

Effects of Non-Thermal Plasma Jet Treatment of Pure/Doped Polystyrene Thin Films on UV-Vis Optical Properties

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ABSTRACT

Non-thermal Cold Atmospheric Plasma (CAP) to improve optical property of pure and doped polystyrene (PS) thin films using He and Ar gas. These thin films were fabricated using the solution cast method. Surface treatment of PS thin films were performed by CAP. To analyze the effect of plasma treatment, the optical properties of the thin films were measured and derived by UV-Vis spectroscopy in wavelength range of 300-700 nm. Absorbance, transmittance, extinction coefficient, energy band gap, and optical conductivity before and after Cold jet plasma treatment (CJT) were compared. The results from Ar and He were similar in effectiveness. The treatment did have an impact on the optical properties of these PS thin films. This data will help to substantiate the use of CJT to enhance optical properties of polymer thin films.

Keywords: UV-Vis absorption spectra, polystyrene thin film, nonthermal plasma jet treatment, cold plasma, Cold atmospheric pressure CAP), Cold jet plasma treatment (CJT)

INTRODUCTION

Many efforts have been directed into the modification of surface roughness resulting in the improvement in grain size and surface energy. As it is the first interface of material which may encounter other materials and an external environment, one of the most important parameters in nanotechnology and thin films is surface and roughness (Hosseinpour et al., 2019). Plasma functionalization is the process by which a bondable surface is treated to improve its adhesive properties, bondability, and pairability. Functionalization enhances properties to characteristics of nanomolecules through surface modifications.

Cold atmospheric pressure has attracted high research interest recently as one of the most versatile non-thermal techniques in surface modification. CAP are discharged plasma that can extend beyond the plasma generation region into the surrounding ambient environments. They can be generated at a discharge voltage around 2kV with discharge gaps in the order of millimeters and are highly energetic photons in the ultraviolet range 100-400 nm (Golda et al., 2020; Yahaya et al., 2021).

Cold plasma jet treatment (CJT) only affects the surface of the treated film and may improve different surfaces for various materials (dielectric, polymers, and metals). CJT has been implemented to reduce etching and chain scission in some polymers. However, sometimes usage of various solvents and different acids may damage the surface and leak into the interior of the material, affecting the interior properties as well (Zendham et al., 2018; Tabares & Junkar 2021).

For example, in some sensor devices, the metallic sensing layer has a short life span that depends on the environment within which the sensor operates (Hosseinpour et al., 2019).

Cold plasmas can be characterized as high pressure, atmospheric pressure, and low pressure according to the pressure conditions and nonequilibrium characteristics. They are an effective source of reactive species such as radicals, metastables, and photons. Due to their high reactivity, they are used in many applications, such as varying on surface roughness for polymer activation, thin film deposition, nanostructuring of surfaces, and for the treatment of biological substrates.

Sometimes warm or hot plasma are used for hardening and smoothing surfaces from friction and erosion point of view. CAP is known as non-thermal because it is a weakly ionized gas that can operate under atmospheric conditions near or just above room temperature Golda et al., 2021; Yahaya et al., 2021; Zendhnam et al., 2018; Tabares & Junkar 2021; France & Short 1998).

Plasma is the predominate state of matter in the known universe belonging to the large family of cold atmospheric pressure plasmas. When energy is added to a solid, in the form of heat or electromagnetic radiation, it transforms into a liquid state, from which gas is obtained through an additional supply of energy. Plasma is created when extra energy is continuing to be added to the gas, it will become partially or completely ionized. Electrons are removed from the atoms that constitute it. Eventually reaching a new state of matter, plasma, made up of free electrons, atoms, molecules (carriers of heat), and ions further exciting ionization and dissociations. One of the most peculiarities of plasma is that they conduct electricity microscopically. On a macroscopic scale, plasmas are electrically neutral (Yahaya et al., 2021; Zendhnam et al., 2018; Tabares & Junkar 2021).

The surface of polymer thin films have been widely studied as well as the properties of inorganic/organic nanocomposite materials. Polystyrene as a polymer has attracted much attention specifically due to its interesting and superior physical and chemical properties. Thin films constructed of inorganic nanoparticles and organic polymers have shown improvements in these same properties and add additional properties. (Ellis et al., 2009; Sangawar & Golchha 2013; Tsuruoka et al., 2013).

These effects depend on the type of gas used. Most are working with Ar and He with a small percentage of reactive gasses as O₂, N₂, He₂. Results may also be influenced by the duration of exposure time and nozzle distance to the sample (Hosseinpour et al., 2019 ; Zendhnam et al., 2018).

In this paper, after solution cast fabrication of pure and doped PS thin films, they were exposed to Ar and He non-thermal plasma to investigate the effects on optical and electrical properties.

EXPERIMENTAL SECTION

Materials

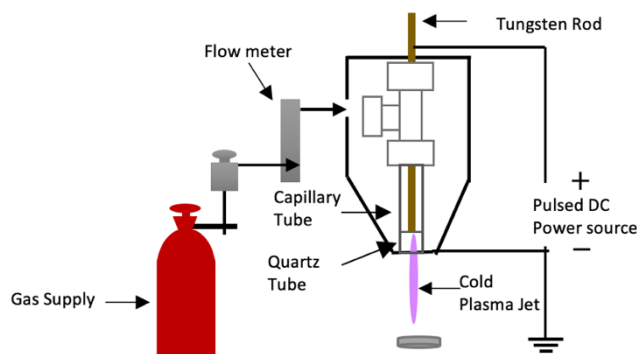
Methyl Ethyl Ketone (C_4H_8O) was purchased from Reagents. Polystyrene ($(C_8H_8)_n$) and all dopants were purchased from Sigma-Aldrich Chemistry as starting materials. Each dopant contained 99% trace metals. The polystyrene latex beads are uniform in size and morphology.

Fabrication Technique

Thin films were fabricated utilizing solution casting method. All glassware used in this study for solution casting was subject to rigorous cleaning. This fabrication technique offers many advantages such as low cost and an easy fabrication technique.

Experimental Set up

The plasma jet set up which can be seen in schematic 1 consisting of two concentric electrodes, where the inner electrode is typically connected to a radio frequency (RF) power at high frequency resulting in ionization of the working gas, which exits the nozzle with a jet-like shape (Hosseinpour et al., 2019). RF plasma treatments may be employed to improve the surface properties of commodity polymers, increasing tetra range of potential applications for these materials (Tabares et al., 2021).



Schema 1. Schematic set up of cold atmospheric jet plasma

With Ar and He being inert gases, would prevent damaging the thin films from oxidation or carbonation. The reactor is flooded with argon (helium) at a rate of 3 standard liter per minute (SLM) monitored by a flow meter with a pulse rate of 6 kHz and width of 1 microsec. The treatment was conducted with a power of 7 kV at a period of 5 minutes for exposure time for plasma on the samples. Distance between the surface and plasma jet was constant at and the films were exposed to CAP perpendicular (normal to the surface). During plasma treatment the jet temperature was monitored and kept constant.

UV-Vis spectroscopy was measured before CJT of the samples. Acquisition of the optical properties were carried out within 5 hours of treatment by Cary 3V UV-Vis Spectrophotometer. The absorption spectra of the samples were recorded in wavelengths 300-700 nm.

RESULTS AND DISCUSSION

Figures 1-5 show UV-Vis of measured thin film samples before and after being exposed to CAP (using He and Ar plasma gas). Although the samples were treated with both gases, the difference in values between He and Ar results were same and combined to one graph. The study was conducted to see if there would be any effect of using either gas.

UV-Vis spectroscopy is a spectroscopy analysis technique using UV electromagnetic radiation source and visible light using spectrophotometer instrument. The spectrophotometer consists of the spectrometer and photometer. The spectrophotometer produces light from spectrum

with certain wavelength and the photometer is a measuring tool of light intensity transmitted or absorbed (France & Short 1998).

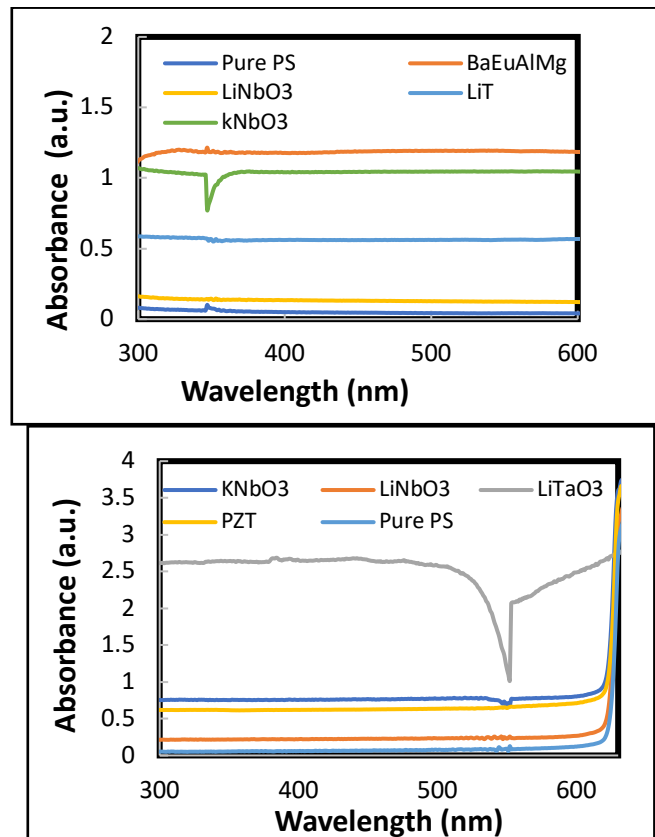


Figure 1. UV-Vis optical absorption spectra for pure PS and doped PS thin films before (L) and after (R) CJT treatment

The wavelength of UV-Vis light is a result from the process of electron transition. If electron transition corresponded with the amount of photon energy, it will cause great absorption along with the amount of energy from the photon (Dewi et al., 2019).

The absorbance peak can be seen to have shifted from wavelength ~ 350 nm in the untreated samples to ~ 550 nm in the treated samples. Perhaps due to the wavelength where in the area took place high absorbance process and photon energy was greater than energy of visible light or attributed to an increase in the grains on the surface. PZT and KNbO_3 absorption values decreased with treatment, while LiTaO_3 increased dramatically and there were no noted changes in pure PS and LiNbO_3 samples. However, in each sample, as the wavelength increases, the absorption spectrum slightly increased by $0.04 \pm \text{nm}$. Optical absorption is an important property for optoelectrical applications.

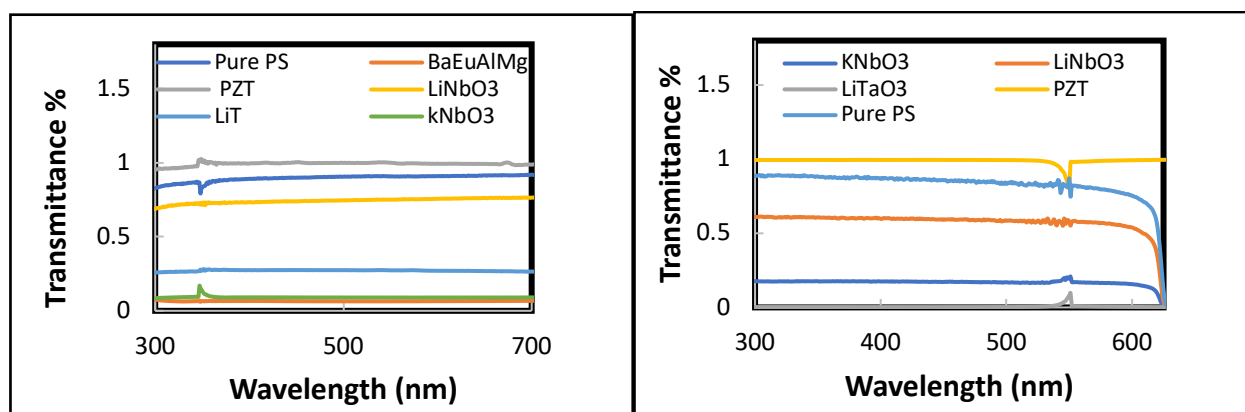


Figure 2. Transmittance % for pure PS and doped PS thin films before and after CJT treatment

The correlation between absorbance A and transmittance T can be written in the form

$$A = \log\left(\frac{1}{T}\right) = \log 1 - \log T.$$

The phenomenon is that transmittance is reversely proportional to its absorbance value. Figure 2 can be reviewed to see the transmittance percent in each sample slightly increased, except for LiTaO_3 and LiNbO_3 . As transparency decreases, the sample absorbs more light.

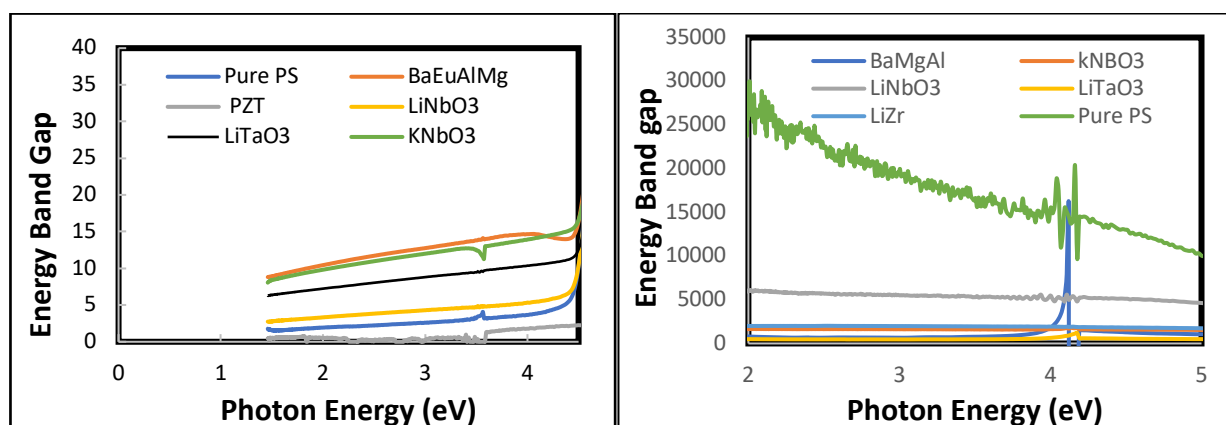


Figure 3. Energy band gap for pure PS and doped PS thin films before and after CJT treatment

The value of the optical energy band gap was determined and plotted. If there is a change in energy band gap – it is evident that the increased/decreased impact in the optical band gap is due to the nonthermal plasma treatment. Thus behavior can suggest a change in degree of disorder in the films due to changes in the polymer structure.

Based on the structure of the energy band, a material can be categorized as a semiconductor, insulator, or a conductor. The conductor has a valence band (low state) and a conduction band (lowest excited state) that do not coincide and the interval in between expresses an energy that cannot be owned by an electron – the band gap. In thin films the optical band gap can be determined by processing the transmittance and absorbance data.

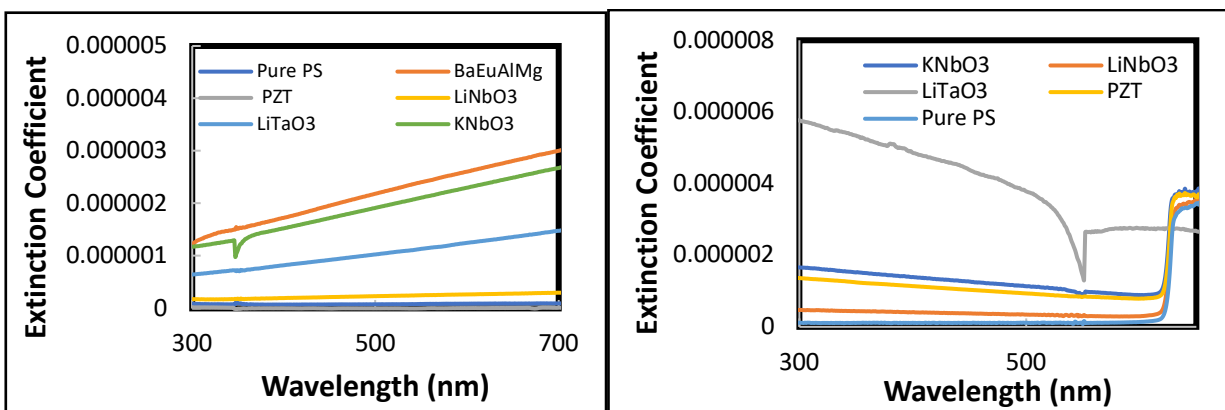


Figure 4. Extinction Coefficient for pure PS and doped PS thin films before and after CJT treatment

The extinction coefficient, shown in figure 4 shows that each sample increases with CJT. This may be due to the increase in absorption coefficient. The extinction coefficient is lower at the longest wavelengths, reverse of the results prior to CJT.

Extinction coefficient, k is related to the absorption coefficient by the relationship:

$$k = \frac{a\lambda}{4\pi}$$

Where λ is the incident photon wavelength. k is a measure of how fast the amplitude of the wave decreases.

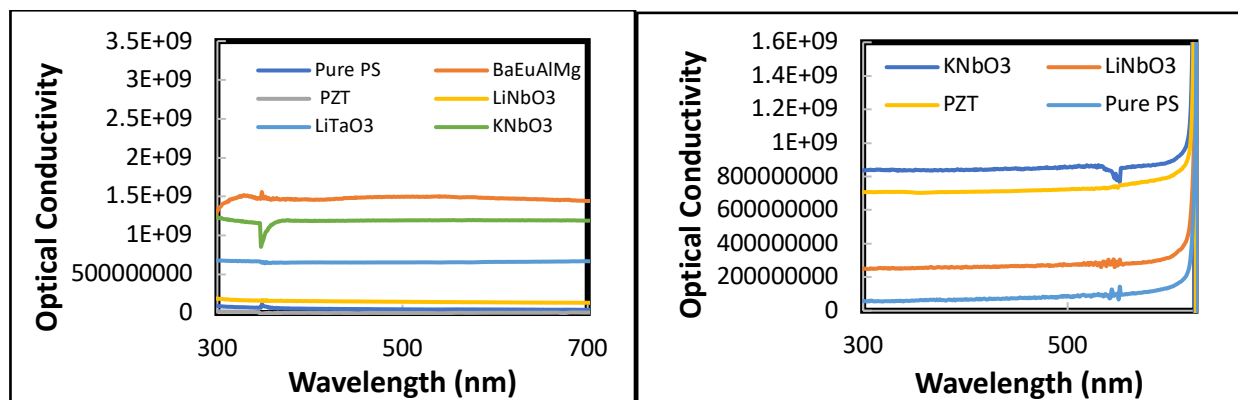


Figure 5. Optical conductivity against wavelength before and after exposure to plasma treatment

The optical conductivity is one of the most powerful tools for studying the electronic states in materials. Figure 5 shows spectrum indicating peak shift in the samples after CJT treatment. It is also evident after exposure the optical conductivity increases as the wavelength gets longer.

CONCLUSION

In this article, we have investigated the impact of nonthermal plasma jet treatment on UV-Vis characteristics of Pure/Doped PS nanocomposites. These thin films were fabricated using the solution cast method and characterized for their optical properties before and after CJT. From these results, CJT does have an impact on the surface of these PS samples, also you can note the

impact on these properties due to the additives (dopants). The optical characteristics such as absorbance, transmittance, energy band gap, optical conductivity, and extinction coefficient (k) were calculated to analyze the properties. The impact of CJT was demonstrated and can be clearly seen in the increase in energy bandgap seen in table 1 below.

Table 1. Comparison of energy bandgap before and after CJT.

Sample	Energy Bandgap Before	Energy Bandgap After
Pure PS	4.3 eV	5.25 eV
PS + LiNbO ₃	4.35 eV	5.44 eV
PS + LiTaO ₃	4.27 eV	5.14 eV
PS + KNBO ₃	4.54 eV	4.8 eV

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