



Volume Fraction Effect for the Film Formation of PS/PVA Composites by Monitoring Photon Transmission Technique

Sibel Eken Korkut^{1*}

^{1*} Yıldız Technical University, Faculty of Arts & Sciences, Department of Chemistry, İstanbul, Turkey, (ORCID: 0000-0001-9637-5541), sibeleken@gmail.com

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Abstract

Film forming of the polystyrene (PS) doped Poly Vinyl Alcohol (PVA) particles were studied by photon transmission (PT) technique. The films were prepared as a mixture of PS and PVA particles at different compositions ranging from 10 to 100 wt % for the optical measurements at room temperature the film formation process was monitored by measuring the transmitted light intensity (I_t) from the samples using PT. The film formation includes two stages: void closure and interdiffusion stages. Percolation model was employed to interpret the distribution of PS particles in PVA lattice. Percolation threshold, R_c , was found to be as 0.4 and the volume fraction of PVA as a power law with exponent 1.01 which is very close to the predicted value, 1.00, by the percolation theory.

Keywords: PS, PVA, Mechanic, Photon Transmission, Activation Energies.

PS/PVA Kompozitlerinin Film Oluşumuna Hacim Kesri Etkisinin Işık Geçirgenliği ile İzlenmesi

Öz

Polistren (PS) katkılı Poli Vinil Alkol (PVA) dağılımının film oluşum süreci foton geçirgenliği (PT) teknikle incelenmiştir. Filmler, oda sıcaklığında optik ölçümler için ağırlıkça %10 ile %100 arasında değişen farklı bileşimlerde PS ve PVA dağılımının bir karışımı olarak hazırlandı. Film oluşum süreci, PT kullanılarak numunelerden geçen ışık şiddeti (I_t) ölçülerek izlendi. Film oluşumunun iki aşamada gerçekleştiği gözlemlendi: boşluk kapanması ve difüzyon aşamaları. PVA kafesinde PS parçacıklarının dağılımını yorumlamak için süzme modeli kullanıldı. Süzme teorisine göre, perkolasyon eşiği R_c 0,4 ve PVA'nın hacim kesri için 1.01 tahmin edilen değer olan 1,00'e çok yakın bulunmuştur.

Anahtar Kelimeler: PS, PVA, Mekanik, Foton Taşınımı, Aktivasyon Enerjisi.

* Corresponding Author: xxxx@xxx.xx.xx

1. Introduction

Latex film formation could be obtained by Theoretical and experimental efforts in literature,(Provdar T., 1996). Film formation process of polymer latex can be explained by three steps: (i) water evaporation, deformation and the annealing process. In the annealing of hard latex system, deformation of particles first leads to void closure(Mackenzie & Shuttleworth, 1949; Sperry, Snyder, Odowd, & Lesko, 1994) and then diffusion across particle–particle boundaries start, i.e. the mechanical properties of hard latex films evolve during annealing. (iii) Coalescence of the deformed particles to form a homogeneous film(Mackenzie & Shuttleworth, 1949) where macromolecules belonging to different particles mix by interdiffusion(Pekcan, 1997; Yoo, Sperling, Glinka, & Klein, 1991).

For the last years, producing new materials by filling polymers with inorganic natural or synthetic compounds is gaining intension (Ray & Okamoto, 2003).

(Hallensleben, 2000; Kelly, DeMerlis, Schoneker, & Borzelleca, 2003). PVA has many advantages for industrial products such as adhesive, coatings, surfactant, films, packaging, biodegradable plastic backing sheet in hygiene products (Hallensleben, 2000), and biomedical applications(Jiang, Liu, & Feng, 2011; Yang, Li, & Nie, 2007).

Here, film formation of PS/PVA composite films. The reason of usage of Polystyrene (PS) is that easily processing, its solubility in many different types of solvents and its clarity which allows dispersion of PVA to be optically observed at the micron scale. After each annealing step of PS/PVA films having various compositions above T_g of PS, I_{tr} , was followed during the film formation. Activation energies were computed with respect to the change of I_{tr} . Percolation threshold, R_c , was found to be as 0.4 (40 wt% PS).

2. Material and Method

2.1. Materials

PS latexes were prepared by polymerization process of styrene (99 % pure from Alfa Asea) as a monomer, dimethacrylate (PolyFluor™ 511 from Polysciences, Inc.) and KPS (Potassium persulphate) was used as an initiator. KPS added after dissolved at 90 °C. Polyvinyl alcohol (PVA) (Boysan Co., Turkey) was purchased in white powder form. 0.01 gr/ml PVA was prepared as a stock.

2.2. PS/PVA Composite Film Preparation

Eight different films by mixing of PS and PVA. A drop cast methode was used for the preparation of the samples. Equal drops were put on a glass plates with the size of 0.5x2.2 cm² after drying of solution. PS volume in matrix as 10, 20, 40, 60, 80, 90, 100 wt %. After drying (at room temperature), all samples were annealed starting from 100 to 270°C.

2.3. Optical Measurements

UV Visible Spectrometer (BW&TEK) was used as a for I_{tr} measurements at room conditions. Film positions should be

perpendicular to the light as in Fig 1. SEM images of pure PS and 40% wt PS films In Fig2a and b, respectively

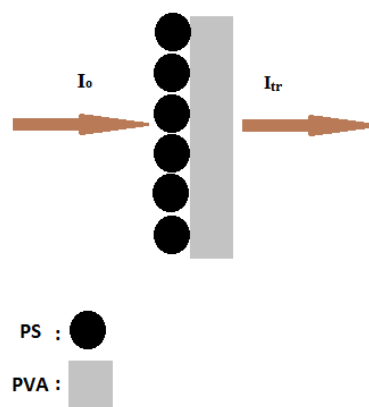


Figure 1. A cartoon figure of the film position to the light and the transmitted light.

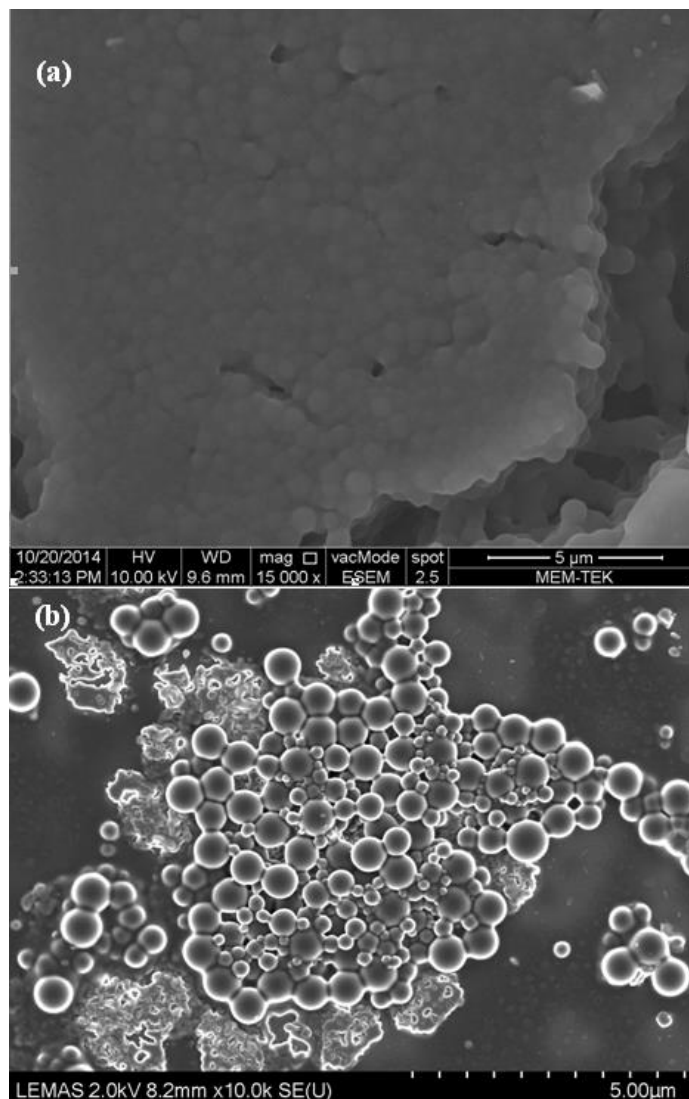


Figure 2. SEM images of pure PS and 40 wt % PS in PS/PVA composites. by FEI - Quanta FEG 250 and HITACHI, respectively.

2.4. Theoretical Considerations

The percolation threshold, p_c for this problem is around 0.6 for so called "site percolation" on a square lattice. An example of percolation is that is the spread of water displacing oil in porous rocks, where neighboring pores are connected by small capillary channels(Sahini & Sahimi, 1994), (Broadbent & Hammersley, 1957).

$$p_{\infty}(p) \approx (p - p_c)^{\beta} \quad (\text{for } p > p_c, \text{ and } p \rightarrow p_c) \quad (1)$$

In a simple cubic lattice p_c is found to be 0.31 for site-percolation and 0.249 for bond percolation models(Stauffer, 1985). The exponent β for a simple cubic lattice is 0.45, for percolation model, however, β is almost the same value as 1.0 in classical model(Stauffer, 1985).

The stages of the film formation process were modelled by the void closure and the interdiffusion models detailed information of which can be found in the studies(Ugur et al., 2011; Yargi, Gelir, Ozdogan, Nuhoglu, & Elaissari, 2016) before and after the healing temperature, respectively.

The relation between the transmittance and the temperature during these stages is given by the following equation

$$I(T) = S(t) \exp\left(-\frac{3\Delta H}{kT}\right) \quad (2)$$

where S is a constant and $I=I_{tr}/(I_{tr})_{max}$, ΔH is the energy of void closure of viscous flow. One mole of material for creating the act of a jump during viscous flow and k is the Boltzmann constant. The activation energies can be calculated by using the linear regression analysis as given in our previous study(Ugur et al., 2011).

3. Results and Discussion

The scattered light intensity, I_{sc} versus PS volume denoted by $R(\text{wt/wt})$ is plotted in Fig 3a, where addition of PS into PS/PVA composite lattice drops I_{sc} , especially below 40 wt % PS content (see Fig 3b). This tendency of I_{sc} can be explained by percolating PS latex in PVA matrix(Stauffer & Aharony, 1994). This percolation can be attributed to I_{sc} (Arda, Kara, & Pekcan, 2013). The below equation can be used:

$$R = \frac{M_{PS}}{M_{PS} + M_{PVA}} \quad (15)$$

where M_{PS} and M_{PVA} stands for the weight of PS and PVA in the matrix. If R is attributed to the occupation probability, p , of PS in the PVA lattice, percolation threshold, P_c becomes R_c , and Eq (1) returns to Eq 16.

$$I_{sc}(R) = (R - R_c)^{\beta} \quad (16)$$

Eq. (16) describes the percolation model for PS distribution in PVA lattice. When R approaches to R_c , the largest cluster of PS spans from one end to the other end of the PVA lattice. In Fig 4, fit of the Logarithmic plot of Eq 16 to the measured points is shown and β , was calculated as 1.01 by the slope of the

straight line the critical exponent, which is quite consistent with the classical model and our previous study(Ugur, Yargi, Gunister, & Pekcan, 2008; Ugur, Yargi, & Pekcan, 2008).

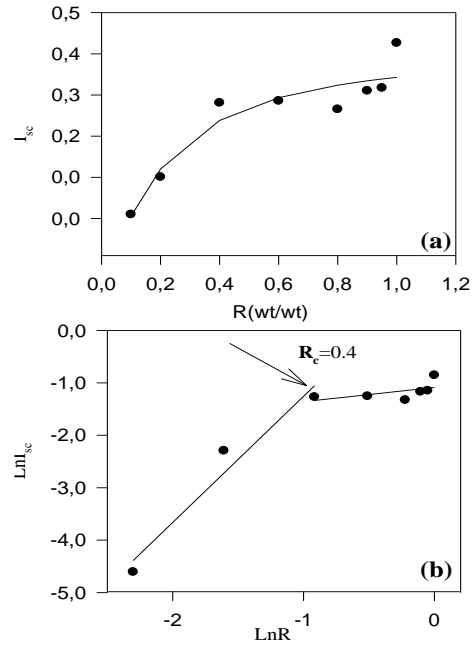


Figure 3. (a)The scattered light intensity, I_{sc} versus PS volume. (b) $\text{Ln}I_{sc}$ versus $\text{Ln}R$ (R is the mass fraction of R)

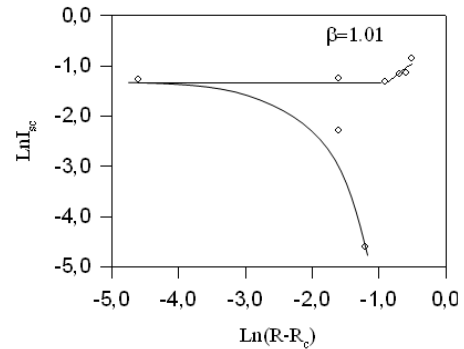


Figure 4. $\text{Ln}I_{sc}$ versus $\text{Ln}(R - R_c)$; β is critical exponent

The composite films with different PS content range in 20-100 wt % were annealed for 10 min at various temperatures. The I_{tr} of the films, versus annealing temperature are seen in Fig. 5. Here, it is seen that I_{tr} first increase and then reaches a saturation level except for the films including 95 and 100 wt % PS. I_{tr} starts to increase at the temperature which is called onset temperature, T_o which moves to the higher temperature with the increasing PS content. In other words, system needs higher temperatures to start film formation processes for higher PS volume. The void closure process is realizing above T_o with the increase of I_{tr} in which the film becomes more homogeneous as a result of decreasing porosity upon closing the voids. This increasing homogeneity of the film increases the transmitted light through the film. After the void closure stage finishes, a new stage which is called as interdiffusion process starts at the healing temperature, T_h , which increase up to a specific PS content and then show almost the same value for the rest of content values where film formation processes can be observed easily.

Observation of interdiffusion process is not possible above the 90 %wt PS content as seen from the Fig 5. In our previous

study, the same behavior was observed with the addition of doping material to PS latex(Ugur, Yargi, Gunister, et al., 2008).

surface than the jump of one mole of polymeric material during the viscous flow.

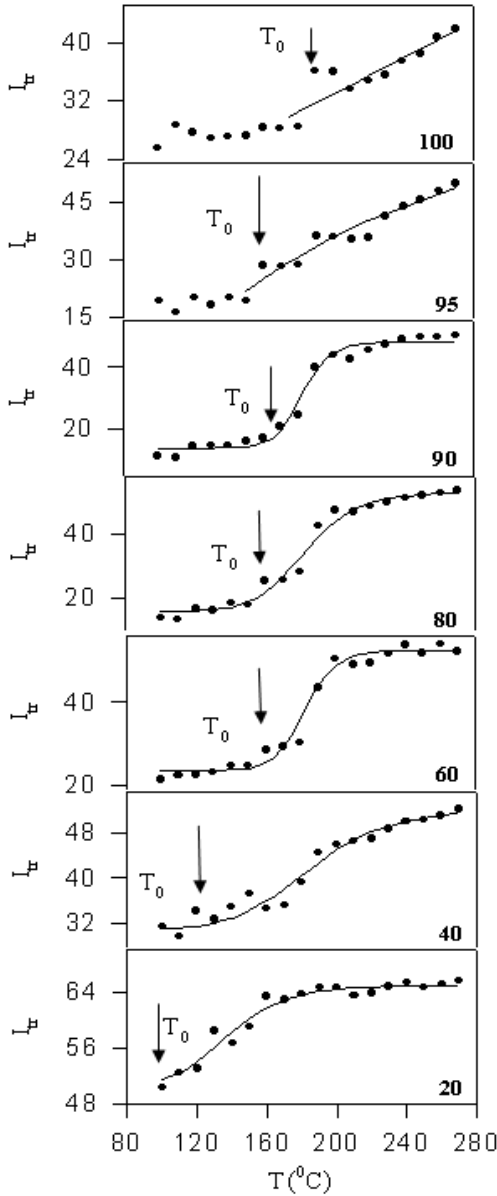


Figure 5. (I_{tr}) change with annealing temperatures depending on PS volume.

Logarithmic plots of I_{tr} vs. T^{-1} are presented in Fig. 6 for different PS contents. The activation energies, ΔE are calculated by the least squares fitting of the data to Eq. 14 and they were plotted versus PS content in Fig.7. Here, it is seen that while the ΔE values increase depending on the increasing PS content, ΔH values are nearly constant. This indicates that the increasing amount of the doping material in the latex film increases the required energy to accomplish the film formation. There may be one reason for not changing so much of ΔH values that aggregation does not become up to T_h values in the composite films which are almost the same for all samples. In other words, viscous flow does not meet up any different potential barrier to overcome before T_h and causes to be almost the same value of ΔH . It is also seen that the ΔE values are much higher than ΔH , because the PS particles can screen the motion of the polymer chains across the junction. In other words, interdiffusion of polymer chains needs more energy to cross over the junction

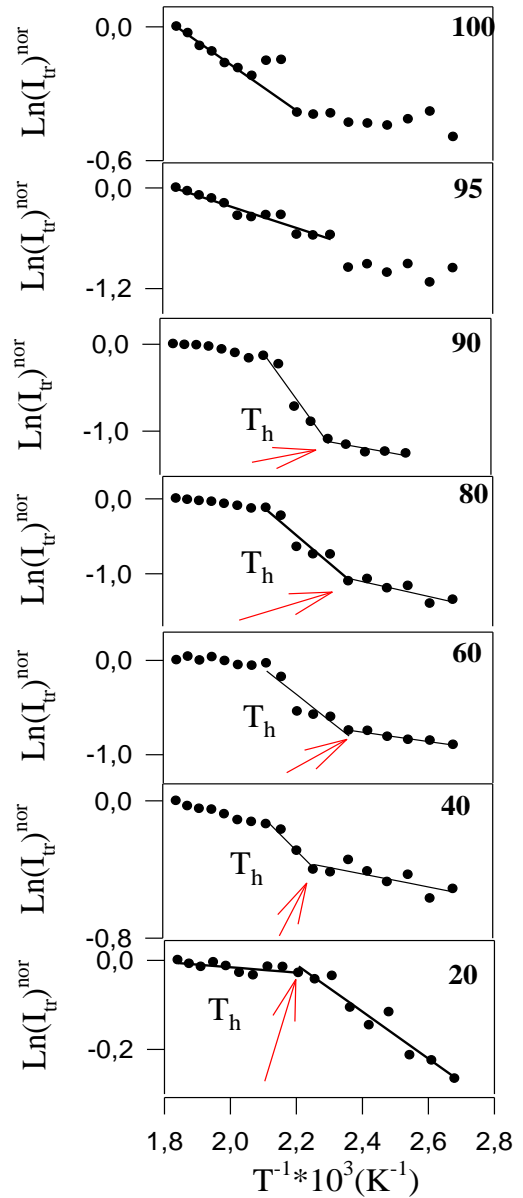


Figure 6. $\text{Ln}I_{tr}$ versus T^{-1} ; for the 20, 40, 60, 80, 90 and 95% PS volume.

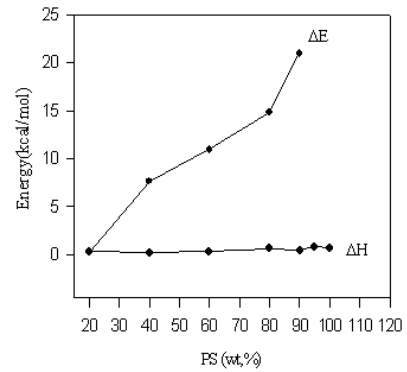


Figure 7. The void closure and interdiffusion energies (ΔH , ΔE) are versus different PS volume.

The behavior of I_{tr} can be explained with our other study (Fig 4)(Yargi et al., 2016) Since there is no mobility between the PS powders up to a certain temperature (T_h), there is no change in light transmittance. However, after the glass transition

temperature, the particles begin to move and the location of the gaps also changes. As the temperature continues to increase, the boundaries of the spheres that begin to fuse begin to disappear and the voids tend to fill. This situation causes the light transmittance to increase up to the fusion temperature. After a certain temperature, the particles cannot move any more either. Because the voids are filled, or because there is a clustering situation depending on the system, it causes the formation of porous structures and a decrease in light transmission. Here, it is not possible to observe the film formation process for composite lattice after the 90 PS wt% value. In other words, for samples with higher PS amount, PT technique is not suitable for to see the detailed I_{tr} change, because the light is blocked by the PS particles and does not allow the transition of itself. In conclusion, it can only be worked below PS 90 wt.%. The morphological changes were found to be consistent with the photon transmission technique results. As seen from Fig. 2a, while pure PS particles has less voids between the spherical particles than the films with 40 wt % PS content as in Fig. 2b. Aggregation which occurs with the addition of PS to the composite films causes the transmitted light intensity to decrease as we have already discussed before.

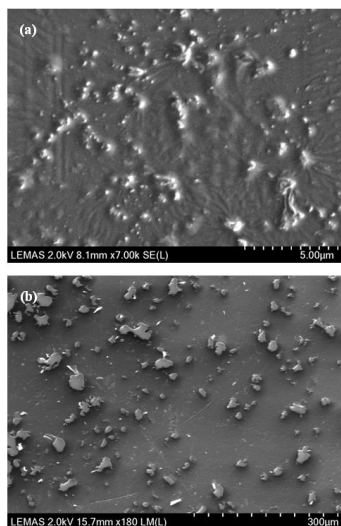


Figure 8. SEM pictures of PVA for the thickness (a) 45 mm, and (b) 170 mm at 90 °C.

4. Conclusions and Recommendations

This work presents a film formation from PS/PVA latexes in terms of mechanical and optical properties. Below 90 wt% PS content, void closure and interdiffusion regions were observed. While, above 90 wt% PS interdiffusion processes was only seen. On the other hand, I_{tr} passing through the films was observed to the PS presence in the composite matrix. Activation energies were also presented. While ΔE increased with PS content, only slightly change was seen in ΔH values depending on doping material.

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