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Improved Surface Properties of Copper/Polymethyl Methacrylate Nanocomposite Films Using DC O2 Plasma

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Films of Polymethylmethacrylate with copper nanofiller were prepared and treated with low temperature oxygen DC glow discharge plasma. FTIR spectroscopy, AFM, water contact angle (WCA) measurements and UV-Vis spectroscopy were used to detect the produced chemical, morphological and optical changes as a function of plasma treatment time. The FTIR spectra, showed a decreasing value of the main characterizing signals of the composite films in addition to the creation of an oxygen containing functional group. The surface morphology of the treated samples was altered according to the increased values of the average surface roughness, obtained from the AFM images. The WCA also, decreased noticeably with increasing treatment time. The UV-Vis spectroscopic analysis showed a decreasing value of the optical absorption in the wave length range 190-270 nm which is an indication to the loss of carbonyl group. The value of direct and indirect optical band gap decreased with treatment time meanwhile, values of the band tail width were significantly increased.

Keywords: *O_2 DC Plasma, Plasma surface modification, Cu/PMMA Nanocomposites films*

Introduction

Research efforts in producing polymeric materials with unique properties have led to the incorporation of nano-particle materials into the polymeric matrices, which facilitates the exchange of properties between the phases and hence, widen their applications [1-6]. Tremendous efforts were made on mixing metal nanoparticles into a polymer matrix to generate new materials called metal nanocomposites [7]. These metal nanoparticles (NPs) have attracted much attention because of their wide range of applications in, optical fibers, waveguides, nonlinear optical switches, imaging materials, household appliances, automotive and various medical applications [8-15].

In this study Cu/PMMA nanocomposite films were prepared and treated with low temperature DC glow discharge oxygen plasma for surface and chemical modification. PMMA is an important polymeric material having several excellent properties such as, low cost, good tensile strength, hardness, high rigidity, transparency, low optical, high light transmittance low glass temperature, high electrical resistivity and thermal stability. PMMA has the chemical structure, $[CH2\ CH\ (CO2H)]_n$ and it is amorphous in nature. It is used in a wide variety of products including airplanes, cars, jewelry and electronic devices, in addition to a large number of medical devices which are made of PMMA such as, cement, contact lenses, blood filters, plastic surgery filler, and tooth filler. Cu NPs have many applications in industry, including its uses in gas sensors, batteries and super conductors. The most important feature characterizing Cu NPs is its antimicrobial activity against many infectious organisms [16, 17].

Nanocomposite materials generally, have excellent bulk physical and chemical properties. However, certain properties such as low surface adhesion,

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low wettability and high electrical resistivity sometimes limit their applications. Different methods have been developed to overcome these problems and obtain the desired surface properties. Among these methods, is the use of non-equilibrium plasmas for surface modifications which is a rapidly growing research fields. Plasma, as a surface modification technique, has the ability to change the surface morphology, chemical structures without affecting the bulk properties of the treated material [18-21]. Plasma's active species and energetic photons generated by the discharge have major contributions to the modification of polymer surface. Four main effects can be induced on the treated surfaces, namely, surface cleaning, ablation, crosslinking and surface chemical functionalization [22]. The literature shows a considerable amount of experimental data regarding the effects of plasma on the surfaces of a large variety of materials. S. Kitova et al. [23] found that, the surface free energy of PMMA and PC increased after treatment with Ar, Ar/H_2O and Ar/C_2H_5OH soft plasma. Darain F.et al. **[**24] improved the surface wettability of PMMA substrates as a result of O_2 plasma treatment. B.L.E. Sánchez et al. [25] enhanced the antibacterial properties, surface wettability and surface roughness of PP/Ag and PP/Cu nanocomposite by argon plasma treatment. F.O. Farag [26] studied the effect of DC N_2 and Ar plasmas on the surface of PS films. The surface free energy and surface roughness of the treated samples were increased remarkably with increasing the plasma treatment time.

The O_2 DC glow discharge treated films were characterized by the, FTIR spectroscopy, AFM, the water contact angle (WCA) measurements in addition to the UV-Vis absorption spectroscopy.

Material and methods

Sample preparation

Cu/PMMA nanocomposite films, with a Cu contentof 1w.t%, were prepared by the solution-casting method.PMMAin the form of grains and CuNPs, of particle size 60 nm, obtained from Sigma-Aldrich Company.2 gram of PMMA granules were dissolved in 40 mL of toluene (with purity 99.99).The mixture was vigorously stirred using a magnetic stirrer till a clear solution is formed. Then 0.02 gm of Cu nanoparticles was added and stirring was continued till a homogenous suspended solution obtained. The solution was poured into a clean glass Petri dish, and the solvent was allowed to evaporate in a dry atmosphere, at room temperature, for several days. After complete dryness, the samples, with a thickness ≈ 0.25 mm, were removed from Petri dish and cut into rectangular sheets (1cm× 2cm).

Plasma treatment

Cu/PMMA nanocomposite films were treated in a DC glow discharge reactor described in details in a previous work [27].The discharge parameters were kept unchanged through the whole experiment. The base pressure of the plasma reactor was 10^{-3} Torr, then it was increased to 0.4 Torr after feeding with oxygen gas and the input power was about 3.5 Watt. The sample is supported on a glass holder and located in the negative glow region of the discharge, about 2cm apart from the cathode.

Sample characterization

Chemical modifications before and after plasma treatment were characterized by Fourier transform infrared spectroscopy (FTIR). The measurements were performed using Bruker Alpha spectrophotometer in the wave number range of ($400cm^{-1}$ - $4000cm^{-1}$) in the absorbance mode. Water contact angle (WCA) measurements were used to examine hydrophilicity modification of the nanocomposite films using a traveling microscope based on taking a high quality photo of the liquid drop. All contact angles are the mean value of four measurements on different locationson the same sample. Surface morphology and roughness analysis of O_2 plasma-treated surfaces were conducted by means of atomic force microscopy (AFM) using a WET-SPM scanning probe microscope (Shimadzu, Japan). UV-Visible spectral analysis was also done to identify the effect of plasma treatment on optical properties of Cu-PMMA nanocomposites films using a Perkin–Elmer Lambda 950 spectrophotometer over a wavelength range 200–900 nm.

Results and discussion

FTIR analysis

The FTIR spectrum of untreated and O_2 plasma treated samples was carried out to examine the chemical modification of the treated films. Figure (1-a) shows the major characteristic absorption bands belonging to the untreated Cu/PMMA film. According to the literature [28-30], the peaks at

2948cm^{-1} and 2992 cm^{-1} are attributed to CH_3 and CH_2 stretching respectively. The intense absorption peak at 1721 cm^{-1} is attributed to C=O vibration in the pendant group $–COOCH_3$ in the PMMA. The peaks at 1441 cm^{-1}and 1062 cm^{-1} are from CH_2 bending vibration and C-O bond stretching respectively. The band between 1385 and 748 are due to α-CH_3 vibrations. All the previous results are attributed to pure PMMA characteristics. However, Cu NPs didn't show any characterizing signals and this may be an indication that Cu NPs could be encapsulated in the PMMA polymer microspheres, and the PMMA layer would shield any characteristic signal due to copper oxidation or contamination [31, 32].

The FTIR spectra of the treated samples Figure (1b - e) have similar peaks to the untreated one, however their intensity showed a decreasing behavior with increasing the treatment time. The peaks between 2948cm^{-1} and 2992 cm^{-1} have their highest intensities in the untreated sample, while getting weakened with increasing treatment time. This can be interpreted in terms of Bouger-Lambert-Beer law, which states that the absorbance in infrared transmission spectra is directly proportional to the concentration of the absorbing functional group as: $A = \varepsilon C h$; where A is the absorbance, ε is the extinction coefficient, C the concentration and h is the sample thickness [30]. This result suggests that the percentage of -CH_3 terminal function groups on the surface of the untreated film is more than the treated one and similarly for the rest functional groups. The diminishing of carbonyl group (C=O), at 1721 cm^{-1}, and the decrease in its intensity with increasing treatment time is an indication to the occurrence of surface crosslinking of the treated samples or due to surface etching by plasma [33].This result is in agreement with previously published work [24, 34, 35], who supported their result by EDX and XPS analysis which proved the reduction of C-atoms percentage and increasing that of O-atoms. The FTIR monitored a new created broad peak extending from 3100 cm^{-1} to 3600 cm^{-1} for samples treated for 45 and 60 min. and this range belongs to the hydroxyl (–OH) group. It is well known that in O_2 plasma, as an oxidative medium, the creation of hydroxyl group is mainly due to the chemical interaction between the active plasma species and the surface atoms [36].This is in addition to the adsorption of moisture from the residual water vapor, which commonly exist in low pressure plasma reactor, or from ambient air just after removing the samples from the plasma chamber.

Surface morphology

The detailed surface morphology of the untreated and treated samples can be seen in the AFM images Figs. (2 and 3) from which the changes induced due to plasma treatment can be examined. Figure (2) shows that, the untreated film appears to be almost flat however, upon plasma treatment many hell-like granules protruded out of the surfaces and their number increased with increasing treatment time.

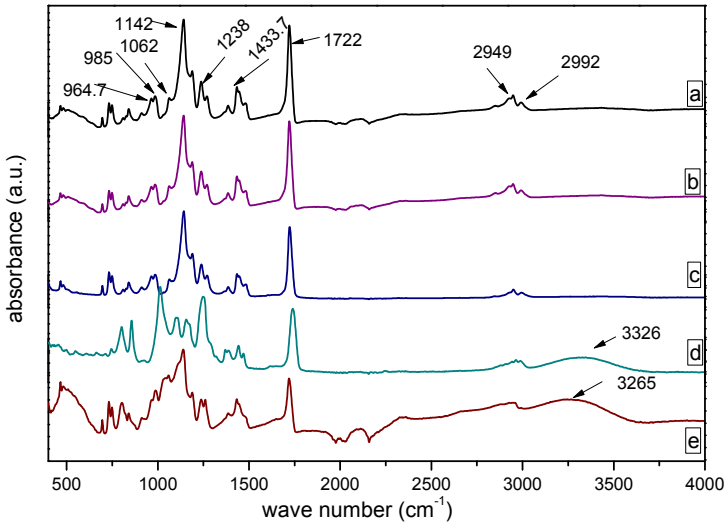

Figure (1): FTIR spectra of untreated [a] and treated films for 15 min [b], 30 min [c],

45min. [d] and 60min. [e]

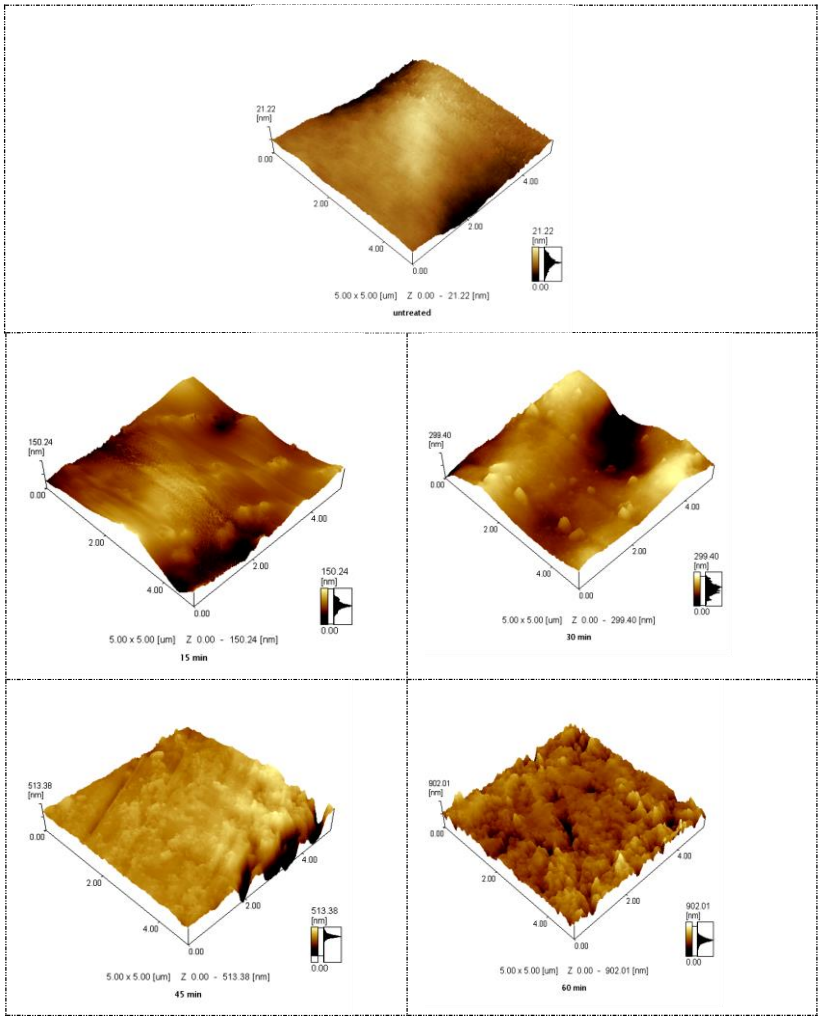

Figure (2): AFM images for untreated and plasma treated samples for different treatment time

This result was confirmed also, by the particle analysis given by the two-dimension AFM images shown in Figure (3). The average roughness increased from 0.8 nm For untreated sample to 1 nm for 15 min, 1.9 nm for 30 min, 1.5 for 45 min and 1.6 for 60 min. Increasing surface roughness with increasing treatment time can be referred to the etching effect due to the bombardment of the most energetic plasma species on the film's surface. It was reported that [37], extensive etching was observed upon treating a polymeric material with O_2 plasma. Atomic oxygen reacts with the surface carbon atoms producing volatile reaction products removed from the surface through a reactive etching process which is also called aching.

Surface wettability

Many applications of polymer nanocomposites, especially in the field of biocompatibility, require the surfaces to be of high wettability. The wettability of the Cu/PMMA films was examined by measuring the WCA for the samples treated with O_2-plasma for different treatment durations. The results, given in Figure (4), shows that the value of WCA of the untreated sample agreed with reported values for pure PMMA [19, 38].This means that, the doped Cu NPs are covered with the polymer matrix so that it has no effect on the value of the contact angle of films. The contact angle showed a decreasing trend with increasing the treatment time. Its initial value was 78.67^o which dropped to 46.5^o after about 90 min of O_2 plasma treatment. According to the literature [39, 40], the decreasing values of WCA can follow the exponential relation:

$$\theta = \theta_{\infty} + (\theta_i - \theta_{\infty})e^{-k\tau} \qquad (2)$$

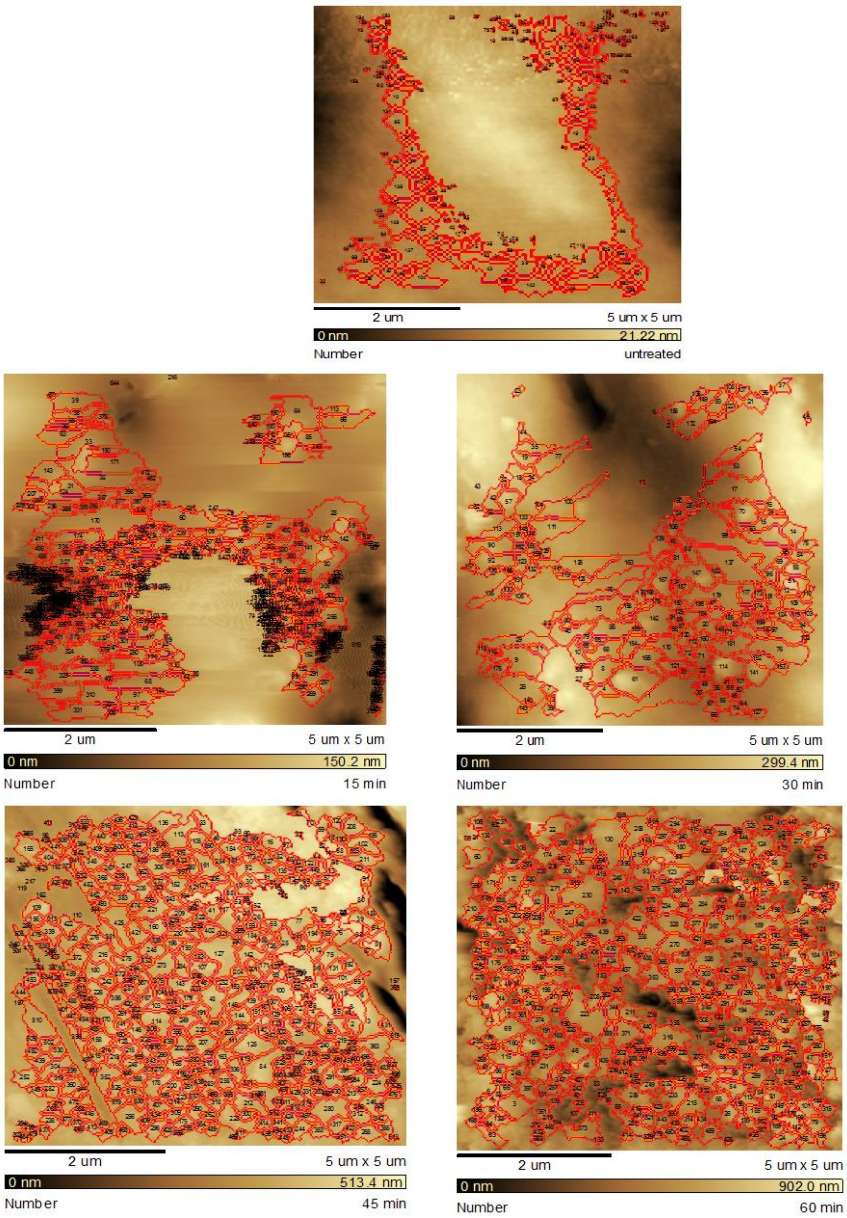

Figure (3): AFM particle analysis for untreated and plasma treated samples for different treatment time

Where θ is the WCA at the corresponding treatment time τ, θ_{∞} is the WCA at maximum treatment time, θ_i is the initial WCA and κ is the surface activation rate constant. According to our experimental data, κ was found to have an average value of 0.03 s^{-1} which is a very small value compared to that reported in the literature [41]. The reason of this can be attributed to the prolonged time of treatment.

It has been established that the hydrophilic properties of plasma treated surfaces are mostly attributed to the changes in their chemical and morphological properties. The FTIR spectra confirmed the chemical changes of the treated surfaces, and it detected the incorporation of –OH polar group on the surfaces of the samples treated for 45 and 60 min. which in turn, increases the surface polarity and hence enhances its wettability. Increasing surface roughness with increasing treatment time, as showed in the AFMimages, is

known to be associated with increasing the effective contact area of the surface.

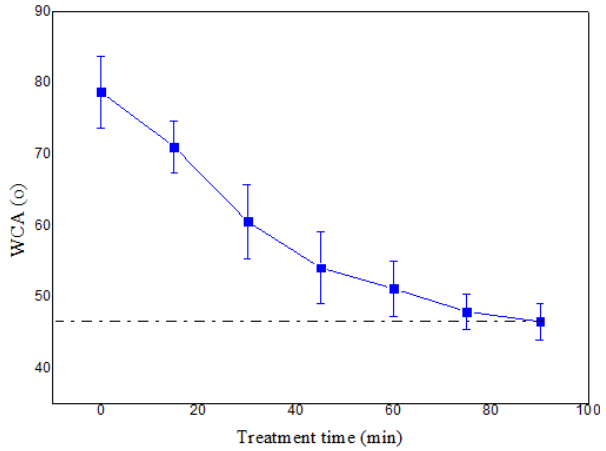

Figure (4): Water contact angle as a function of plasma treatment time

UV-Vis analysis

Figure (5) shows the UV–Vis absorption spectra of unirradiated and O_2 plasma irradiated Cu/PMMA nanocomposite films in the wavelength range of 200–900 nm. A remarkable decrease in the optical absorption with increasing treatment time for the irradiated samples can be observed in the wavelength range 190-270 nm. This decrease could be attributed to the loss of carbonyl group (C = O) due to the oxidative decomposition of the double bonds or plasma etching effect during irradiation with O_2 plasma [42]. In the wavelength range 270-900 nm, the optical absorption increases with increasing the irradiation time. Also, it can be noticed the existence of a shift in the absorption edge of the spectra toward the longer wavelength for plasma irradiated samples. This shift is an indication for the reduction in optical energy gap and could be attributed to the induced defects in the polymeric materials by the irradiation [43, 44].

The values of indirect and direct optical energy band gap were determined by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2}$ versus the photon energy (hv) according to Tauc's equation [45] from the extrapolation of the straight parts of the curves $[(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^{2}$ versus (hv)] to the energy axis as showed in Figure (6). The band tail width (Urbach energy) values were obtained by using Urbach rule from the inverse of the slope ln (α) versus the photon energy (hv) [46].

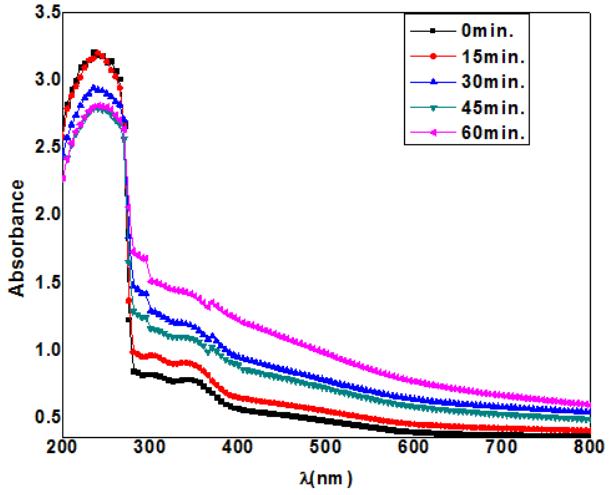

Figure (5): UV-viss absorption spectra of Cu/PMMA nanocomposite samples treated with O_2 plasma for different irradiation times

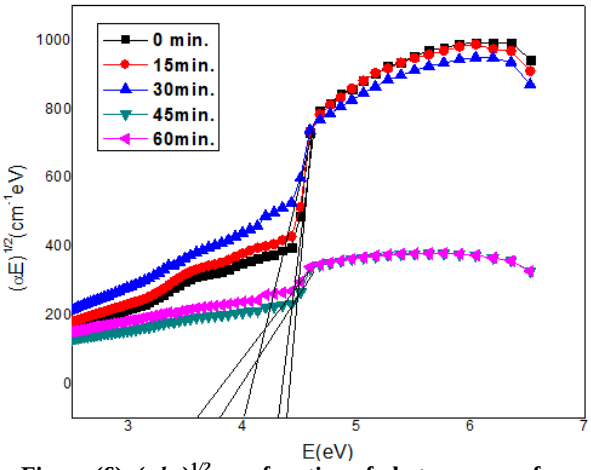

Figure (6): $(\alpha h\nu)^{1/2}$ as a function of photon energy for unirradiated and O_2 plasma irradiated Cu/PMMA nanocomposite films

The calculated values of the optical energy band gab; E_g, and band tail width (Urbach energy), E_u, for Cu/PMMA films upon exposure to the DC O_2 plasma for different exposure time are tabulated in Table (1). It has been observed that both direct and indirect optical energy band gap decrease while Urbach energy increases with increase in the exposure time. It has been also observed that the values of indirect energy gap are lower than those for direct energy gap for the same exposure time. The decrease in optical energy band gap upon plasma exposure could be attributed to the scission process of polymer chain which results in unsaturation and creation of free radicals leading to increasing the conductivity of Cu/PMMA composite samples [47]. The decreasing behavior of optical energy gap with the exposure time is

similar to that reported by Farag, et al. [48]. On the other hand, the increasing of E_u values with the plasma treatment may be attributed to the increase of the width of localized states which is an evidence for increasing the disorder in the treated Cu/PMMA films [49].

Table (1): Optical energy band gap (E_g) and band tail width (E_U) of pristine and oxygen plasma irradiated Cu/PMMA nanocomposite films

Treatment time (min.)	In direct E_g	Direct E_g	E_u
0	4.43	4.5	0.183
15	4.22	4.40	0.211
30	4.12	4.41	0.361
45	3.8	4.35	0.317
60	3.58	4.30	0.526

Conclusion

In this work, an investigation was carried out for the enhancement of surface hydrophilicity and optical properties of Cu/PMMA nanocomposite films, due to low power oxygen DC plasma. The results showed that even with such low power treatment, the film's surfaces showed significant alterations. The FTIR spectra showed a decreasing in the value of the main characterizing signals of the composite films in addition to the creation of -OH group, which leads to the increase of surface polarity. The surface morphology of the treated samples was altered according to the increased values of the average surface roughness, obtained from the AFM images. The WCA also, decreased noticeably with increasing treatment time. The UV-Vis spectroscopic analysis showed a decreasing value of the direct and indirect optical band gap in the main time values of the band tail width were significantly increased as a function of treatment time.

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