

FILM FORMATION PROCESS OF PS/PBA LATEX BLENDS DEPENDING ON PARTICLE SIZE

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Introduction

Film from an aqueous colloidal suspension of polymer particles takes places in different stages[1].; (i) water evaporation and subsequent particle packing, (ii) deformation of the particles, (iii) coalescence of the deformed particles to form a homogeneous film[1]. Dry films of a single component latex have poor mechanical properties[1]. In order to get films with good mechanical and barrier properties composite latex systems involving two or more different polymer compositions can be used[2]. Parameters affecting the mechanical properties of such blends are the properties of the neat constituents, the composition, the particle sizes, the particle size ratio, the morphology and interfacial interactions. Latex dispersions having a well-controlled, bimodal particle size distribution are gaining attention due to their potential to enable control of the dispersion rheology, the film formation characteristics, and the final film properties. The aim of the present work was to study the influence of hard/soft latex fraction and hard particle size on the morphology and film formation behaviours of PS/PBA latex blends.

Experimental

Materials

Hard PS Latexes; Two different hard polystyrene (PS) latexes with diameters 900 nm (LgPS) and 320 nm (SmPS) were synthesized via a surfactant-free emulsion polymerization process. The hard latex samples are composed of pyrene (P) labeled polystyrene and has a $T_g=105$ °C. The only difference between the LgPS and SmPS latex's recipes were the solids contents of the latex (their sizes).

Soft PBA Latex; The soft latex samples are composed of Poly(n-butyl acrylate) (PBA) and were prepared by semicontinuous process. They are fairly monodisperse, having all very similar mean diameters (97nm) and has a T_g (=41 °C) below room temperature.

Film Preparation; Blends films were prepared by mixing different fractions (by weight) of the hard PS and soft PBA dispersions. Since, our aim is to study the particle size effect of hard latex on film formation behaviour of hard/soft latex composite, we prepared two series of blends;

Series 1: small-hard PS and soft PBA (SmPS/PBA)

Series 2: large-hard PS and soft PBA (LgPS/PBA)

Hard/soft latex blends were prepared by mixing hard/soft latices with the following weight compositions for each series: 100/0, 80/20, 60/40, 50/50, 30/70, 20/80 and 10/90. Then these dispersions were cast into glass plates and allowed to dry at room temperature. After drying, samples were separately annealed above T_g of PS at temperatures ranging from 100 to 250°C.

Methods

Fluorescence measurements: After annealing, each sample was placed in the solid surface accessory of a Perkin-Elmer Model LS-50 fluorescence spectrometer. Pyrene (P) was excited at 345 nm and fluorescence emission spectra were detected between 360-600 nm. All measurements were carried out in the front-face position at room temperature.

Photon transmission Measurement: Photon transmission experiments were carried out using Variant Carry-100 UV-Visible (UVV) spectrometer. The transmittances of the films were detected at 500 nm. A glass plate was used as a standard for all UVV experiments and measurements were carried out at room temperature after each annealing processes.

Atomic Force Microscopy Measurements: Micrographs of the blend films were recorded with SPM-9500-J3 Shimadzu and NanoScope (R) IIIa multimode scanning probe atomic force microscopies (AFM).

Results and Discussion

The plot of fluorescence intensity (I_p) versus annealing temperature, T for 0, 20, 50, 70, 80 and 90 wt% PBA content blend films for Series 1 is shown in Fig 1. It is seen that I_p intensity from blends with 0-50 wt% PBA content for series 1 (Fig 1) and 0-70 wt% PBA content for series 2 first increases by showing a maximum at a certain temperature called healing temperature, T_h . Then, due to further annealing, I_p decreases. The increase and decrease of I_p upon annealing of these blend films can be explained with the void closure and interdiffusion processes, respectively[3]. However, I_p intensity from blends which have (70-90) wt%PBA for series 1 (Fig 1) and (80-90) wt%PBA for series 2 behave quite differently. I_p intensities from the blends prepared with low PS content are weak and almost remains unchanged

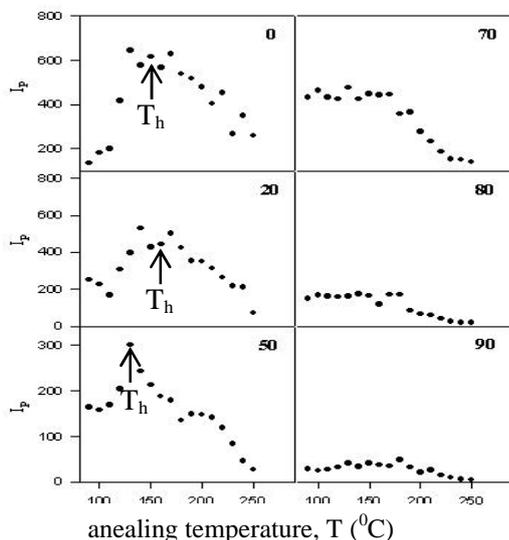


Fig 1 I_p vs T for series 1 with different PBA content.

during annealing indicating that no film formation process takes place in a traditional way.

The change in transmittance of the blend films upon annealing for Series 1 is shown in Fig 2 with increasing 0, 20, 50, 70, 80 and 90 wt% PBA component. I_{tr} present a dramatic increase above a certain temperature called minimum film formation

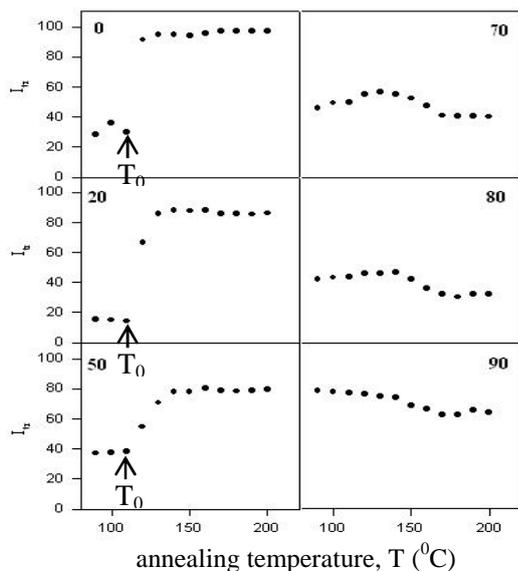


Fig 2 I_{tr} vs T for series 1 with different PBA content.

temperature, T_0 above a certain amount of PBA. I_{tr} increases reaching a maximum and then remains constant for 0-50 wt% PBA content blend films (series 1) and 0-70 wt% PBA content blend films (series 2) with annealing. The increase in I_{tr} with annealing temperature primarily due to the closure of voids[3] between PS particles by viscous flow in these films. However, above these ranges of PBA, I_{tr} almost doesn't change with annealing temperature for both series indicating that no void closure process takes place. The increase in I_{tr} and I_p (up to T_h) intensities in the (0-50) wt% PBA range for series 1 and (0-70) wt% PBA range for series 2 can be explained by void closure[3] and surface smooting with annealing. Decrease in I_p above T_h can be understood by interdiffusion between polymer chains[3].

The related void closure (ΔH_p and ΔH_{tr}) and interdiffusion (ΔE) activation energies were obtained and are listed in Table 1 for both series. It is seen that activation energies do not change much by varying the blend composition in the films. Both ΔH and ΔE values of LgPS/PBA blends is larger than those of SmPS/PBA blends. This implies that the viscous flow and interdiffusion processes are significantly affected by the hard PS particle size. The driving force for film formation is proportional to the inverse of the particle size, according to descriptions of film formation driven by capillary forces[1]. Since the specific surface area or the total surface energy of SmPS particles is much larger than of LgPS particles, they require less energy to complete viscous flow process. Furthermore, the polymer chains contain more free volume and less interactions between segments in SmPS chains leading to higher conformational energy and less interaction of polymer chains. Polymer chains in the SmPS particle are in a highly confined state due to the spatial limitation compared to that of the random-coil state[4] in LgPS particles. Therefore, SmPS particles need less energy to accomplish interdiffusion process in comparing with LgPS particles.

Table 1 Activation energy values of both series

PBA (wt%)	SmPS/PBA			LgPS/PBA		
	ΔH_p	ΔH_{tr}	ΔE	ΔH_p	ΔH_{tr}	ΔE
0	3.6	11.2	9.6	5.2	17.2	28.8
20	3.9	9.3	11.2	1.6	12.7	42.6
40	3.2	7.9	6.4	1.6	5.2	25.8
50	2.9	3.2	7.2	1.6	9.4	26.2
70	-	-	-	1.8	3.7	8.9

The T_0 and T_h temperatures are ca. 110 °C and 130-150 °C for the SmPS/PBA blends, 140-160 °C and 170-200 °C for the LgPS/PBA, respectively. Although T_0 and T_h do not change so much within the each series with PBA content, both are shifted to higher temperatures with the size of hard PS. In other words, the film formation process of SmPS/PBA blends occurs at much lower temperature. AFM micrographs also confirmed SSF and UVV data.

Conclusion

It was concluded that the higher the hard particle size, the lower the critical weight fraction of hard particles leading to percolation. Compared to the LgPS/PBA blend, the sintering of SmPS/PBA blend occurred at much lower temperatures and require less energy.

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