

Electrical and Optical Properties of Plasma Polymerized Eucalyptus Oil Films

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ABSTRACT: Electrical and optical properties of the plasma polymerized eucalyptus oil (PPEo) films are discussed in this article. As part of our electrical studies, we have found that the conduction mechanism in the PPEo film is a Schottky type. We have also found that iodine doping can enhance the conductivity of the film. IR studies revealed that PPEo film is a highly crosslinked polymer, and UV-vis-

NIR studies revealed the information that optical band gap energy of the PPEo film had been reduced as a result of iodine doping. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1102–1107, 2003

Key words: plasma polymerization; thin films; UV-vis spectroscopy; iodine doping; eucalyptus oil

INTRODUCTION

Plasma polymerization is one of the methods that has been widely used to produce polymer films from organic and organometallic compounds.¹ These films can be effectively utilized for replacing brittle metallic components with flexible polymer materials in electronic circuits, which is the current trend in the electronics industry and materials research fields.^{2,3} Plasma polymerization method normally yields highly crosslinked, highly branched, and highly insulating materials.⁴ However, many attempts have been made to enhance the conductivity of these polymers by adopting different treatments such as doping, thermal treatments, and so forth.⁵ In order to make use of a given material in electronic circuits, it is essential to know the conduction mechanism that prevails in that material. As part of our aim to utilize natural resources effectively in the electronics research field, we attempted to produce plasma polymerized eucalyptus oil films (PPEo) from eucalyptus oil, which is a natural oil. We extensively studied the conduction mechanism of the polymer formed; in addition, we also tried to enhance the conductivity of the plasma polymer films by doping with iodine. To our best knowledge no one had ever tried to prepare a polymer film from eucalyptus oil by any method, including radio frequency (RF) plasma polymerization method.

EXPERIMENTAL

The experimental setup (Fig. 1) for making PPEo films consists of a deposition cell made of a borosilicate glass tube, which is about 0.5 m long and has an outer diameter of 0.035 m, fitted with a monomer inlet, an iodine vapor inlet, an air inlet, a pressure gauge, and an evacuation system (rotary pump). The flow rates of monomer and iodine vapor into the deposition cell were controlled with needle valves. The power from RF (13.56 MHz) oscillator power supply was capacitively coupled to the deposition chamber by means of copper foils wrapped around the tube. The film was produced in an RF plasma under a monomer vapor pressure of 0.2 Torr and at a current density of 20 mA/cm². For the studies of electrical conductivity, samples in the form of metal-insulator-metal (M-I-M) sandwich structure with a square area of 0.25 cm² were prepared. For M-I-M structures we have used Al and Ag as electrodes. The electrodes were deposited to a thickness of ca. 2000 Å by conventional thermal evaporation technique under a pressure of 2×10^{-5} Torr on cleaned glass substrates. Electrical measurements were carried out in a metal chamber (under a pressure of 1×10^{-2} Torr). The current flowing through the films was measured using an electrometer amplifier (Keithley, Model 617). Unless otherwise specified regarding the applied voltage, every reading was taken by administering a biased voltage of 2 V to the samples. Doping was carried out by admitting iodine vapor separate from, but simultaneously with, monomer vapor into the deposition cell at the time of plasma polymerization. For IR studies of the doped and undoped films, the films were scraped from the glass substrate and pelletized after mixing with KBr;

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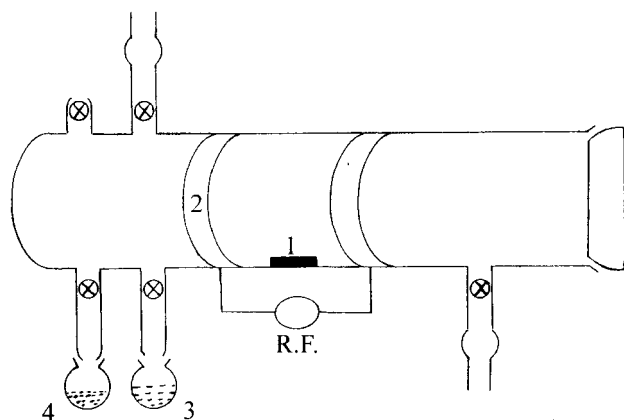


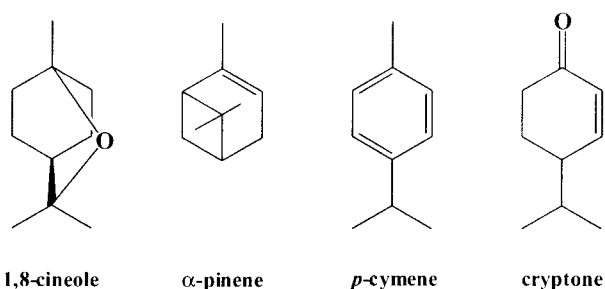
Figure 1 Plasma polymerization setup. 1 = substrate; 2 = copper foils; 3 = monomer; 4 = iodine.

these pellets were used to record IR spectra. The IR spectra were recorded on a Shimadzu IR 470 spectrophotometer under identical conditions. For energy gap studies ultraviolet-visible-near infrared (UV-vis-NIR) spectra of the doped and undoped films were recorded using a Hitachi 3410 spectrophotometer.

RESULTS AND DISCUSSION

Optical studies

The eucalyptus oil used in the present work contained as many as 11 components in major levels. The most abundant component is 1,8-cineole, which is by far more abundant (at least 70%) than other components such as α -pinene, *p*-cymene, and cryptone.⁶⁻⁸ The chemical structures of these compounds are given below:



Despite the complexity of the composition of the eucalyptus oil, attempts have been made to elucidate the structure of PPEo films, using the IR spectra of the monomer and PPEo films.

Figure 2 depicts the IR spectra of eucalyptus oil and PPEo films prepared with and without iodine doping. The peaks at 787, 985, 1016, 1053, and 1080 cm^{-1} in the monomer and at 1067 cm^{-1} in the polymer spectrum were assigned to C-H in-plane bending. The peak at 1169 cm^{-1} in the monomer spectrum was ascribed to either C—O—C asymmetric stretch and/or skeletal

vibration of isopropyl group, and the peaks at 1215, 1234, 1273, and 1306 cm^{-1} to C—C stretch vibrations. The peaks at 1375, 1466, 1526, and 1652 cm^{-1} in monomer and 1377, 1459, and 1655 cm^{-1} in the polymer were assigned to in-plane vibration of ring structures. Observation of these peaks in the polymer spectrum indicates that ring structures of the monomer have not been affected very much during plasma polymerization. Further, the peak at 1734 cm^{-1} of monomer and 1707 cm^{-1} of the polymers could be assigned to C=O stretch of carbonyl compounds and carbonyl units derived from the monomer components or introduced by post-oxidation, respectively. The slight variation in the position of a polymer peak in comparison with the corresponding position of a monomer peak may be due to the change of state of the monomer (liquid) and polymer (solid).⁹

The peaks at 2881 and 2968 cm^{-1} in the monomer and at 2871 and 2958 cm^{-1} in the polymer spectrum represent the C—H stretch vibrations in the monomer and polymer, respectively, which were not affected to a great extent during polymerization. The strong band at 3467 cm^{-1} in the spectra of both iodine-doped and undoped polymer films and in monomer indicates the presence of O—H bonds.

The fact that characteristic C—H and C—C bending modes are absent or reduced in intensity in the spectra of both iodine-doped and undoped polymer films indicates the possibility of highly crosslinked polymers. Since the eucalyptus oil contained many components in major levels as mentioned earlier, it is practically impossible to arrive at any definite conclusions regarding the structure of the plasma polymers. There were almost no distinguishable differences between the IR spectra of PPEo and iodine doped PPEo polymer films, indicating that iodine was not chemically bonded to the chain of the polymer during doping. However, we found through our electrical and optical

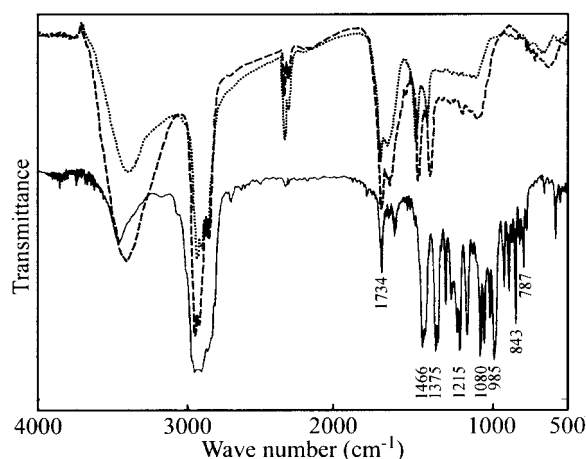


Figure 2 IR spectra of Eucalyptus oil (—), PPEo (---), and iodine-doped PPEo (·····).

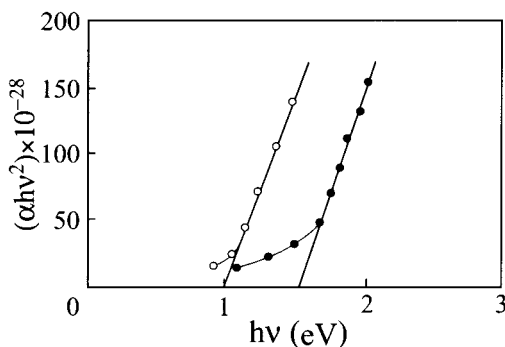


Figure 3 Relationship between $(\alpha hv)^2$ and the photon energy (hv) for PPEo (●) and iodine-doped PPEo (○).

studies that there was some considerable increase in the conductivity as well as remarkable reduction in the band gap energy on iodine doping. We assume that during iodine doping, iodine may fill up the voids in the polymer, giving higher connectivity and continuity for the doped films, which may in turn lead to an increase in the conductivity.^{10–12}

Figure 3 shows a plot of $(\alpha hv)^2$ versus hv where α stands for the absorption coefficient and hv for the photon energy. The plot has a linear portion that, when extrapolated, cuts the energy axis. The energy at this intersection corresponds to the threshold of optical absorption and hence the optical band gap values. Thus, the optical band gap energies of undoped and iodine-doped PPEo films were estimated to be 1.53 and 1.0 eV, respectively. A similar change in the optical band gap values on iodine doping has also already been reported for some other materials.^{12–15}

Electrical studies

While discussing the conduction mechanism through the polymer films, we have to consider following conduction mechanisms such as (1) space charge limited conduction, (2) tunneling, (3) Schottky, and (4) Poole-Frenkel mechanisms.^{12,16,17}

Figure 4 depicts the current density–voltage relationship of the polymer film sandwiched with Al as

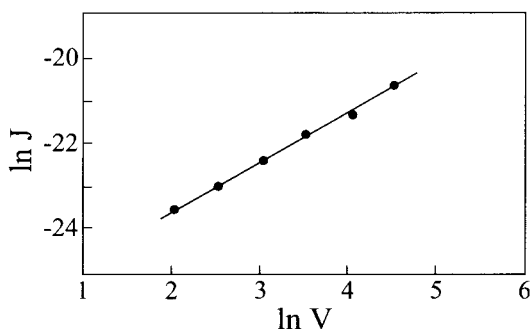


Figure 4 Current density (J)–Voltage (V) relationship for a PPEo film with a thickness of 2000 Å ($\ln J$ vs. $\ln V$).

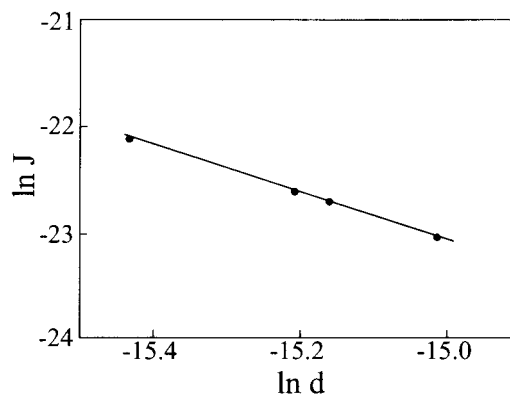


Figure 5 Effect of the film thickness (d) on the current density (J) of PPEo film ($\ln J$ vs. $\ln d$).

electrodes as $\ln J$ (current density) against $\ln V$ (applied voltage). The plot is for a film thickness of 2000 Å. The graph shows that there is no breakdown in the sample even at higher voltage, indicating that it can withstand even at the high applied electric field (1.3×10^8 V/m). The slope of this plot is 1.2. Generally, such a plot between current density and applied voltage with a slope equal to or greater than 2 suggests the possibility of space charge limited conduction.^{12,18–21} However, in the present case the slope is smaller than the value required to establish that the conduction mechanism is space charge limited conduction.

Figure 5 shows a plot of $\ln J$ versus $\ln d$ for films of thicknesses (d) between 2000 and 3000 Å. The plot reveals that $\ln J$ is inversely proportional to $\ln d$. The slope for this plot is 1.76. For space charge limited conduction, the thickness dependence of current density is expressed by $J \propto d^{-t}$ where t is a parameter that depends upon the trap distribution and ideally is equal to 3.^{12,21} However, the value 1.76 is much lower than that required to establish that the film has space charge limited conduction. From this observation and the inference from Figure 4, we can rule out the possibility of the space charge limited conduction in the PPEo film.

Tunneling is another possible conduction mechanism. For tunneling to occur, the film thickness needs to be of the order of 100 Å. However, in the present case, we conducted experiments on the films of thicknesses ranging from 2000 to 3000 Å. Hence the mechanism of tunneling conduction can be ruled out.

Figure 6 presents the plot between $\ln J$ and $d^{1/2}$. A straight line of this graph indicates that the conduction mechanism may be either Schottky or Poole-Frenkel.^{12,19,21} Comparison of the experimentally obtained β coefficient values with theoretical values is the easiest method to differentiate between Schottky and Poole-Frenkel mechanisms.^{12,20} Experimental values of β coefficient can be obtained from the plot $\ln J$ versus $V^{1/2}$.^{12,18,19,21} Figure 7 shows such plots for the

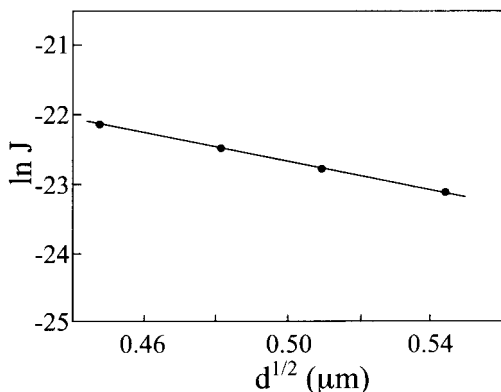


Figure 6 Dependence of the current density (J) on the square root of the film thickness ($d^{1/2}$) ($\ln J$ vs. $d^{1/2}$).

film with a thickness of 2000 Å. Beyond the ohmic region, a straight line portion is obtained, indicating that $\ln J$ is proportional to $V^{1/2}$ in this region. Obtaining the slope from the straight line, we can calculate the experimental value of β coefficient, β_{exp} , with the help of eq. (1),^{12,18,19}

$$\beta_{\text{exp}} = skTd^{1/2} \quad (1)$$

where s is the slope of the graph plotted between $\ln J$ and $V^{1/2}$, k is the Boltzmann constant, T is the temperature in Kelvin, and d is the film thickness in meters.

The theoretical coefficients β_S and β_{PF} are obtained from eqs. (2) and (3), respectively, taking high frequency dielectric constant of PPEo film as 3.0, which was obtained from optical transmission studies in the VIS-NIR region. We have used the relation $\epsilon = n^2$ to obtain the high frequency dielectric constant of the film, where n is the refractive index of the material.²² To calculate the refractive index of the material we have adopted Manificier's method.²³

$$\beta_S = (e^3/4\pi\epsilon\epsilon_0)^{1/2} \quad (2)$$

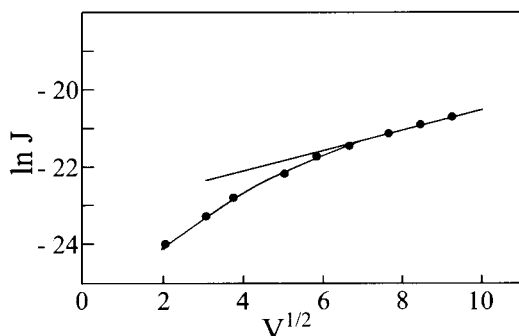


Figure 7 Relationship between the current density (J) and the square root of the voltage ($V^{1/2}$) for the Al-PPEo-Al symmetric electrode configuration for film thickness 2000 Å ($\ln J$ vs. $V^{1/2}$).

TABLE I
Comparison of Experimental and Theoretical β Coefficients

	β ($\text{eVm}^{-1/2}\text{V}^{-1/2}$) ^a	
Experimental	β_{exp}	1.5×10^{-5}
Theoretical	β_S	2.06×10^{-5}
	β_{PF}	4.12×10^{-5}

^a Film thickness = 2000 Å.

$$\beta_{\text{PF}} = (e^3/\pi\epsilon\epsilon_0)^{1/2} = 2\beta_S \quad (3)$$

In Table I the experimental value of β is compared with the theoretical values of β_S and β_{PF} , which shows that the experimental and theoretical values coincide with the Schottky type mechanism.

The asymmetric electrode method^{12,19,20} is a generally accepted and reliable method to confirm which conduction mechanism, Schottky type or Poole-Frenkel type, actually prevails in the material. Hence a graph is plotted with J versus $V^{1/2}$ for the asymmetric electrode M-I-M configuration. Ag and Al were used as the electrode metals and the PPEo film with thickness 2000 Å as the insulator. Figure 8 represents two straight lines, one with Ag and the other with Al positively biased. The plots do not coincide and show a significant and reproducible difference in the current density values for opposite directions of the applied field. Theoretically, for Schottky type conduction, a work function difference of about 0.06 eV between two electrode metals should result in many orders of difference in current levels for opposite directions of the applied field.^{12,24} In the Ag-PPEo-Al asymmetric electrode configuration, the work function difference is ca. 0.25 eV. Thus many orders of difference in current density values can be expected for opposite directions of the applied field. Contrary to the expected result, Figure 8 shows only a small but reproducible difference. This

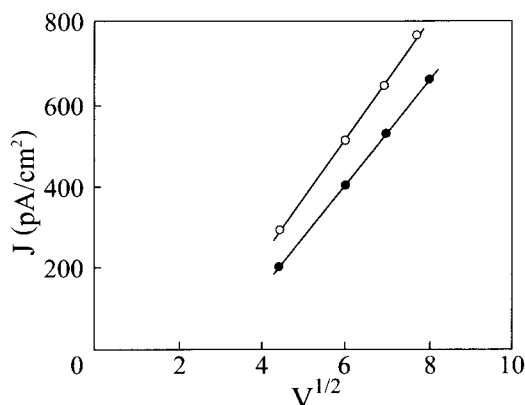


Figure 8 Relationship between the current density (J) and the square root of the voltage ($V^{1/2}$) for the Ag-PPEo-Al asymmetric electrode configuration (\circ Ag positive; \bullet Al positive) for film thickness 2000 Å (J vs. $V^{1/2}$).

fact may be due to the presence of surface states at the polymer electrode interface, which can change the potential barrier.^{12,19,20,24} Mizutani et al.²⁵ have suggested that the phenomenon of equalization of the metal polymer contact barriers may take place owing to the presence of surface states, which results in the small difference in the barrier heights when dissimilar electrode configurations are employed.

To establish that the conduction mechanism is a Poole-Frenkel one, the plots in Figure 8 should be identical. In other words, to point out the conduction mechanism as Poole-Frenkel, the current density should be independent of electrode materials and polarity of the electrodes. In that case we can strongly suggest that the conduction mechanism is bulk controlled Poole-Frenkel one rather than electrode controlled Schottky type one.^{12,17} However, in our case it happened in other way. Thus the small but reproducible and significant difference in current density values for opposite directions of different applied fields can be related to electrode-dependent Schottky type conduction mechanism.

Figure 9 shows current voltage characteristics of the undoped and iodine-doped PPEo films. It may be noted that current increased about two times due to iodine doping; namely, the conductivity of the PPEo film with a thickness of 2000 Å was increased from 3.1×10^{-16} to 5.9×10^{-16} (Ωm)⁻¹ upon doping with iodine. Similar behavior was obtained with the films of different thicknesses.

Temperature effects

The dependence of current on temperature in the symmetric configuration (Al-PPEo-Al) has been studied in the temperature range 303–423 K. In Figure 10, $\ln(J/T^2)$ is plotted against $1000/T$. From the slope of the graphs we can determine the metal polymer barrier heights. The figure is plotted for different bias voltages. The straight line plots of this graph further confirm Schottky type conduction mechanism in the PPEo

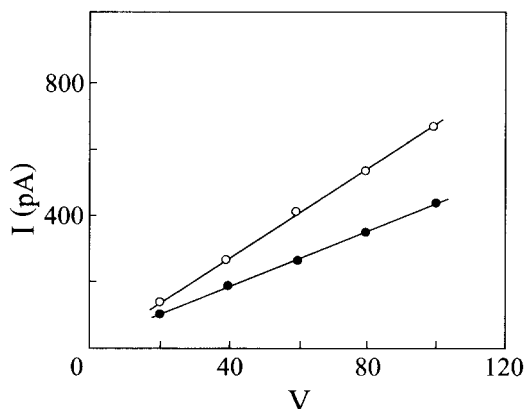


Figure 9 I-V characteristics of PPEo (●) and iodine-doped PPEo (○) films with a thickness of 2000 Å.

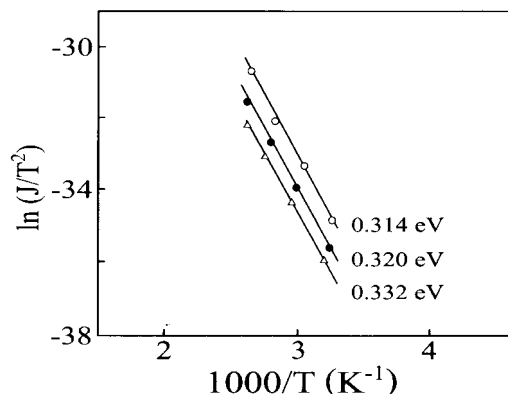


Figure 10 $\ln(J/T^2)$ versus $1000/T$ relationship for applied voltages of 2V (△), 4V (●), and 9V (○).

films.^{19,21} The activation energy decreases from 0.332 to 0.314 eV as the bias voltage increases from 2 to 9 V.

CONCLUSIONS

We have investigated the electrical and optical properties of the plasma polymerized eucalyptus oil films in detail. Conduction studies have led us to the conclusion that the conduction is an activated process and the activation energy decreases with the increase in the applied field, which represents a case of an extrinsic conductivity where the change in activation energy is determined by the number of extrinsic carriers. The conduction current varies with the field direction and the nature of the electrode metals. The major conclusion we can draw from these observations is the very clear dominance of the Schottky type mechanism in the PPEo films. The presence of the surface states were responsible for the small difference in the barrier heights compared to the expected change due to the work function difference of the metal electrodes. Considering the conductivity and band gap energy of the material, a modification can be brought about by incorporation of a proper dopant like iodine.

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