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Araştırma / Research

WETTABILITY, OPTICAL AND CHEMICAL CHARACTERISTICS OF PLASMA-POLYMERIZED D-LIMONENE THIN FILMS

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ABSTRACT

In this study, organic based polymer thin films were obtained on various substrates using D-Limonene essential oil, which is an organic compound by radio frequency (RF) plasma polymerization technique. The optical band gap and absorption spectra of thin films were investigated by Uv-VIS spectra and depending on the increased RF power, the optical band gap of the thin films was found to be 3.19, 3.25 and 3.31 eV, respectively. WCA analyzes were also performed to determine the wettability properties of thin films and all thin films had hydrophilic properties and these properties were significantly affected by increased RF power. Considering both the morphological and optical properties of plasma polymerized (pp) D-Limonene thin films, it is thought that these films may be an alternative to those already used in current electronic applications due to their organic compound-based nature.

Keywords: Polymerisation, organic thin films, RF, D-Limonene.

PLAZMA POLİMERİZE D-LİMONENE İNCE FİLMLERİN ISLANABİLİRLİK, OPTİK VE KİMYASAL ÖZELLİKLERİ

ÖZET

Bu çalışmada, radyo frekansı (RF) plazma polimerizasyon tekniği ile organik bir bileşik olan D-Limonene esansiyel yağı kullanılarak çeşitli alt tabakalar üzerinde organik bazlı polimer ince filmler elde edilmiştir. İnce filmlerin optik bant aralığı ve absorpsiyon spektrumları Uv-VIS spektroskopisi kullanılarak incelenmiş ve artan RF gücüne bağlı olarak, optik bant aralığı sırasıyla 3,19, 3,25 ve 3,31 eV olarak belirlenmiştir. İnce filmlerin ıslanabilirlik özelliklerini belirlemek için WCA analizleri de gerçekleştirilmiş ve tüm ince filmlerin hidrofilik özelliklere sahip olduğu ve bu özelliklerin artan RF gücünden önemli ölçüde etkilendiği belirlenmiştir. Plazma ile polimerleştirilmiş D-Limonene ince filmlerin, hem morfolojik hem de optik özellikleri göz önünde bulundurulduğunda, bu filmlerin organik bileşik tabanlı olmaları nedeniyle, mevcut elektronik uygulamalarda kullanılanlara alternatif olabileceği düşünülmektedir.

Anahtar kelimeler: Polimerizasyon, organik ince filmler, RF, D-Limonene.

1. INTRODUCTION

Recently, cross-linked polymers have been actively used in light emitting diodes, sensors and solar cells [1-6]. However, various organic materials, organic conductors, organic semiconductors and insulators, are also used in organic devices. Due to its wide application area, the importance of polymer materials has increased dramatically. In organic materials, the molecules are connected to each other by weak Van Der Waals bonds,

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*Corresponding author / Sorumlu yazar. Tel.: +90 04422314016; e-mail / e-posta: obayram@bayburt.edu.tr which allow the resulting material to be flexible [7]. The solid-state structure of the polymer materials, unlike inorganic materials, is based on the van der Waals interaction between the polymer chains. In polymers, 'π-conjugated bonds', which lead to delocalized and π-orbitals also greatly, affect the optical and electrical properties of the materials [8]. The formation of conjugated polymers depends on the thin film techniques and some important parameters of these techniques. Conjugation polymers are obtained by conventional polymerization, electrochemical polymerization and plasma polymerization techniques. It is understood from the literature that the most suitable method for obtaining these polymers is plasma polymerization technique. Using this technique, the resulting product is cost-effective and environmentally friendly, and thus significantly increases the importance of the technique. Furthermore, compared with other polymerization techniques, the process of obtaining a thin film in the plasma polymerisation technique takes place in a single process, and thus this technique allows minimizing external factors. In this technique, it is possible to polymerize all the volatile compounds present in the plasma environment by optimizing the coating parameters. The plasma polymers have mechanical and thermal stability with the substrate and are well adhere to the substrate surface. These polymer surfaces have also a smooth, pinhole-free and homogeneous structure.

In the literature, mechanical [6], chemical [9-11] and optical [12] properties such as refractive index, extinction coefficient and optical band gap of thin films obtained by plasma polymerization technique have been investigated by many researchers [13-17]. In the study conducted by Bazaka et al. [18], biocompatibility and antibacterial activities of polymers obtained by using radio frequency plasma polymerization technique were investigated. Essential oil components, which are natural products, have been obtained on the glass substrates under the optimum (optimal) coating parameters. The polymeric coatings obtained were shown to exhibit significantly resistance to various bacteria and viruses, and their antibacterial effects were compared with the antibiotics used against these bacteria. They found that both antibacterial activities and biocompatibility levels of polymeric coatings were better than antibiotics. In another study by Easton et al. [10], they obtained polymeric organic thin films on glass substrates using the RF plasma enhanced chemical vapor deposition (RF-PECVD) technique from the 1.8 Cineole essential oil component. They determined that thin film coatings they obtained were 220 nanometers thick by Spectroscopic Ellipsometry. Fourier Transform Infrared (FTIR) spectroscopy was performed to determine the chemical structure of monomer and polymer materials and these structures were compared to confirm the chemical structure of the polymer. However, the refractive index and absorption coefficient of the thin films were calculated as 1.543 (500 nm) and 0.001 (500 nm), respectively. Atomic Force Microscopy (AFM) images of thin films were obtained and the surface roughness of the films was determined.

The researchers also revealed that the polymeric coatings obtained by taking contact angle measurements of thin films showed hydrophobic properties. In a study by Jacob et al., they stated that they obtained an alternative to organic semiconductor materials, which are widely used in organic electronics. According to this study, polymeric coatings were obtained from Lavandula Angustifolia essential oil component on glass substrates by using RF-PECVD technique. The thickness of the coatings obtained varies between 200 nm and 2400 nm. Forbidden energy ranges of the coatings were determined as 2.93 eV, the absorption coefficient and refractive indexes were determined as 0.01 and 1.565. Polymeric coatings obtained from Lavandula Angustifolia essential oil component, which is a natural product, have been seen as a remarkable material among organic semiconductors because of their low cost and environment friendly compared to other organic devices [19]. In a previous study by us [20], Polymer thin films were obtained by using Cinnamaldehyde essential oil by using RF-PECVD technique and the effect of RF power on some structural properties of these films was investigated.

In the study, it was determined that the applied RF power has an effect on the structural and morphological properties of the films. Thin films were found to be semiconductor and optically transparent. In this study, it was aimed to obtain polymeric thin films on glass surfaces by using RF plasma polymerization technique from D-Limonene essential oil components, which are terpene alcohol. Thin films were obtained at 25, 50 and 75 RF power and 30 minute coating time. Polymeric thin films were also characterized by AFM, RAMAN, FTIR, Uv-VIS spectroscopy and Water Contact Angle (WCA) measurement.

2. MATERIALS AND METHODS

D-Limonene essential oil, 98% pure, was purchased from Sigma Aldrich. The RF plasma polymerization system was installed by Nanovak vacuum systems company (Ankara, Turkey). The system consists roughly of quartz glass, vacuum pump, RF power supply and matching units. Quartz and Potassium bromide (KBr) glass were used as substrate material. Substrates were washed sequentially with ethanol and propanol and rinsed with deionized water. In addition, substrates were cleaned with ultrasonic cleaner. Before the film coating process, the plasma polymerization system was operated and the surface of the substrate was subjected to Argon (Ar) plasma treatment. By applying the Ar plasma to the vacuum medium, it is intended to remove the possibly foreign atoms from the substrate surface. The Ar plasma was performed for about 1 minute. After surface cleaning with Ar plasma, the pressure of the vacuum chamber was adjusted to approximately 20 mTorr with the help of a vacuum pump. The D-Limonene compound, which was then used as the monomer material, was sent to the plasma system with the help of a sensitive valve. Using a precision valve, it is intended to control the flow rate of the monomer to the vacuum medium. At a constant flow rate, the pressure of the vacuum chamber was determined to be about 380 mTorr. With the help of an RF power supply, voltage is applied to the vacuum chamber and plasma is obtained from the monomer in this pressure. All thin films were grown at 30 min coating time and at a pressure of about 380 mTorr. RF power values are set to 25, 50 and 75 W respectively. The schematic representation of the RF plasma polymerization system is given in Figure 1.

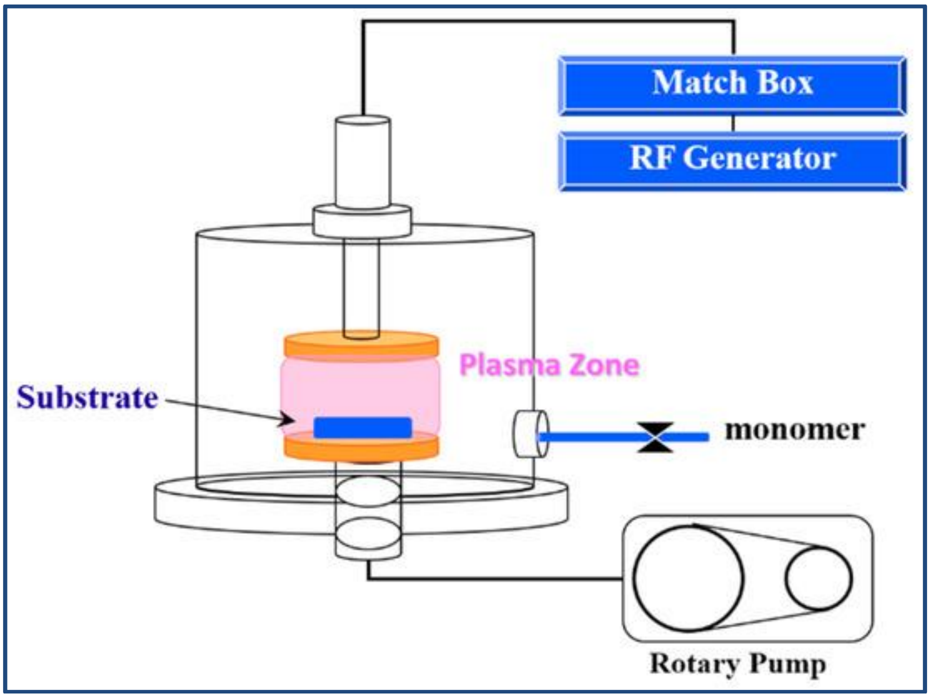

Figure 1. Schematic representation of RF-Plasma Polymerization system [10]**.**

3. RESULTS AND DISCUSSION

3.1 Chemical properties of plasma polymer thin films

Figure 2. shows the FTIR spectra of polymer thin films and precursor monomer. FTIR spectra reveal functional groups and chemical bonds of precursor and pp D-Limonene films. Hydroxyl groups (O-H) were detected at about 3700 cm^{-1} [13, 18, 19] for polymer thin films and 3300 cm^{-1} for the precursor monomer. Depending on the RF power, the OH groups for the polymer thin film are shifting from 3300 cm^{-1} to 3700 cm^{-1}, and there is a reduction in the intensity of these OH peaks. Bonds at 2976, 2929, 2894 and 2798 cm^{-1} [13, 19] in the FTIR spectra of the monomeric material are C-H stretching vibrations. These bonds are more pronounced in polymer thin films. However, the C-H stretching band of monomer is sharper and more intense than polymer thin films. The C-H bending vibration of the monomer material was detected at 1452 cm^{-1} and 1376 cm^{-1} [13, 18-20], respectively, but this vibration band is 1365 cm^{-1} more broader for polymer thin films. The C-H bending vibration of the polymer thin films was very poor, but no significant difference was detected due to RF power. The C-O stretching band was detected at 1112 cm^{-1} [18, 19] for the monomer material, but none of the polymer thin films could be detected. However, C-H deformation peaks were observed at 1002 cm^{-1} [18, 20], 923 [18], 837, 692 and 567 cm^{-1}, respectively, with strong peak to weak peak order. In this region, which is defined as the fingerprint region in the polymer thin films, many peaks could not be detected but only one C-H deformation peak was detected at 636 cm^{-1}.

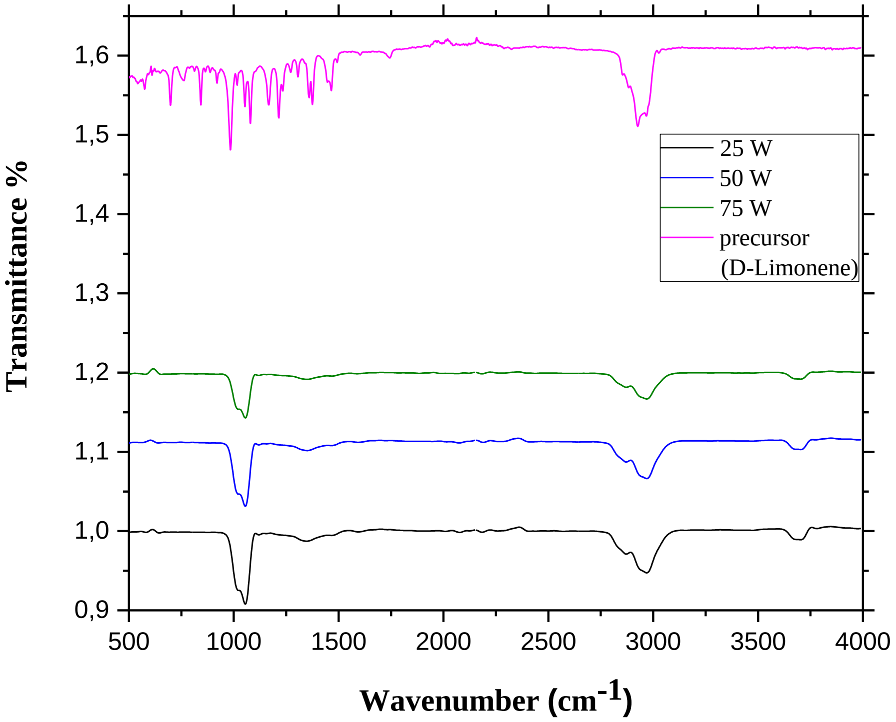

Figure 2. FTIR spectra of precursor materials and pp D-Limonene films at various RF Powers.

Characteristic peaks for polymer thin films obtained from D-Limonene precursor monomers were also determined by Raman spectroscopy. The spectra of polymer films obtained at 25 W and 50 W RF energies showed significant peak at approximately 2920 cm^{-1} [21, 22] wavenumber. This strong peak is thought to represent the C-H stretch. However, the peak corresponding to the C-H bending band at 1440 cm^{-1} [21] was detected for polymer films obtained at 25 W and 50 W RF power. For the polymer thin film obtained at 75 W RF power, these peaks could not be detected in the Raman spectroscopy. The weaker of the peaks intensity detected in the Raman spectrum of this thin film can be explained by the thin film thickness. If the film thickness is too low, the beam sent to the surface by Raman spectroscopy damages the polymer due to the high energy it has, and therefore, it is considered that sufficient information cannot be provided about chemical properties from this surface. This is confirmed by the FTIR spectra of thin films. The presence of characteristic peaks was determined for all thin films obtained on the KBr substrate.

3.2 Optical properties of pp D-Limonene thin films

The absorption spectra of the polymer thin films and the optical band values were determined by UV-Vis spectroscopy and optical absorption spectra were presented in Figure 4. From the absorption spectra of the thin films, it is understood that the maximum absorption for all thin films is obtained at a wavelength of 320 nm. The highest absorption value was detected in thin films obtained at 75 W and 50 W RF power. The sharp peaks determined at about 320 nm can be explained as follows. Due to the photon absorption, electrons are pushed from the valance band into an empty band, which causes a significant increase in the absorption coefficient. However, there are significant differences in this peak intensity depending on the RF power. The difference in these peaks is thought to be due to the thickness of the thin films (13). In general, in the wavelength range of 400 to 850 nm, the absorption electrons are attributed to the transition from π (binding) to π* (antibaking). This transition causes absorption peak in the absorption analysis of thin films. The optical band gap (E_g) can be determined from the following equation between the absorption coefficient (α) and the photon energy (hν) [23].

$$(\alpha h\,\nu)^n = C\,(h\,\nu - E_g)$$

where, C and n is constant, E_g is the band gap value of the material and h is the Planck's constant. The optical band gap of thin films was obtained at a range of 3.19-3.31 eV. In addition, as the RF power increased, a slight increase in the optical bandgap of the thin films was detected. These values indicate that thin films have approximately semiconductor properties (~ 3.00 eV). Furthermore, the semiconductor property of thin films can be further increased by doping. In addition to the semiconductor properties, the fact that these thin films are obtained from organic compounds and that the resulting product is environmentally friendly increases the potential for their use as an alternative material in electronic circuits.

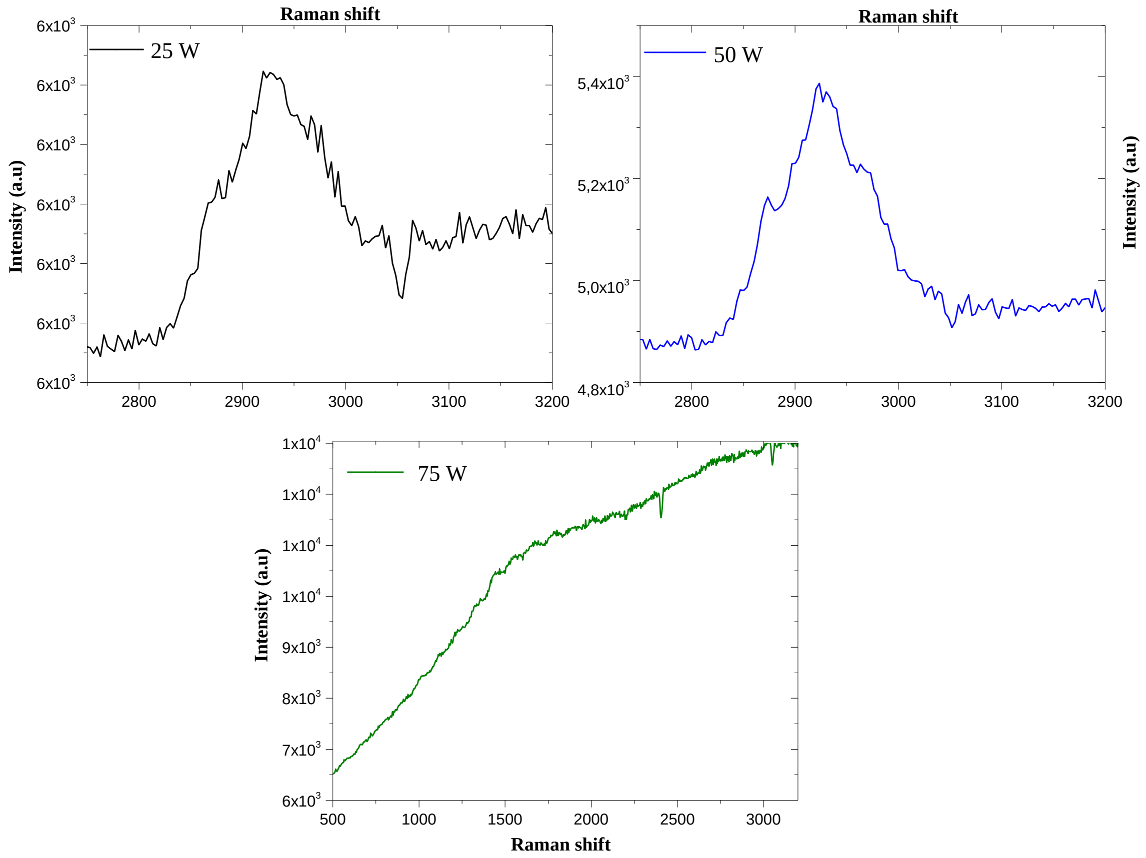

Figure 3. Raman spectra of pp D-Limonene thin films.

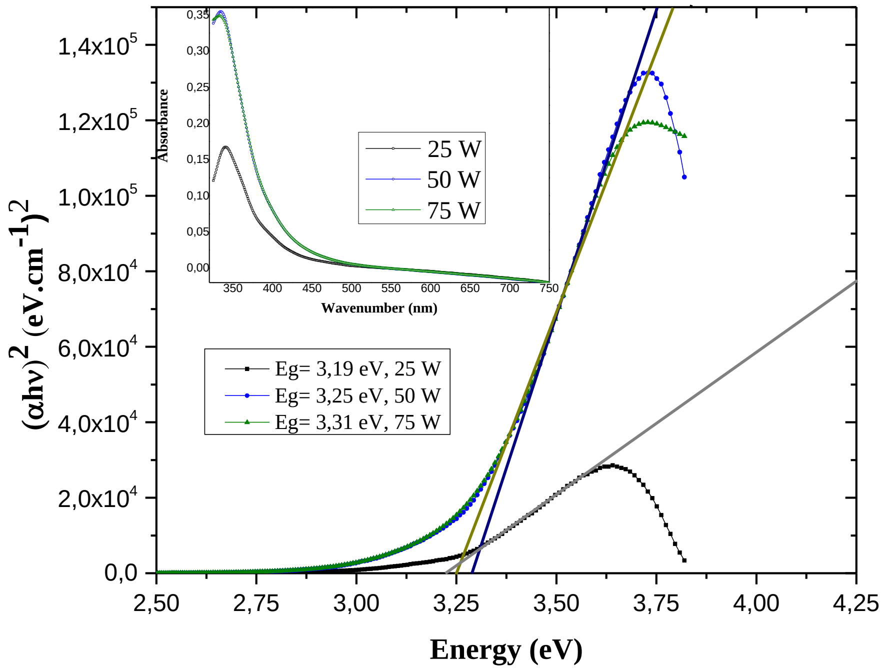

Figure 4. Tauc graph plotted for synthesized D-Limonene.

3.3 Morphological properties of pp D-Limonene thin films

The surface morphological characteristics of the thin films were analyzed using AFM and the AFM images of the thin films are given in Figure 5. These analyzes were performed using 5x5 μm^2 area for each thin film. Average surface roughness (R_a) and maximum peak height (R_{max}) are important factors for optical and electronic applications of thin films. It is generally desirable that the surface is very smooth and homogeneous. Significant differences were found between these values of polymer films obtained at different RF energies. The R_a values were determined to be 0.19 nm, 0.21 nm and 0.36 nm, respectively, with increasing RF power. The R_a values of thin films tend to increase with RF power. These results are in good agreement with the literature [11, 19, 20, 24]. However, in a study conducted by Bazaka et al., they suggested that Ra values of thin films obtained by increasing RF power decreased. Easton et al. also noted that the increase in RF power resulted in a decrease in the R_a values of the thin films. The R_{max} values of the polymer films tend to increase by 1.29 nm, 1.46 nm and 8.14 nm, respectively, with increasing RF power. These morphological features of the thin films reveal that all thin films are nearly homogeneous, nonporous and smooth. However, significant differences have been identified for these properties with increased RF power. In particular, the surface roughness of the thin film obtained using 75 W RF power is quite different from other thin films. This is due to the fact that when the thin film is obtained, the etching process is effective as well as the deposition process. From Raman spectroscopy and AFM images of all thin films, it is understood that the surface morphology of the thin film obtained at 75 W RF power is not homogeneous and contains almost no characteristic peak. However, considering the spectrum obtained from Raman spectroscopy, it does not mean that no thin film are formed on the substrate surface. Because the images obtained from the AFM analysis show that the surface roughness of the thin film obtained at 75 W RF power is considerably higher than the others. This is attributed to the idea that thin film is formed on the substrate surface. As a result, it is understood from both AFM images and Raman spectroscopy that the thin film obtained at 75 W RF power does not have homogeneous morphology, but growth is observed in some regions, even if not all of the surface.

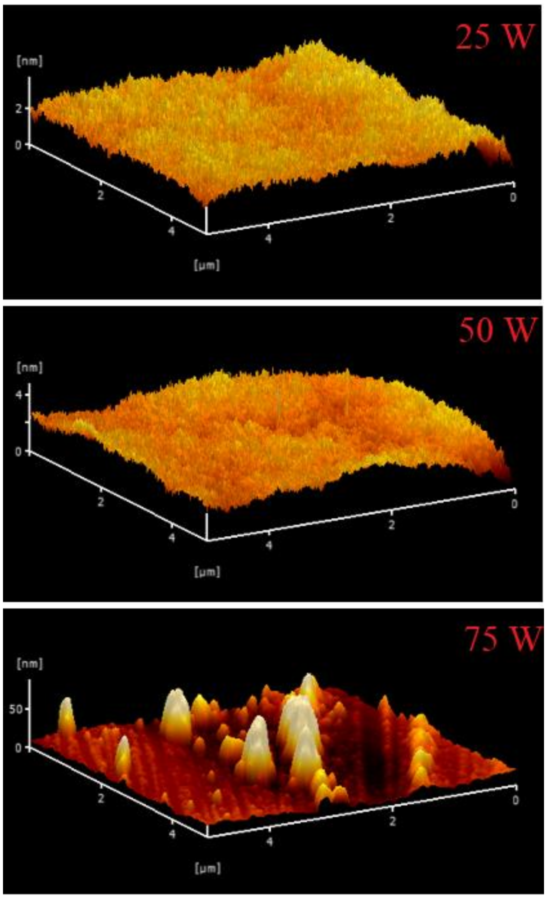

Figure 5. AFM images of pp D-Limonene thin films obtained at various RF Powers.

3.4 Wettability properties of pp D-Limonene thin films

The measurement of the contact angle between a solid surface and a liquid drop is widely used to determine the wettability characteristic of the surface. If the contact angle between the solid surface and the liquid droplet is less than 90 degrees, it is hydrophilic and if it is greater than 90 degrees, it is called hydrophobic surface. Figure 6. shows the contact angle measurements of thin films. The contact angle measurements of thin films were measured as 45, 71 and 72 degrees, respectively; with increasing RF power (25 W, 50 W and 75 W). These results imply that all thin films are hydrophilic. However, the hydrophilic character tends to decrease with increasing RF power. The reduction of the hydrophilic property can be explained as follows. The most important is the surface energy described by some researchers, depending on the surface roughness. AFM analyzes of thin films reveal that the average roughness values of the surface increase significantly with increasing RF power. It is thought that thin film surface energy decreases with increasing surface roughness. Another important parameter is the presence of the OH hydroxyl group in the polymer obtained from the monomer. Surfaces having a hydroxyl group are generally of hydrophilic character [25]. In this study, decrease in peak intensities of OH hydroxyl group from FTIR spectra of thin films was detected by increasing RF power [20, 26]. The decrease in peak intensity of the hydroxyl group implies an increase in the hydrophobic property of the surface. It is understood that the contact angle results of thin films and the decrease in the peak intensity of the hydroxyl group obtained from the FTIR spectra are compatible with each other.

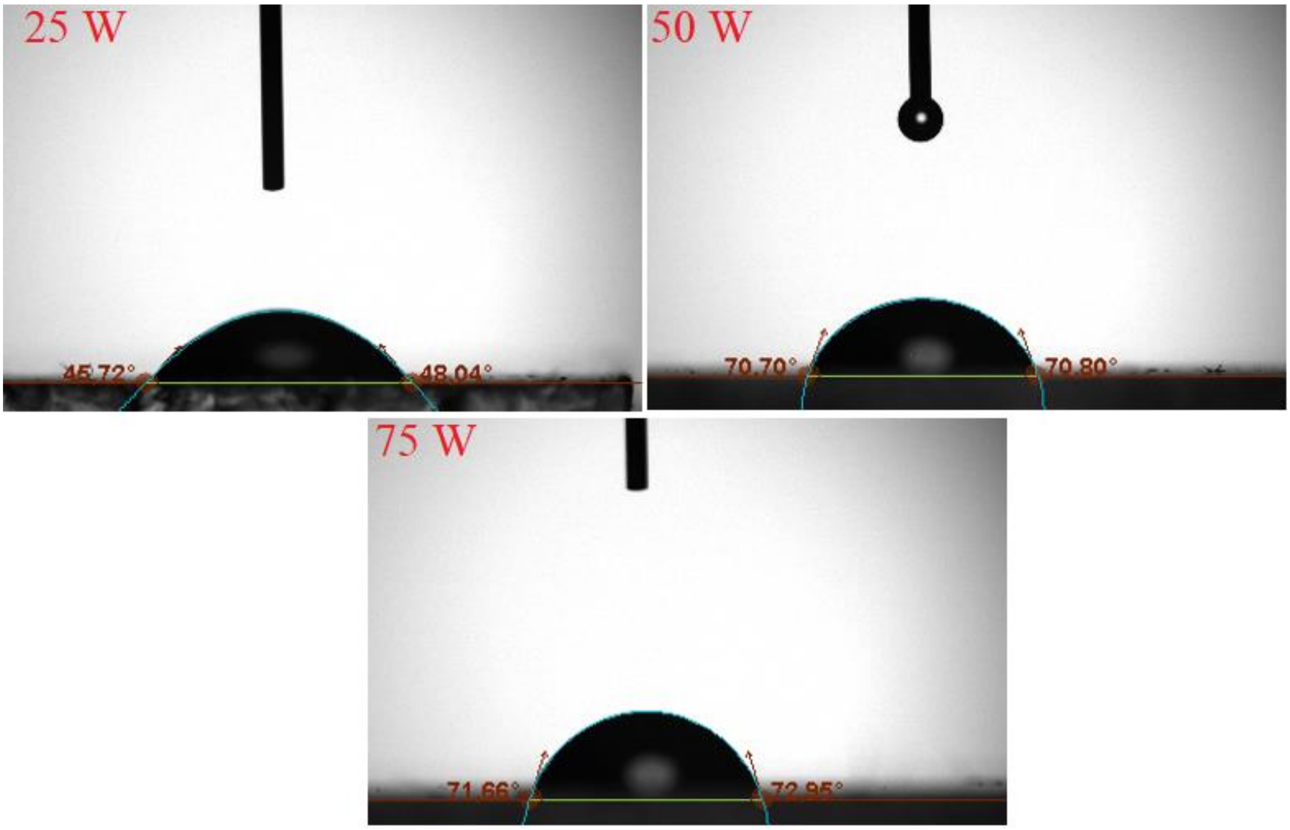

Figure 6. Contact angle measurements of pp D-Limonene thin films.

4. CONCLUSION

Plasma polymerized D-Limonene thin films were grown on KBr and quartz substrates using various RF power values. AFM analysis of thin films reveals that the film surfaces have smooth, pinhole and homogeneous structure. In this study, it can be said that the film obtained using 25 W RF power has a more homogenous and smooth morphology than others. However, it is thought that the film obtained with the power of 75 W RF does not have the desired thin film properties in terms of both roughness and homogeneity. The chemical properties of all thin films were examined by both FTIR and Raman spectroscopy, and the results of these analyzes showed that the chemical properties of the monomer were largely preserved. Using Uv-VIS spectroscopy of all thin films, a sharp peak was determined at about 320 nm, and the intensity of this peak was determined to be weaker at 25 W RF power. The optical band gap of the D-Limonene films was between 3.19 eV and 3.31 eV. All thin films had a hydrophilic character but according to both the film morphology and the presence of OH groups, this characteristic shifted slightly to the hydrophilic character. Optimization of the coating parameters in the plasma polymerization technique, it is possible to obtain surfaces with the desired optical and chemical properties. Thus, the film properties obtained in this study can be further improved. In addition to this study, D-Limonene monomer is known to have antibacterial properties. It is thought that these thin films can also be used in the biotechnology field by obtaining antibacterial surfaces by using this technique.

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