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# A modulated DSC characterization of morphology of composite latex particles

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**Abstract**

A modulated differential scanning calorimetry (MDSC) method combining transmission electron microscopy (TEM) for characterizing the morphology of composite latex particles has been developed. Sulfonated polystyrene (S-PS)/poly(methyl methacrylate) (PMMA) (50:50 by weight) composite latex particles were prepared as model samples. PS particles were prepared by self-emulsification using lightly S-PS in co-solvents/water. For the preparation of S-PS/PMMA composite latex particles, the guest methyl methacrylate (MMA) monomers first diffused into swollen S-PS particles in S-PS aqueous dispersions, and then the MMA monomers were polymerized. Based on the MDSC method, one can determine quickly whether and what kinds of composite latex particles are prepared. Combing TEM, morphological parameters, such as the radius of core, diffused-phase thickness and thickness of shell of the composite latex particles, can be obtained.

*Keywords:* Self-emulsification; Composite latex particles; Modulated DSC

## 1. Introduction

Composite latex particles are produced in a wide variety of morphologies for applications in various polymer products [1]. The physical properties are achieved by balancing polymer composition, molecular weight and latex particle morphology. Control of particle morphology in composite latex is important for many latex applications such as adhesives, coatings, graphic arts, and impact modifiers, etc. [2]. Morphology is a subject of intense interest and a great deal of effort is being expended to learn how to control and characterize the final structure of the latex particles [3,4], because of the importance to their final properties. The ability to predict the final morphology of the latex particles has improved markedly since the introduction of free energy analyses of the phase separated particles [2]. Such analyses have highlighted the importance of the interfacial tensions at the polymer/water and polymer/polymer interfaces. The variation of these interfacial tensions with important parameters such as surfactant level, polymer type, initiator end group, and monomer concentration can be utilized to predict all possible equilibrium of the latex particle morphology. However information on concentration distribution in such latex particles cannot be obtained [2]. Only can such information be obtained, composite latex particles for different purposes can be designed. In this communication, we developed a modulated differential scanning calorimetry (MDSC) method to characterize the morphology of the latex particles.

## 2. Experimental

### 2.1. Materials

Methyl methacrylate (MMA), supplied by Aldrich Chemical, was distilled under vacuum. Polystyrene ($M_w = 110\,000$), supplied by Yanshan Chemical Ltd., China, was purified by dissolving in tetrahydrofuran and precipitated by using water, and dried under vacuum at 70 °C for 48 h prior to use.

### 2.2. Sulfonated reaction

Sulfonation was carried out in 1,2-dichloro-ethane at 50 °C following the procedure described by Weiss and Sen

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[5]. Sulfonation agent was acetyl sulfonate, which was prepared by the reaction of concentrated sulfuric acid with acetic anhydride.

### 2.3. *Emulsification of lightly sulfonated polystyrene(S-PS)*

Solutions of 5% S-PS were prepared in toluene/ethanol (1:5 by volume), cyclohexanone/acetone (1:1 by volume) and 1,2-dichloroethane/ethanol (1:1 by volume) co-solvents, respectively. Emulsification was carried out by adding deionized water slowly, with constant agitation at room temperature, into a solution of S-PS. During adding, the conductivity and viscosity of the solution were measured. When the conductivity of the solution reached a constant value, phase inversion was considered to be completed, and then addition of water was stopped. After phase inversion, oil-in-water emulsion was formed [6].

### 2.4. *Preparation of polystyrene/poly(methyl methacrylate) (PMMA) composite latex particles*

MMA monomers with initiator (BPO) were dropped into the oil-in-water emulsion of S-PS. It was expected that MMA diffused into the polystyrene nanocapsules. After stirring for 1 h, heated the system to 80 °C, and then the system was kept for 8 h at 80 °C. S-PS/PMMA (50:50 by weight) composite latex particles were performed in three different co-solvents/water called S-PS/PMMA-1, S-PS/PMMA-2 and S-PS/PMMA-3.

### 2.5. *Transmission electron microscopy (TEM)*

TEM experiments were carried out to examine the morphology for these samples mentioned above. The oil-in-water emulsion of S-PS, and emulsion of S-PS/PMMA composite latex particles were diluted by water. Dropped them on a copper-coated grid, and then dried in air at room temperature, respectively. The residual monomer and other volatile matters were removed under vacuum before the TEM experiments were taken. The specimens were unstained, and examined by means of JEM-1010 electron microscope.

### 2.6. *Thermal analysis*

The morphology of the S-PS/PMMA composite latex particles was analyzed by means of MDSC (TA Instrument DSC2920). The composite samples were heated from room temperature to 170 °C with a heating rate of 3 °C/min. An oscillation amplitude of ±1.0 K, an oscillation period of 60 s were employed. The baseline and temperature of the calorimeter was calibrated by using empty pans and indium. The heat capacity was calibrated by using sapphire and standard polystyrene.

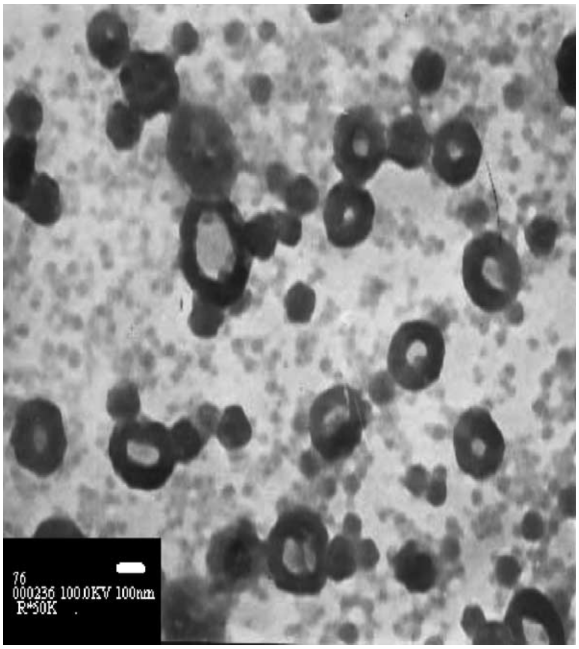

Fig. 1. TEM photograph of the S-PS latex particles.

## 3. Results and discussion

Fig. 1 shows the TEM result for the S-PS particles, indicating that it has a cavum-structure. This will afford the location for polymerization of guest monomers. Fig. 2 shows the TEM result for the S-PS/PMMA-2 composite latex particles. The cavum-structure disappeared. The

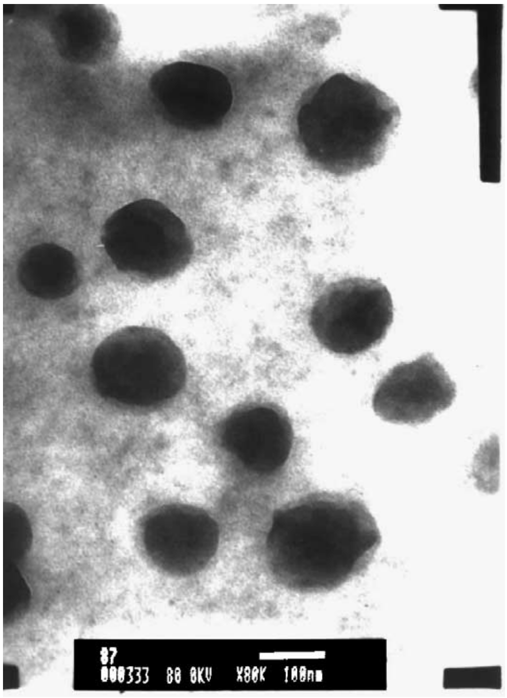

Fig. 2. TEM photograph of S-PS/PMMA-2 composite latex particles.

S-PS/PMMA-1 and S-PS/PMMA-3 have the same TEM results as S-PS/PMMA-2. From the TEM results, the average particle size can be obtained. The average particle size was found to be 120 and 112 nm for S-PS/PMMA-2 and S-PS/PMMA-3, respectively. From the TEM results, the only information that can be given is that the morphology of the S-PS/PMMA composite latex particles is a mixed structure of S-PS and PMMA components. It is not clear how the PMMA distributed in the S-PS particles: uniformed, separated or gradient?

It has been demonstrated that the differential of heat capacity, $\mathrm{d}C_p/\mathrm{d}T$, with temperature signal is very sensitive to the change of component in polymer blends [7]. For a fully miscible two-component polymer blend, $\mathrm{d}C_p/\mathrm{d}T$ with temperature signal is a single Gaussian function of temperature. For a fully immiscible two-component polymer blends, $\mathrm{d}C_p/\mathrm{d}T$ with temperature signal is a two-separated Gaussian function of temperature. For a partially miscible two-component polymer blends, $\mathrm{d}C_p/\mathrm{d}T$ with temperature signal is a sum of multiple Gaussian functions of temperature [7].

For a three-phase polymer system, polymer 1, polymer 2 and interfacial phases (diffused interface between phases), we have [7]

$$\frac{\mathrm{d}C_p}{\mathrm{d}T} = \left[\frac{\mathrm{d}C_p}{\mathrm{d}T}\right]_1 + \left[\frac{\mathrm{d}C_p}{\mathrm{d}T}\right]_2 + \Psi \tag{1}$$

$\Psi$ is the differential of heat capacity versus temperature signal for the interfacial phase. For simplicity, in this paper, we use the Gaussian function to describe the change of $\mathrm{d}C_p/\mathrm{d}T$ versus temperature at the glass transition, i.e.,

$$\left[\frac{\mathrm{d}C_p}{\mathrm{d}T}\right]_1 = \frac{\Delta C_{p1}}{\omega_{\mathrm{d}1}(\pi/2)^{1/2}} \exp\left[\frac{-2(T - T_{\mathrm{g}1})^2}{(\omega_{\mathrm{d}1})^2}\right] \tag{2}$$

$$\left[\frac{\mathrm{d}C_p}{\mathrm{d}T}\right]_2 = \frac{\Delta C_{p2}}{\omega_{\mathrm{d}2}(\pi/2)^{1/2}} \exp\left[\frac{-2(T - T_{\mathrm{g}2})^2}{(\omega_{\mathrm{d}2})^2}\right] \tag{3}$$

$\omega_{\mathrm{d}1}$ and $\omega_{\mathrm{d}2}$ are the half width of the glass transition peak for polymers 1 and 2. The glass transition temperature as a function of distance from a discrete phase boundary between polystyrene and poly(bisphenol-A carbonate) has been studied theoretically [8]. Consider that the interfacial phase is divided into $N$ sub-systems. Each sub-system has average concentration, $\{\langle\phi^1\rangle, \langle\phi^2\rangle, \ldots, \langle\phi^n\rangle\}$. For the $N$ sub-systems, there is a glass transition temperature spectrum, $\{T_{\mathrm{g}}^1, T_{\mathrm{g}}^2, T_{\mathrm{g}}^3, \ldots, T_{\mathrm{g}}^n\}$. Assume that the differential of heat capacity versus temperature signal, $\Psi_i$, for $i$th sub-system can still be described by the Gaussian function. For the glass transition temperature spectrum, the $\Psi$ is as follows:

$$\Psi = \sum \Psi_i = \sum \frac{\Delta C_{pi}^{\mathrm{g}}}{\omega_{\mathrm{d}i}^{\mathrm{g}}(\pi/2)^{1/2}} \exp\frac{-2(T - T_{\mathrm{g}i}^{\mathrm{g}})^2}{(\omega_{\mathrm{d}i}^{\mathrm{g}})^2} \tag{4}$$

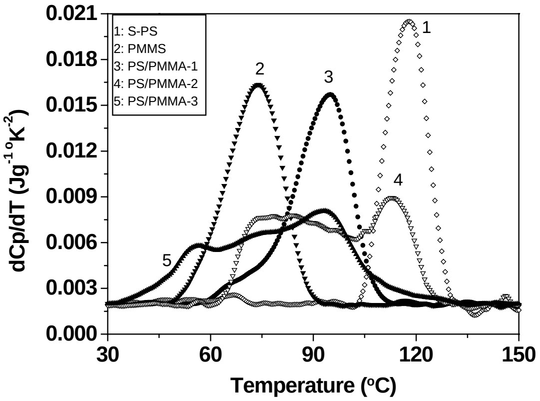

Fig. 3. Differential of heat capacity with temperature signals for different S-PS/PMMA composite latex particles.

$\Delta C_{pi}^{\mathrm{g}}$ is the increment of heat capacity, $T_{\mathrm{g}i}^{\mathrm{g}}$ the glass transition temperature and $\omega_{\mathrm{d}i}^{\mathrm{g}}$ the half width of the glass transition peak for the $i$th sub-system.

Fig. 3 shows the $\mathrm{d}C_p/\mathrm{d}T$ with temperature signals for S-PS, PMMA and S-PS/PMMA (50:50 by weight) composite latex particles prepared with different co-solvents/water. The $\mathrm{d}C_p/\mathrm{d}T$ with temperature signals were smoothed. The smoothing resulted in about 3% error for the calculation of the increment of heat capacity. The effect of the different slope of the heat capacity below and above the glass transition region on the derivative of the heat capacity was discussed in [9,10]. Although TEM results were the same for S-PS/PMMA-1, S-PS/PMMA-2 and S-PS/PMMA-3, Fig. 3 indicate that the MDSC results were significantly different. S-PS/PMMA-1 is fully miscible composite latex particles. The glass transition temperature of the S-PS/PMMA-1 can be described by $T_{\mathrm{g}} = \omega_1 T_{\mathrm{g}1} + \omega_2 T_{\mathrm{g}2}$ approximately. $\omega_1$ and $\omega_2$ are the weight fractions, and $T_{\mathrm{g}1}$ and $T_{\mathrm{g}2}$ are the glass transition temperatures of the S-PS and the PMMA, respectively.

The $\mathrm{d}C_p/\mathrm{d}T$ with temperature signals of S-PS/PMMA-2 and S-PS/PMMA-3 indicate that the two systems are partially miscible composite latex particles. However the morphologies of S-PS/PMMA-2 and S-PS/PMMA-3 are very different. It can be seen clearly that the glass transition temperature of S-PS/PMMA-3 shift to low temperature, which indicates PMMA in the S-PS/PMMA-3 has lower molecular weight. PMMA of lower molecular weight plasticized the S-PS phase. The $\mathrm{d}C_p/\mathrm{d}T$ of MDSC with temperature signal is, indeed, very useful one for the analysis of the distribution of one component in another component in composite latexes.

In order to provide quantitative information for the distribution of one component in another component in composite latexes, we re-draft the $\mathrm{d}C_p/\mathrm{d}T$ with temperature signals for the S-PS/PMMA-2 and the S-PS/PMMA-3 shown in Figs. 4 and 5, respectively.

According to Eqs. (1)–(4), information on the morphology of these composite latex particles can be obtained

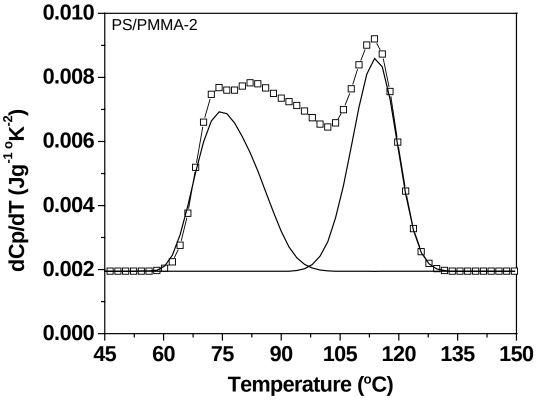

Fig. 4. Peak resolution results for the S-PS/PMMA-2 composite latex particles. For clarity, the intermediate peaks were removed because the sum of the intermediate peaks represents the diffused-phase signal.

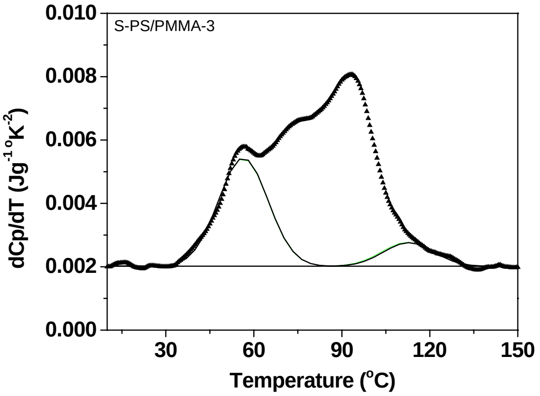

Fig. 5. Peak resolution results for the S-PS/PMMA-3 composite latex particles. For clarity, the intermediate peaks were removed because the sum of the intermediate peaks represents the diffused-phase signal.

combining their TEM results. A three-phase structure: pure PMMA phase (core), pure S-PS phase (shell) and a PMMA and S-PS diffused-phase for the S-PS/PMMA-2 was obtained by peak resolution [7]. For clarity, the intermediate peaks were removed because the sum of the intermediate peaks represents the diffused-phase signal. Morphological parameters are shown in Table 1. However, it is necessary to indicate that the baseline step in the derivative of the heat capacity caused by the different slope of the heat capacity is very small, which result in a neglected error in the analysis of the morphology of the composite latex particles. The radius of the core and the thickness of the shell and the diffused-phase were calculated based on the assumption of that both S-PS and PMMA had the same density.

The morphology of the S-PS/PMMA-3 composite latex particles was also analyzed. A three-phase structure: pure PMMA phase (core), pure S-PS phase (shell) and a PMMA and S-PS diffused-phase for the S-PS/PMMA-3 was obtained. The morphological parameters are shown in Table 2. The glass transition temperature of the PMMA core-phase in the S-PS/PMMA-3 composite latex particles was found to be 57 °C, which is lower than that of pure PMMA as prepared in this report, which resulted from lower molecular weight. Indeed, different co-solvents have significant influences on the morphology of S-PS/PMMM composite latex particles. The analysis of the effect of co-solvents on the morphology of the S-PS/PMMA is beyond the scope of this paper.

From above analysis, it is believed that combing TEM and MDSC, information of the morphology of polymer composite latex particles can be provided. According to the information, the design and control of the morphology of polymer composite latex particles with

Table 1
Morphological parameters of S-PS/PMMA-2

| Phase | $T_g$ (°C) | $\Delta C_p$ (J/g K) | Weight fraction (%) | Radius of the core, thickness of the shell and diffused-phase (nm) |
|---|---|---|---|---|
| PMMA phase (core) | 74 | 0.092 | 29 | 27 |
| S-PS phase (shell) | 114 | 0.095 | 33 | 8 |
| Diffused-phase | – | 0.116 | 38 (21% PMMA and 17% S-PS) | 25 |
| Pure S-PS as prepared in this report | 116 | 0.292 | – | – |
| Pure PMMA as prepared in this report | 74 | 0.314 | – | – |

$\Delta C_p$ (S-PS/PMMA-2) = 0.303 J/g. The average diameter of the particles is 120 nm.

Table 2
Morphological parameters of S-PS/PMMA-3

| Phase | $T_g$ (°C) | $\Delta C_p$ (J/g K) | Weight fraction (%) | Radius of the core, thickness of the shell and diffused-phase (nm) |
|---|---|---|---|---|
| PMMA phase (core) | 57 | 0.082 | 26 | 26 |
| S-PS phase (shell) | 115 | 0.027 | 10 | 3 |
| Diffused-phase | – | 0.193 | 64 (24% PMMA and 40% S-PS) | 30 |
| Pure S-PS as prepared in this report | 116 | 0.292 | – | – |
| Pure PMMA as prepared in this report | 74 | 0.314 | – | – |

$\Delta C_p$ (S-PS/PMMA-3) = 0.301 J/g. The average diameter of the particles is 118 nm.

different properties and for different purposes could be achieved.

## 4. Conclusions

A MDSC method for characterizing the morphology of composite latex particles was developed. Based on the MDSC method, one can determine quickly whether and what kinds of composite latex particles are prepared. It is believed that combing TEM and MDSC information of the morphology of polymer composite latex particles can be provided. According to the information, the design and control of the morphology of polymer composite latex particles with different properties and for different purposes could be achieved.

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