

Surface Modification of PS/C₆₀ Nanocomposite Films by Nitrogen Glow Discharge Plasma for Improving Hydrophilic and Optical Properties

Naglaa. M. Elsayed, Omar. F. Farag, Mohammed. H. Elghazaly and Doaa. A. Nasrallah*

Physics Department, Faculty of Science, Zagazig University, Egypt

Abstract: Fullerene C₆₀-polystyrene nanocomposite films were fabricated using solution casting method and modified using N₂-DC- plasma with varying treatment time. Plasma treatment aimed to enhance surface wettability and optical parameters for industrial applications. For chemical modifications and new functionalities, the plasma treated films were examined by FTIR spectroscopy, water contact angle (WCA) and surface free energy and the results recorded the formation of new functional groups and decreasing CA with treatment time during which the surface free energy increases from 23 to 68 mJ/m². Optical properties were investigated by UV-Vis. spectroscopy in the wavelength range of 200- 800 nm which illustrated a decreasing direct and indirect optical energy band gap, Eg, with treatment time, while the optical constants showed clear changes with plasma exposure.

Keywords: Surface modification, Optical properties, Hydrophilicity, Surface energy.

I. Introduction

Due to recent developments in the field of nanotechnology, there has been growing interest in polymer-matrix composites in which nano-sized fillers are distributed homogeneously (known as filler/polymer nanocomposites), due to their unique optical, electric and magnetic properties[1]. So Nowadays, polymer nanocomposites play major roles in biomedical, electronic and optical devices[2]. The polymer analyzed in this work, polystyrene (PS), has conduction characteristics and dielectric strength that make it a promising insulator for organic electronics applications [3]. However, like most polymers, polystyrene is chemically inert and thus needs to be functionalized for applications that require increased wettability, adhesion, or covalent immobilization of chemical and biological ligands [4]. Polystyrene (PS) is one of the polymers capable to content nano-carbonic particles [5]. So incorporation of fullerene and nanotubes into chemical composition of polymers gives one more opportunities for their study and application as composite materials (films, fibres) serving different purposes. We select this system as both the fullerene and polymer are well-defined, high purity, molecular species, and the 'nanoparticle' has an unambiguous surface chemistry and geometry. Further, fullerenes and derivatives find wide applications in thin film composites and organic photovoltaics [6] due to their unique structural, electronic and spectroscopic properties[7].

Modern industry requires components that are made from materials with desired mechanical, chemical, optical and electrical properties, and are coated with different films often incompatible with the substrates. In such cases, the surface properties should be modified without modification of the bulk properties [8]. To modify the surface properties of polymers, low-pressure cold plasma treatment is commonly used as a dry process. Plasma is a complex source of energy for surface modification, due to the large variety of components, as excited and ionized particles, photons, radicals, all these species being capable to induce chemical reactions, both in the plasma volume and at its interface with solid surfaces [9]. Plasma can interact with the polymers through the formation of cross-linkages between adjacent polymer chains or by chain scission.

Improving the surface hydrophilicity is induced by forming of new oxygen containing groups on the surface, such as carbonyl, carboxyl or hydroxyl [10] depending on the treatment conditions and gas composition which contribute to the polymer treatment, resulting in etching, activation and/or crosslinking [11]. In this work PS/C₆₀ nanocomposite films were treated with DC glow discharge N₂ plasma under different exposure times with an intension of improving the intrinsic low-surface properties. The surface hydrophilicity of the treated samples were examined by measuring the contact angle as a function of treatment time. Also, the determination of the optical constants of PS/C₆₀ nanocomposite films such as refractive index and extinction coefficient is an important for optical applications. Furthermore, the refractive index and optical band gap are the fundamental parameters of an optical material, because these are closely related to the electronic properties of the material[12].

II. Experimental And Methodology

PS/C₆₀ nanocomposite films were prepared by using solution - cast technique. PS of molecular weight 135,000 in the form of grains and Fullerene (C₆₀) of molecular weight 720.64 were supplied by Sigma- Aldrich company. PS and Fullerene (C₆₀) were dissolved using a magnetic stirrer separately in toluene with purity 99.99

%, then the solution added to each other to obtain a solution with a concentration 1×10^{-4} mol % the complete dissolution was obtained at room temperature for half-hour. A mixture of the solution was cast onto a clean glass Petri dish and left to dry at room temperature for a week. After drying, the samples were cut into rectangular substrates (1 cm \times 2 cm) with thickness range 0.22- 0.25 mm.

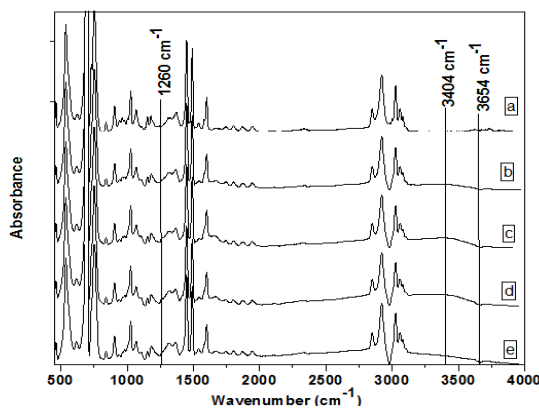
PS/C₆₀ nanocomposite films were exposed to DC glow discharge plasma of low – power was generated in Pyrex tube of (18 cm) long and (13 cm) diameter closed at each end with aluminum plate .The base pressure is attained into the tube at (10^{-3} Torr) by using a rotary pump (Edwards H. vacuum pump, model ED 200) then N₂ gas is allowed to inter the tube throw a controllable needle valve. Two plane circular stainless steel disks of (5 cm radius) represent the two electrodes are connected to each other with four isolated rods keeping the spacing constant at (7 cm). The two electrodes move axially forward and backward as a unit controlled by a handle outside the tube. Plasma properties were kept constant during the experiment, as the gas pressure was 0.4 Torr, and the discharge power was about 3.5 W. The samples were supported on a glass holder and put in front of the cathode at the edge of the negative glow. The exposure time was varied from 15 to 120 minutes.

FTIR Analysis was using an infrared spectrometer device, Vertex 70 Bruker Optics in the range of 4000- 400 cm⁻¹ for knowing the possible functional groups present with before and after plasma treatment .The hydrophilicity of PS/C₆₀ nanocomposite films is usually expressed in terms of wettability that can be estimated by contact angle measurements. Measurements were carried out with distilled water at room temperature. The volume of the liquids drop was about 5 μ l using a microsyringe. The contact angle was measured at least at five different locations on the sample to check the homogeneity of treatment. Ultra violet and visible (UV/VIS) absorbance, transmittance and reflectance spectra of pristine and plasma treated PS/C₆₀ nanocomposite films were recorded over a wavelength range 200–900 nm using a Perkin–Elmer Lambda 950 spectrophotometer. The optical transmission and reflectance spectra were analyzed to determine optical constants such as refractive index n, extinction coefficient k, and absorption coefficient α . Analysis of the absorption coefficient was also carried out to determine the optical band gap.

III. Results And Discussion

3.1. FTIR analysis

The most important characteristics of the surface of samples are determined by the functional groups present in the surface layer. Fourier transform infrared (FTIR) spectroscopy is used for this purpose. Figure.1 represents IR-spectra of PS/C₆₀ nanocomposite films before and after N₂ plasma treatment with changing treatment time. The absorption bands of PS as obtained from the untreated film are classified as The bands at 3059, 3025 cm⁻¹ due to the C-H aromatic stretching vibration, the bands at 2921 and 2849 cm⁻¹ are identified as the stretching vibration of the aliphatic C-H bonds. The bands at 1600 cm⁻¹ and 1492, and 1450 cm⁻¹ are assigned to the phenyl ring stretching, and the bands at and 1027, 752, and 695 cm⁻¹ correspond to aromatic C-H deformation and skeletal vibration. Due to the interaction between C₆₀ and aromatic ring of the PS, there may be overlap between bands corresponds to C₆₀, which are reported to be at 1429, 1181, 577, and 528 [13] and Phenyl ring bands of PS within ranges [14] and[5]. The FTIR spectrum shows a significant difference between untreated and treated samples. Two bands appeared in the range 3200 - 3700 cm⁻¹, this region belongs to ν (N-H) imine group and ν (-OH) hydroxyl group. At 1260 cm⁻¹ a medium peak appeared in all samples attributed to C-N stretch . The incorporation of O₂ and N₂ functionalities on the sample's surfaces is an indication to surface activation by N₂ plasma and the formation of free radical sights on the nanocomposite film's surfaces. The activated surface either adsorbs moisture from ambient air just after removing from the plasma chamber or abstract residual O₂ in the plasma chamber [15].The appearance of imine, hydroxyl and C-N functionalities on the examined samples is the mean reason of wetting enhancement.



Figure(1): FTIR spectra of nitrogen plasma treated PS/C₆₀ nanocomposites with the treatment times (a):0 min, (b):15 min, (c):30 min, (d): 60 min and (e): 120 min.

3.2. Wettability and Surface free energy

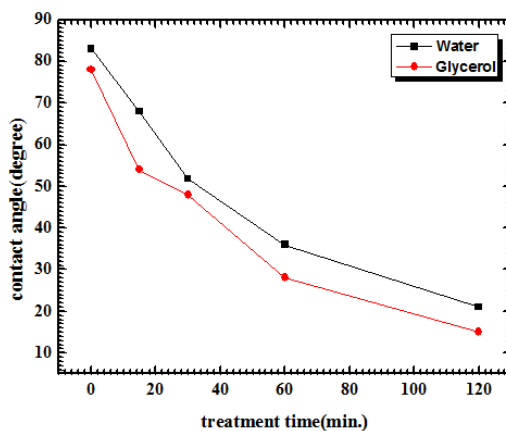
Low temperature plasma treatment is known as one of the well recognized and effective means of improving the surface wettabilities of many polymeric surfaces. Wettability can be regulated by changing chemical composition of the surface, it is governed by molecular interaction of the outer most surface layer of a few a angstrom units. The average values of contact angle ,thus, obtained was used for surface energy calculations. Surface free energy, that is, the sum of polar force and dispersive force using the water and glycerol contact angles, before and after plasma exposure were evaluated by applying Owens-Wendt method [16].

Where γ_l , γ_l^p and γ_l^d are the total surface energy, polar and dispersion components of the surface free energy of the liquid respectively. The values of γ_l , γ_l^p and γ_l^d , required for solid surface energy calculation were obtained from the Table1.

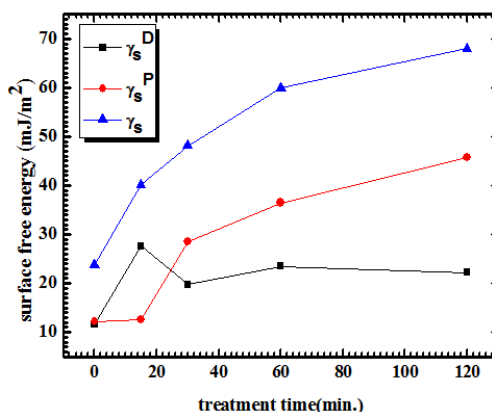
Table 1: Surface energy of liquids[17].

Liquid	γ_{LV} (mN/m)	γ_{LV}^d (mN/m)	γ_{LV}^p (mN/m)
Distilled water	72.8	22.6	50.2
Glycerol	63.4	40.6	22.8

The change in the contact angle on PS/C₆₀ nanocomposite films as a function of plasma exposure time is shown in Figure 2.It can be noticed that as the exposure time increases, the contact angle decreases. It is considerably, decreased to about 59-55% of its original value at an exposure time of 30 min. This percentage of reduction reduced as the exposure time increased as it reaches to about 25-23% of its original value at 120 min. The change in the surface free energy on PS/C₆₀ nanocomposite films as a function of plasma exposure time is shown in Figure 3. The values of total surface energy, γ_s , were estimated for the PS/C₆₀ films by adding polar and dispersive components, γ_s^p , γ_s^d . It was found that values of γ_s increase as treatment time increase from 23 mJ/m² reaching its maximum value of 68 mJ/m² at 120 min. Decreasing the liquids contact angle and subsequent increasing total surface energy with increasing treatment time is a good evidence of the formation of polar functional groups and increasing surface roughness.



Figure(2): Variation of contact angle with respect to treatment time

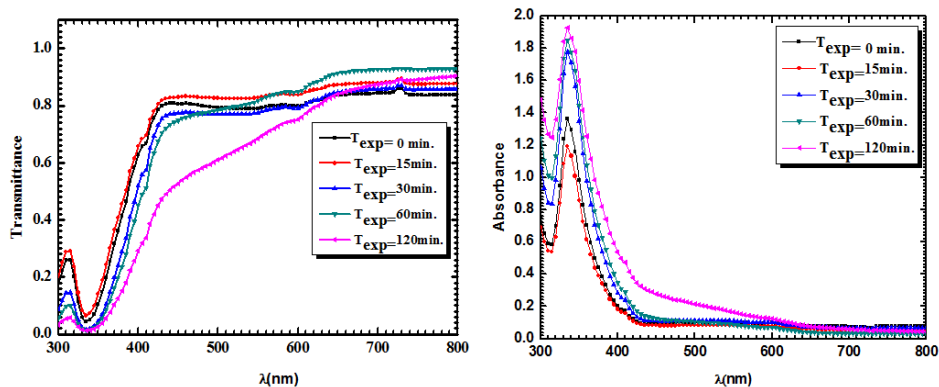


Figure(3): Surface energy of PS/C₆₀nanocomposite film with respect to treatment time.

3.3. Determination of optical constants

Figure 4 shows the transmittance spectra obtained for untreated and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations. It is well known that the transparency of a bulk film strongly depends on the surface roughness and an increase in the average roughness will result in a decrease in transmittance due to light scattering effects, but the action of some species present in the plasma promotes chain scission, and this could lead to etching and material removal, thus promoting changes in surface roughness which in most cases positively contributes to a transparency decrease [18].

The optical absorbance for treated PS/C₆₀ nanocomposite films was evaluated by recording the UV-visible absorption spectra for various N₂ plasma glowing duration as shown in Figure 4, the reference used for absorption measurements is untreated PS/C₆₀ nanocomposite film. The absorption value of the plasma treated film was increased when compared to the untreated film.



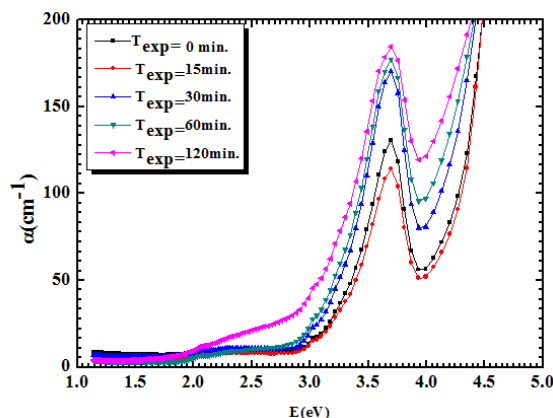
Figure(4): The UV-Visible transmission and absorption spectra for pristine and plasma treated PS/C₆₀ nanocomposites films for different durations.

The variation of the optical bulk absorption coefficient, α , with wavelength is a unique parameter of the medium. The importance of the absorption coefficient is related to the valuable information that can be obtained, such as the electronic band structure and the optical energy band gap. The absorption coefficient can be estimated from the optical absorption spectrum owing to the following equation [19] :

$$\alpha(\nu) = 2.303A/d \tag{2}$$

where A is the absorbance and d is the film thickness.

Figure 5 shows the absorption coefficient (α) as function of photon energy ($h\nu$) for pristine and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations. It is clear from this figure that the values of (α) showed increase with increasing in the exposure time.



Figure(5):The absorption coefficient as a function of the photon energy for pristine and plasma treated PS/C₆₀nanocompsites films for different durations.

The index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen. The refractive index of the films was calculated by the following equation [20] :

$$n = \left(\frac{1 + R}{1 - R} \right) + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (3)$$

where R is the reflectance and k is the extinction coefficient.

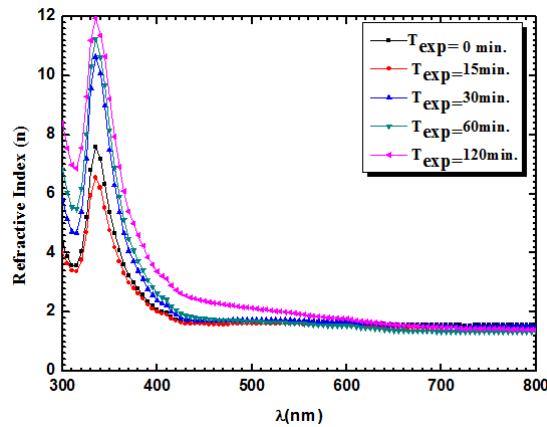
Figure 6 shows the refractive index as function of wavelength for pristine and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations. It is clear from this figure, that the refractive index decrease with increasing λ. Meanwhile the values of (n) increase with the increasing plasma exposure time. The reason of such behavior may be attributed the etching action of the plasma which increase roughness of film surface.

The extinction coefficient (k) describes the properties of the material with respect to light of a given wavelength and indicates the absorption changes when the electromagnetic wave propagates through the material. The extinction coefficient (k) was calculated using the following equation [21] :

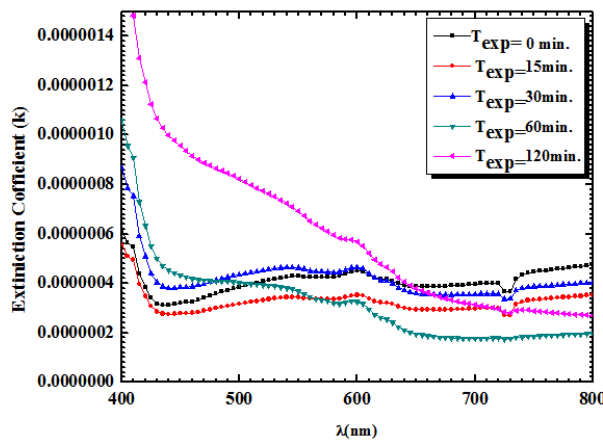
$$k = \alpha\lambda / 4\pi \quad (4)$$

where λ is the wavelength and α is the absorption coefficient.

Figure 7 shows (k) as function of wavelength for pristine and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations. It is clear from this figure, that the values of the extinction coefficient showed increase with the increase in the exposure time.



Figure(6): The refractive index as a function of wavelength for pristine and plasma treated PS/C₆₀nanocompsites films for different durations.

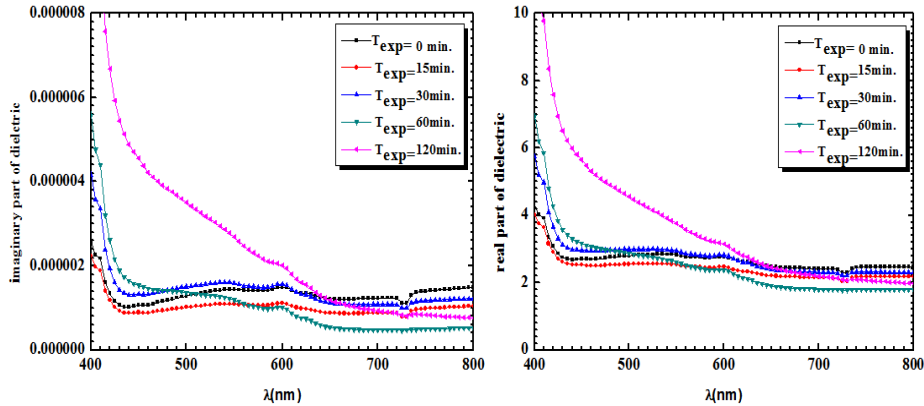


Figure(7): The extinction coefficient as a function of wavelength for pristine and plasma treated PS/C₆₀nanocompsites films for different durations.

The complex dielectric constant is defined as the response of the material toward the incident electromagnetic field. The complex dielectric constant of compound ε is divided into two parts real ε_r, and imaginary ε_i. The real and imaginary parts of dielectric constant (ε_r and ε_i) were calculated by the following equations [22] and [23]:

$$\begin{aligned} \epsilon_r &= n^2 - k^2, \\ \epsilon_i &= 2nk \end{aligned} \quad (5)$$

Figures (8.a and b) show the real and imaginary parts of dielectric constant (ϵ_r and ϵ_i) as function of wavelength for pristine and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations. It is clear from these figures, that (ϵ_r and ϵ_i) for pristine and nitrogen plasma treated PS/C₆₀ nanocomposite films decrease with increasing λ . Also the values of (ϵ_r and ϵ_i) showed increase with the increase in the exposure time. It is concluded that the variation of ϵ_r mainly depends on n^2 because of small values of k^2 , while ϵ_i mainly depends on the k values which are related to the variation of absorption coefficients.



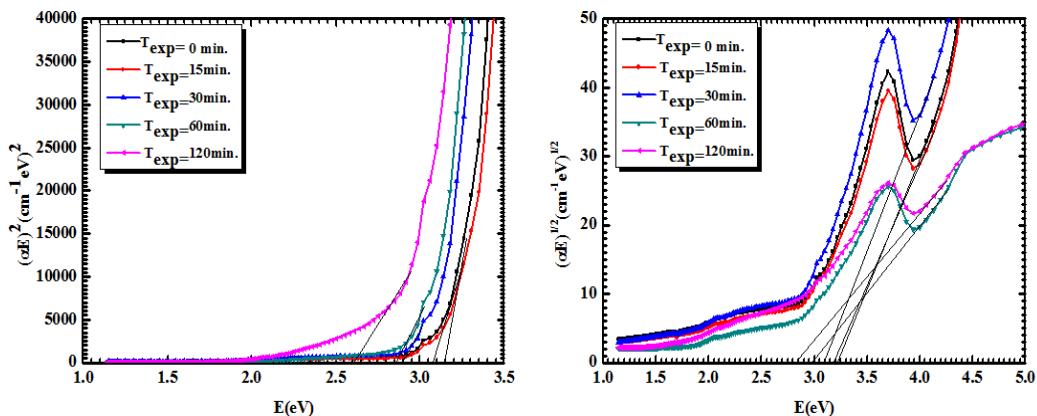
Figure(8. a and b): The real part (ϵ_r) (a) and imaginary part (ϵ_i) (b) of dielectric constant as a function of wavelength for pristine and plasma treated PS/C₆₀ nanocomposites films for different durations.

3. 4. Determination of optical band gap

The optical band gap is the value of optical energy gap between the valance band and the conduction band. The optical band gap of the samples is determined from the absorption spectra near the absorption edges. The relation between the optical energy band gap, absorption coefficient and energy ($h\nu$) of the incident photon is given by [24] and[25]:

$$\alpha h\nu = B(h\nu - E_g)^r \tag{6}$$

where α is the absorption coefficient, ν is the frequency, h is the Planck's constant, B is a constant, E_g is the optical energy band gap between the valence and the conduction bands and r is the power that characterizes the transition process. Specifically, r can take the values 1/2, 3/2, 2, and 3 for transitions designated as direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively. The usual method to determine the optical energy band gap is to plot a graph between $(h\nu\alpha)^{1/r}$ and $h\nu$. The best fit of indirect transitions is obtained for $r = 2$, meanwhile for a direct transition the best fit is obtained for $r = 1/2$. The indirect optical energy band gap is determined by plotting $(\alpha h\nu)^{1/2}$ against the photon energy ($h\nu$). The extrapolation of the straight parts of the curves to the energy axis ($h\nu$) yields the indirect optical energy band gap. To obtain information about direct and indirect transition, the optical energy gap was determined from the analysis of spectral dependence of the absorption near the fundamental absorption. Figure (9. a and b) show the dependence of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ on the photon energy ($h\nu$) for untreated and nitrogen plasma treated PS/C₆₀ nanocomposite films at different durations respectively. The values of optical energy band gap for pristine and plasma treated samples are tabulated in Table 2. It was found that, PS/C₆₀ nanocomposite films revealed a decrease in energy gap with increase in the exposure time, this may be due to the decrease of the crystalline nature by plasma exposure which in turn decrease the band gap[26].



Figure(9. a and b): $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of the photon energy spectra for pristine and plasma treated PS/C₆₀nanocompsites films for different durations.

Table 2: Displays the values of optical energy band gaps for pristine and plasma treated samples

Treatment time (min.)	E _g (indirect) (eV)	E _g (direct) (eV)
0	3.26	3.96
15	3.2	3.87
30	3.07	3.82
60	2.99	3.75
120	2.83	3.64

IV. Conclusion

Low power, low pressure N₂-DC- plasma has been used to modify the surface and optical properties of PS/C₆₀nanocompsites films . Samples prepared and exposed to N₂-DC- plasma for varying treatment time. The plasma treatment increased polar functional groups onto the surface of the PS/C₆₀nanocomposite films causing decrease in contact angle and increase in surface energy, which in turn, enhance the surface wettability. The Refractive index (n) and the real and imaginary parts of the dielectric constant were showed clear changes with plasma exposure, while the values of direct and indirect optical energy band gap are decreased with the plasma exposure time.

References

- [1]. Mitsuru Tanahashi, *Materials*, 2010, 3, 1593.
- [2]. Pragatheeswaran A, Abdul Kareem T and Anu Kaliani A , *Plasma Science & Technology (PLASMA-2008) IOP Publishing Journal of Physics* , 2010, 208, 012109.
- [3]. Prime D, Paul S, Josephs-Franks P. ,W. *IEEE Trans. Dielectr. Electr. Insul*, 2008, 15, 905.
- [4]. Evgeniya H. Lock, Dmitri Y. Petrovykh, Paul Mack, Tim Carney, Richard G. White, Scott G. Walton and Richard F. Fernsler, *Langmuir* , 2010, 11, 8857.
- [5]. Alekseeva OV, Bagrovskaya NA, Noskov AV, *Processing of the International Conference, Nanomaterials applications and properties*, 2013, 2 , 03NCNN 24-1.
- [6]. Alejandro Sanz, Him Cheng Wong, Alisyn J. Nedoma, Jack F. Douglas, Joeao T. Cabral, *Polymer* , 2015, 68, 47.
- [7]. Ahmed R M and El-Bashir S M, *International Journal of Photoenergy*, 2011, 801409 ,1.
- [8]. Alenka Vesel and Miran Mozetic, *Journal of Physics*, 2009, 162 , 012015.
- [9]. Borcia C., Borcia G. and Dumitrascu N., 28th ICPIG, July 15-20, 2007, Prague, Czech Republic, 13 ,700.
- [10]. Manas D, Manas M, Stanek M, Danek M, *Arch. Mater .Sci. Eng.*, 2008, 32, 69.
- [11]. Agrawal N K, Awasthi K, Vijay Y K and Swami KC, *Journal of Advanced Electrochemistry*, 2013 ,2, 31.
- [12]. Yakuphanoglu F , Barim G, Erol I , *Physica B*, 2007, 391, 136.
- [13]. Donald S. Bethune, Gerard Meijer , Wade C. Tang, Hal J. Rosen, William G. Golden, Hajime Seki, Charles A. Brown and Mattanjah S. de Vries, *Chemical Physics Letters*, 199 1, 179, 2 12 .
- [14]. Jung-Woon Kim, Kun-Ji Kim, Sooyeon Park, Kwang-Un Jeong, and Myong-Hoon Lee, *Bull. Korean Chem.Soc.*,2012, 33, 9.
- [15]. Idage S B and Badrinarayanan S, *Langmuir* 1998, 14, 2780.
- [16]. Subedi D P, Madhup D K, Adhikarai K and Joshi U M, *Indian Journal of Pure and Applied Physics*, 2008, 46, 540.
- [17]. Nagla. M. Elsayed, Magdy. M. Mansour, Omar. F. Farag and Mohammed. H. Elghazaly N₂, N₂-Ar and N₂-He DC Plasmas for the improvement of Polymethylmethacrylate surface wettability, *Adv. Appl. Sci. Res.*, 2012, 3,1327.
- [18]. [18] Khalaf Ibrahim Khaleel, Awatif Sabir Jasim, Mohamad Abdul Kareem Ahmed, Vijay Y K and Subodh Srivastava, *International Journal of Recent Research and Review*, 2012 ,3, 2277 .
- [19]. El-Khodary A, *Physica B: Condensed Matter*, 2010, 405, 4301.
- [20]. Dragoman D and Dragoman M, *Optical characterization of solids*. 1st ed, Springer, Berlin, 2002.
- [21]. Dorrnian D, Abedini Z, Hojabri A, Ghoranneviss M, *Journal of Non-Oxide Glasses*, 2009, 1,217 , 229.
- [22]. Seraphin B O, *Optical Properties of Solid New Developments*, Company, American Elsevier Publishing, New York, 1976.
- [23]. Ghanipour M and Dorrnian D, *Journal of Nanomaterials*, 2013,1,10.
- [24]. Tauc J, *Amorphous and Liquid Semiconductors*, Plenum Press, New York, 1979, pp159.
- [25]. Mott N and Davis E, *Electronic Process in Non-Crystalline Materials*, 2nd Edition, University Press, Oxford, 1979.
- [26]. Atta A and El-Sayed SM, *journal of Engineering and Technology Research*, 2015, 7 , 10.