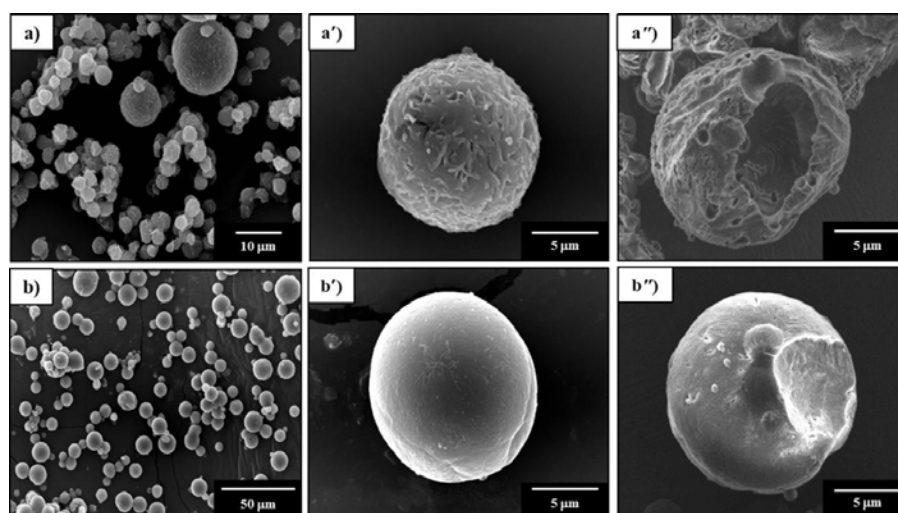

Figure 7. SEM images of P(LA-*co*-GMA) microspheres and cross-sectioned microspheres prepared by PIE (a, a′, a″) and suspension crosslinking (b, b′, b″) methods.

Table 2. Results on average size and gel contents of P(LA-*co*-GMA) microspheres prepared from PIE and suspension crosslinking methods.

Method	Yield (%)	Average diameter (μm)		PSD	Gel contents (%)
		1st mode	2st mode		
PIE	81	1.1	11	1.8	50 ± 1.7
Suspension	83	1.7	19	1.7	32 ± 3.3

The cross-sectioned SEM images illustrate that microspheres prepared by PIE method have hollow structure (Figure 7a″), while those prepared by a traditional suspension technique display solid structure (Figure 7b″). This phenomenon describes the influence of the solvent evaporation rate through the polymer droplets. In PIE process, the aqueous phase is gradually dropped to the oil phase, in which droplets are formed at the phase inversion point. During the addition of aqueous phase period, solvent can evaporate while the copolymer is undergoing crosslinking reaction. The particles finally form hard hollow structure. In contrast, the suspension crosslinking technique leads to immediate formation of droplets at the early stage of the process, which gradually undergoes crosslinking to generate solid structure [19, 20].

Gel content value is indicative of the degree of crosslinking of the cured microspheres, as summarized in Table 2. The materials prepared by PIE method show a gel content of 50%, while those from the suspension crosslinking is lower at 32%. This is probably because in the PIE method, the copolymer and the initiator are homogeneously mixed in the polymers droplets covered by surfactant molecules at the interface. This help preventing the copolymer and initiator molecules to migrate from the droplets. When the temperature is raised to the decomposition point of the initiator, the polymer droplets are readily crosslinked. On the other hand, in the suspension reaction, the initiator molecules are dispersed heterogeneously. Therefore, the initiator and copolymer chains take time to migrate and initiate free radical reaction.

Thermal property of the cured microspheres are examined by DSC experiments. The endothermic transition temperature of each samples are determined from the first heating thermograms as shown in Figure 8. Neat copolymer shows a T_m at 137 °C with undetectable T_g in the experimental temperature range, likely due to its low molecular weight and high size distribution. In contrast, microspheres prepared from both PIE and suspension methods exhibit T_g and T_m characteristics, in which those prepared from PIE technique shows higher values than the counterparts obtained from suspension crosslinking method. This clearly indicate higher efficiency of the curing reaction to form larger chain structures. Interestingly, an additional exothermic peak is observed after T_m for both samples. The result firmly reflects further crosslinking reaction (T_{cure}) [21], associated with remaining acrylate groups in the copolymer structure and residual BPO curing agent. The results suggest that the excess curing agent does not completely decompose at the fabrication temperature (80 °C) [8]. When the copolymer chains are reheated to a liquid state at around 140-170 °C, a regeneration of free radical leads to further crosslinking reaction. The much higher area of the curing peak observed in the suspension

microspheres indicates higher degree of additional curing reaction. This is in good agreements with results from the degree of crosslinking of the original microspheres, as previously discussed.
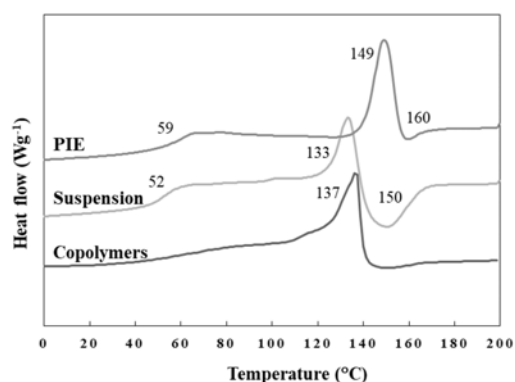

Figure 8. DSC thermograms (1st heating scan) of P(LA-*co*-GMA) copolymers and microspheres prepared by PIE and suspension methods.

4. CONCLUSIONS

P(LA-*co*-GMA) microspheres have been successfully prepared by a phase inversion emulsification (PIE) process. Important reaction parameters have been verified and optimized. The association between PVA and SDS surfactant/co-surfactant system leads to an enhancement in colloidal stability of the microspheres and a decrease in size distribution of the particles when slower addition rates of the aqueous phase are employed. The resulting particles are semi-crystalline in nature, reflected by their rough wrinkled surface morphology of lamellar crystalline structures, containing crosslinked network structure, with about 50% gel content. This results in variations in structures and properties of the resulting microsphere. These materials with tunable properties can be applied in many fields, especially in cosmetic and biomedical applications.

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