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Plasma Impact on the Structural and Optical Properties of Polycarbonate/polyester Blend

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ABSTRACT

The polycarbonate / polyester (PC / PS) blend is one of the very distinctive blends which is distinct by its high degradation resistance and hence it is characterized by a good thermal stability. In the research in hand, the authors used X ray diffraction and UV spectroscopic methodologies to get information concerned with the influence of plasma (1 - 3 min.) on the structural and optical characteristics of the blend film. The changes of the optical band gap (Eg) and the refractive index (n) with the plasma exposure time were interpreted. An increase in n (1.5663 - 1.5764) associated with a reduction of Eg (6.71 - 6.58 eV) was noticed when augmenting the exposure time up to 3 minutes. These trends were assigned to the dominance of chain crosslinks. The plasma radiation encourages the transesterification interaction between the PC and the PS leading to a more compact structure of the copolymer.

1. INTRODUCTION

Polycarbonate (PC) and polyester (Ps) are two thermoplastic materials that are frequently utilized in a variety of applications. PC is a manufactured amorphous polymer with outstanding transparency that makes it suitable for use in optical data storage devices such as CDs and DVDs. Additionally, they are utilized in further engineering fields including construction, and transportation. Meanwhile, Ps is a semi - crystalline polymer that is utilized in several industrial applications, including films and fibers. The PC-Ps mixes have garnered interest recently in industry [1]. The polymer mix is among the most fascinating areas that helps to progress industry [2]. New high-performance polymers are produced in this sector. For instance, the Bayfol class of nuclear track detectors (NTDs) is produced by combining polyester (Ps) with polycarbonates (PC). A crucial component of industrial mixes is the PS and PC mix.

In comparison to the combined polymers, the resulting mix exhibits good physical and chemical properties that are chemically stable [3]. The transesterification process was thought to be the most critical one to occur between PC and Ps, leading to a unique copolymer structure with distinct IR function groups [4,5].

These copolymers have a remarkable ability to maintain its original dimension, spectacular serviceability, and strong mechanical and thermal characteristics, of both polycarbonate and polyester. The polymer characteristics are altered due to the breakdown of the polymeric chains caused by plasma irradiation, and the creation of biochemically active free radicals that serve to generate novel covalent bonds resulting in chains crosslinks [6]. Additionally, the γ irradiation causes lattice flaws, changing the characteristics of the polymer[7].

Optical and electrical instruments frequently involve the descriptions of the optical characteristics of polymers exposed to radiation [8]. Polymeric materials' refractive indices reveal information about their essential characteristics [9]. Additionally, the irradiation-induced color changes are used to evaluate the substance's optical properties. This becames a significant approach used to evaluate the changes of the physical characteristics of polymers after being exposed to radiation. This is

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a crucial piece of scientific proof for their use in dosimetry and commercial requirements [10]. Researches were conducted to demonstrate the importance of the changing colors of polymers exposed to radiation in the dosimetry sector [11–13]. They investigated if the color alteration approach offered the principles that had to be taken into account while developing radiation sensors. The color change in the DPF exposed to radiation was attributed to the free radicals produced, which facilitated the development of conjugated bonds [14]. Furthermore, the radical species, the released benzophenones, and the highly conjugated bonds or reorganized isopropylidene radicals were held responsible for the color change in the treated PC.

The current research focuses on whether it is possible to change the Bayfols' optical and structural characteristics in order to improve its performance in a variety of purposes.

2. EXPERIMENTAL

2.1 Materials

Bayfol DPF CR 1-4 is a PC/Ps blend film of chemical configuration, average thickness and density of $C_{16}H_{14}O_3$, 380μm and 1.23 g/cm^3, respectively. It is fabricated by Farbenfabriken BayerA.G., Leverkusen (Germany).

The samples were exposed to plasma using a plasma source described in details in a previous work [15].

2.3 Analysis of the exposed samples

The XRD was measured applying a Shimadzu 6000 diffractometer, which is noted for its Cu-k radiation. The X-rays had a wave length of 1.54 Å and the diffraction patterns were taken in the 2θ at a rate of 2° per minute, ranging from 10° to 30°.

The Tomos UV-1800 Spectrophotometer was applied to measure UV spectra at wavelengths ranging from 280 to 800 nm.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The change in the ratio of ordered to disordered regions due to plasma exposure was investigated using XRD. Figure (1) shows the XRD curves for the exposed and non-exposed Bayfol films for the samples recorded within 2θ (10-30 degrees).

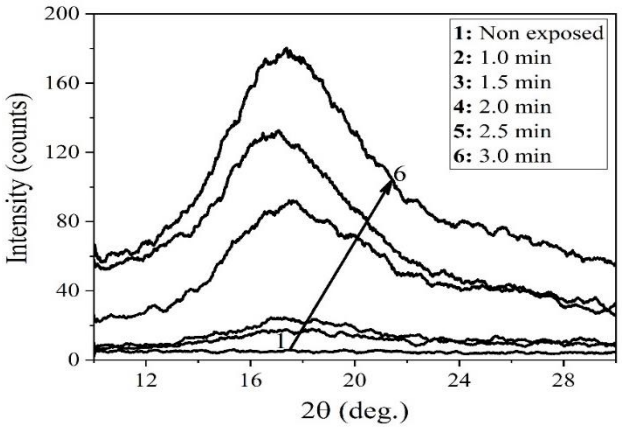

Fig. (1): XRD spectra of the exposed and non-exposed films

The results indicate a disordered halos (2θ = 14-22°) implying disordered regions' dominance. As can be seen, integral intensity, or the area under the curve, decreases as exposure duration increases up to 3 minutes. As a consequence of crosslinking, which decreases crystallinity, the disorder nature of the samples increases. Crosslinking causes the integral intensity to decrease, resulting in the breakdown of ordered structure. This reduction shows that plasma exposure causes regular lamellas to crosslink, resulting in non-arranged lamellas. Another issue which improves the crosslinks mechanism is the transesterification reaction among PC and Ps, resultant in a novel construction of copolymers [4,5].

3.2 Optical analysis of plasma exposed Bayfol films

3.2.1 Absorption

Figure (2) shows the absorbance of UV spectra of the exposed and non-exposed Bayfol films in order to compute band-gap configuration changes owing to plasma exposure and provides insight into optically induced electronic transitions.

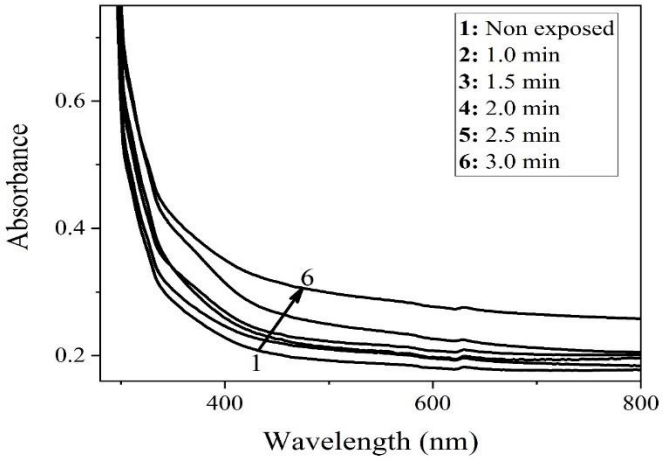

Fig. (2): Absorbance pattern of exposed and non-exposed Bayfol films in UV–Vis

At about 280 nm, a prominent absorption band was discovered, which was minimized when the wavelengt h was increased up to 800 nm. The n−π* transition carbonyl group C=O and π− π* phenyl groups were responsible for the decrease in absorbance with wavelength [16]. It can also be caused by the development of color centers at wavelengths of 280 nm [17]. Photo-chemical reactions begin in the Bayfol matrix at that wavelength due to UV absorption, which causes macromolecules to form singlet or triplet ones [16]. The act of plasma destroys the C-H bond for wavelengths larger than 280 nm.

Furthermore, increasing the plasma exposure duration to 3 min enhanced the absorption of the films. It is attributed to the formation of conjugated bonding. As a result, a smaller optical band-gap is expected as exposure time is increased [18].

The following formula relates the extinction coefficient k to the refractive index:

$$n^* = n + ik \qquad (\mathbf{1})$$

The refractive index's real and imaginary components are indicated by n and k, respectively.

The value of k is calculated using the following formula:

$$k = \frac{\lambda\alpha}{4\pi} \qquad (\mathbf{2})$$

where λ is the incident light's wavelength. The absorption coefficient α may be computed using the following equation:

$$\alpha = 2.303 \times \frac{\text{Absorbance}}{\text{Sample's thickness}} \qquad (\mathbf{3})$$

The coefficient of absorption, α, denotes the amount of the light absorbed by the substance, and is thus used to depict differences in the band's configuration.

3.2.2 Band-Gap

The values of the band gaps, E_g were obtained by a direct transition method, which is called Tauc's equation that presents the information about the band-gap structure transitions [19]

$$\alpha h\nu = B(h\nu - E_g)^n \qquad (\mathbf{4})$$

Where hν signifies the energy of the incoming photon, B denotes a constant, and the index n denotes the nature of the electronic transition. Direct transitions have n values of $\frac{1}{2}$ or $\frac{3}{2}$, but for indirect transitions, it equals 2 or 3 depending on if they are allowed or disallowed, correspondingly [20]. Drawing the correlation of $(\alpha h\nu)^{1/n}$ and hν, then extrapolating the straight portion of the curve to cross the hν axis, is used to get E_g as shown in Figures (3-5). Band-gap tends to decrease upon the increase of the plasma exposure time to a maximum of 3 min. Crosslinking is responsible for the narrowing of the optical band gap. As a result of the produced defects, the amorphous state of the Bayfol films is improved, and localized bands are formed in the E_g zone, resulting in lower-energy micrelectronic transitions. That is, the creation of chain scissions, bonding and unsaturated bonds is caused by the generation of free radicals as a result of plasma radiation on Bayfol. Raising the plasma exposure period increases the rate of free radicals generation and the formation of conjugated and unsaturated bonds, resulting in a reduction of E_g [18].

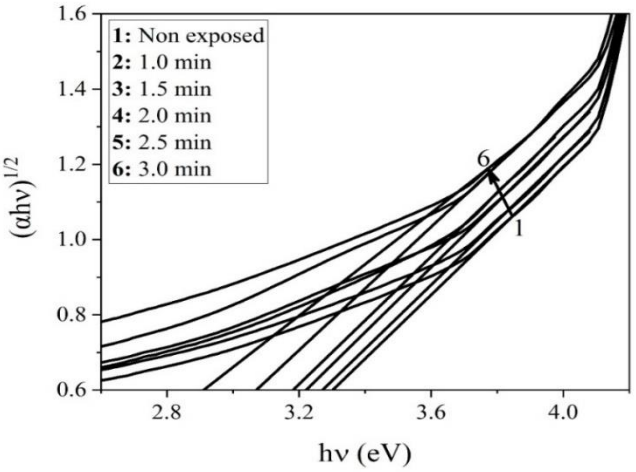

Fig. (3): A plot of $(\alpha h\nu)^{1/2}$ against hν

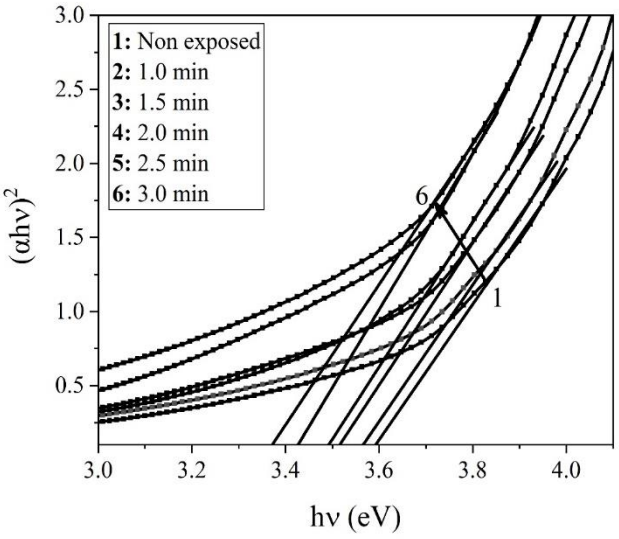

Fig. (4): $(\alpha h\nu)^2$ against hν

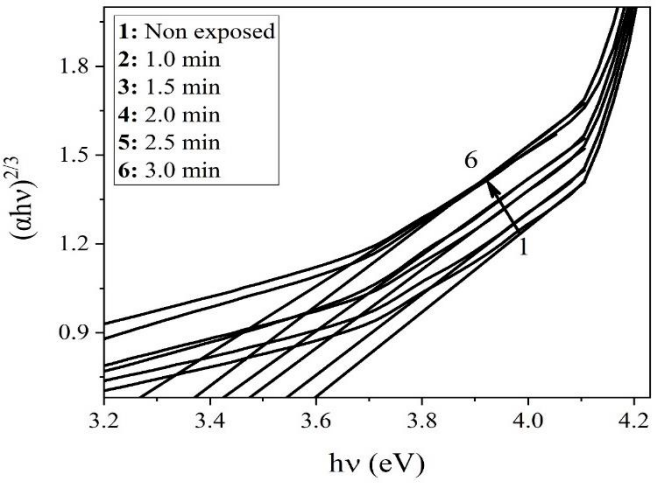

Fig. (5): $(\alpha h\nu)^{2/3}$ against hν

The optical band-gap and electronic transition type were calculated using the optical dielectric loss shown in Figure (6) and Tauc's model shown in Figure (3-5).

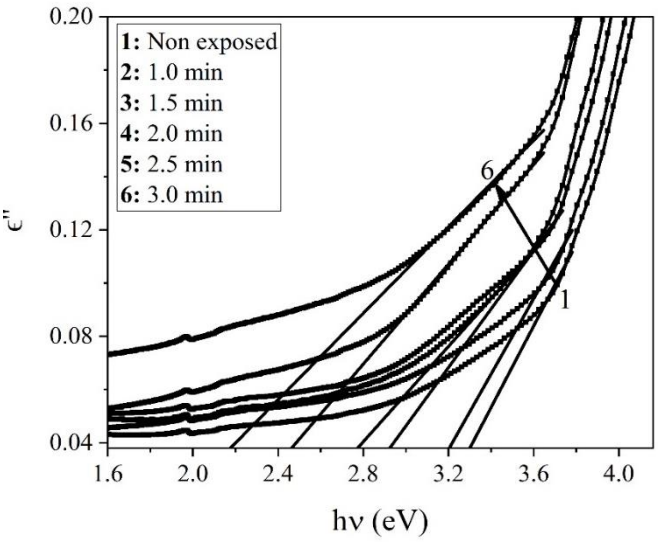

Fig. (6): The optical dielectric loss against hν

This is because the optical dielectric function is highly dependent on the band structure of the substance. Furthermore, using UV spectroscopy to analyze the optical dielectric function is quite valuable in establishing the band structure of the entire material [20]. The imaginary component of the optical dielectric function ε″ [21,22] is applied to explore the electrical transition among unoccupied and occupied states. The optical dielectric loss ε″ can be computed applying the formula below:

$$\varepsilon'' = 2nk \qquad (5)$$

The extinction coefficient is k, and the refractive index is n. Figure (6) shows the optical dielectric loss spectra for the exposed and non-exposed Bayfol. As shown in Table (1), the optical band-gaps of the films estimated using the optical dielectric loss are quite close to those expected using Tauc's model. As a result, the electronic transition type is the only authorized direct transition[22].

Table (1): E_g (calculated from Tauc's model and ε″ vs. *hν*) for the non-irradiated and irradiated Bayfol samples

Exposure time (min)	E_g calculated from ε″ vs. *hν*	E_g calculated from Tauc's Model (eV)		
		E_g^2	$E_g^{½}$	$E_g^{⅔}$
0	٣,٠٥	٣,٥٧	٢,٦٠	٣,١٢
١	٢,٩٣	٣,٥٤	٢,٥٧	٣,٠٥
١,٥	٢,٥8	٣,٥٠	٢,٥٣	٢,٩٦
٢	٢,٣5	٣,٤٧	٢,٤٨	٢,٩٠
٢,٥	٢,٠6	٣,٤٠	٢,٣٤	٢,٨٧
3	١,٧1	٣,٣٥	٢,٠٣	٢,٦٧

3.2.3 Materials Structure and Refractive Index

The following formula is used for calculating the refractive index, n, for Bayfol films [23]:

$$\left(\frac{n^2-1}{n^2+1}\right) = 1 - \sqrt{\frac{E_g}{20}} \qquad (6)$$

Figure (7) demonstrates how the refractive index varies as the time interval of plasma exposure rises.

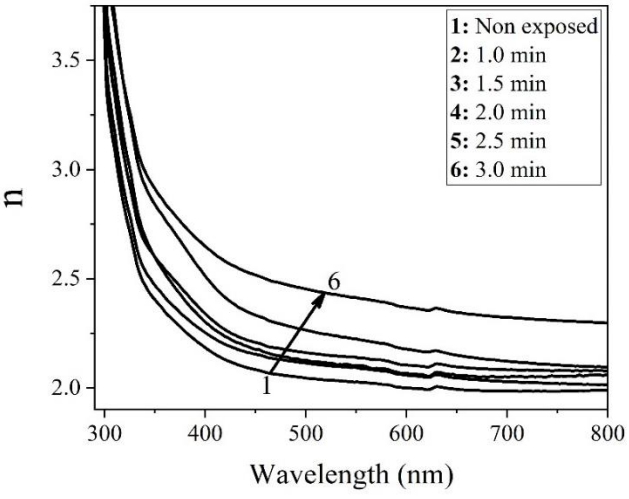

Fig. (7): A plot of refractive index changes vs. plasma exposure time

The index of refraction is increasing on growing the exposure time up to 3 minutes. This pattern matches that of E_g which indicates the authorization of crosslinks. Chain scissions produce active free radicals which allow for the formation of covalent bonds via crosslinking. This explanation is in a good agreement with what was previously discovered [24].

The dielectric properties primarily give information on the solid-state optical properties [25]. The dielectric constant varies with hν, indicating that strong photon-electron interactions developed in the films at this energy level.

According to the following formula, the dielectric constant is correlated to *n* and *k* [26].

$$\varepsilon' = n^2 - k^2 \qquad \textbf{(7)}$$

The values of $\underline{\varepsilon''}$ were evaluated and displayed in Figure (8) vs. wavelength. As the exposure time is prolonged to 3 minutes, the dielectric constant rises. This implies that plasma exposure improves the density of states inside the forbidden gap of the blend [27].

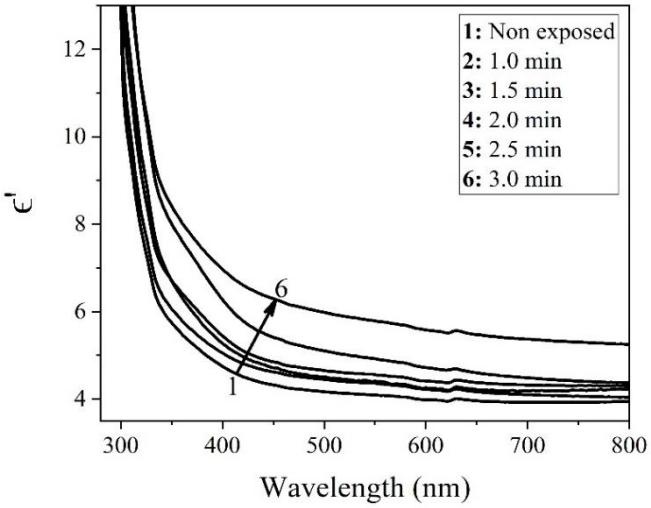

Fig. (8): Optical dielectric constant vs. h*ν*

4. CONCLUSION

Plasma irradiation of Bayfol films causes crosslinking dominance, which alters the structural and optical properties of the films under investigation. Due to a plasma exposure length of up to 3 minutes, the amorphous regions grew larger, and the Bayfol gained flexibility. As a result, the polymer proposed in the current study could be a good fit for applications requiring bendability without breaking. The optical band-gap value dropped significantly as the plasma exposure time was increased to 3 minutes, although the refractive index and optical dielectric constant values rose. Such changes in the optical features may lead to improvements in the Bayfol films' optical qualities, making them suitable for the use in switches, filters, optical coatings, and other applications.

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