FTIR analysis of plasma-polymerized toluene films using a PECVD method

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Abstract

Plasma-polymerized toluene films were successfully grown using a plasma-enhanced chemical vapor deposition method (PECVD). The films were deposited on a glass substrate at room temperature. Structural investigations, using an FT-IR spectrometer, confirmed that all films have structure of toluene compound. Variation of polymer-like film properties with change of microwave power and toluene to argon ratio was studied systematically. The C-H stretching peak increased as the microwave power increased, indicating a higher degree of cross-linking in the film. These findings suggest that toluene films may have a promising role in corrosion protective applications.

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Introduction

Plasma-enhanced chemical vapor deposition (PECVD) has attracted considerable interest in the field of synthetic polymers [1-5]. It is a very efficient approach to produce homogeneous organic coatings or thin films on large area substrates, including metals, glass, and thermally sensitive substrates such as porous and nanostructured plastics [6-9]. Plasma polymerization is an innovative technique for depositing organic films. It is used to fabricate polymer-like films from a variety of organic materials. The films created by plasma polymerization are structurally distinct from conventional method [10, 11]. Polymers synthesized by plasma are being identified as a new branch of polymer chemistry [12]. During the polymerization process, which is started by high-frequency electromagnetic waves, the monomers are fragmented into ions, electrons, and radicals [5]. The radicals adsorb, condense, and polymerize on the substrate (Fig 1). The process is carried out at low pressure and temperature, resulting in a polymerized film with a higher cross-linking density than conventional films.

This study aims to understand the toluene plasma deposition mechanism and study the chemical structure of the deposits by FTIR analysis. Microwave plasmas have attracted significant attention concerning their high-frequency (2.45 GHz) effects on the properties of polymer-like organic films, compared to radiofrequency (MHz) discharge [12]. Variation of polymer-like film properties with change of deposition parameters such as plasma microwave power and toluene to argon ratio needs to be studied systematically. Plasma polymerized coatings have significant potential as corrosion barrier films [13-18]. In the current

work, a polymer-like film was successfully deposited on a glass substrate with good structural properties, allowing it to be applied for corrosion protection on metal substrates.
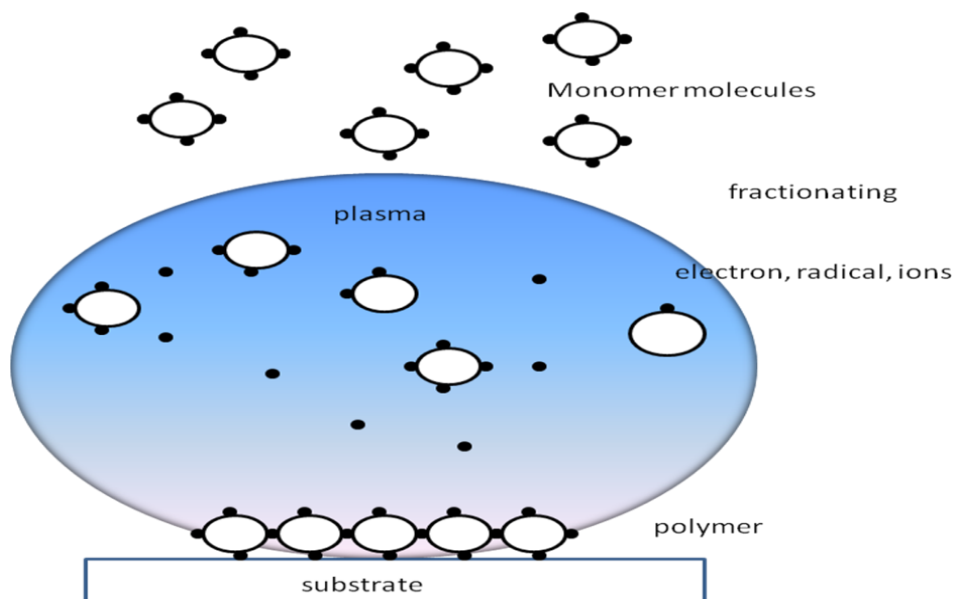

Fig.1. Mechanism of Plasma Polymerization

Experimental procedure

Polymer-like organic films were deposited on glass substrates using plasma-enhanced chemical vapor deposition (PECVD) method. Toluene monomer (C_7H_8) was used as organic precursor. Plasma polymerization was carried out in a cylindrical stainless steel vacuum chamber. The chamber, with a diameter of 14 cm, has four inlet ports. One is used for the flow of argon gas and the injection of toluene monomer. The toluene is placed in a glass evaporation cell and coupled to the T-shaped tube using needle valves. The second port is connected to a vacuum system that allows atmospheric air to be pumped out of the

chamber. The microwave source is connected to the third port via the waveguide rectangular tube to concentrate all the power inside the chamber. The fourth port has a glass window to monitor the plasma process. A wide-range manometers having Pirani and Penning gauges monitors the chamber pressure. The chamber was evacuated from atmospheric air to 10^{-5} Torr. Microwave plasma (0- 900 W- 2.45 GHz) was used to generate a glow discharge necessary to initiate the deposition process. Glass substrates, with dimensions of (1.5×1.5) cm^2, were used to deposit the films. The film quality is directly impacted by the substrate conditions. To achieve a homogeneous, defect-free deposition, the glass substrates were cleaned using distilled water and acetone. Then they were exposed to Ar plasma in situ to create an oxygen-free surface and improve film adhesion. This process was carried out at 720 watt of Mw power and lasted up to 20 min. The PECVD process was run at 100-800 W Mw power, a deposition time of 10-25 minutes, and a toluene/argon ratio of 10-100%. Fourier transform infrared (FTIR; Varian Inc 640-IR), was used to record the infrared spectra, within the 700 - 4000 cm^{-1} wavelength range, and a spectral resolution of 4 cm^{-1}. Film thicknesses based on the interference phenomenon were measured using the variable thickness method (wedge-shaped) [19]. Fig.2 shows how fringes in a wedge-shaped air film can be used to determine the thickness of the film. The average film thickness (t) was calculated according to Equation. (1):

$$t = LN\lambda / 2(x_2-x_1) \qquad (1)$$

Where t is the thickness of the film, L is the length of the air wedge, N is the number of dark fringes lying between the positions x_1 and x_2, λ is the wavelength of sodium lamp (5894 A^0) and x_2, x_1 are the positions of dark fringes at two distance points.
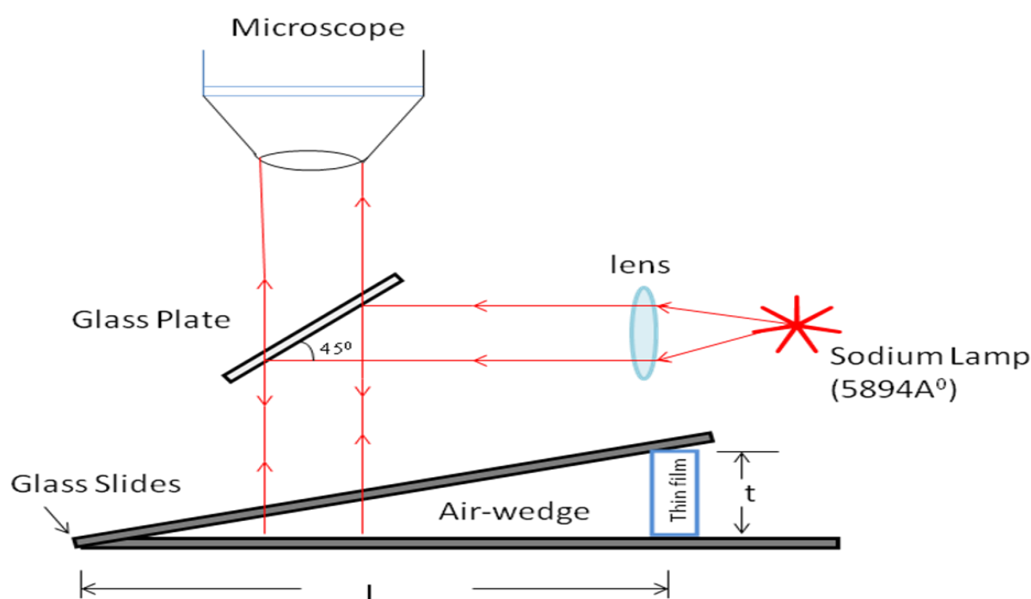
Fig. 2. Determination of the thickness of toluene film by obtaining fringes in wedge shaped method

Result and discussion

FT-IR spectroscopy was used to identify structures of the films. The resulting spectrum can be used to measure the concentrations of functional groups in plasma polymerization and thus the crosslink density of hydrocarbon plasma polymers. Fig. 3 shows the IR spectra of the liquid toluene which used as a monomer in this study. The spectrum confirms the standard pattern of the general liquid toluene [20]. The IR spectrum of liquid toluene shows two peaks belongs to C-H stretching bonding of the aromatic group at $720 \sim 800$ cm^{-1} and 3000 cm^{-1}. In addition, one peak related to the aromatic C=C stretching bonding appears at approximately $1540 \sim 1640$ cm^{-1}. Fig. 4 (a-d) shows the IR spectra of glass surface coated with toluene films at different toluene ratios and microwave power. All of the transmittance spectra confirm the structure of toluene compound.

The C-H stretching peak increases as the microwave power increases and toluene ratio decreases. This is possibly explained by the fact that toluene benzene ring was broken by the plasma polymerization surface treatment. Hence, the toluene films exhibit a higher degree of cross-linking with increasing microwave power. This improvement in cross-linking by plasma contributes to the increased densification of deposited films. The aromatic C=C stretching peak did not show significant changes with the increment of microwave power but increased with decreasing toluene ratio. Yu et al. [31] reported that the C-H stretching peak increases with RF power for their toluene film prepared by the PECVD method. Raynaud et al. [21] studied the gas phase composition of hexamethyldisiloxane microwave plasma films using FTIR spectroscopy under different power conditions. They reported that the microwave power change the amount of CH_x groups in the film. The band lies around 3400 cm owing to O-H vibration. It may suggest the presence of oxygen in the film, even though it was not incorporated into the plasma polymerization process. The presence of radicals enables the incorporation of O-containing groups through reactions with oxygen. It is probably due to the residual air inside the reactor during film deposition. Adding argon gas with toluene precursor during plasma polymerization was to prevent powder formation. The powder is formed by the reaction in the gas phase instead of an interface reaction between the gas (toluene vapor) and the surface (glass). The parameters that may promote the gas-phase reaction include: High flow rate, long treatment times, high power conditions, monomers with a fast reaction rate, and a higher activation frequency [21]. Argon gas increases the working pressure and decreases the toluene flow rate, thereby preventing powder formation. The estimated value of toluene film thickness (t) using the wedge-shaped method is 58± 5μm
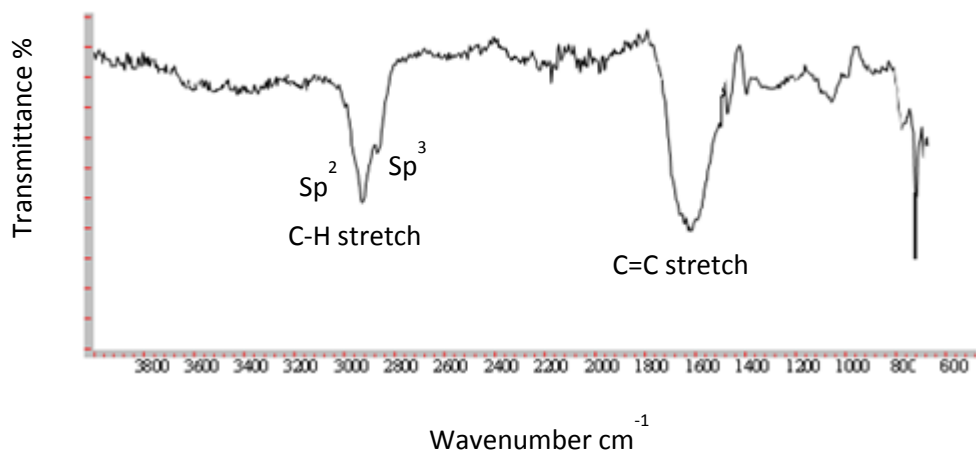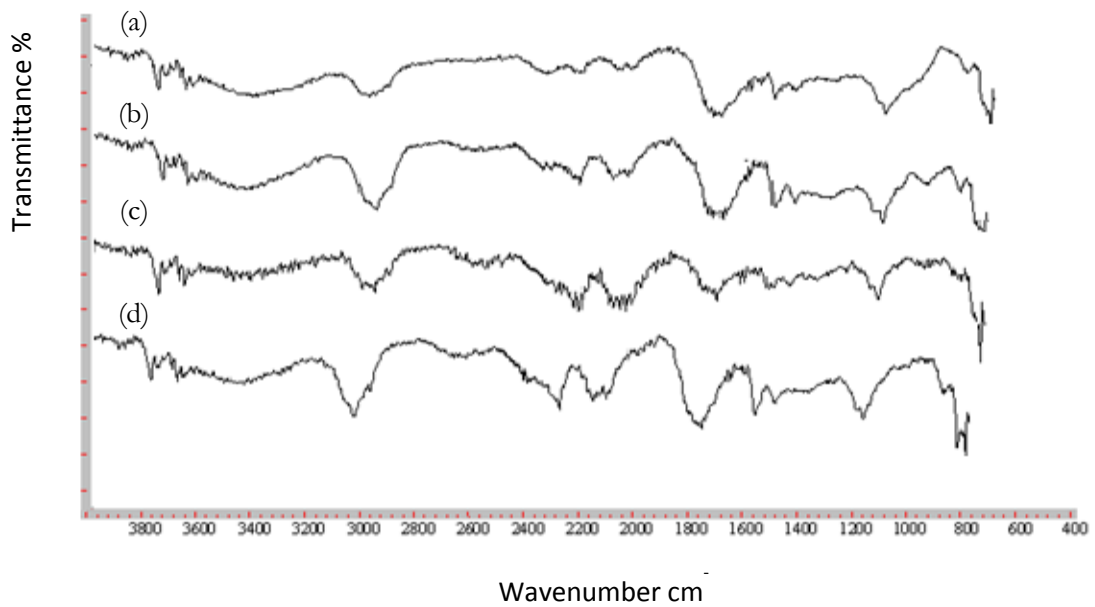
Fig.3. FTIR spectra of toluene liquid

Fig. 4. FT-IR spectra of the glass substrates coated with the toluene films: (a) 15% toluene-540 W, (b) 15% toluene-720 W, (c) 720 W- 30% toluene and (d) 720 W- 15% toluene

Conclusion

Polymer-like organic films were deposited on glass substrate at room temperature by the PECVD method using toluene as the precursor. From the results of FT-IR analyses, the C-H stretching peak of toluene films had a significant dependence on the Mw plasma power. Toluene films exhibit a higher degree of cross-linking with increasing microwave power, which increases the densification of deposited films. Adding argon gas during plasma polymerization prevents powder formation. Toluene films with a polymer-like structure were investigated as a promising candidate for metal corrosion prevention.

Acknowledgements

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