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RESEARCH ARTICLE - PHYSICS

Preparation and study the structural and optical properties of PS.$Cu_{(etx)2}$ thin films for UV shield application

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Abstract

Thin films of polystyrene PS and polystyrene doped by copper complex $Cu_{(etx)2}$, have been prepared on glass (quartz and pyrex) substrates by the spin coating method. The effect of $Cu_{(etx)2}$ weight ratios (0, 0.02, 0.04, 0.06) wt% on the morphology, structural, and optical properties have been studied. The X-ray diffraction results showed that the pure PS thin films have an amorphous structure. Adding $Cu_{(etx)2}$ improves the crystalline structure by turning it into a polycrystalline state. FE-SEM images showed that the morphology of all samples was almost similar, smooth, and with few defects. The optical measurements showed that in general, PS and PS.$Cu_{(etx)2}$ thin films exhibited high absorption in the UV region and increased with $Cu_{(etx)2}$ weight ratios, as well as a high absorption coefficient (α>$10^4 cm^{-1}$) in the visible range with a direct allowed optical energy band gap E_g, and its value decreased from 3.8 eV for PS thin films to 3.05 eV for PS.$Cu_{(etx)2}$ thin films with 0.06 wt%. The research focused on the preparation of UV shield thin films as a practical application of the current study.

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Keywords: Polystyrene, PS.$Cu_{(etx)2}$, Thin films, UV shield.

1. Introduction

Polystyrene (PS) is a vinyl polymer, versatile for manufacturing a wide variety of consumer products. Its chemical structure represents a long hydrocarbon chain, with a phenyl group attached to every other carbon atom [1][2]. The first industrial production of polystyrene was carried out by BASF in Germany in 1930. Polystyrene, the basis of the styrenic plastics family, is a high-molecular-weight linear polymer, they are characterized by being extraordinarily light, although resistant [3]. Depending on the application, the densities range from 10 kg/m^3 to 35 kg/m^3. Its density is closely related to its mechanical resistance properties. Expanded polystyrene has an excellent thermal insulation capacity. Some of its applications are directly related to this property: for example, when it is used as an insulating material for different building enclosures or in the field of packaging and packing of fresh and perishable foods. Its natural color is white; it is identified by its transparency and fragility; it can be easily colored and processed; it has the characteristic property of being a polymer with high mechanical strength, thermal insulation, behavior in water and water vapor, dimensional stability, stability against temperature, and performance to atmospheric factors [1][4]. There are four types of polystyrene commonly known as: crystal, high impact (HIPS), expanded (EPS) and extruded [5]. Polystyrene is regulated according to its processing characteristics; it contains 3-4% mineral oil and is used in disposable plates, cups and utensils. A high heat resistant grade has the highest molecular weight and lowest additive level and is used for sheet extrusion, thermoforming and oriented packaging. Polystyrene can be processed by almost every conventional industrial process for thermoplastics, from injection molding, rotational molding, foaming, etc. Parts made from polystyrene can be decorated by almost any existing method such as printing, painting, vacuum metallizing and hot stamping. In addition, two parts of the same material can be joined with adhesives, solvents or thermal welding [6]. Polymer-based composites are one of the most common materials due to their light weight and high durability. Polymers are used in this category as a base material, which is usually supported by various synthetics such as nanomaterials, semiconductor oxide, glass fibers, carbon, nylon, etc. This type of composite material is distinguished, compared to polymeric materials, by the possibility of using it in different electronic applications. These materials are also characterized by hardness, durability, dimensional stability, and a higher deformation temperature than polymers [7]. Thin film deposition technology has made impressive progress in recent years. This progress has been due primarily to the need to achieve new products and devices applicable in the optical and electronic industries. The rapid progress made in solid-state opt-electronic devices would not have taken place without the development of new film deposition processes, through which very high-quality films with excellent characteristics are obtained. Another beneficial factor is the greater and better knowledge of the physics and chemistry of films, surfaces, interfaces and microstructures, also supported by the advance in analytical instrumentation. The importance of obtaining thin films can be deduced from devices such as computers or solid-state microelectronic devices, all of them based on materials whose structure is formed by thin film deposition [8]. Ultraviolet UV radiation cannot be seen or felt. While some people are exposed to artificial sources of ultraviolet radiation (for example, in medicine, industry, disinfection and cosmetics), all people are exposed to ultraviolet radiation from the sun. Exposure to small amounts of ultraviolet radiation is beneficial to health and plays an essential role in the production of vitamin D. However, excessive exposure to ultraviolet radiation has negative health consequences because ultraviolet radiation is a carcinogenic factor in humans. It also affects many electronic and optical devices. Therefore, prevention from it is very important [9]. This paper presents a study of PS and PS.$Cu_{(etx)2}$ thin films prepared by using the spin coating method, which is a simple and inexpensive method for producing polymer films. A simple and practical approach for preparing films is demonstrated by doping $Cu_{(etx)2}$ into PS polymer. The study also aims to prepare films used to protect electronic devices that deteriorate when exposed to ultraviolet rays.

2. Experimental procedure

In this study, polystyrene polymer powder from High Media Company with molecular weight 32,000 g/mol and chloroform $ChCl_3$ with purity 99.98% was used as solvent from BDH Company Chemical Ltd. Poole. England, and for doping, copper complex $Cu_{(etx)2}$ was used which was prepared in the same way in the two studies [10][11], these two references can be consulted for more details. A solution of polystyrene with a weight concentration of 0.27 wt% was prepared by dissolving 0.2 gm of PS it in chloroform, then 5 ml of the solution was taken and $Cu_{(etx)2}$ was added to it with weight ratios (0, 0.02, 0.04, 0.06) wt% and these solutions were stirred for half an hour. Then the required films were prepared using the spin coating method on glass substrates (quartz for optical properties and pyrex for other properties) at a speed of 1500 rpm for 30 seconds. Spin coating is a method used to produce uniform thin films, which consists of four steps. The first step consists of applying a small amount (drop or drops) of material in the center of the substrate. In the second step, the substrate is rotated at high speed to spread the material, which is coated due to centrifugal force. The rotation continues for a certain time while the fluid exits through the edges of the substrate. In step three, the substrate rotates at a constant speed, and according to the viscosity of the fluid, the thickness characteristics are controlled. In the last step, the film drying stage occurs; here the rotation stops, and the evaporation of the solution begins, in which the dissolved polymer grows as a thin film on the substrate. X-ray diffraction was used to study the crystal structure of the samples using a Philips X-ray device, FE-SEM type TESCAN MIRA3 was used to analyzed the morphology of samples, and spectrophotometer (SHIMADZU UV-1650 PC) was employed to curry out the optical measurements.

3. Results and discussions

X-ray diffraction tests were used to look at the crystal structure of pure polystyrene thin films and what happened when $Cu_{(etx)2}$ was added to them. Figure 2 shows the X-ray diffraction pattern of pure polystyrene and doped thin films with $Cu_{(etx)2}$. It is clear that pure polyester thin films have a noncrystalline structure, and this is consistent with Vishwesh et. al., [12]. Most polymers have an amorphous structure, but when they are converted into films or fibers, a distinctive peak or group of peaks appears as a result of the beginning of the appearance of some of their crystalline structures. The crystal structure of the polystyrene thin films changed clearly after the $Cu_{(etx)2}$ was added. Two new peaks appeared at angles $2\theta=11.2^o$ and $2\theta=19.97^o$, these two peaks are attributed to the changes that occur in the crystal structure of polystyrene when the $Cu_{(etx)2}$ is added to it, as a reaction occurs between the complex and the polymer chains, which in turn leads to the formation of new crystalline phases within the polystyrene matrix that improve the crystal structure [13]. Calculating the crystal size of PS.$Cu_{(etx)2}$ thin films using the Scherrer equation [14], also reveals that the crystal size increases as the weight ratio of $Cu_{(etx)2}$ increases (see Table 1). This indicates an improvement in the crystal structure of the PS.$Cu_{(etx)2}$ thin films when they are doped with the $Cu_{(etx)2}$, in addition to their transformation into polycrystalline thin film structures[15].

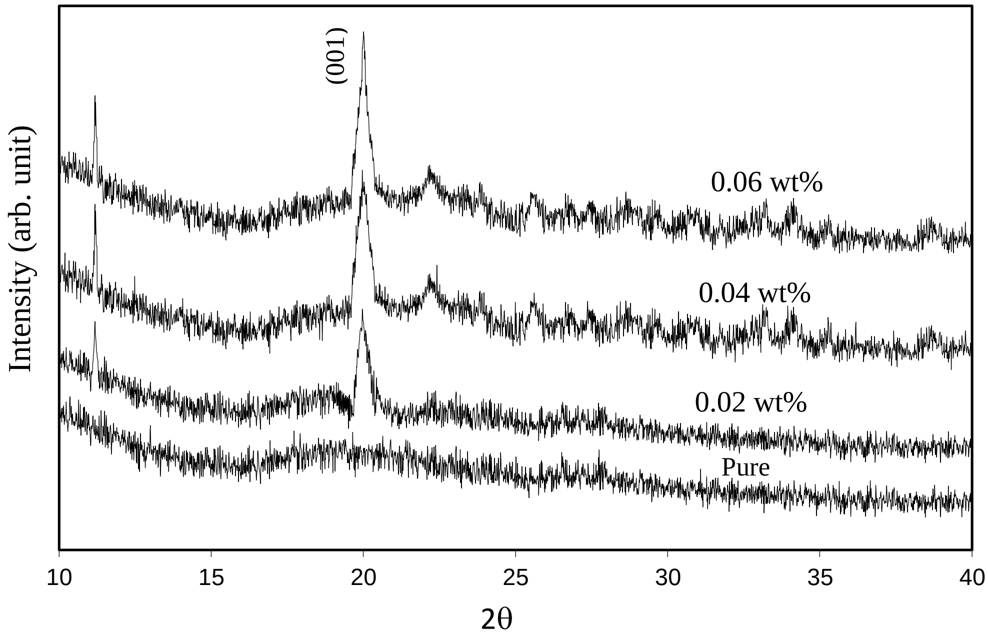

Fig. 2. The XRD spectra of pure PS thin films and doped with $Cu_{(etx)2}$ at different wt%.

Figure 3 shows the FE-SEM images of pure polystyrene and doped thin films with $Cu_{(etx)2}$. It is noted that the morphology of all prepared thin films is almost similar, with high homogeneity and few defects such as cracks and agglomerations. It is noted that the pure polystyrene thin film has good homogeneity with some defects such as agglomerations and simple cracks. A slight improvement appears after doping at 0.02 %wt $Cu_{(etx)2}$, and this improvement increases with increasing the %wt ratios of $Cu_{(etx)2}$, and the least defects and the best morphology are at the 0.06 %wt $Cu_{(etx)2}$, where high homogeneity and no cracks and only some agglomerations are present. This improvement is attributed to the effect of the interaction of the $Cu_{(etx)2}$ with polystyrene, which leads to improving the bonding forces between the molecules of the material and improving the interfacial stability, thus improving the morphological thin films [16]. The optical properties of polymers, such as gloss, transparency, clarity, haze, cooler, surface appearance, and refractive index, are closely related to our perception of the quality and visual performance of a polymer product. Polymer optical property testing will give you information to speed up development and optimize and find the best application for it. For the optical study of PS and PS.$Cu_{(etx)2}$ thin films deposited glass substrates, Absorption A and transmittance T spectra were taken as a function of the incident wavelength. Figure 4 shows the absorption spectra for the PS and PS.$Cu_{(etx)2}$ thin films at different wt% of $Cu_{(etx)2}$ in the ultraviolet, visible and near infrared (UV-Vis-NIR) region, corresponding to a wavelength range of 200 to 900 nm, From the figure, it is noted that the absorption spectrum of pure PS thin films has a very high absorption at short wavelengths up to wavelength 270, after which it begins to decrease as the wavelength increases, i.e., in the visible and near infrared regions. As for the PS thin films that have been doped with $Cu_{(etx)2}$, it is noted that the range of a high absorption

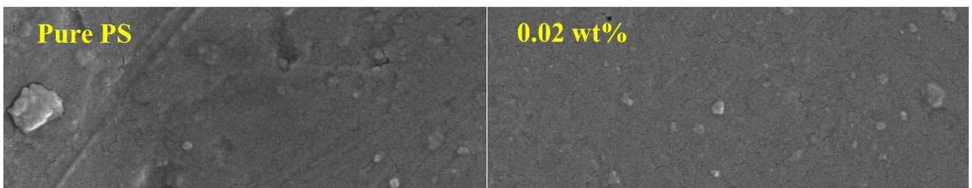

Fig. 3. FE-SEM images of Pure PS thin films and doped with $Cu_{(etx)2}$ at different wt%.

at short wavelengths increases until it reaches 330 nm at a doping ratio of 0.06 wt%, after which it begins to decrease with increasing wavelength. Two other things are noted upon doping: the first is an increase in absorption in general with increasing doping ratio, as well as the appearance of two peaks at wavelengths 410 nm and 595 nm. This is attributed to the effect of $Cu_{(etx)2}$ on the absorption spectrum of polystyrene through the appearance of new energy levels, which increases electronic transitions and absorption of incident beam photons, i.e. the presence of specific electronic transitions at wavelengths 410 and 595 resulting from the energy levels of the $Cu_{(etx)2}$ [13]. Figure 5 shows the transmittance spectra for the PS and PS.$Cu_{(etx)2}$ thin films at different wt% of $Cu_{(etx)2}$ in the ultraviolet, visible and near infrared (UV-Vis-NIR) region, corresponding to a wavelength range of 200 to 900 nm, it is noted that the behavior of transmittance spectra is the opposite of the behavior of absorption spectra, and this is expected, based on the relationship between transmittance and absorption [17].

$$A= \log_{10} T$$

Figure 6 shows the absorption coefficient spectra for the PS and PS. $Cu_{(etx)2}$ thin films at different wt% of $Cu_{(etx)2}$ in as function to energy incident photons. To calculate the band gap, it is necessary to know the absorptaion coefficient α, equation [17]: -

$$\alpha= 2.3 \frac{A}{t}$$

where t is the thin film thickness

From the figure, it is noted that all samples have an absorption coefficient greater than 10^4 cm^{-1} in the visible wavelength region and that the absorption coefficient increases as the doping ratios of $Cu_{(etx)2}$ in the PS thin films increase, and its highest values of α are at high energies (short wavelengths). One of the most important parameters that can be determined using UV-Vis characterization is the energy band gap E_g for a polymer material. The band gap represents the energy range between the valence band and the conduction band of a material, indicating the minimum energy value that the electron must obtain to manifest itself as a conductor. Therefore, the determination of band gap in materials is of great interest when defining their photoelectronic applications. To find the band gap of a material, the Tauc method is used, which, starting from the absorption spectrum of a sample, poses the Davis-Mott equation, that relates the absorption coefficient with the difference between the energy of the photon and the band gap of the material, as presented in the following equation [18]:

$$(\alpha h\nu)^{\varepsilon}=k(h\nu-E_g)$$

k and ε a constant.

The ε value dependent on the nature of the material and is related to the probability of its electronic transitions, it takes the values: ε =1/2 for allowed direct transitions, ε =2 for allowed indirect transitions, ε =3/2 for prohibited direct transitions, ε =3 for prohibited indirect transitions[18-19]. The band gap of the PS and PS. $Cu_{(etx)2}$ thin films they were calculated using the Tauc equation, taking into account that the transition type is allowed direct transitions, depending on the value of the absorption coefficient, as this type of transition occurs when the absorption coefficient value is $\alpha > 10^4$ cm^{-1}. [18-19] , This method uses x trapolation on the x-axis of the linear segment of the Tauc graph $(\alpha h\nu)^{1/2}$ vs. hν. Figure 7 shows the results of the Tauc graphs obtained from plotting the hν as a function $\alpha h\nu)^{1/2}$ for the PS and PS. $Cu_{(etx)2}$ thin films at different wt% of $Cu_{(etx)2}$. From this figure and Table 1, it was noted that the energy gap values for pure PS thin film were 3.8 eV and decreased with increasing $Cu_{(etx)2}$ doping to reach 3.05 at a doping 0.06 wt%. The variation of the E_g band gap due to doping is the result of the introduction of $Cu_{(etx)2}$ into the structure causes the gap to decrease, where doping leads to the creation of new local state within the optical energy gap, which leads to a reduction in the energy required for the transfer of electrons from the valence band to the conduction band. In addition to the effect of improving the crystal structure and increasing the crystal size, it also leads to an increase in the regularity of the crystal structure and thus a decrease in the energy gap [20]. From the above calculations, it is noted that the UV absorbance of the prepared samples increases with the increasing $Cu_{(etx)_2}$ doping, and the 0.06 wt% is the best absorber of UV rays and can be used in UV shields.

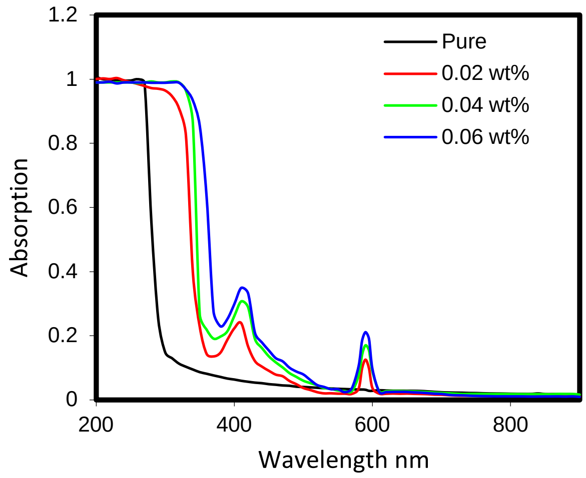

Fig. 4. The variation of absorption spectra with wavelength of pure PS and doped thin films at different $Cu_{(ext)2}$ wt% .

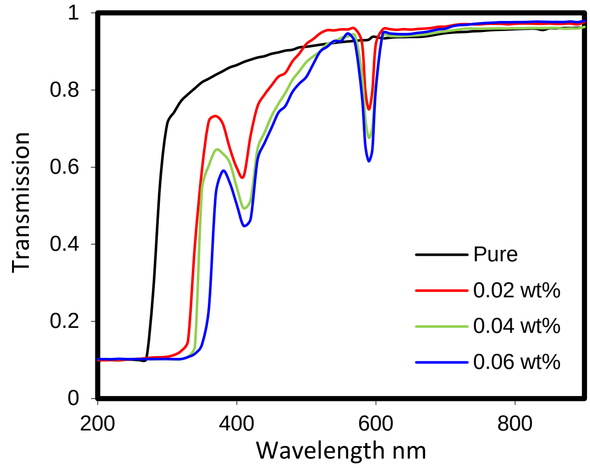

Fig. 5. The variation of transmission spectra with wavelength of pure PS and doped thin films at different $Cu_{(ext)2}$ wt%.

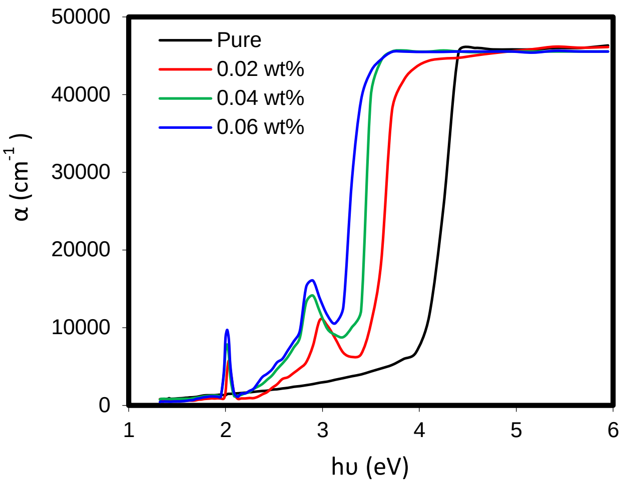

Fig. 6. The variation of **α** with hυ of pure PS and doped thin films at different $Cu_{(ext)2}$ wt%.

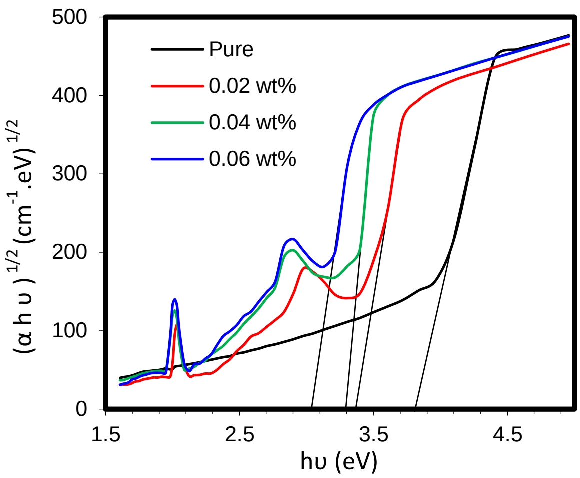

Fig. 7. The variation of $(\alpha h \upsilon)^{1/2}$ with hυ of pure PS and doped thin films at different $Cu_{(ext)2}$ wt%.

Table 1. Table 1. Effect of $Cu_{(etx)2}$ on parameters of the PS. $Cu_{(etx)2}$ thin films.

$Cu_{(etx)2}$ wt%	C.S nm	E_g eV
0	0	3.8
0.02	15.01	3.4
0.04	16.63	3.3
0.06	18.65	3.05

4. Conclusions

The research findings indicated that doping polystyrene thin films with the $Cu(etx)_2$ improved their crystalline structure and increased crystallite size. Furthermore, it reduced surface imperfections and enhanced the homogeneity of the thin films. Doping resulted in enhanced optical characteristics, characterized by heightened absorption in the ultraviolet UV spectrum and a reduction in the energy band gap from 3.8 eV for pure PS thin films to 3.05 eV at a doping of 0.06 wt% from $Cu_{(etx)_2}$. The optical measurements verified the significant UV absorption of the produced samples, with the 0.06 wt% $Cu_{(etx)_2}$ sample demonstrating the maximum UV absorption. These results validate the films' efficacy as proficient UV shields, rendering them appropriate for use as protective layers in optical and electrical domains.

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