



Comparison of the effect of plasma treatment and gamma ray irradiation on PS-Cu nanocomposite films surface

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ARTICLE INFO

Article history:

Received 24 December 2017

Received in revised form 3 February 2018

Accepted 15 February 2018

Available online 18 February 2018

Keywords:

DC plasma

Gamma irradiation

Surface modification

PS-Cu nanocomposites

Hydrophilicity

Spreading coefficient

ABSTRACT

Polystyrene-copper (PS-Cu) nanocomposite films were treated with DC N₂ plasma and gamma rays irradiations. The plasma treatment of PS-Cu film surface was carried out at different treatment times, gas pressure 0.4 Torr and the applied power 3.5 W. On the other hand, the treatment with gamma rays irradiation were carried out at irradiation doses 10, 30 and 50 kGy. The induced changes in surface properties of PS-Cu films were investigated with UV-vis spectroscopy, scanning electron microscopy (SEM) and FTIR spectroscopy techniques. In addition, the wettability property, surface free energy, spreading coefficient and surface roughness of the treated samples were studied by measuring the contact angle. The UV-vis spectroscopy analysis revealed that the optical band gap decreases with increasing the treatment time and the irradiation dose for plasma and gamma treatments, respectively. SEM observations showed that the particle size of copper particles was increased with increasing the treatment time and the irradiation dose, but gamma treatment changes the copper particles size from nano scale to micro scale. The contact angle measurements showing that the wettability property, surface free energy, spreading coefficient and surface roughness of the treated PS-Cu samples were increased remarkably with increasing the treatment time and the irradiation dose for plasma and gamma treatments, respectively. The contact angle, surface free energy, spreading coefficient and surface roughness of the treated PS-Cu samples are more influenced by plasma treatment than gamma treatment.

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Introduction

Polystyrene (PS) is one of the most widely used polymer today; it has a wide range of excellent physical properties such as light weight, wide band gap, high stability, transparent and low cost material [1–3]. The addition of nanometals such as Ag, Au and/or Cu to PS resulting in a new materials known as PS-metal nanocomposites which combined the excellent physical properties of PS and excellent electrical conductivity of metals [4]. The applications of such materials are always limited due to low surface free energy, inertness and high hydrophobicity of their surfaces. Therefore, are need modification to their surfaces properties to suit the different applications.

Among various surface modification techniques, we concerned with the application of DC glow discharge plasma and gamma treatments to modify the surface properties of PS-Cu nanocomposite films. Irradiation of polymeric materials with gamma rays causes various effects as: ionization, free radicals formation, the breakage of C–H and C–C bonds, chain scission, cross-linking,

Hydrogen releases, carbonization and displacing atoms [5–8]. Moreover, the oxidation of the irradiated samples when exposed to the atmospheric air [6]. Therefore, the properties of the polymeric materials such as the: (1) optical, (2) electrical, (3) mechanical and (4) surface including wettability, surface free energy and spreading coefficient become modified [9–12]. The extent of modification depends on the irradiation dosage and material characteristics [13]. On the other hand, glow discharge plasma contain charged and neutral particles, such as electrons, ions, atoms, molecules and radicals. Depending on the gas composition and treatment conditions, the energetic plasma species (electrons, ions, fast atoms, free radicals and UV photon) participate in polymer surface treatment, resulting in three main effects: (i) etching, (ii) activation and (iii) cross-linking [14]. These effects alter the optical, electrical, dielectric and surface properties of the treated polymeric material [15].

The main goal of the present study is to compare the effect of DC glow discharge plasma and gamma treatments on the surface of PS-Cu nanocomposites films. The induced changes in optical properties and the surface morphology were investigated by UV-vis spectroscopy and scanning electron microscopy (SEM). The

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changes in chemical composition of treated surface were carried out by FTIR spectroscopy. Also, the modifications in wettability, surface free energy and spreading coefficient were investigated.

Materials and methods

Samples preparation

The studied PS-Cu samples were fabricated by the casting method. Polystyrene (PS) of molecular weight 135,000 in the form of grains, copper nanoparticles (CuNPs) of particle size 60 nm and toluene with purity 99.998% were supplied by Sigma-Aldrich company. 1 gm of PS was dissolved in 20 ml of toluene and stirring this mixture by using a magnetic stirrer at room temperature for one hour to get the complete dissolution. While the above system was still in liquid state, the desired amount of copper powder was added for the production of PS-Cu nanocomposite samples. The copper powder content in the prepared samples was 1 wt% and the mixture was stirred continuously until homogenous solutions were obtained. The obtained solution was then poured into a clean glass Petri dish. The evaporation of toluene was carried out by placing the samples in a dust free chamber at room temperature for one week. The films thickness were in the range of (0.22–0.25 mm), it were determined using digital micrometer at different places in each film and an average was taken.

Plasma treatment

The details of DC plasma unit used for surface treatment of the PS-Cu films were described elsewhere [16]. The samples were inserted inside the plasma reactor at the interface between the cathode fall region and the negative glow region and supporting them on a glass rode. In DC N_2 plasma treatment, the treatment conditions were kept constant, as the working gas pressure was 0.4 Torr, the plasma power was about 3.5 W and the treatment time was varied from 15 to 60 min. The size of the treated samples was (1 × 2 cm).

Gamma treatment

The irradiations of PS-Cu samples were performed at room temperature and in air by using the gamma cell 220 excel Co^{60} irradiation facility, which is available in the National Center for Radiation Research and Technology (NCRRT), Atomic Energy Authority, Cairo, Egypt. The PS-Cu samples were exposed to irradiation dose varied from 10 to 50 kGy.

Characterization techniques

UV-vis Spectroscopy

The induced changes by plasma and gamma treatments in the optical absorption and optical energy band gaps of the pristine and treated PS-Cu nanocomposite samples were studied by recording UV-vis spectra of samples using UV-vis spectrometer (Perkin-Elmer Lambda 950) in the wavelength range from 200 to 1000 nm.

Scanning Electron Microscope (SEM)

For surface morphology investigation, the scanning electron microscope quanta fei 250, was used to reveal images of the surfaces before and after treatment with plasma and gamma rays irradiations.

Weight loss analysis

In order to quantify the etching effects on the surface of PS-Cu films, a microbalance was used to measure the weight of the samples before and after the treatment. The etching effect in terms of weight loss was calculated by the following equation [17]:

$$\text{Weightloss (\%)} = \left[\frac{(W_p - W_{pt})}{(W_p)} \right] \times 100 \quad (1)$$

where W_p and W_{pt} are the weight of pristine and treated samples, respectively.

Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectra were taken for pristine and treated PS-Cu samples to determine the chemical functional groups which may be formed on the surface of the PS-Cu films upon treatment. The samples were examined by using **an infrared spectrometer device, Vertex 70 Bruker Optics**.

Contact angle measurements

The improvement in the hydrophilicity(wettability), surface free energy(SFE) and spreading coefficient of the PS-Cu films were determined by using the measured values of contact angles of two test liquids namely deionized water and glycerol on the surface of the samples by a travelling microscope. Measurements were performed with deionized water and glycerol at room temperature. The volume of the test liquid drop was about 5 μ l using a microsyringe. Measurements were repeated eight to ten times at different points on the surface of the same sample and the average value was taken.

Results and discussion

SEM analysis

To determine the size and distribution of the copper nanoparticles in addition to the surface morphologies of the sample's surface, scanning electron microscopy was performed. Fig. 1 represent SEM micrograph of PS-Cu nanocomposite samples before and after plasma treatment for different exposure time. CuNP, like most of nano-materials, are reported to have high surface energy so that they have the tendency to agglomerate [18], however in Fig. 2a, low magnification indicates how well-distributed the filler throw the composite film, with mean particle size of 72 nm, the bright spots appearing in the photos corresponds to the presence of CuNP. As the treatment time increases CuNP agglomerate and connect to each other in the form shown in Fig. 1b–d resulting in an increase in the nanoparticles size. The mean values of particle size after plasma treatment are tabulated in Table 1. This result can attributed to the chain scission and degradation of the PS matrix due to plasma. This was explained as, [19–20] chain scission induces polymer chain mobility. When chains relaxes, stresses released and this helps CuNPs to move and agglomerate thus, increasing the mean particle size. Also according to the FTIR analysis for samples treated with plasma for different times in section 3.5, we noticed changes in the intensity of the main peaks characterizing the composite films which an indicator for PS chain scission.

Law magnification SEM image in Fig. 1d shows surface wrinkles of the PS-Cu sample upon plasma exposure for 60 min. As these wrinkles make the surface have more contact points i.e. increases the film's surface area so that, it is suggested to enhance the surface wettability.

SEM analysis also carried out for the samples treated with gamma-irradiation with doses 10, 30 and 50 KGy and the resulted images are given in Fig. 2. The images show a clear hexagonal

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