

EFFECT OF PARTICLE SIZE ON THE FILMING PROCESS OF POLYSTYRENE LATEX STUDIED BY AFM*

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Abstract The film formation process of micro-PS particles (diameter 742 nm) and nano-PS particles (diameter 29 nm) was studied by atomic force microscopy and differential scanning calorimetry. During a step heating process, the particles were annealed for 0.5 h at each selected temperature. It was found that the deformation and interdiffusion temperatures of the micro-PS particles are ca. 120–130°C and 140–150°C, that of the nano-PS particles are 90°C and 100–110°C respectively. The DSC traces of nano-PS particles showed that there was an exothermic peak near T_g after annealing for 0.5 h at the selected temperatures below 90°C; otherwise, the exothermic peak disappeared after annealing at 100°C or above. Compared with the micro-PS particles, the sintering process of nano-PS particles occurs at much lower temperature determined by the confined state of polymer chains with higher conformational energy in nano-particles, and completes in a much narrower temperature range driven mainly by the larger total surface energy.

Keywords Polystyrene latex, Filming process, Particle size effect

INTRODUCTION

Over recent years, the application of waterborne latex-based coatings has been expanding rapidly as a kind of environment-friendly polymeric material^[1]. Traditionally, the film formation process of polymer latex is considered in terms of three sequential steps: (i) water evaporation and subsequent packing of polymer particles, (ii) deformation of the particles and close contact between the particles if their T_g is less than, or close to the drying temperature, and (iii) coalescence of the deformed particles to form a homogeneous film^[2].

Many studies of the latex filming process, utilizing a variety of techniques, have been published. Transmission electron microscopy (TEM) of latex films has been the traditional method for examining the film morphology^[3]. Roulstone *et al.*^[4] and Wang *et al.*^[5] used freeze-fracture transmission electron microscopy (FFTEM) to investigate the deformation, coalescence and fusion process in poly(butyl methacrylate) (PBMA) particles in the latex film with a particle diameter of 114–400 nm. The molecular interdiffusion phenomena in the third step have also been extensively studied by techniques such as non-radiative energy transfer (NRET) method^[6] and small-angle neutron scattering (SANS)^[7].

Atomic force microscopy (AFM) is a powerful technique for observing the surface morphological changes during the latex film formation, since it is able to provide high-resolution images of the film surfaces and without the need for pretreatment of samples. The time and temperature dependence of particle deformation/flattening at the surface of PBMA latex has been measured by Goh *et al.*^[8] and Lin *et al.*^[9, 10], respectively.

Besides the influence of time and temperature on the film formation process in the second and third steps, attention was also paid to the effect of particle size on the sintering temperature of latex filming. Goudy *et al.*^[11]

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observed that smaller PS particle latex (size = 0.24–1.05 μm) resulted in a faster rate of the interparticle fusion. In this work, we focus our attention on the filming behavior of nano-PS latex particles, in which the polymer chains showed novel condensed characters, comparing to that in the micro-particles or in the bulk^[12, 13]. The morphological alterations on film surfaces at various annealing temperatures were observed by AFM. The deformation and interdiffusion temperatures of both micro-PS particles and nano-PS particles were measured. The thermal behavior of the particles during sintering was also investigated by differential scanning calorimetry (DSC).

EXPERIMENTAL

The synthesis of the latex particles used in the present study were described in our previous articles by using conventional dispersion polymerization and microemulsion polymerization, respectively^[13,14]. The particles were harvested and purified by centrifugation, washing for several times with methanol and distilled-deionized water (DDI water) until the electroconductivity of the centrifugate were very close to that of DDI water, and were dried under vacuum at room temperature. The particle sizes were checked by TEM using a Hitachi-800H microscope. On average, the diameters of the micro-PS and nano-PS particles are *ca.* 742 nm and 29 nm, the molecular weights of individual polymer chain (M_w) are 1.75×10^5 and 1.64×10^6 respectively, measured by gel permeation chromatography (GPC, PL-GPC-210). Based on static laser-light scattering (LLS, DLS-700) measurements, the weight average molar mass of the nano-PS particle (designated as M_s) in aqueous suspension is *ca.* 6.34×10^6 . And based on the M_s/M_w value, it was calculated that there are *ca.* 4 polystyrene chains in each nano-PS particle on average^[13].

Part of the purified PS particles were re-dispersed in DDI water. The film was prepared by spreading a drop of the diluted dispersion directly onto a freshly cleaved mica, followed by drying in air for 72 h, and then in vacuum for 24 h at room temperature.

The film formation processes were observed from a Nanoscope IIIa (Digital Instruments) scanning probe microscope, equipped with a high temperature heater accessory (MMHTRS-1, Digital Instruments). The film formation was performed on the high temperature heater accessory using a step heating process from room temperature to 140°C and the film was annealed for exactly 0.5 h at selected temperatures, followed by cooling down to room temperature for *in-situ* AFM imaging. The film was heated again to a higher selected temperature with the same procedure. With a 4979JVH scanner, it is possible to scan the film surfaces at almost the same location after each annealing step. Samples were transferred into a convection oven under nitrogen atmosphere for annealing at temperatures higher than 150°C. The AFM images of the samples were observed using the tapping-mode with a silicon cantilever of resonance frequency 250–300 kHz. During heating, the cantilever was also heated at a temperature a little bit lower than the annealing temperature, to protect the tip from contamination.

Thermal behavior measurements of the particles after step heating were performed on a Perkin-Elmer DSC-7 instrument, with a scanning range and heating rate of 30–200°C and 10 K/min, respectively.

RESULTS AND DISCUSSION

Figure 1 displays a series of AFM images which show the changes of morphology of the micro-PS film (diameter 742 nm) during the annealing steps. The film surface morphology in the images remained unchanged when the annealing temperatures were lower than 110°C, as shown in Fig. 1(a) and (b). After annealing at 120°C for 0.5 h, a slight deformation of some micro-PS particles was observed by measuring the changes of peak-to-trough distance through the section lines^[9–11]. The peak-to-trough distance was reduced compared to that of the same particles annealed at lower temperatures, although it was hardly distinguished from the top view of the AFM image shown in Fig. 1(c).

The flattening of micro-PS particles can clearly be seen in Fig. 1(d), scanned after the film was sequentially annealed at 130°C for 0.5 h. Compared with the morphology shown in Fig. 1(a)–(c), it is noted that the flattening

of particles occurs more easily where the particles are more closely packed. Mazur *et al.*^[15] also reported that the sintering of particles with lower packing densities requires higher annealing temperature or longer annealing times. Interpenetration of polymer chains between the adjacent particles was scarce because the interfaces between most particles still existed at this annealing temperature.

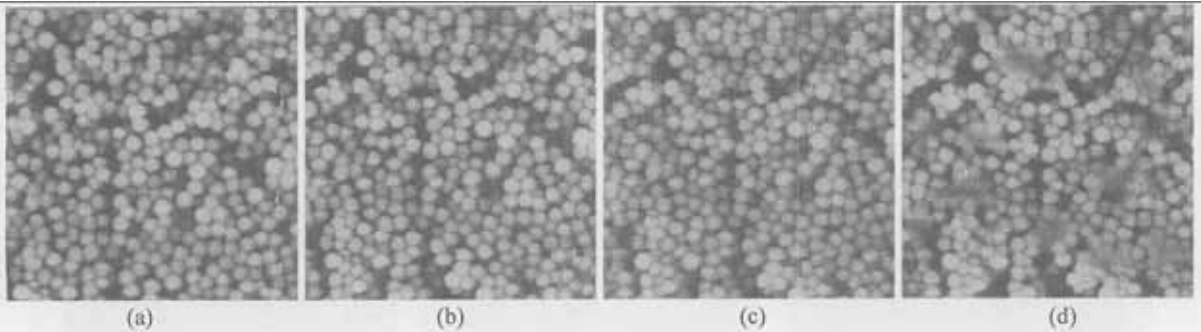


Fig. 1 AFM images of the morphology of the PS particles with average diameter of 742 nm at room temperature (a), after annealing at 110°C (b), 120°C (c) and 130°C (d) for 0.5 h
Image size: 15 μm $\times$ 15 μm

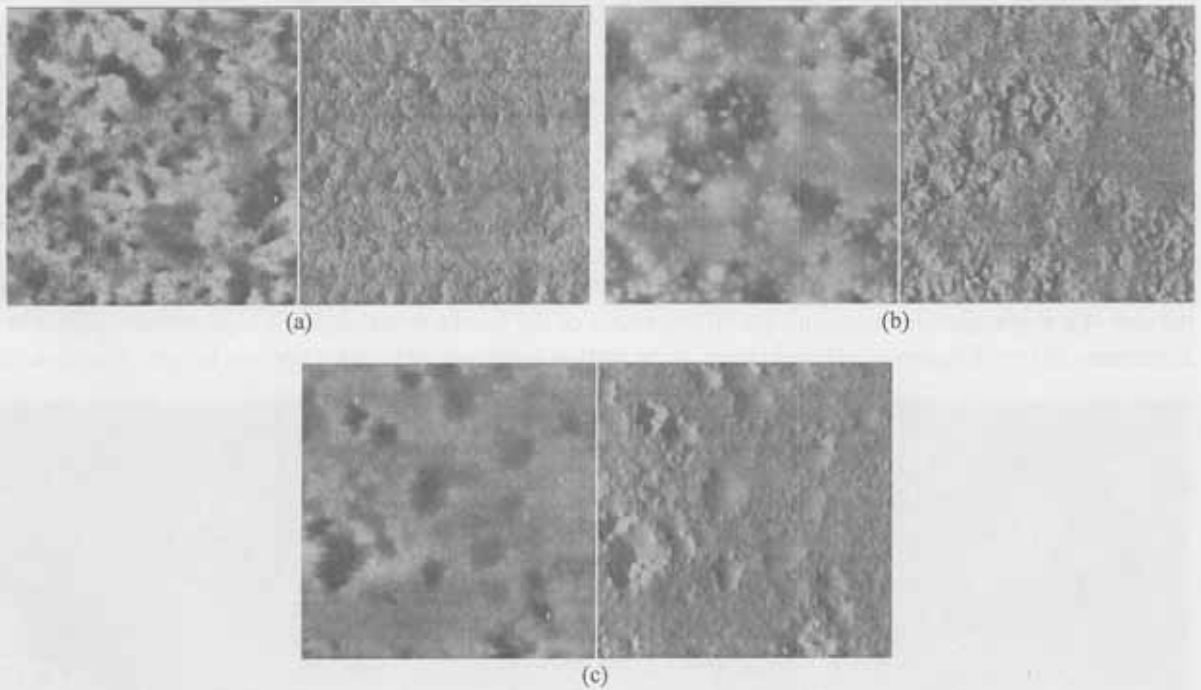


Fig. 2 AFM images of the morphology of the PS particles with average diameter of 742 nm after annealing at 140°C (a), 150°C (b) and 180°C (c) for 0.5 h
Left: height image, Right: phase image; Image size: 15 μm $\times$ 15 μm

The particles on the surface of film flattened completely after annealing at 140°C (Fig. 2a). However, the contours of a large number of the particles remain discernible, as shown more clearly in the phase image of Fig. 2(a), together with several homogeneous domains. When the annealing temperatures attained 150 (Fig 2b), 160 and 170°C (images are similar to Fig. 2b), the contours of most particles became blurred and, only a part of them was still visible. It has been indicated^[2] that the greater the interdiffusion between polymer chains at the particle surface, the greater will be the loss of particle definition. Our results imply that the interdiffusion of the

polymer chains between the adjacent micro-PS particles occurs at 140–150°C and continues to 160–170°C. Figure 2(c) shows that a relatively homogeneous film was formed after annealing to 180°C for 0.5 h.

The film process of nano-PS particles was quite different from that of micro-PS, as shown in Figs. 3 and 4. The contour of the particles is clearly seen in the images when the annealing temperature was below or at 80°C (Fig. 3a and b). Significant deformation of the contours is observed after annealing at 90°C (Fig. 3c), which is much lower than the deformation temperature of micro-PS particles, and also lower than the T_g of bulk PS. However, as shown in Fig. 3(c), it is noted that the particle's boundaries are still visible, this implies that the interparticle diffusion of polymer chains is limited after annealing at 90°C.

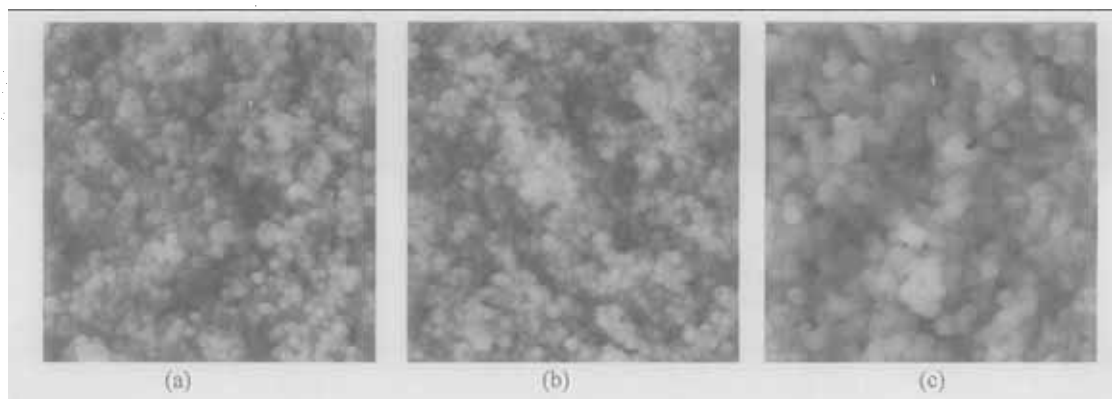


Fig. 3 AFM images of the morphology of the PS particles with average diameter of 29 nm at room temperature (a), after annealing at 80°C (b) and 90°C (c) for 0.5 h
Image size: 1.5 μm $\times$ 1.5 μm

After the film was annealed at 100°C for 0.5 h, the contour of individual particle are barely distinguishable although distinct contrast is still obvious among the homogeneous domains, as shown in the height image and phase image of Fig. 4(a). In the images of Fig. 4(a), there are larger domains with a dimension much bigger than the size of a single particle, indicating the disappearance of the interfaces among these adjacent particles, or the appearance of interdiffusion of polymer chains at the particle interfaces, although it may not be very extensive.

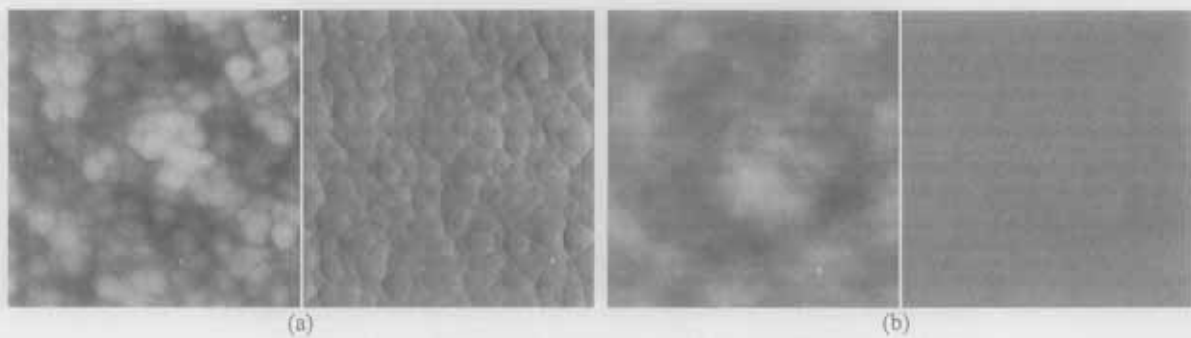


Fig. 4 AFM images of the morphology of the PS particles with average diameter of 29 nm after annealing at 100°C (a) and 110°C (b) for 0.5 h
Left: height image, Right: phase image; Image size: 1.5 μm $\times$ 1.5 μm

Figure 4(b) shows that the surface topology of the whole film after sintering at 110°C for 0.5 h becomes fairly homogeneous, indicating that interdiffusion of the polymer chains and sintering take place to a certain extent.

As mentioned before, the deformation and interdiffusion temperatures of the micro-PS particles with a diameter 742 nm are around 120–130°C and 140–150°C, respectively. This result agrees with our previous one

which was measured by laser confocal fluorescence microscopy (LCFM)^[16, 17]. Compared to that, the sintering temperature of the nano-PS particles is obviously lower. Goudy *et al.*^[11] reported that both the peak-to-peak distances and the peak-to-trough heights of close-packing PS particle (diameter 0.24–1.05 μm) arrays measured by AFM remained constant for an annealing temperature of 95°C (a little lower than the bulk T_g of PS) with a long annealing time of 17 h. Their experiments also revealed that films comprised of smaller latex particles (diameter 0.240 μm) are more susceptible to fusion than those comprised of larger latex particles (diameter: 0.375 μm) annealing at 105°C for 17 h. TMA measurements show that the densification of acrylic copolymer particles (diameter 140 nm) was mostly completed within the temperature range of 70–90°C, which is in the immediate vicinity of T_g (72°C), measured with a heating rate of 10 K/min, while the sintering of larger particles requires higher temperature or longer time^[15]. We could infer that the extent of particle size confinement causes the sintering of the nano-PS particles (*i.e.* with a diameter of 29 nm in this work) to take place at the extremely low annealing temperature.

The DSC scans in Fig. 5 show that exothermic peaks appear at ca. 106, 107, and 110°C for the samples without sintering and after annealing for 0.5 h at 80 and 90°C. The exothermic enthalpy of the peaks was ca. 2 J/g. Mahr^[18] first observed such exothermic peak during the first heating cycle of polystyrene colloids with a particle size of 109 nm and associated this irreversible measurable energy with the loss of the high specific surface area and the disappearance of surface energy at sintering. Similar thermal behavior was also found for polymer particles such as poly(vinylidene chloride) (diameter 37 nm) and acrylic copolymers (radius 70 nm)^[15, 18]. Guar *et al.*^[19] attributed this kind of exotherm of PS nano-spheres (diameter 85 nm) to stress release. But no such exothermic peak was observed on both the first and second traces of the micro-PS particles as shown in Fig. 6. This implies that the exothermic process is significantly affected by the particle size. With smaller diameter (*i.e.* < 120 nm), the nano-PS particles have larger surface area or surface free-energy and, more important, the polymer chains in the nano-spheres lie in a highly compact state due to the spatial limitation compared to that of the random-coil state^[13, 20] either in micro-particles or in bulk.

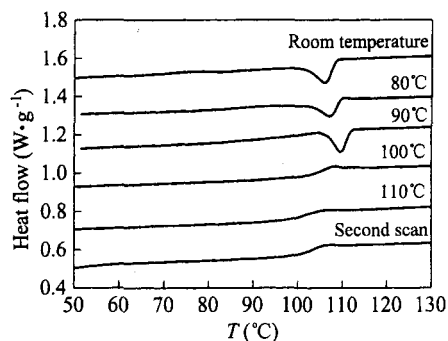


Fig. 5 DSC traces of PS particles with diameter 29 nm after sintering at various temperatures for 0.5 h
Heating rate: 10 K/min

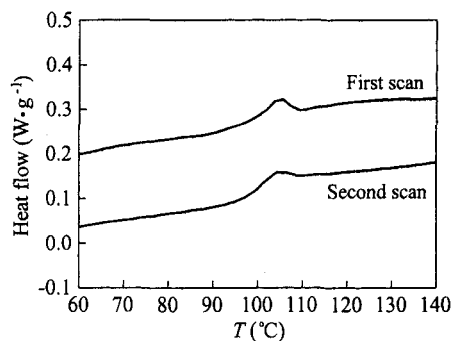


Fig. 6 DSC traces of PS particles with diameter 742 nm
Heating rate: 10 K/min

The maximum of the exothermic peak shifted to higher temperature when the annealing temperature was increased, but not over the bulk T_g . The mobility of the polystyrene chains in the particles was increased, and the spherical shape of the particles deformed when the nano-PS particles were annealing at 90°C. Presumably, this causes some loss of freedom in the backbone motion as the aromatic ring of nano-PS is cooled down to room temperature. The original interface between the adjacent particles remains and with limited interpenetration of PS chains after annealing at 90°C for 0.5 h, as shown in Fig. 3(c). The enthalpy of the exothermic peak remains similar to that of particles without annealing.

However, the exothermic peaks disappear after sintering at 100°C or above, only their decrements in heat flow which are represented by the glass transitions could be seen at ca. 104°C and 102°C for the sintering

temperatures of 100°C and 110°C respectively. This indicates that the surface energy has already been released during the sintering period, causing dissolution of the interface between the adjacent particles. This corresponds to the interdiffusion and interpenetration of PS chains at the interface of these particles, even though it may not be very extensive, at a sintering temperature around the bulk T_g (*i.e.* 100°C), *ca.* 40 K lower than that of micro-PS particles, and also the relaxation of the chain conformation from a confined state to a bulk random coil state at 100–110°C. The second heating scan of nano-PS after cooling from 200°C to ambient temperature also showed only a glass transition at 102°C without the exothermic peak, just like the DSC traces of micro-PS particles (Fig. 6) and bulk atactic PS.

Li *et al.*^[21] simulated the conformation of a single polystyrene chain (SPSC, $M_w = 4.16 \times 10^6$) in θ solution by the RIS-Monte Carlo model. It was shown that for PS with a particle diameter of 24 nm, the conformational energy of the single chain particle is 0.93 J/g higher than that of a free state (Gaussian coil) PS chain. On the other hand, if the particle diameter is larger than 120 nm or there are 20 or more PS chains in a particle within a diameter of 24 nm, the conformational energy of the SPSC is equal to that of a Gaussian PS chain. Qian *et al.*^[12] found that the single-chain polystyrene glass prepared by microemulsion polymerization has a higher conformational temperature than that of the ordinary multichain PS based on FTIR measurements. The density of the nano-particle is *ca.* 10% lower than bulk PS in this work^[20, 22]. The polymer chains contain more free volume and less interactions between segments in nano-PS chains, which were confirmed by the solid state NMR measurements and other methods^[20, 22]. With $M_w = 1.64 \times 10^6$, the root-mean square end to end distance of a Gaussian coil should be *ca.* 80 nm, which implies that the polymer chains in the nano-PS particle (diameter 29 nm) are in a highly confined state, leading to higher conformational energy than those of bulk PS and micro-PS chains. Therefore, it is reasonable to think that the higher conformational energy and less interaction of polymer chains are the major reasons for the sintering of nano-PS particles at a lower temperature.

After the samples were annealed above the deformation temperature, the sintering process of nano-PS particles was completed within the temperature range of 90–110°C, which is narrower than that of micro-PS particles (*i.e.* 120–180°C). It has been found that a smaller particle sized latex produces a faster rate of interparticle fusion, caused by the greater capillary force between the smaller particles^[11] Song *et al.*^[1] showed that the surface molecular diffusion in the latex film is driven by the surface tension or surface free energy. The specific surface area or the total surface energy of nano-PS particles (diameter 29 nm) is much larger than that of micro-PS particles (diameter 742 nm). Also the interfacial capillary forces for nano-PS should be larger. It is reasonable that the filming process completed within a narrow heating temperature range, or with a fast rate, was determined by the large total surface energy of nano-PS particles. The appearance of an exothermic peak in the first DSC scan of nano-PS particles at the temperature around T_g (Fig. 5) can mainly be attributed to a rapid release of the surface energy resulting from the occurrence of interdiffusion at the interface of the adjacent particles and thus results in a loss of specific surface area. And the decrease of the excess conformational energy of polymer chains from the confined state to the random coil state may also be a contribution. No exotherm is observed in the DSC scans of micro-PS particles because their total surface energy is much less than that of nano-PS particles and releases slowly over a longer period.

CONCLUSIONS

The film formation process of micro-PS particles (diameter 742 nm) and nano-PS particles (diameter 29 nm) was studied by means of AFM and DSC. During a step heating process, the particles were annealed for 0.5 h at each selected temperature. The deformation and interdiffusion temperatures were found to be *ca.* 120–130°C and 140–150°C for the micro-PS particles, and 90°C and 100–110°C for the nano-PS particles, respectively. Compared to the micro-PS particles, the sintering of nano-PS particles happens at much lower temperature determined by the confined state of polymer chains with higher conformational energy in the nano-particles, and the process is completed more rapidly, being driven mainly by the larger total surface energy.

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