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Synthesis and Surface Characterization of a Novel Plasma-polymerized (α -Pinene)-based Thin Film

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Abstract. α -Pinene is a bicyclic compound that is commonly sequestered from coniferous plants like pine trees. Several properties of pinene have been investigated, such as its isomerization capabilities and biological activity. However, the viability of pure pinene as an organic thin film has not yet been explored. In this work, we report the synthesis of an α -pinene-based organic thin film deposited on Al and glass substrates via plasma polymerization and its subsequent surface characterization. It was determined that the film generally became more hydrophobic as the α -pinene loading and the deposition time increased. More importantly, it was shown that specifying a pinene-Ar ratio of 50:50 yielded the highest contact angles at 94.22° and 110.38° for deposition times of 6.0 and 9.0 minutes, respectively. These results signify that a pinene-based organic thin film has been produced through the plasma polymerization synthesis route.

1. Introduction

The thin film industry has progressed considerably to adapt to the current needs and trends of the market. For major thin film industries, such as microelectronics, the thin film is typically sourced from metals and metal oxides. Thin films have also been reported to be suitable for pharmaceutical and biomedical applications, such as thin-film drug delivery and bioactive coatings for prosthetics. [1,2] While some inert and known biocompatible metals (e.g. Ti) have been routinely used for such applications, there is still a need to provide an alternative thin film that offers environmental sustainability, biocompatibility, and cost-efficiency.

To this end, the research for organic thin films have gained traction in the recent years. Due to its composition, organic thin films can naturally degrade or decompose, thereby promoting environmental sustainability. [3]

It is with this motivation that Gerchman, et al. developed a thin film based on the organic compound limonene. [4] Limonene is a member of the terpene class of compounds—organic substances that are cycloaliphatic or aromatic in nature. [4,5] The cost of its production is cheap, as it is often sourced from the by-products of the citrus production industry. i.e. from waste peels of fruits such as oranges and lemons.

Another potential compound that can be formed into a thin film is α -pinene. α -Pinene ($C_{10}H_{16}$), as shown in Figure 1, is a monoterpene organic compound typically extracted from the resin of pine trees and other coniferous flora. [6] Literature indicates that pinene has been known to exhibit antimicrobial and anti-inflammatory properties, with the (+)- α -pinene enantiomer showing promise as a human anti-osteoarthritic drug. [7]



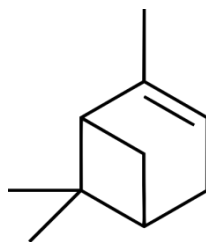


Figure 1. Structure of α -Pinene, the more abundant form of pinene in nature

Conventional polymerization routes prove to be difficult for compounds such as limonene and pinene because of the low conversion rates and its inefficiency arising from degradative chain transfer reactions. [8] Instead, the use of plasma polymerization affords the production of thin films from any organic precursor. Utilizing a stable plasma between two electrodes produces a myriad of reactive species like electrons, ions and radicals that bombard the organic molecule. [4,8] These highly energetic interactions initiate bond cleavage in the organic precursor, resulting in the fragmentation, rearrangement, and eventual crosslinking of the latter onto the substrate. [4,9]

Apart from its versatility, the plasma polymerization route is advantageous because of its ease of use. Several studies, prior to the work of Gerchman, et al., have reported the usage of plasma polymerization in creating organic thin films out of terpenoid substances. The work of Bazaka, et al., for instance, synthesized terpinen-4-ol using radio frequency (RF) plasma polymerization technique. [10] Pegalajar-Jurado, et al. and Chan, et al. have likewise used RF plasma polymerization to produce thin films based on 1,8-cineole and carvone, respectively, and explore their antimicrobial and biocompatibility properties. [11,12] While pinene belongs to the same family of compounds as the others previously mentioned, there have been no prior studies dealing with its synthesis and utilization as a thin film.

With these in mind, the present work is primarily geared towards synthesizing an (α -pinene)-based organic thin film via plasma polymerization. Subsequently, the study aims to characterize the surface morphology of the thin film formed and explore the effects of the deposition parameters, specifically the deposition time and the (α -pinene)-Ar gas ratio, on the said properties. However, due to constraints in time and resources, additional surface characterizations were not employed.

2. Methodology

2.1. Sample Preparation

Eighteen samples of 1 x 1-inch Al slabs were grinded with 1500 and 2000 grit size sandpaper. Then, the metal sheets were subjected to a series of cleaning in different solvents (deionized water, ethanol, acetone) via ultrasonication for 30 minutes. For characterization purposes, the same washing process was done to three 1 x 1-mm glass slides.

2.2. Plasma Polymerization

Deposition of pinene thin film was done via plasma polymerization in a customized RF plasma system in Plasma-Material Interactions Laboratory (PMIL). For the plasma polymerization of pinene, a base pressure of 10-15 Pa was first attained before introducing Ar and α -pinene (British Drug Houses Ltd.) gases. RF power was then set at 50 W to initiate plasma formation. Two levels for the deposition time were used (6.0 and 9.0 minutes). Meanwhile, three levels for the gas ratios were used: 25-75, 50-50, and 75-25 percent pinene-to-argon. The gas ratios were measured via partial pressure, i.e. 25-75% pinene-to-argon implies the use of 25 Pa of pinene to 75 Pa of Ar for the plasma polymerization process.

2.3. Characterization

Sessile drop test method was conducted to each treated Al samples by dropping 5.0 μ L of deionized water onto the metal surface using a micropipette. The droplets' images were captured using a high magnification camera (DinoCapture 2.0) and the contact angle was processed using ImageJ.

Surface analysis, including surface morphology and homogeneity, was done via FESEM (InTouchScope, UP Baguio) in SEI mode with an accelerating voltage of 10 keV and a working distance of 19 mm. Analysis of the chemical composition of the plasma polymerized α -pinene was done via FTIR-ATR ranging from 4000 cm^{-1} and 500 cm^{-1} .

3. Results and Discussion

Shown in Figure 2 below is the trend for the average H_2O contact angles obtained for the plasma-polymerized pinene thin films. As seen in the figure, there was a consistent increase in hydrophobicity of the treated Al surface as the deposition time was increased from 6.0 to 9.0 mins. The said trend occurred for all the samples with constant pinene-Ar gas ratio but varied time of exposure. The phenomenon observed implies that heightened exposure time deposited more α -pinene layers as compared to that with minimum time of deposition since prolonged deposition amplifies the probability that the ionized solvent would interact with the metal surface.

Using the same figure, it can be noticed that the trend observed for varying gas ratios deviated from ideality. In line with Le Chatelier's Principle, it was expected that additional amounts of the organic reactant would eventually result to a superior hydrophobicity of the surface. [13] However, the results showed that the best gas ratio was at 50% pinene and 50% Ar. It can be inferred that the lowest setting was governed by Ar sputtering. On the other hand, the highest pinene-Ar ratio resulted to insufficient amount of Ar gas that will ionize the bulky organic precursor and carry it to the substrates. Thus, the lack of ionizing gas possibly resulted to the inefficient deposition of α -pinene.

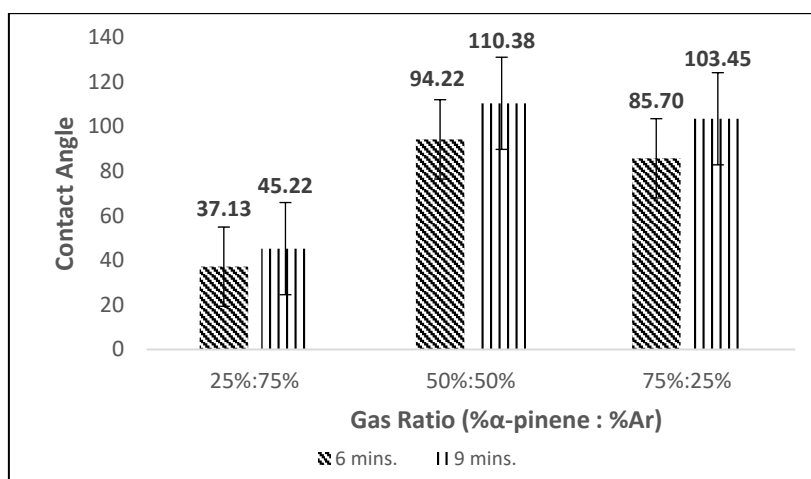


Figure 2. Water contact angle trend for hydrophobicity assessment

FTIR-ATR was done to determine the chemical composition of the deposited α -pinene thin films. Figure 3 shows the FTIR spectral diagram of the plasma polymerized α -pinene of varying monomer proportions. It is observed that several peaks associated with α -pinene were generally no longer present, such as those in 2800-2900 cm^{-1} corresponding to $=\text{C-H}$ stretching, while formation of new bands occurred especially at around 2300-2400 cm^{-1} . However, it is shown on Figure 3 that the thin film with 75% α -pinene loading showed low-intensity peaks corresponding to the spectra of the monomer. This is evidenced by the broad and low-intensity peak at 2900 cm^{-1} as well as in 1000 and 1400 cm^{-1} , all suggesting the presence of unpolymerized pinene in the film.

Due to the formation and breaking down of bonds, the plasma polymerized polymer thin film is not considered as a poly(α -pinene) homopolymer, rather it is a polymer derived from α -pinene. The bands of the plasma polymerized pinene were also less well-defined; this implies that there has been a decrease in the bond homogeneity. This decrease in bond homogeneity can be correlated to the crosslinking that occurs during plasma polymerization; in this process, plasma polymers usually have random bonding and cross-linking. [4,14]

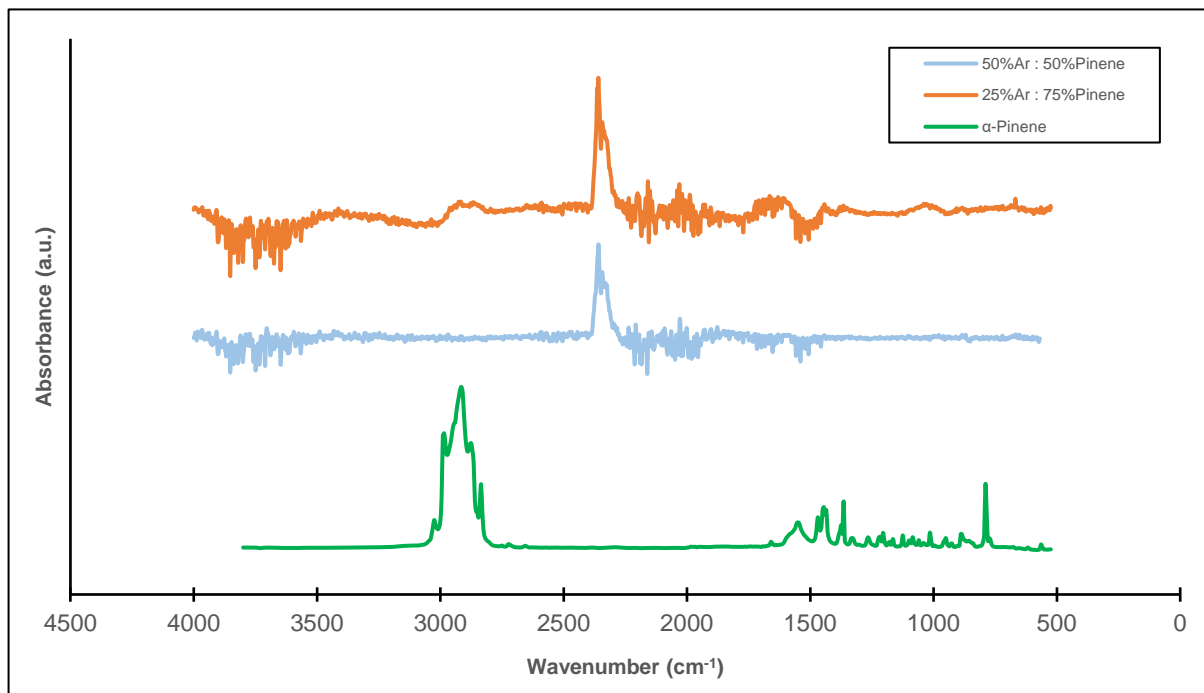


Figure 3. FTIR spectra for the pinene-based thin films with 6.0 minutes deposition time and the indicated gas ratios. FTIR spectra of α -pinene (NIST, 2018) included for comparison

Figure 4 shows the SEM images of the plasma polymerized pinene deposited under 9 mins., with varying gas ratios. It is observed from the figure that for samples deposited with 25:75 and 50:50 gas ratios, no features were apparent, signifying a uniform deposition of the plasma polymerized pinene. A smooth surface finish was observed for the thin film, this implies that the formation of a flat plasma-polymerized pinene was able to level the surface roughness and imperfections of the substrate. However, for the sample with 75:25 gas ratio, bubble-like features were observed, and this is possibly due to the impurities present on the surface of the silicon glass wafers.

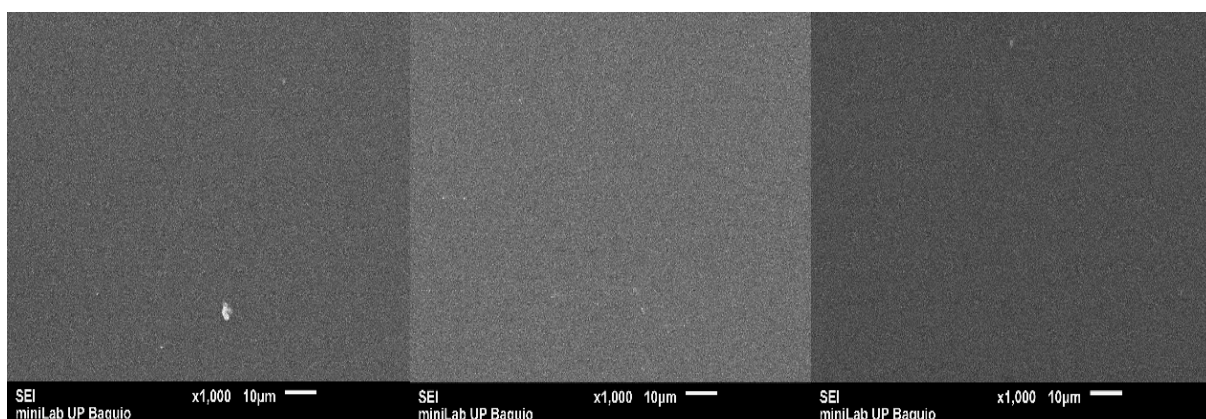


Figure 4. FESEM micrographs of the plasma-polymerized pinene thin films deposited on Si substrates taken at 1000x. A pinhole-free image is seen despite varying α -pinene concentrations of 25%, 50%, and 75% (from left to right)

4. Conclusions

A thin film layer of α -pinene was successfully deposited onto the Al substrate. IR analysis suggested that the composition of the thin film only reflects select hydrocarbon bonds and that the plasma polymerization route eliminated the unsaturation present in the α -pinene precursor. On the other hand,

inspection of the surface morphology of thin film revealed a featureless, pinhole-free surface, consistent with the typical morphology of plasma-polymerized films. For each pinene-Ar gas ratio, it was observed that the hydrophobicity of the Al surface significantly improved as deposition time was increased from 6.0 to 9.0 minutes. The pinene-Ar gas ratio that exhibited the superior hydrophobicity was found out to be at 50:50 gas ratio, regardless of the deposition time, with average water contact angles at 94.22° and 110.38° for samples subjected to 6.0 and 9.0-minute deposition times, respectively. The findings in this work suggest that α -pinene can indeed be deposited as a thin film. This may prove to be significant in the development of organic thin films for a variety of applications such as coating for medical equipment and in the study of organic thin film transistors for flexible electronics applications.

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