Infrared Spectroscopy Analysis of (3-Aminopropyl)triethoxysilane (APTES) Coating

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Background

Organic coatings can act as a barrier between metal surfaces and the environment. The coating increases the durability of the metal by providing resistance to stress, weather, and physical aging (Popov 2015). Silane bonding agents can be used to enhance the adhesion between organic coatings and metal. (3-Aminopropyl)triethoxysilane (APTES) is a coupling agent which contains an active group on one end which can react with organic molecules, like synthetic resin, and alkoxy groups on the other end which is connected to a silicon atom. This end can react with hydroxyl groups present on the surfaces of minerals, glass, and inorganic materials (*3-Aminopropyltriethoxysilane* n.d.). Therefore, an even coating of APTES is beneficial towards meditating an effective bond between the organic coating and the metal surface.

In this project I used Fourier-transform infrared spectroscopy (FTIR) to obtain infrared spectrums of two different APTES coatings- one was coated through vapor deposition which presented a thinner, more uniform coating, and the other was produced through soaking which produced a thick, non-uniform coating.

FTIR spectroscopy is a type of infrared (IR) spectroscopy, and the principle behind it is that molecules are made up of atoms and different molecules are composed of different compositions of atoms. Compounds are composed of identical units of molecules, and hence different compounds are made up of different arrangements of atoms. When we irradiate a compound with wavelengths of IR light, the functional groups (specific groups of atoms characteristic to a compound) within the molecules of the sample will move around. Different functional groups absorb different wavelengths of infrared light; hence IR spectroscopy is a way to narrow down what the structure of a molecule is. After the sample is irradiated with IR light, we can produce an IR spectrum of the compound which is a graph relating the relative absorbance or transmittance of specific wavelengths of light.

In this project I primarily helped Prof. Chen develop a new method to coat APTES on glass substrates, which is different from traditional methods of sample preparation for FTIR characterization. This new method uses those two methods listed above to coat APTES on microscope cover glass rather than sandwiching APTES powder between two KBr cell windows, which is the traditional method for preparing a sample for FTIR detection. I had to then manually process the spectrums. In developing and verifying this new method, a lot of trial and error has been taken to preliminarily verify that this new microscope glass-based technique works for sample preparations for FTIR spectral characterization.

Materials and Methods

The coating protocols were co-developed and benchmarked by Prof. Chen and Mr. John Halford (M.S.) at the Department of Mechanical Engineering. Mr. Halford also helped prepare the coatings. The IR spectroscopy technique is mentored under Dr. Jack Zhang's guidance.

Materials and Equipment

Materials used included a 1 in. × 1 in. microscope cover glass, anhydrous toluene (> 99.8%), 100 ml of (3-Aminopropyl)triethoxysilane (APTES) (99%), KBr 25x4mm FTIR Cell Window, and a 5.3 oz tube of Seedburo SD200G Desiccator Silicone Grease. A Perkin Elmer Spectrum RX1 FTIR Spectrometer was used to scan the two coatings. Spectragryph, an optical spectroscopy software, was used to manually edit the raw scanned data.

At the beginning of this project, we attempted to sandwich the APTES powder between two KBr cell windows, which is the traditional procedure for preparing a sample for transmission-based FTIR detection. However, we discovered that this procedure was difficult to accommodate the coating procedure developed.

Therefore, we carried out the microscope glass protocol to determine whether microscope glass (rather than KBr) is suitable for FTIR detection. After discovering the glass protocol worked, I proceeded to analyze the difference in the FTIR detection results of the two coatings.

Sample cleaning

1. Glass samples were sonicated in 75% alcohol for 8 minutes. Then they were sonicated in DI water for 10 minutes.
2. Afterwards, the glass samples were bathed in boiled DI water for 10 minutes.
3. Then, the glass samples were baked at 200 F for 1 hr.
4. Once the glass samples were baked, they were treated by air plasma at 560 mTorr, high power, for 30 seconds.

Coating

Coating with vapor deposition: this produced Coating 1

1. Two plasma-treated glass samples were placed in a glass jar.
2. One drop (around 1 ml) of 99% APTES was dripped in the jar without touching the samples.
3. The lid of the jar was loosely covered.
4. The jar was placed in a thermal vacuum chamber. The chamber was set at a pressure of 500 mTorr and temperature was set to around 60 C.
5. Under the powerful vacuum and elevated temperature, the APTES drop dipped into the jar from earlier gradually evaporated and deposited onto the glass samples.
6. The coating was left to sit for 24 hours.

Coating with the soaking method: this produced Coating 2

1. The APTES solution was diluted in the anhydrous toluene at the 1 volume % ratio.
2. Once the glass samples were treated by plasma, they were immediately soaked in the APTES/toluene solution.
3. The glass samples soaked for 24 hrs. Two samples were soaked at a time.

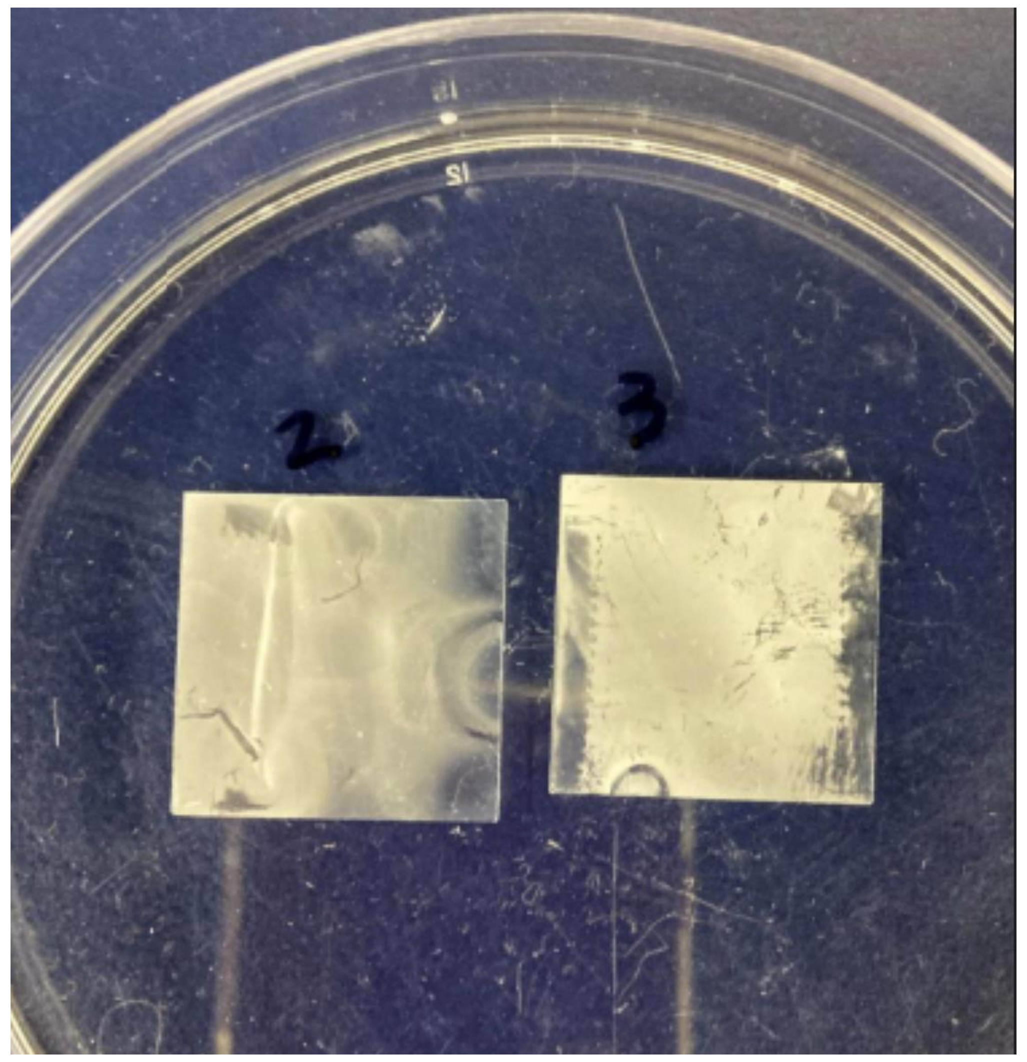


Fig. 1. Coating 1, on the left, is the glass sample coated through vapor deposition. The APTES coating appears to be thin and more uniform. Coating 2, on the right, is the glass sample coated through soaking. It looks thicker and nonuniform.

Results and Discussion

Figure 2 shows the IR spectrum of Coating 1 and 2. The y-axis is in units of "Intensity", and as seen in Figure 3, this means as in the intensity (I) of the transmitted light once it reaches the spectrometer's detector after passing through the coating samples. The Beer-Lambert Law relates the passage of light through a translucent medium to the medium's properties (*Beer Lambert Law* 2021). Coating 1 and 2 delivered distinct spectral peaks which suggests that Coating 1 and 2 are inherently different in uniformity, which aligns with the visible observations of their differences in uniformity as seen in Figure 1. The presence of distinct coating quality between the two coating methods implicates that coating APTES on microscope cover glass is feasible for preparing coatings for FTIR spectrum analysis. This result highlights that the microscope cover glass coating protocols developed in this project could stand as an alternative to the traditional KBr lens sandwich-based sample preparation approach. However, this statement needs to be verified with further research.

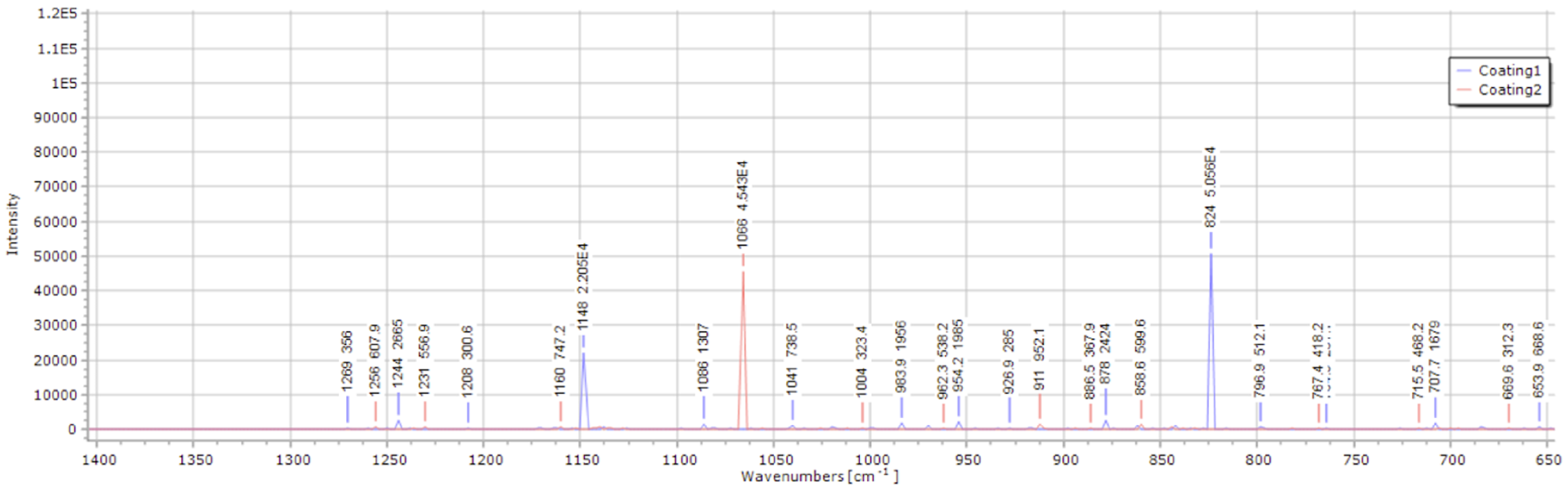
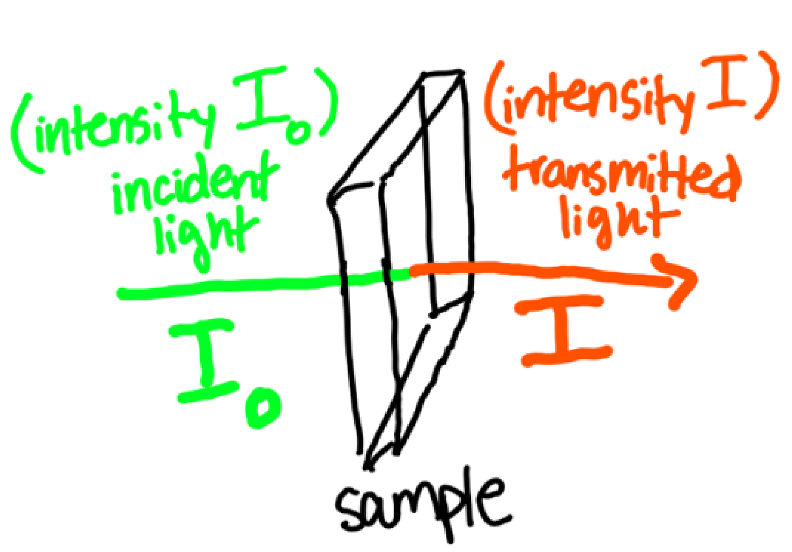


Fig. 2. IR spectrum of the fingerprint region for Coating 1 and 2 in Spectragryph. Coating 1 is the microscope cover glass coated through vapor deposition, and Coating 2 is the microscope cover glass coated through the soaking method.



$$T = \frac{I}{I_0}$$

$$A = \log_{10} \frac{I_0}{I}$$

Fig. 3. Image depicting relationship between incident light, I_0, and transmitted light, I, in relation to the Beer-Lambert Law. In the formulas to the right, "T" means transmittance of the translucent medium, and "A" means absorbance of the translucent medium.

Conclusion

We were able to coat APTES on microscope cover glass and operate the spectrometer to produce spectra of Coating 1 and 2. The spectral peak distinctions between the two coating methods imply that both differ from each other in terms of coating uniformity, suggesting that the developed microscope cover glass protocol for APTES is viable for FTIR spectral characterization.

My personal achievements include being able to operate a FTIR spectrometer and learning to edit raw spectral data in an optical spectroscopy software. Academically, this project has allowed me to deepen my understanding in IR spectroscopy, along with broadening my understanding of the Beer Lambert Law.

Initially for this project, we were aiming to utilize FTIR spectroscopy to analyze APTES coated on aluminum alloy samples, however after finding out that the spectrometer allocated for this project only allows for transmission mode for detection, meaning that the samples have to be translucent enough for infrared light to pass through, that lead to the development of the glass sample protocol. Furthermore, another limitation was figuring out how to operate Spectragryph. Initially, my goal was to have the y-axis as transmission, but I was unable to confidently convert intensity over to transmission. Hence, our presented data is in its primitive form. Future research could include converting the y-axis to either transmission or absorbance and comparing the labeled peaks on our experimental spectrum to reference literature concerning APTES. Then, we could introduce more coating methods and observe which condition allows for the experimental peaks to align most accurately to reference spectra. This could tell us which coating method produces the most even coating, which is beneficial towards APTES's purpose, which is acting as a glue between organic and inorganic materials.

References

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