Surface & Coatings Technology 206 (2011) 947–950

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Evaluation of physico-chemical properties of plasma treated PS–TiO_2 nanocomposite film

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ARTICLE INFO

Available online 2 April 2011

Keywords:
Nanocomposite
Polystyrene–TiO_2
Crystalinity
RF plasma
Wettability

ABSTRACT

In this work, we use TiO_2 nanoparticles with average particle size 30 nm and polystyrene for production nanocomposite thin films. After polystyrene was dissolved in toluene, then TiO_2 nanoparticles was added to the solution with different percentage. The obtained solutions were coated on quartz substrate using spin coater. The effect of argon RF plasma (13.6 MHz, with treatment time 30–120 s) on the optical properties, crystallinity, and the surface energy of PS-TiO_2 nanocomposite has been investigated. Some characterization techniques viz., X-ray diffraction analysis (XRD), UV–visible spectroscopy and contact angle measurement were used to study the induced changes on the properties of the treated PS–TiO_2 nanocomposite. Crystalinity and optical properties remained unchanged at the same conditions. Moreover, the surface energy of treated sample varied comparing to the respective untreated samples.

1. Introduction

Polymer nanocomposites attracted great attention due to their unique properties and possibility for numerous applications in modern technology [1–4]. The properties of polymer nanocomposites are mostly a simple combination of the properties of incorporated inorganic nanoparticles and polymeric matrix, although sometimes the appearance of completely new characteristics can take place due to synergistic effects. The properties of polymer nanocomposites are influenced by type, size, shape and concentration of incorporated particles, as well as their interaction with polymer matrix [5–8].

Practical applications for radiation processing of materials have been evolved since the introduction of this technology more than 50 years ago. The main applications are for modification of polymer materials through radiation cross-linking, degradation and grafting. Radiation processing, using plasma, gamma-rays, electron-beams (EB), UV and X-rays or laser beams has been demonstrated on a large commercial scale to be very effective means of improving end-use properties of various polymers [9,10].

Polystyrene (PS), an important material in the modern plastic industry, has been used all over the world, due to its excellent physical properties and low-cost. PS and its related plastic products are non-biodegradable in natural environment. The waste PS plastics do not decompose in landfills. A large amount of disposable PS plastic commodities causes serious environmental problems, called “white pollution”. PS nanocomposites become active research area because the addition of very small amounts of nanoparticles brings about a large enhancement of the mechanical properties and thermal properties of the polymer [11,12]. However, the reports about the photodegradation properties of PS nanocomposites are very few [13].

Surface modification processes of low-temperature plasma were first developed in 1960s [14]. Low temperature plasma has many remarkable advantages for surface modification applications. For instance, it has free radicals, charged particles, especially energetic electrons. These particles not only have high enough energy to activate, ionize or bond-break reactant molecules, but also would not decompose or ablate the materials. It will only change the surface properties of the materials rather than the bulk properties, causes no pollution to the environment, and can reduce energy consumption [14,15]. Radio frequency (RF) plasma has been employed for wide-range powder processing of polymer, metals and ceramics. The inductive coupling of an oscillating electrical energy typically forms the RF plasma. It displays unique characteristics, which can be used advantageously in thermal processing of advanced materials. Moreover, the technique induces changes in hydrophilicity, adhesion, wetting, printing and friction properties of polymers. These effects have considerable technological importance in the areas of adhesion, coating and printings, composition fabrication and interfacial compatibility [10,16].

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doi:10.1016/j.surfcoat.2011.03.136

In this work, nanocomposite films at different TiO_2 percentage were fabricated by spin coating methods. Reference (untreated) and samples treated by Ar plasma characterized via, FTIR, XRD and UV–Vis. and contact angle measurement.

2. Experimental and methods

Commercial Polystyrene (PS, Pars Petrochemical company in Iran) and Titanium dioxide (TiO_2, Degussa company in Germany) powders of 30 nm with 80% anatase and 20% rutile phases were used.

Various weight percents (2–8%) of TiO_2were added to polystyrene–toluene solution and stirred in ultrasonic device with a magnet stirrer to prevent agglomeration. To coat the obtained homogenous solutions on quartz substrates, a spin coater of 1000 rpm was used for 2 min.

Radio frequency glow discharge plasma (EMITECH KX1050) was used to produce 30 W Ar plasma. Samples were treated with the plasma for 30, 60, 90, 120 s and 5 min. Visually, there are no drastic differences between untreated and plasma treated samples.

Static contact angles (water and diiodomethane) were measured (Kruss G10) using the sessile drop method. All contact angles were the mean value of 5 measurements on different position of the film. Polar and disperse parts of the surface energy were obtained based on Owens and Wendt methods [17]. Crystallinity of the samples was studied using X-ray diffraction measurement (Philips Powder Diffractometer type PW 1373 goniometer). The XRD was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 A° and the diffraction patterns were recorded in a 2θ range (4°–80°) with scanning speed of 2°/min.

To study the structural changes including the alteration in position and intensity of the characteristic bands the Fourier transform infrared (FTIR, Shimazu FTIR spectrophotometer 8300) with 400–4000 cm^{-1} wave number were used. The $PS–TiO_2$ morphology has been studied using a scanning electron microscopy (JEOL JSM-6335 F).

3. Results and discussion

3.1. XRD characterization

X-ray diffraction pattern of the Degussa TiO_2 P25 was shown in Fig. 1a. The XRD analysis showed the presence of about 80% anatase and 20% rutile phases. The average crystalline size of anatase and rutile was about 30 nm obtained from XRD data with the Scherer equation [22].

Fig. 1b shows the X-ray diffraction pattern of the PS sample. The pattern is characterized by the appearance of halos extending in 2θ range from 10° to 24°. Halos show that the amorphous phase is dominant in the compound.

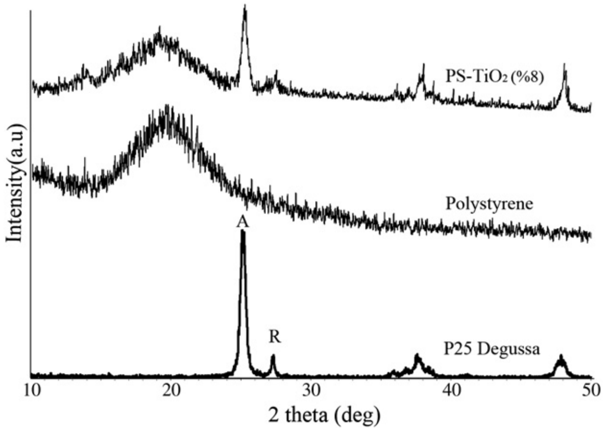

Fig. 1. X-ray diffraction patterns (a) Degussa TiO_2 P25 (b) PS and (c) PS/TiO_2 nanocomposite.

The typical X-ray diffraction pattern of the control $PS–TiO_2$ nanocomposite film is shown in Fig. 1c. No significant alteration is observed between $PS–TiO_2$ nanocomposite reference and plasma treated ones. It indicates that the degree of crystallinity remains mainly invariant.

3.2. FTIR characterization

Typical FTIR spectra of $PS–TiO_2$ (8 wt.%) obtained in this work are given in Fig. 2a. In a comparison, the spectra of the polystyrene (curve b) and TiO_2 nanoparticles (curve c) are included in this figure. It is noted that the characteristic peaks of TiO_2 particles are located at around 696 cm^{-1}. The broad peak at 3450 cm^{-1} corresponds to the stretching motion of the surface hydroxyl or the water adsorption and the peak at 1640 cm^{-1} corresponds to the bending vibration of the OH bonds of the adsorbed water. The peak at 1330 cm^{-1} is due to the stretching of residual organic functional groups. As expected, the characteristic peaks of TiO_2 appear in the case of the $PS–TiO_2$ film (curve a). Furthermore, as shown in Fig. 3, the spectra of the $PS–TiO_2$ (2 wt.%) film show no discernible difference from the pristine polystyrene (Fig. 2, curve b). The figure also shows that the spectrum lines due to aromatic ring vibrations at 3081, 3060, 3026, 1602 and 1493 cm^{-1} and due to the aliphatic backbone of the polystyrene macromolecule at 2922, 2851 and 1452 cm^{-1}.

In Fig. 3 the IR spectra of the Ar plasma-treated $PS–TiO_2$ compared with the spectrum of the untreated $PS–TiO_2$. Fig. 3 shows new peak at 1165 cm^{-1} that was created after plasma treatment. The peak is related to the peroxide group [18]. The new peaks at 1600 and 3284 cm^{-1} attributed to the hydroxyl groups [19,20], were observed. It suggests that after Ar plasma treatments some polar groups were created on the $PS–TiO_2$ surface.

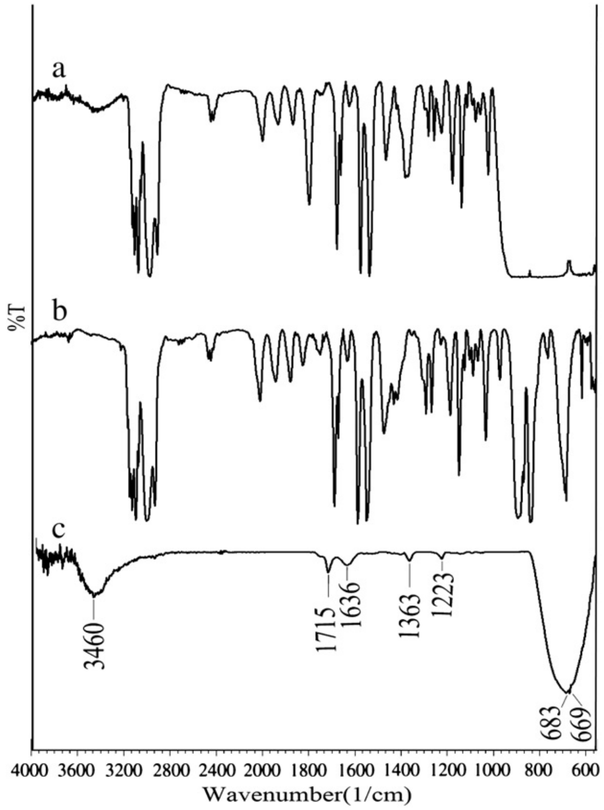

Fig. 2. Typical FTIR spectrums (a) $PS–TiO_2$, (b) PS film and (c) TiO_2 nanoparticles.