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Mechanistic Study on Latex Film Formation in the Presence of Alkali-Soluble Resin Using Atomic Force Microscopy

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SUMMARY: The mechanism of film formation of emulsifier-free monodisperse poly(n-butyl methacrylate) (PBMA) latex in the presence of postadded alkali-soluble resin (ASR), namely poly(styrene/alpha-methylstyrene/acrylic acid) (SAA) was followed using atomic force microscopy (AFM). The film morphology and peak-to-valley distance (Δz) of latex particles in the film was monitored at different annealing temperatures as a function of annealing duration. The Δz of the PBMA particles in films containing SAA was found to be higher than those in the pure PBMA films. The AFM results suggest very strongly the formation of a hard surface layer of SAA over the soft PBMA particle, and the migration of free SAA to the latex film surface during annealing. The SAA layer adsorbed on and surrounding each PBMA particle retards the viscoelastic flow of the PBMA particles and slows down the gradual coalescence of the particles in film formation. Annealing at high temperature, the PBMA particles fuse at a faster rate than the SAA due to its lower T_g compared to that of SAA. The difference in the rates of fusion of the SAA and PBMA phases leads to the formation of indentations on individual particles at high annealing temperature and long annealing duration.

Introduction

The film formation process depends on latex characteristics (nature of polymer, particle size and distribution, particle morphology, nature and amount of surfactants, etc.) and experimental conditions (annealing temperature, rate of water evaporstion, etc.). Recently, alkali-soluble resin (ASR) containing carboxylated random copolymers was used as a polymeric surfactant in the emulsion polymerization of polystyrene and poly(methyl methacrylate) latex particles[1)]. Several patents describing the applications of durable emulsion polymers, prepared using these types of resins can be found in the literature[2-3)]. Another variation of this is to post-add the ASR to monodisperse surfactant-free poly(n-butyl methacrylate) (PBMA) latex prepared by emulsion polymerization in the absence of any

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surfactant and their film formation behavior was studied. In the present work, we reported the morphology of latex film of monodisperse surfactant-free PBMA latex, containing post-added ASR such as poly(styrene/alpha-methylstyrene/acrylic acid) (SAA) visualised by atomic force microscopy (AFM)[4-6]. Some very interesting morphological features were observed such as the formation of a hard shell of SAA surrounding a soft PBMA core and a SAA-rich layer at the film surface. This core/shell structure of the latex particles produces a cellular type film[6] such as that described by Joanicot[7] previously. The large difference in the T_g of the two polymers (115°C for SAA versus 32°C for PBMA) gives rise to a difference in diffusion rates which result in uneven fusion of the core and shell. At sufficiently high annealing temperature, the shell eventually ruptures enabling greater flow of the PBMA in the bulk beneath the film surface. Cellular-type of polymeric films consisting of particles with a hydrophilic cell wall surrounding a hydrophobic core has been shown to deform on stretching[8] and to undergo rupturing of the shell by thermal treatment[7]. It was found that after rupturing and fragmentation, the cell wall material is expelled as large lumps immersed in a continuous latex matrix.

AFM is a particularly powerful tool in the study of latex film morphology because it can provide high-resolution three-dimensional images of the film surface without any sample pretreatment[9]. It allows quantitative data of the particle peak-to-valley dimensions to be obtained directly.

Experimental

The alkali-soluble resin, poly(styrene/alpha-methylstyrene/acrylic acid) (SAA), with M_n = 4,300 g mol^{-1}, M_w = 8,600 g mol^{-1}, acid number = 190 and T_g = 115 °C was purchased from Morton Inc., USA and used as received. PBMA latexes were prepared by emulsifier-free emulsion polymerization. The number average particle size (D_n) and polydispersity (D_w/D_n) of the latex particles were determined by Capillary Hydrodynamic Fractionation (Model CHDF-1100, Matec Applied Sci., USA) and were found to be 370.0nm and 1.004 respectively.

A known weight of a SAA solution at 1.0 wt %, obtained by dissolving the resin in distilled, deionized water adjusted to pH 9, was added slowly to 10.0g of PBMA latex (solids content = 1.0 wt %) at 25 °C and then allowing the mixed dispersion to equilibrate with mild agitation for 24h. A series of mixed dispersion containing various weight of SAA solution was prepared in this manner. Latex films were prepared by placing a few drops of a mixed

PBMA and SAA onto freshly cleaved mica surface and allowed to dry at 25 °C in a desiccator. Aging of the film was carried out in a convection oven for various periods of time. All films were imaged in air at 25 °C using a Nanoscope III AFM (Digital Instruments, Inc., Santa Barbara, CA, USA) using the TappingMode. The scans were done under ambient condition without any sample surface treatment. The peak-to-valley distance of a film was obtained using the cross-section analysis of AFM instrument.

Results and Discussion

The peak-to-valley distance (corrugation height) of latex particles in films was monitored by AFM at different annealing temperatures as a function of annealing time. Fig. 1 shows the peak-to-valley distance (Δz) for PBMA latex films and PBMA latex films containing 10 wt % SAA as a function of annealing time. It can be seen that Δz for PBMA latex films containing SAA is much higher than those of pure PBMA latex films at all annealing temperatures. It can be deduced that the SAA, with a high T_g and adsorbed on the particle surface retards the viscoelastic flow of the PBMA polymer molecules. Therefore, the presence of adsorbed SAA decreases the mobility of the PBMA molecules and slows down the gradual coalescence of film formation. The peak-to-valley distance of PBMA latex films decreases exponentially with annealing time, indicating the deformation of particles follows an exponential decay relationship with time[10]. Fig. 1(B) also shows the decrease in Δz is dependent on the annealing time: there is a slow exponential decrease with annealing time initially followed by a much steeper decrease at longer annealing time. This change in the rate of flattening of the film surface is also dependent on the annealing temperature: the higher the annealing temperature, the earlier this second stage is reached during annealing.

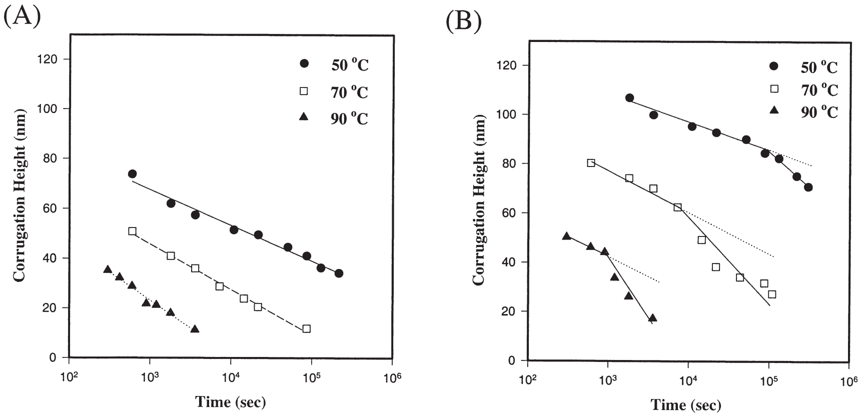


Fig. 1: Plots of peak-to-valley distance (corrugation height) of (A) PBMA latex films and (B) PBMA latex films containing 10 wt % SAA vs. annealing time at 50, 70, and 90 °C.

The migration of the SAA to the surface of the latex film during annealing is clearly demonstrated by the FTIR spectrophotometer with attenuated total reflectance (ATR FTIR, A Perkin-Elmer model 2000)$^{4)}$. The accumulation of SAA at the interstices of the arrays of PBMA particles is clearly discernible from the three-dimensional surface image of PBMA latex film containing 10 wt % SAA annealed for 10 minutes at 90°C (Fig. 2). As the annealing temperature is raised, SAA molecules migrate to the surface of the latex film and concomitantly accumulate in the valleys between the particles due to the incompatibility of the SAA and PBMA. Thus the second steeper decrease of Δz with annealing time corresponds to both the viscoelastic flow of PBMA latex particles and the migration of SAA to the film surface.

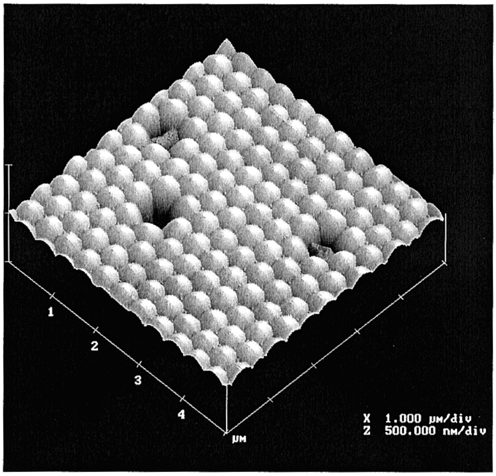


Fig. 2: Three-dimensional surface image of PBMA latex film containing 10 wt % SAA annealed for 10 minutes at 90°C.

Since the T_g of SAA is higher than that of PBMA, the morphology of the latex film formed from the mixed dispersion is thus expected to change with the amount of SAA adsorbed on the latex surface and the annealing temperature of the film. Fig. 3 shows the three dimensional AFM surface images of PBMA latex films containing 20 wt % of SAA annealed at various temperatures for 30 min. Very interesting features of film morphology are observed. The polyhedral cellular structure is apparent before annealing. As annealing temperature was increased, the tops of the individual latex particles in the outermost layer (latex film surface) starts to soften forming small indentations at 90 °C and this feature is apparent at 110 °C. When the annealing is raised to 130 °C, a temperature well above the T_g of both PBMA and SAA, the morphology of the film was transformed to one with regular arrays of depressions. This is clear manifestation that the indentations at the tops of the individual particles have eventually sagged in and develop into these depressions on the PBMA latex films. Occasional vacancies or "holes" formed by missing latex particles in the hexagonal arrays are observed within the layer, which can be attributed to the presence of vacancies in the layer below.

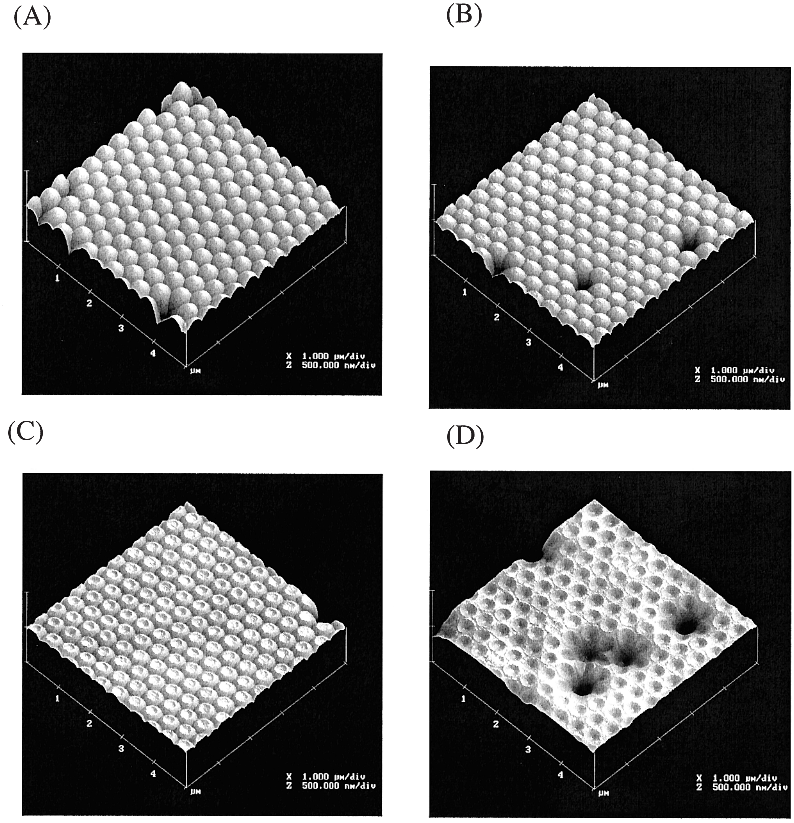
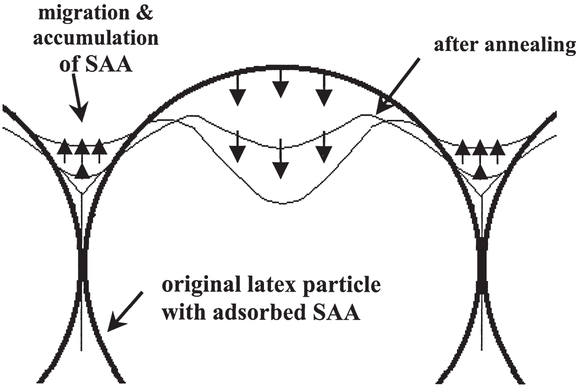


Fig. 3: Three-dimensional surface images of PBMA latex films containing 20 wt % SAA before annealing (A); and annealed for 30 minutes at 90 °C (B), 110 °C (C) and 130 °C (D).

The incompatibility of the SAA and PBMA causes, during annealing, the migration and enrichment of the more hydrophilic SAA at the interstices space between the PBMA particles at air/polymer interface. Deformation and rupturing of the SAA shell surrounding the PBMA particle at high annealing temperatures leads to coalescence of the PBMA particles below the surface layer of SAA. As the annealing proceeds, the PBMA particles are more susceptible to fusion due to its lower T_g than that of the SAA. The SAA does not fully coalesce if the annealing temperature is not high enough to melt it completely. The difference in the rates of fusion of the two phases leads to the formation of indentations of the individual latex particles and the sagging of certain regions of the surface layer. The surface morphology of the PBMA latex film containing SAA molecules, particularly the development of indentations on the top of latex particles on the outermost surface is represented schematically in Fig. 4. At high annealing temperature and duration, the indentations at the tops of individual particles have eventually sagged in, giving rise to the regular arrays of "depressions" in the film surface.

Fig. 4: A schematic representation of the film formation process of PBMA latex particles in the presence of high concentration of SAA during annealing. The upward arrows indicate migration of SAA to the interstices at the air/polymer interface.



Conclusion

The unique morphology of the film surface is consistent with the formation of a SAA-rich surface layer of the film on top of regular arrays of PBMA particles beneath which are themselves surrounded by shells of SAA. The hard shell of the SAA retards the viscoelastic flow of the PBMA particles and slows down the gradual coalescence of film formation. The interesting feature of the morphology showing indentations of the particle tops within the surface layer could be attributed to the much faster coalescence, during annealing, of the PBMA latex particles as compared to SAA with a much higher T_g.

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