

DETERMINATION OF ACTIVATION ENERGIES AND TENSILE CHARACTERISTICS OF POLYMER LATEXES DEPENDING ON DIFFERENT HEATING METHODS AND THICKNESSES

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Abstract

In this work, film formation from composites of polystyrene (PS) latex particles and poly vinyl alcohol (PVA) was studied using both infrared radiative heating (IRH) and standard convectional heating techniques. Photon transmission (PT) techniques of PS/PVA composite films and tensile strength of pure PVA films were investigated for the film formation process at each temperature and different film thicknesses, respectively. Results showed that the activation energy required for the completion of film formation decreased considerably in IRH annealing technique and IRH heating also causes more homogenous and more flat film surface than films annealed in the oven. Ductility properties were enhanced with the thicker PVA films.

Key words: heating, photon transmission, activation energy, glass transition

1. INTRODUCTION

Recently, IR radiation has been applied to dry foods (Chandra et. al., 2007) and waterborne polymers (Jeong 2010; Menard 2007). The drying time of aqueous solutions of poly (vinyl alcohol) was reduced from 120 min, to only 15 min for combined convective and IR radiative drying (Jeong 2010). In convective heating in an oven, heat diffuses from the film surface and the time for homogeneous distribution of temperature through the film directly depends on this heat diffusion. However, in IRH process, the electromagnetic energy can be focused directly on the film which leads a drastic decrease in time to reach a homogeneous distribution of temperature through the film. In convective heating in an oven, heat diffuses from the film surface and the time for homogeneous distribution of temperature through the film directly depends on this heat diffusion. However, in IRH process, the electromagnetic energy can be focused directly on the film which leads a drastic decrease in time to reach a homogeneous distribution of temperature through the film. Several experimental techniques were used to observe latex film formation such as electron (Eckersley et. al., 1994) and atomic force microscopies (Cannon et. al., 1994), neutron scattering (Chevalier et. al., 1996), non-radiative energy transfer conjunction with time resolved (Pekcan et. al., 1990), and steady state fluorescence (Uğur et. al., 2005). Photon transmission (Arda et. al., 1999; Arda et. al., 2001) and reflection (Pekcan et. al., 1998) techniques have been elaborated for latex film formation processes. Film formation from soft (low- T_g) and hard (high- T_g) latex dispersions can occur in several stages. In both cases, the first stage corresponds the wet initial stage. Evaporation of solvent leads to second stage in which the particles form a close packed array, here if the particles are soft they are deformed to polyhedrons. Hard latex particles remain essentially discrete and undeformed during drying. The mechanical properties of such films can be evolved after all the solvent is evaporated by annealing process. In both cases, the first stage corresponds to the wet initial stage. Evaporation of solvent leads to second stage in which the particles form a close packed array, here if the particles are soft they are deformed to polyhedrons. Hard latex however stays undeformed at this stage. Annealing of soft particles causes diffusion across particle-particle boundaries which leads to a homogeneous continuous material. In the annealing of hard latex system, however, deformation of particles first leads to void closure (Sperry et.al., 1994; Mazur, 1995; Mackenzie and Shuttleworth, 1949; Vanderhoff, 1970) and then after the voids disappear diffusion across particle-particle boundaries starts. The last stage of film formation is the

coalescence of the particles where macromolecules belonging to different particles mix by interdiffusion (Pekcan, 1994).

In this study, the film formation of PS/PVA composites depending on two different heating processes, IRH and convective heating using PT technique and effect of only PVA content at different thicknesses were investigated. After each annealing step, the transmitted light intensity, I_{tr} was measured to investigate the film formation process. The increase in I_{tr} was explained by void closure up to healing temperature, T_h , and above T_h it was explained by the interdiffusion processes for both IRH and convective heating. In order to see the changes in the uniaxial tensile properties of the pure PVA films, the PVA films having different thicknesses changing from 45 to 178 μm were tested by using a tensile tester. It was observed that the tensile properties of PVA films were enhanced with increasing film thickness up to around 165 μm . The tensile properties decreased slightly for the PVA films having thickness higher than 165 μm . However, many of them remained remarkably higher than corresponding values for film thickness equal to 45 μm .

2. EXPERIMENTAL

2.1 Materials

Fluorescent PS latexes were prepared via a surfactant free emulsion polymerization process of styrene monomer (99 % pure from Alfa Asea) using (Potassium persulphate) KPS as initiator. The fluorescent latexes were prepared by adding fluorescent monomer dimethacrylate (PolyFluorTM 511 from Polysciences, Inc.) in pre-polymer solution. The water-soluble radical initiator KPS was dissolved in water and added when the polymerization temperature reached 90 °C. In all polymerizations, deionized water was used. Commercially available Polyvinyl alcohol, PVA (Boysan Co., Turkey, include Acetic acid ethenly, ester, polymer with ethanol, 92-100%, powder form and water soluble, white color, melting point is 220-240 °C, PH is 4.5-6.5) was used as supplied in white powder form. A stock solution of PVA was prepared by following the manufacturers regulations: PVA were dispersed in deionized (DI) water with in the proportions of 0.01 gr PVA; 1 ml DI water by bath sonication for 3h. PVA is a good stabilizing for dispersions enabling preparation of polystyrene composites from dispersions of PVA in polystyrene solution.

2.2 Film Preparation

Two different films with (0 wt% PVA and 50 wt% PS/PVA contents) and two sets were prepared from the dispersion of PS/PVA composites by placing the same number of drops on a glass plates with the size of 0.8x2.5 cm² and allowing the water to evaporate. One set was prepared for the convective heating and the other set was prepared for IRH. Then the samples were separately annealed above T_g of PS, 105 °C, for 10 min at temperatures ranging from 100 to 270 °C in both oven and under IR lamb. The temperature was maintained within ± 2 °C during annealing for oven and ± 1 °C for IRH. After annealing, each sample was placed in the UV-Visible spectrometer, Perkin Elmer Lambda 35 for the photon transmission measurements. The transmittances of the films were detected at 500 nm. A glass plate was used as a standard for all transmittance experiments and measurements were carried out at room temperature after each annealing processes. The sample position and the transmitted light, I_{tr} , are presented in Fig 1

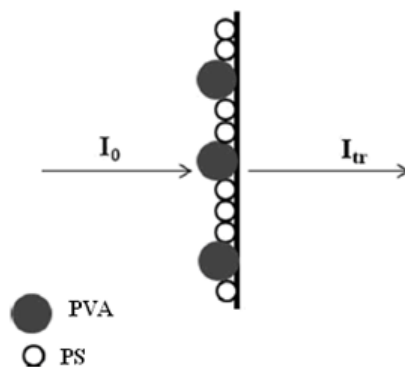


Figure 1. Schematic illustration of sample position and incident light (I_0), Transmitted light (I_{tr}) intensities.

2.3 Tensile Testing Method

Uniaxial tensile tests of PVA films having a gauge length of 20 mm were made on a Lloyd tensile testing machine LF Plus (AMETEK Lloyd Inst., UK) with a crosshead speed of 20 mm/min at room conditions ($T=25\text{ }^{\circ}\text{C}$; $\text{RH}=60\%$). The tested PVA films had the same width of 5 mm but varying thicknesses from 45 to approximately 200 μm .

2.4 Calculation of the activation energies

The activation energies for the void closure process are calculated by using the following equation (Pekcan et. al., 1990).

$$I(T) = S(t) \exp\left(-\frac{3\Delta H}{kT}\right) \quad (1)$$

where $S(t) = (yt/2AC)^3$, k is the Boltzmann's constant, ΔH is the void closure energy and I is the transmittance at 500 nm. For a given time the logarithmic form of Eq. 1 can be written as follows

$$\ln I_f(T) = \ln S(t) - \left(\frac{3\Delta H}{k_B T}\right) \quad (2)$$

By using the least square fitting, the void closure energy can be calculated by using the Eq. 2 for the latex films. The activation energies for the interdiffusion process are calculated by using the Eq. 3.

$$I(T)/I(\infty) = A \exp(-\Delta E / 2kT) \quad (3)$$

Where k is the Boltzmann's constant, ΔE is the interdiffusion energy and I is transmittance at 500 nm. Similar procedure with the calculation of the void closure energies is used to calculate the interdiffusion energy. The activation energies for the PS and PS/PVA films annealed by the convective heating in the oven and IRH monitored by PT technique was given in Table 1.

kcal/mol	PS-I _{tr}	PS/PVA-I _{tr}
ΔH -OVEN	2,30	0,53
ΔE -OVEN	2,78	1,01
ΔH -IR	0,67	NC
ΔE -IR	1,08	NC

Table 1. Experimentally obtained void closure (ΔH) and interdiffusion energies (ΔE). NC: Cannot be calculated

Since the theoretical models which describe the latex film formation are discussed in literature in detail (Ugur et. al., 1990; Arda 2007), the information about these models was not given in this manuscript.

3. RESULTS AND DISCUSSION

The behavior of I_{tr} can be explained with the schematic picture given in Fig.2.

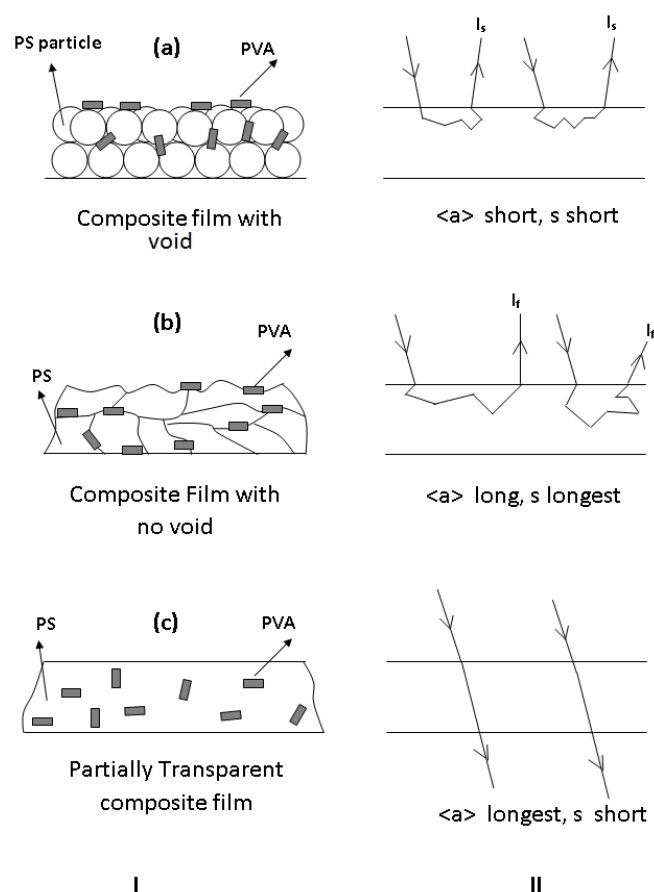


Figure 2. Schematic illustration of the stages of the latex film formation and the path of the light inside the film at each stage. (a) The initial stage of the film formation. Film mostly has voids inside. (b) The voids inside the film are disappeared upon annealing. (c) The final stage of the film formation. Here the partially transparent film is obtained due to the interdiffusion of the polymers through the boundaries.

In Fig. 2a, at the early stages of the film formation, the composite film possesses many voids which results in short mean free, $\langle a \rangle$, and optical, s , paths of photons. At this stage most of the light is scattered which yields low I_{tr} . Fig. 2b represents a film in which interparticle voids disappear due to the annealing. The mean free path and the optical path are the longest for this case and I_{tr} reaches its maximum value because of the increasing efficiency of the excitation due to the long s . Finally, as seen in Fig. 2c, a partially transparent film with longest $\langle a \rangle$ but shorter s values was formed. Since the optical path is very small compared with the previous condition, the excitation efficiency decreases considerably resulting in low I_{tr} intensity. Transmitted light intensity, I_{tr} , versus annealing temperatures is plotted in Figs. 3 and 4 for the PS films without and with PVA (%50 PS, %50 PVA), respectively.

I_{tr} first starts to increase after a certain onset temperature, called the minimum film formation temperature T_o , and then reaches a maximum at the healing temperature, T_h , which is the transition

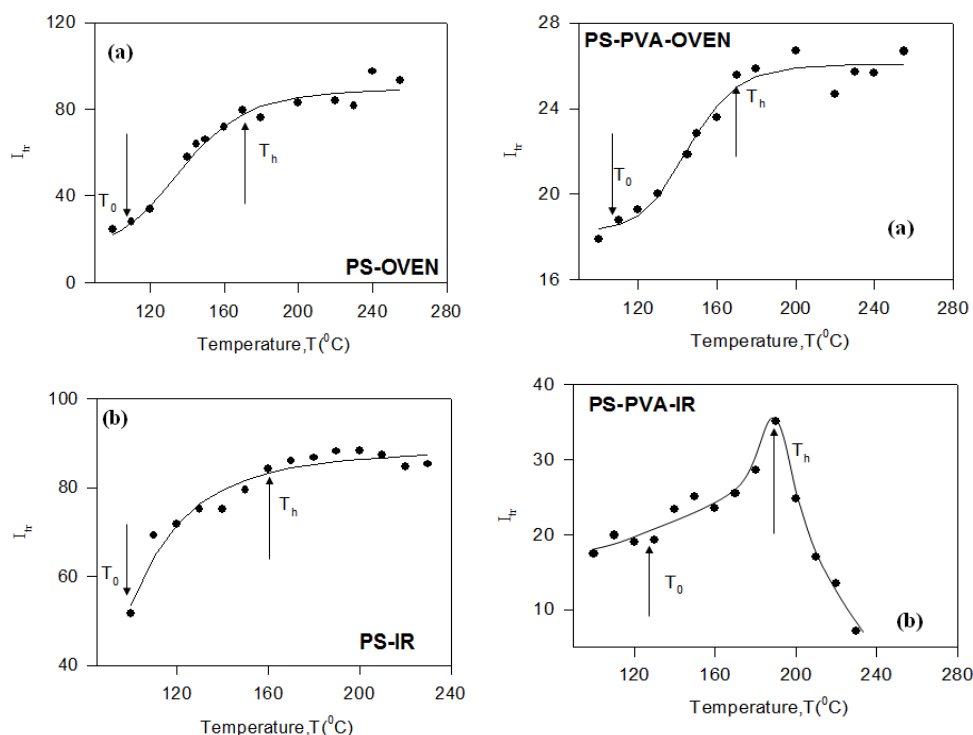


Figure 3. Transmitted light intensity (I_{tr}) versus temperature for the pure PS latex film annealed by (a) conventional heating in the oven and (b) by IRH. (Left Side)

Figure 4. Transmitted light intensity (I_{tr}) versus temperature for the PS/PVA (50% wt) composite latex film annealed by (a) conventional heating in the oven and (b) by IRH (Right Side)

temperature from void closure to interdiffusion process. The increase in I_{tr} above T_o can be explained by the evaluation of the transparency of the PS and PS/PVA latex films upon annealing. Most probably, increased I_{tr} corresponds to the void closure process; i.e., polymer starts to flow upon annealing and voids between particles can be filled. After T_h since the motion of the polymers through the boundaries during the interdiffusion process does not change the average optical properties of the latex films, the increase rate of the transmittance is very small (Ugur et. al., 1990; Arda 2007). Just for the PS/PVA latex film annealed by IRH technique; I_{tr} decreases after reaching maximum as seen in Fig. 4(b). This point will be discussed in the following paragraphs. For pure PS films, both T_o and T_h values are close to each other in both infrared and convective heating techniques as seen in Fig. 3. But the rate of increase and the initial value of the transmittance are higher for the film annealed by IRH Fig. 3(b). Also the void closure (ΔH) - interdiffusion (ΔE) energies obtained from Fig 5 are 2.30 - 2.78

kcal/mole and 0.67 - 1.08 kcal/mole for PS films annealed by the convective heating in the oven and IRH, respectively, as given in Table 1.

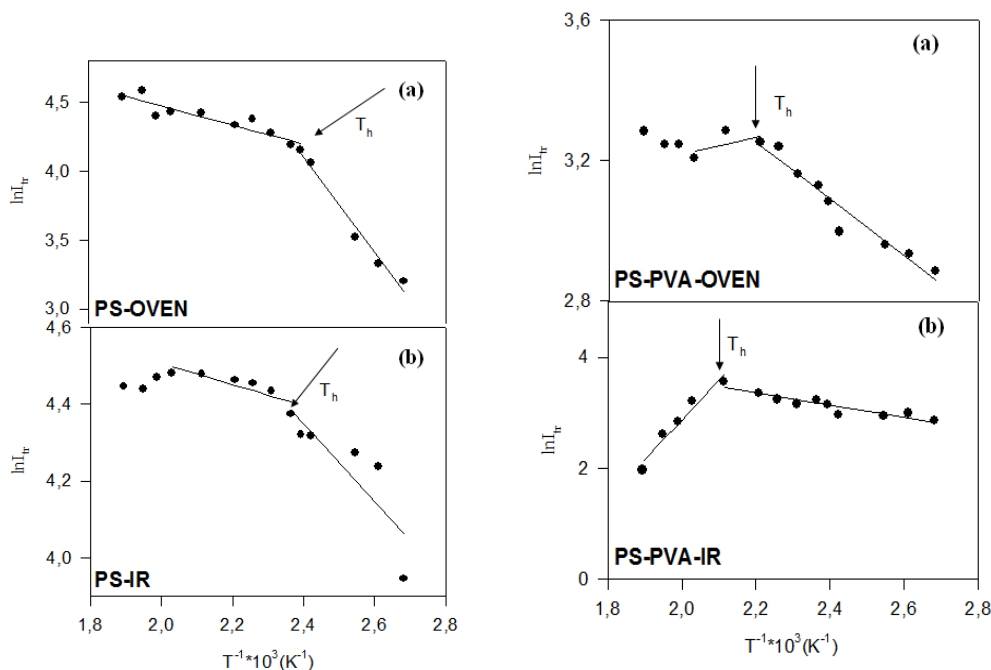


Figure 5. Logarithmic plots of I_{tr} data vs. inverse of annealing temperatures (T^{-1}) for the pure PS latex films annealed for 10 min in (a)oven and (b) IRH. Data are fitted to Eq 2 and Eq 3 to produce ΔH_{tr} , (right slopes) and left slope of the linear relations produces ΔE_b values, respectively which are listed in Table I. (Left Side)

Figure 6. Logarithmic plots of I_{tr} data vs. inverse of annealing temperatures (T^{-1}) for the PS/PVA composite films annealed for 10 min in (a) oven. Data are fitted to Eq 2 and Eq 3 to produce ΔH_{tr} , (right slopes) and left slope of the linear relations produces ΔE_b values, respectively which are listed in Table I. and (b) Logarithmic plots of I_{tr} data vs. inverse of annealing temperatures (T^{-1}) for the PS/PVA composite films annealed for 10 min by IRH.(Right Side)

These results clearly indicate that less energy is required for the void closure and interdiffusion processes for the pure PS latex films when IR heating is used for the film formation. The transmittance variations with respect to the annealing temperature for the PS/PVA composite latex films annealed by the convective heating in the oven and IRH are shown in Fig. 4. The void closure and the interdiffusion processes are clearly observable for the composite films annealed in the oven and the required energies for these processes are calculated as 0.53 kcal/mole and 1.01 kcal/mole, respectively (see Fig 6). It is also seen that ΔE values are higher than ΔH values for both PS and PS/PVA composites. Since PS particles can screen the motion of polymer chain across the junction, then, a single chain needs more energy to overcome this difficulty. Therefore, a single chain needs more energy to execute diffusion across the polymer-polymer interface, than bulk polymer needs to accomplish the viscous flow process. Another interesting point that, the obtained void closure and interdiffusion energies from PS/PVA composites is less than PS particles for the two technics as seen in table I. This result shows that addition of the PVA particles makes easier film formation processes. Probably, when PVA particles heated around the T_g value starts to fill the voids between the PS particles and decreases the aggregation in two polymer system and causes being more homogenous film structure. For the PS/PVA film annealed by IRH, different situation was observed: the transmittance decreased abruptly after reaching maximum value as seen in Fig. 4(b). This decrease in the transmittance is probably due to the physical deformation of the film. Because some dark spots were

observed on the surface of the PS/PVA film annealed by IRH after a certain temperature. Before the maximum I_{tr} , probably the void closure and the interdiffusion processes occur very fast and nearly simultaneously. So it cannot be possible to distinguish these processes during the film formation for the PS/PVA composite film annealed by IRH. The void closure and the interdiffusion energies for the composite film annealed in the oven could be calculated as 0.62 and 18.00 kcal/mole, respectively as in table 1. These energies are in accordance with the energies calculated from the transmittance measurements which clearly indicate that the energy for the motion of the polymers through the boundaries is much higher than the void closure energy. The mechanical properties of pure PVA films with six different thicknesses varying from 45 to 178 μm were also investigated at room temperature.

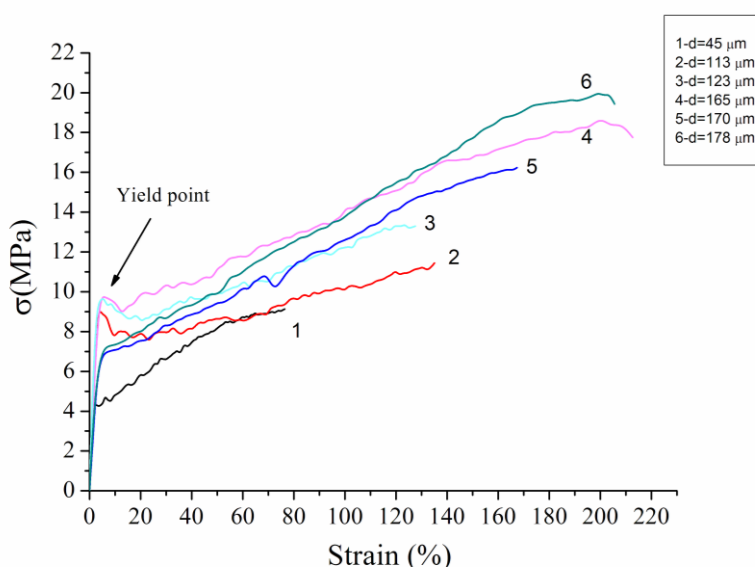


Figure 7. Effect of thickness on the stress-strain curve of PVA film at room conditions.

As shown in in table 2 and Fig. 7, elastic modulus or Young's modulus being a measure of stiffness increased significantly, as d increased up to 123 μm , and then had a slightly decreasing tendency.

Table 2. Tensile properties of PVA films with different thickness

d : thickness of PVA film; σ_y : yield stress; ϵ_r : strain at break; σ_r : breaking stress

d (mm)	σ_y (MPa)	σ_r (MPa)
0.045	4.31	9.14
0.1125	8.97	11.45
0.123	9.63	13.29
0.165	9.73	17.75
0.17	6.93	16.23
0.178	7.21	19.43

The value of Young's modulus became consistent with the value of 0.4 GPa to 5.6 GPa determined for PVA film with different thickness in different studies (Paiva et. al., 2004; Xu et. al 2009; Zhang et. al 2014; Chan et. al 2009; Chen et. al 2005; Chan et. al 1999; Fukomori et. al 2013) which indicate a great variety for the Young's modulus. It was also observed in these studies that the breaking strength and breaking extension had a wide varying range from 0.35 to 83 MPa and from 53% to 350% strain for different thickness, respectively, with which measured values of the extensibility and the tensile strength of the PVA films with different thickness as tabulated in Table 1 were seen to be consistent. It is seen that the increase in the thickness of the PVA films increased significantly the mechanical strength. For example, as the thickness of the films increased around four times, the tensile strength increased around twice. Moreover, while the thickness of the films increased up to 165 μm , the toughness of the films increased greatly. That is, the absorbed energy per unit volume of the films prior to fracture increased. With the increase in the toughness, the films became tougher, that is, stronger and more ductile at the same time which indicates that the PVA films withstand both higher stresses and strains values. This may lead to increase roughnesses over the surface of the PVA films. This situation causes the surface tension caused by different ways and enhances their mechanical strength. This case resembles the increase in the energy needed to overcome the potential energy barrier met as a result of the aggregation formed in the latex structure by the addition of PS to PVA. As indicated above, while the intensity of the transmitted light from PS/PVA films increased as the PS content increased up to 40% in the PS/PVA composite latex, for the films having higher PS content than 40%, the intensity of the transmitted light from the films decreased, that is, the amount of scattering increased. In other words, it becomes more difficult to observe the film formation with the photon transmission technique for the concentration value higher than that. In addition, the great increase in the strain at break or extensibility of the films as seen in Figure 7 with increasing the thickness of the PVA films is an expected result because due to increase in the PVA concentration, cracks with the micro size present in the film structure fill and as it gets thicker, the surface tension in the medium increases. In order to overcome this difficulty, it is needed to apply more stress or force. In the optical measurements, as also explained in the percolation model, the increase in the amount of the PVA in the PVA/PS composite films enables the films to obtain a more homogenous structure. This homogeneity results in the formation of more transparent film formation optically.

4. CONCLUSION

This study mainly focused on the effect of the IR heating on the film formation process of the pure PS and PS/PVA composite latex films. The film formation stages of the pure PS latex films annealed by the convective heating in the oven and by IRH could be measured by PT technique. When the IRH technique is used for the film formation of the pure PS latex films, the void closure and the interdiffusion activation energies decreases considerably as seen in Table 1. The latex films annealed by IRH are more homogeneous than the latex films annealed by the convective heating in the oven. Finally, it can be concluded that the IRH technique speeds up the film formation process for the latex films. From the results of tensile testing measurements, the tensile properties of PVA films were enhanced clearly with increasing film thickness up to around 165 μm . The films became tougher, more ductile and stronger with higher extensibility. As the film thickness increased from 45 to 165 μm , breaking stress, strain at break, and the toughness values increased approximately twice, 3 times, and 6 times respectively when compared with the values obtained for d equal to 45 μm .

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