Spin Coating and Beer's Law Analysis of Polystyrene Films
With and Without Bet-Carotene Dye Using UV-VIS spectroscopy

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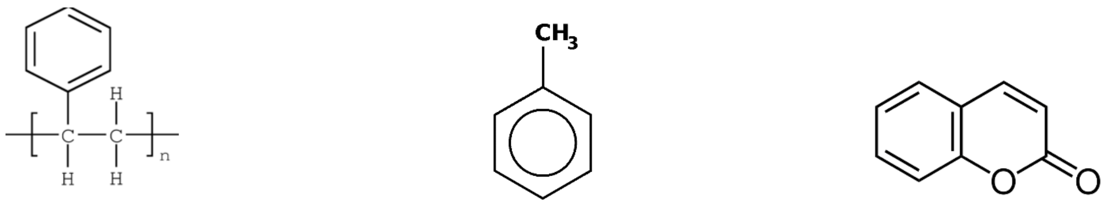
Abstract

The objective of this laboratory was to use spin coating to prepare thin films of polystyrene (PS) on glass substrates in order to analyze how spinning speed and the liquid precursor solution can be used to control film thickness. Furthermore, the UV-VIS response of the thin layers after beta-carotene was introduced into the PS solutions was measured to calculate wavelength dependent absorption coefficients of beta-carotene by applying Beer's Lambert law. Finally, Beer's Law was analyzed in term of the capability of describing the measured spectral trends of the beta-carotene. It was concluded that film thickness increases with an increase in the viscosity of a solvent whereas it decreases with increase of spinning speed and spinning time. Using 105 UV-Vis Spectrophotometer, the absorption peaks were found at 380 nm for the thin film of PS and 460 nm after the addition of beta-carotene dye. The absorption coefficient for beta-carotene was calculated to be 139.7 cm^{-1}. This implies that absorption increases with the increase of thickness, which directly follows from the Beer-Lamber-Law, for which Beer's law cannot describe the spectra trend.

Introduction

Film formation is scientifically known as the adaptation of a coating film from a liquid or fluid form into a solid. [1] One of the most widely used technique in forming organic and inorganic films is spic coating. The technique is preferred because it offers low cost, high speed, and flexibility with a diverse array of materials systems. Spin coating produces a uniform, adherent, defect-free polymeric film of desired thickness over a specific surface. [2] Three stages are involved in the spin coating procedure. The first stage is dispensing where the surface is flooded with precursor solution. An initial slow rotation step is run to evenly distribute the initial volume, which is named a spread cycle. The second stage is acceleration where the initially dispensed substrate is accelerated as quickly as possible to a final spin speed. In general, high ramp rates are associated with better film uniformity. This results from minimized solvent evaporation during the acceleration to final speed. [2, 3] It is worthwhile to note that as precursor viscosity will increase with solvent evaporation, a changing viscosity over time will impact uniformity if substantial evaporation is allowed. [2] The third stage is resist flow, in which the precursor layer obtains a relatively uniform and symmetric flow profile, which establishes the final film thickness profile. Once this structure is formed, the remainder of the high speed spinning stage promotes final solvent evaporation. The most significant parameters that control film formation are spinning speed, time, and viscosity. [1, 2]

The materials used in this laboratory are polystyrene (PS), toluene, and beta-carotene. PS is a worldwide utilized thermoplastic polymer used to make “foam” cups, DVD cases, etc. A precursor solution of polystyrene can be prepared by dissolution of PS in toluene, a clear water-insoluble liquid which is a mono-substituted benzene derivative. [2] Beta-carotene is a chemical compound that is the red-orange pigment found in many plants and fruits such as carrots and pumpkins since it absorbs in the blue/green portion of the EM spectrum. Beta-carotene shows an orange color when added to an otherwise colorless host material like PS. [2] The structures of polystyrene, toluene and beta-Carotene are shown in Figure 1.



Polystyrene Toluene Beta-Carotene

Figure 1: Molecular Structures of Polystyrene, Toluene, and Beta-carotene.[2]

The Beer-Lambert Law, as shown in Equation 1, is used to calculate the absorption coefficient of beta-carotene. [2]

$$I_T = I_O e^{-\alpha x} \tag{1}$$

where I_T is the intensity of the light transmitted, I_0 is the initial intensity of the light, α is the absorption coefficient, and x is the path length, in this case the thickness of the thin film in cm.

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Experimental Procedures

Polystyrene-Toluene solutions at different percentages of toluene were prepared in order to get different film thickness and see its effect on the absorption of beta-carotene as well using a UV-VIS spectrophotometer. The model of spin coating equipment used in this experiment was WS-400B-6NPP/LITE. The model of UV-VIS spectrophotometer was 105 UV-VIS SPETROPHOTOMETER. First, the solutions were placed on stir plate with stir bar until Toluene got solved in PS completely. Another set of solutions were prepared by adding Beta-carotene at constant concentration. Then, a glass slide was placed on the spin coater stage and the vacuum pump was activated and the pressure set to above 20 in order to hold the sample in place during spinning. The solution was dispensed onto the slide using a micropipette. Using a micropipette, a 600 microliter of solution was distributed onto the slide. Each one of the eight solutions, two sets (with and without beta-carotene) of four different concentrations, was spin coated on the substrate based on the chart below.

Table 1. Solutions of Polystyrene Dissolved in Toluene

Solution #	PS wt%	Toluene wt%
1	8	92
2	12	88
3	18	82
4	25	75

The UV/Vis spectra of each sample were measured from 360-500 nm in 20 nm increments. Given that, $A = \log_{10}(1/T) = \log_{10}(I_o/I_T)$ where T equals transmittance, Equation 1 was rearranged to Equation 2 to use the absorption data generated by UV/Vis spectroscopy to find the absorption coefficient.[2]

$$ln(T) = -ax \quad (2)$$

Results and Discussion

Table 2 shows the thickness of PS films as a function of solution concentration and spinning conditions. It was observed that thickness of the PS films increases with the increase of Toluene. Given the properties of toluene, the findings indicate that an increase in the viscosity of a solvent increases the thickness of the film being made during spin coating process. This outcome agrees with the literature. [2, 3] Studies have also shown that film thickness decreases with increase of spin speed and spin time. [2, 4]

Table 2. Film thickness as a function of solution concentration and spinning conditions.

Solution #	PS wt%	Toluene wt%	Speed (rpm)	Time (secs)	Thickness (µm)
1	8	92	1500	60	1
2	12	88	1500	60	2.1
3	18	82	1500	60	4.5
4	25	75	1500	60	11

The absorption spectra for PS without Beta-Carotene, as shown in Figure 2, indicate absorption peaks at wavelength of 380 nm, which is in the ultra-violet region. This agrees with the expected results of its appearance; since it is out of the visible range, it appears colorless to the human eye. The maximum absorption of PS is moving to a shorter wavelength because PS has a large energy gap between the bonding and anti-bonding orbitals as shown in its molecular structure in Figure 1. [1,2]

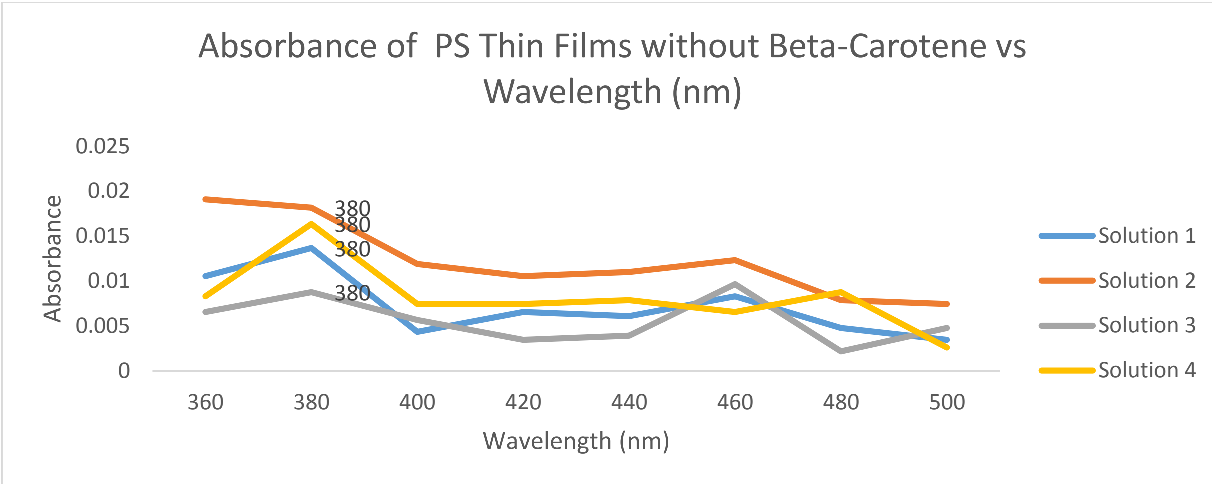

Figure 2. Absorption Spectra for PS thin films without Beta-Carotene

After the addition of beta-carotene, a shift to the right, to the visible range, was observed as shown in Figure 3. Specifically, the Absorption Spectra for PS thin films showed a peak at 460 nm, which agrees with the expected result. In the visible light spectrum, a wavelength of 460 nm is associated with the blue region, which appears orange to the human eye. Moreover, absorption in beta-carotene at ~470 nm can be explained by the transitions between bonding and antibonding $\pi \rightarrow \pi^*$ states. [2, 4]

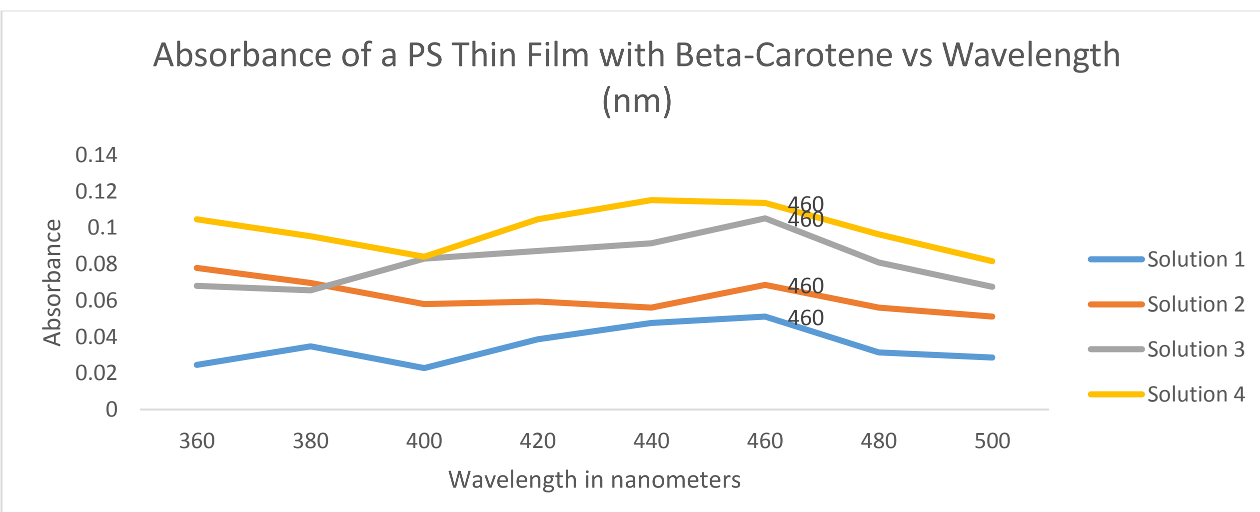

Figure 3. Absorption spectra of PS thin films with the addition beta-carotene.

It was also determined that the peak of true absorption of beta-carotene is at 460 nm, which demonstrates the optical properties of beta- beta-carotene. The molecular of beta-carotene can explain why it appears orange. Beta-carotene has alternating double and single bonds, as shown in Figure 1. The more delocalisation there is, the smaller the gap between the highest energy pi bonding orbital and the lowest energy pi anti-bonding orbital. [1] Therefore, it takes less energy in beta-carotene than in PS to promote an electron because the gap between the levels is less. Less energy means a lower frequency of light gets absorbed, which is equivalent to a longer wavelength.[1]

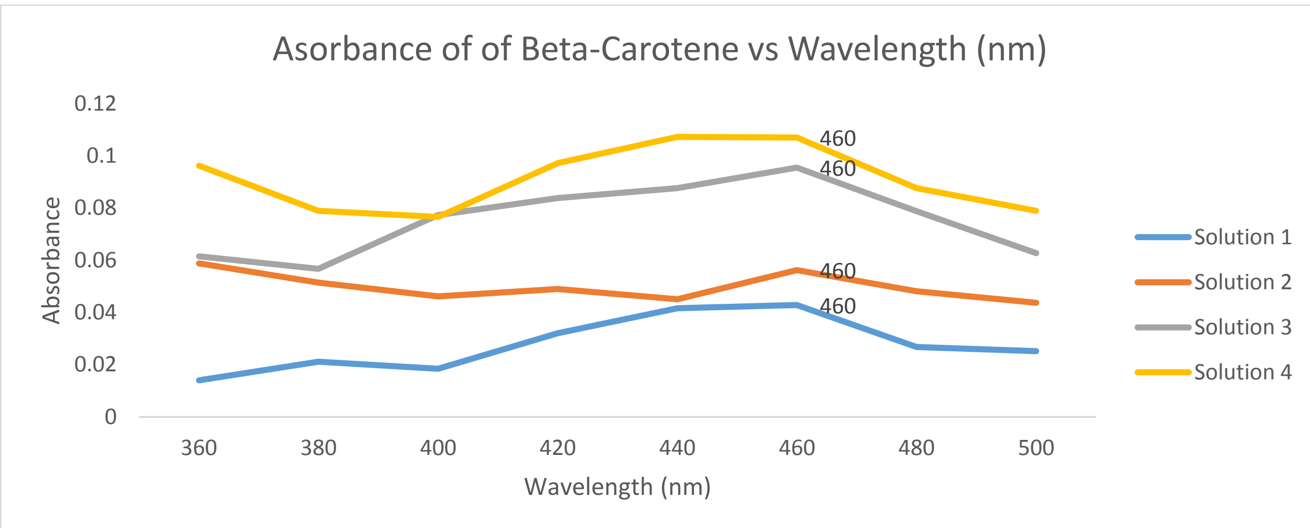

Figure 4. The true absorbance of beta-carotene in PS thin films.

Using the Beer-Lambert Law as stated in Equation 2, the absorption coefficient was determined to be 139.7 cm^{-1}, taken as the slope of the logarithm of peak transmittance and the film thickness in cm as demonstrated in Figure 5.

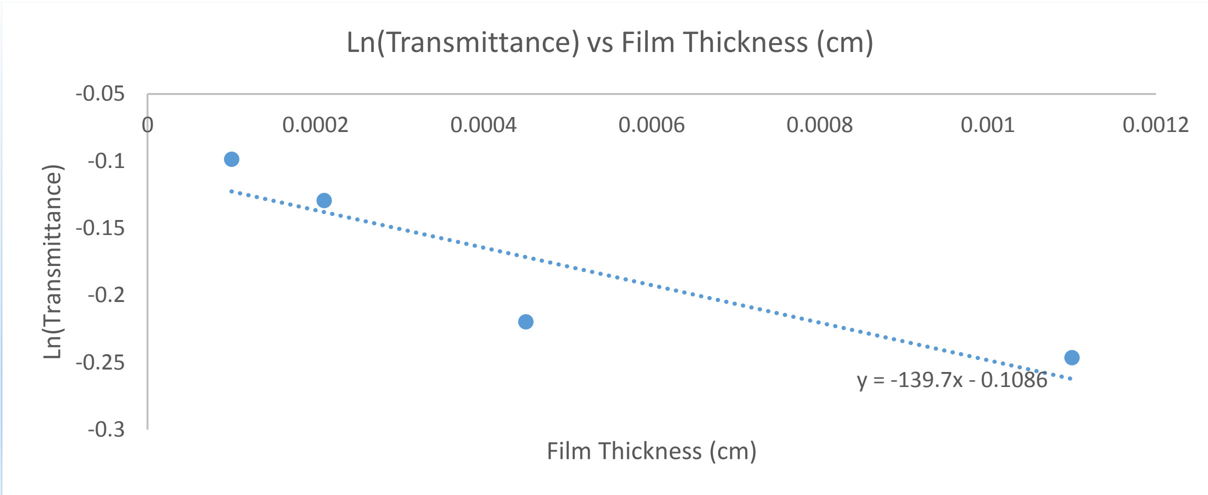

Figure 5. The absorption coefficient of Beta-Carotene is determined as the slope of the logarithm of transmittance and the film thickness in cm using the Beer-Lambert Law.

The experimental value determined for the absorption coefficient of Beta-Carotene agrees with the value reported in the literature with a relative error of 18.3%. It was reported that the absorption coefficient of Beta-Carotene is 171 cm^{-1}. [4] Variation in results can be explained by the fact that the films were not formed to a precise thickness during the spin coating process. Given the beta-carotene optical properties, it is worthwhile to note that Beer's Law does not describe the measured spectral trends because it does not account for thickness. [1, 2] However, the Beer-Lambert Law exposes an exponential dependence between the amount of light transmitted and the thickness of the absorbing medium. The concentration of absorbing centers in the sample also influences the amount of absorption. [2, 3]

Conclusions

The objective of this laboratory was to use spin coating to prepare thin films of polystyrene (PS) on glass substrates in order to analyze how spinning speed and the liquid precursor solution can be used to control film thickness. Furthermore, the UV-VIS response of the thin layers after beta-carotene was introduced into the PS solutions was measured to calculate wavelength dependent absorption coefficients of beta-carotene by applying Beer's Lambert law. Finally, Beer's Law was analyzed in term of the capability of describing the measured spectral trends of the beta-carotene.

This experiment succeed in demonstrating the effects of in the process of spin coating and thin film formation. It also succeed in explaining that the spectra trends cannot be explained using Beer's Law due to its independence of thickness. Instead, Beer-Lambert law was used to show the absorption coefficient. Analysis of spin coating was made possible by forming thin films of four PS solutions with increasing concentrations of Toluene. It was determined viscosity, spinning speed and time control film thickness. Film thickness increases with an increase in the viscosity of a solvent whereas it decreases with increase of spinning speed and spinning time. After that, the films were examined in a 105 UV-Vis Spectrophotometer. The absorption peaks were found at 380 nm for the thin film of PS and 460 nm after the addition of beta-carotene dye. Using the Beer-Lambert law the absorption coefficient for beta-carotene was calculated to be 139.7 cm^{-1} which compares to a literature value of 171 cm^{-1} with 18.3% error. This implies that absorption increases with the increase of thickness, which directly follows from the Beer-Lamber-Law. [2, 4]

References

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[2] L. Reynolds, Experiment Description-Spin Coating and Beer's Law, MSE 255 Course Locker.

[3]J.R. Dives, Concise Metals Engineering Data Book, (ASM International, Ohio, 1997).

[4] S.Flack *et al*., Journal of Applied Physics, volume 56, p. 1199, (1984).