Latex Film Formation Study by Using Photon Reflection Method

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Abstract : Photon reflection method was used to monitor the evolution of transparency during film formation from latex particles. Latex films were prepared from Poly (methyl methacrylate) (PMMA) particles, which were annealed at elevated temperatures in various time intervals during which reflected photon intensity, I_{rf} was measured. I_{rf} first decreased and then increased as the annealing temperature is increased. Decrease in I_{rf} was explained with the void closure mechanism. Increase in I_{rf} against temperature was attributed to increase in crossing density at the junction surface. The void closure constant, B and the back and forth activation energy (ΔE_{rf}) were measured and found to be around 24×10^3 K and 49 kcal/mol respectively.

INTRODUCTION

Latex films are generally formed by coalescence of submicron polymer particles in the form of a colloidal dispersion, usually in water. The term "latex film" normally refers to a film formed from soft latex particles (T_g below room temperature) where the forces accompanying the evaporation of water are sufficient to compress and deform the particles into transparent, void-free film. However, latex films can also be obtained by compression molding of a film of dried latex powder composed of relatively hard polymers such as Polystyrene (PS) or Poly (methyl methacrylate) (PMMA) that have T_g above room temperature. Hard latex particles remain essentially discrete and undeformed during drying. The mechanical properties of such films can be evolved after all the solvent has evaporated, by an annealing process which first leads to void closure and then interdiffusion of chains across particle-particle interfaces. Eckersley and Rudin[1] suggested that since polymer is a linear viscoelastic material, the deformation of particles and / or the shrinkage of voids due to capillary and interfacial forces can be considered to be additive to the film formation mechanism.

Transmission electron microscopy (TEM) has been the most common technique used to investigate the structure of dried films[2),3)]. Pattern of hexagons, consistent with face centered cubic packing, are usually observed in highly ordered films. When these films are annealed, complete disappearance of structure is sometimes observed, which is consistent with extensive polymer interdiffusion. Small – angle neutron scattering (SANS) has been used to study latex film formation at the molecular level. Extensive studies using SANS have been performed by Sperling and coworkers[4)] on compression molded PS films. Direct – non radiative energy transfer (DET) method has been employed to investigate the film formation processes from dye labeled hard[5)] and soft[6),7)] polymeric particles. The steady state fluorescence (SSF) technique combined with DET has been used to examine healing and interdiffusion processes in dye labeled hard latex systems[8),9)]. Recently we have reported photon transmission studies for latex film formation from Polystyrene particles[10),11)].

In this work evolution in transparency of films formed from hard latex particles were studied by measuring the reflected I_{rf} photon intensities. It was shown that the variation in transparency is related to the variation in I_{rf}. Latex films were annealed in equal time intervals at elevated temperatures above the glass transition (T_g) of Poly (methyl methacrylate) (PMMA) and I_{rf} intensities were measured by modified UV – Visible (UVV) spectrophotometer.

EXPERIMENTAL

In UVV experiments, hard latex particles having two components were used[12)]; the major part, PMMA, comprises 96 mol % of the material and the minor component, Polyisobutylene (PIB) (4 mol %), forms an interpenetrating network through the particle interior[13)] very soluble in certain hydrocarbon media. A thin layer of PIB covers the particle surface and provides colloidal stability by steric stabilization. (These particles were prepared by Mr. B. Williamson in Prof.M.A. Winnik Laboratory in Toronto). Films were prepared from the dispersion of particles by placing same number of drops on glass plates with the size of 0.9×3.2 cm^2 and allowing the heptane to evaporate. Samples were weighed before and after the film casting to determine the film thicknesses. Average size for the particles was taken to be 2 μm to calculate the number of layers in the films.

In this work UVV experiments were carried out to measure I_{rf} from the annealed latex film samples. Annealing process of the latex films were performed in an oven in air above T_g of

PMMA after evaporation of heptane, in 30, 15 and 10 min time intervals at elevated temperatures between 110 and 210 °C. The temperature was maintained within ± 1 °C during annealing. After annealing, each sample was placed in the model Lambda 2S UV-Visible spectrophotometer of Perkin Elmer. I_{rf} of films were detected between 300-400 nm. Another glass plate was used as a standard for all UVV experiments. In order to measure the reflected intensity I_{rf} from latex film, UVV spectrophotometer is slightly modified as presented in *Figure 1* where two mirrors were placed in triangle position on the path of the light beam, which hits the surface of film sample to produce I_{rf} intensity.
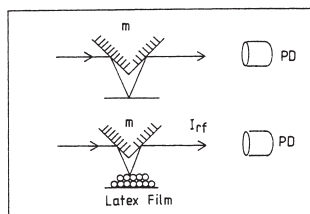
Fig. 1- Cartoon representation of modified UVV spectrophotometer. PD presents photo diode an M shows the triangular mirror system. I_{rf} is the reflected light intensity.
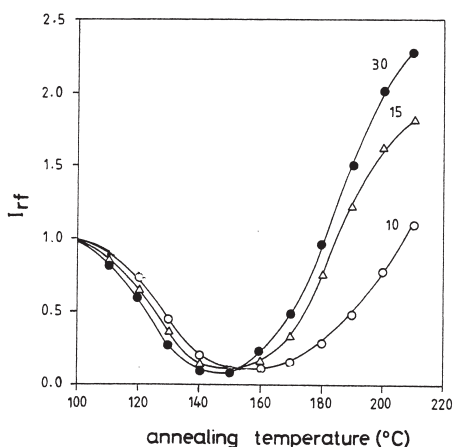
Fig. 2- Plot of reflected photon intensity I_{rf} versus annealing temperature. Numbers on each curves indicate the annealing time int

RESULTS AND DISCUSSION

Reflected photon intensities, I_{rf} are plotted versus annealing temperature for 30, 15 and 10 min time intervals in *Figure 2*. It is seen that all I_{rf} curves first decreased by showing a minimum then increased to larger values at each annealing time intervals. Initial decrease in I_{rf} is attributed to homogenization of the film surface due to the void closure process. In other words polymeric material flows to fill up the voids between particles and as a result latex film reflects less photon. However annealing the film above 160 °C, reflected photon intensity starts to increase and more

photons can reach to the photo diode as the interfaces starts to heal and disappear. This picture can be visualized by taking into account the photon's mean free path <a> which is very short at the beginning of film formation where many interparticle voids exist. At this stage films reflect more photons, however as the film is annealed, interparticle voids start to disappear and <a> increases, as a result I_{rf} starts to decrease. Finally when all the voids have disappeared, I_{rf} reaches the minima at 160 °C where <a> becomes maximum[14]. Above 160 °C, after all voids have disappeared, the film gradually becomes a flat mirror. Then as the interfaces heal due to interdiffusion of chains, the quality of the film (mirror) improves and the film reflects more photons, resulting increase in I_{rf}. Here it has to be noted that because of the geometry of the light beam, reflected light primarily measures the surface quality of the film.

Void Closure Kinetics

In order to quantify the behavior of I_{rf} below its minima, we introduce the phenomenological void closure model. The void closure kinetics can determine the time for optical transparency and film formation[15]. In order to relate the shrinkage of spherical void of radius, r to the viscosity of surrounding medium, η an expression was derived and given by the following relation[16].

$$\frac{dr}{dt} = -\frac{\gamma}{2\eta}\left(\frac{1}{\rho(r)}\right) \tag{1}$$

where γ is surface energy, t is time and $\rho(r)$ is the relative density. It has to be noted that here surface energy causes a decrease in void size and the term $\rho(r)$ varies with the microstructural characteristics of the material, such as the number of voids, the initial particle size and packing.

The temperature dependence of viscosity of most amorphous polymers near their T_g an be describe by Vogel-Fulcher (VF)[17],[18] equation as

$$\eta = A\exp\left(\frac{B}{T-T_o}\right) \tag{2}$$

where A, B and T_0 are constants for a given polymer. For most glasses T_0 is typically about 50 K lower than T_g. Integrating *Eq. (1)* and combining it with *Eq. (2)* the following equation is obtained

$$t = -\frac{2A}{\gamma} \exp\left(\frac{B}{T - T_o}\right) \int_{r_o}^{r} \rho(r)\, dr \qquad (3)$$

where r_o is the initial void radius at time t=0.

Eq.(3) will be employed to interpret the data of photon reflection to explain the void closure mechanism as follows.

When film samples annealed for 10, 15, and 30 min time intervals a continuous decrease in I_{rf} intensities were observed, until they reached to minimum. In order to quantify these results *Eq.(3)* can be used where we assume that the voids are spherical (i.e. $\rho(r) \propto r^{-3}$). Then integration of *Eq.(3)* produces the relation

$$t = \frac{2AC}{\gamma}\left(\frac{1}{r^2} - \frac{1}{r_o^2}\right)\exp\left(\frac{B}{T - T_o}\right) \qquad (4)$$

where, C includes the related constants for the relative density, $\rho(r)$. Here an assumption can be made that I_{rf} intensity is proportional to void radius, r. i.e. as voids disappear, I_{rf} decrease. Then *Eq.(4)* is inverted and can be written as

$$I_{rf} = S(t)\exp\left(\frac{B}{2(T - T_o)}\right) \qquad (5)$$

where $S(t) = (2AC / \gamma\, t)^{1/2}$, here it is naturally considered that initial radius of void r_0 is much larger than r, which then resulted the omission of r_0^{-2} compare to r^{-2}.

On the right hand side of *Figure 3a* and *b* logarithmic plots of I_{rf} versus $(T-T_0)^{-1}$ for films annealed in 30 and 15 min are presented respectively, where, ln I_{rf} increased linearly for all

samples, which indicate that the model chosen for void closure mechanism works well for our UVV data. In other words the slopes of the right hand side of *Figure 3* produce B values according to *Eq.(5)*. B values are found to be around 24.6×10^3 K. These values are six times larger than the values obtained for acrylic $(4 \times 10^3$ K$)$[19] and 60 times larger than that was found for water borne acrylic lattices[15]. Smaller value for copolymer of MMA and 2-ethyl-hexyl acrylate lattices were attributed to the plasticizing effect of water[15]. In our case no such plasticizing effect is expected, because our PMMA latex has glass transition of 380 K which is very high compared to water borne acrylic lattices ($T_g \approx 280$ K). The values of B$=24.6 \times 10^3$ K for our system seems to be quite reasonable for our hard latex particles and measured values of B suggest that heptane has no plasticizing effect on PMMA latex particles.

Crossing Density at Junction Surface

When film samples were annealed at elevated temperatures in equal time intervals, a continuous increase in I_{rf} intensities above 160 °C were observed (see *Figure 2*). The increase in I_{rf} was already explained in the previous section, by the increase in transparency of latex film due to disappearance of particle-particle interfaces. As the annealing temperature is increased some part of polymer chains
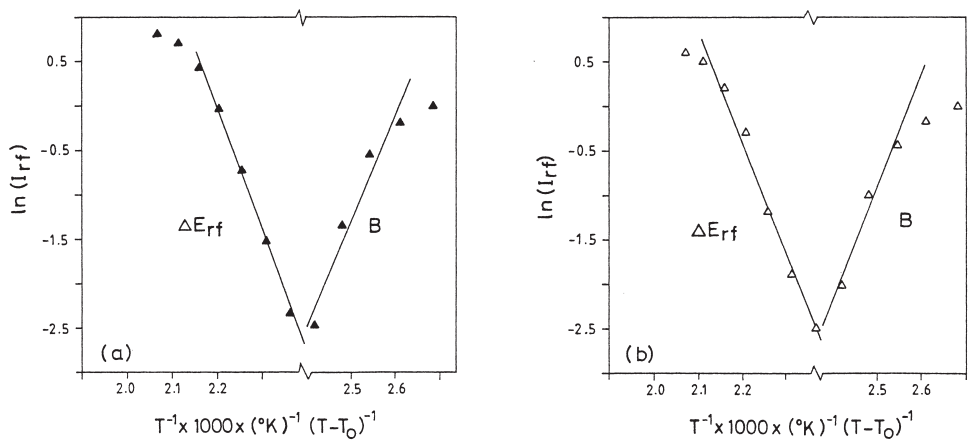

Fig. 3- Logarithmic plots of the data in *Figure 2* versus reverse of annealing temperature $(T)^{-1}$ and $(T-T_0)^{-1}$ for a-30, b-15 min time intervals.

may cross the junction surface and particle boundaries start to disappear, as a result the reflected photon intensities increase due to the creation of high quality, transparent mirror film. In order to quantify these results, the Prager-Tirrell (PT) model[20] for the chain crossing density was employed. A homopolymer chain with N freely jointed segments of length L was considered by PT, which moves back and forth by one segment with a frequency v. Here, $v/2$ is called the "diffusion coefficient" of a segment in one dimensional motion. The total "crossing density" $\sigma(t)$ (chains per unit area) at junction surface was calculated by PT from the contributions $\sigma_1(t)$ due to chains still retaining some portion of their initial tubes, plus a remainder, $\sigma_2(t)$. Here the $\sigma_2(t)$ contribution comes from chains which have relaxed at least once. In terms of reduced time $\tau = 2vt/N^2$ the total crossing density can be written for small τ values as follows

$$\sigma(\tau)/\sigma(\infty) = 2\pi^{-1/2}\tau^{1/2} \tag{6}$$

In order to compare our results with the crossing density of the PT model, the temperature dependence of $\sigma(\tau)/\sigma(\infty)$ can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient

$$v = v_o \exp(-\Delta E/kT) \tag{7}$$

Here ΔE is defined as the activation energy for the back and forth motion of a chain. Combining *Eq.(6)* with *Eq. (11)* and assuming that I_{rf} is proportional to the crossing density $\sigma(T)$, the following phenomenological equation can be written

$$I_{rf}(T)/I_{rf}(\infty) = R_o \exp(-\Delta E_{rf}/2kT) \tag{8}$$

where $R_o = (8v_o t/\pi N^2)^{1/2}$ is a temperature independent coefficient.

Logarithmic plots of I_{rf} versus T^{-1} are presented on the left hand side of *Figure 3a* and *b* for films annealed in 30 and 15 min time intervals. The activation energies, ΔE_{rf} are produced by fitting the data to *Eq.(8)* and the averaged value is found to be as 49.5 kcal/mol. This value is very close to our previous findings[7),8)] for the raptating PMMA chains.

In conclusion, this paper presents a simple (UVV) method together with void closure and crossing density model (PT) to measure void closure constant, and the activation energy for reptating polymer chain during latex film formation.

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