Microstructure and Thermal Behavior of Poly(*o*-anisidine)/Poly(ethylene terephthalate) Composite

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ABSTRACT: Poly(*o*-anisidine)–Poly(ethylene terephthalate) composite film was prepared by chemical oxidative polymerization method. The composite film shows a conductivity of about $15.6 \text{ K } \Omega^{-1} \text{ cm}^{-1}$ with 3.5 wt. % of POA. Fourier Transform infra-red (FT-IR) and UV–vis spectral analyses reveal the existence of hydrogen bonding interactions between the groups in PET and POA. X-Ray diffraction analysis informs that the amorphous characteristic of PET is affected by the presence of POA in the composite. UV–vis spectral results demonstrate that there exists cross-linking in the composite film when the POA in the composite undergoes doping and dedoping. AFM micrographs confirm the formation of genuine composite between POA and PET. [DOI 10.1295/polymj.37.489]

KEY WORDS Poly(*o*-anisidine) / Poly(ethylene terephthalate) / Composite Film / Hydrogen Bonding / Characterization /

π -Conjugated polymers with phenylene or aromatic heterocyclic units, such as polyaniline (PANI), polypyrrole and polythiophene, have attracted as conductive polymers in these years.^{1–5} In the class of conducting polymers, PANI holds a special place due to its attractive characteristics such as high air stability, high electrical conductivity and ease of preparation. However, the poor solubility in common organic solvents leads to relatively poor processibility and further restricts its widely practical application. As a typical derivative of aniline, *o*-anisidine (OA) is often used to copolymerize with other aromatic monomers to increase the solubility and processability.^{6–9}

Several methods have been described to improve the processibility of conducting polymers.^{10,11} One of the approaches to improve the physical property of the electrically conducting polymers is to convert them into composite systems with common polymers, thus combining the desirable properties of both the polymers.^{12–14} Different methods were employed to prepare the composite films, such as mechanical mixing,¹⁵ casting of solution containing the components of the blend,¹⁶ polymerization of one polymer to another¹⁷ and electrochemical methods.^{18,19}

The present work deals with the preparation of the composite of poly(*o*-anisidine), POA with poly(ethylene terephthalate), PET. Composite films prepared with different weight ratios of the two components have been characterized for microstructure, morphology and thermal behavior.

EXPERIMENTAL

o-anisidine, OA (Merck), potassium peroxodisulphate, PDS (Merck), hydrochloric acid (Merck) and ammonia (Merck) were used as received. PET film was used after Soxhlet extraction with acetone to remove adhering impurities and was dried at room temperature.

Preparation of the Pure Composite Film

Scheme 1 describes the methodology adopted for the preparation of pure transparent and conducting composite PET–POA films. Preparation of pure PET–POA film (doped with HCl) was done by sequential steps: polymerization of OA in the presence of PET in HCl to result acid-doped PET–POA with unbound POA, neutralization with aqueous ammonia, removal of unbound POA to obtain pure PET–POA neutral composite and doping the composite with HCl. For the removal of unbound POA from the composite film, conversion of acid doped composite to neutral form was needed. The unbound POA was soluble in NMP and hence removed by Soxhlet extraction.

Acid Doped Form of the Composite

Films of the composite were prepared by chemical oxidative polymerization for various concentrations of *o*-anisidine, OA by using potassium peroxydisulphate (PDS) as the oxidant. A solution of monomer

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Scheme 1. Preparation of pure composite film.

(30 mM OA) was prepared in 1 M HCl and cooled below 273 K using the freezing mixture. A pre-cooled (below 273 K) solution of PDS (20 mM) was then added drop wise to the monomer solution containing PET film with constant stirring over a period of 20 min. The solution was further stirred for 1 h. Transparent HCl doped composite film (along with unbound homopolymer (POA)) of PET was formed. The film was washed with 1 M HCl continuously till the filtrate was colorless.

Neutral Form of the Composite

The acid doped composite was converted to neutral form by treating the doped composite films with 1 M aqueous ammonia solution at room temperature for 1 h.

Removal of Unbound POA from the Composite

The HCl doped composite film having unbound POA was converted into neutral form by treatment with ammonia and was dried at 60 °C for 5 h. Then, it was dispersed in *N*-methyl pyrrolidone, NMP and Soxhlet extracted. The unbound POA was found to dissolve out from the mixture and the NMP solution became blue colored. Visible spectrum was recorded using Shimadzu UV-2401 PC UV-vis spectrometer

for estimating the POA content at various Soxhlet extraction time intervals. Soxhlet extraction was repeated several times till NMP did not contain POA in it. Thus, the pure composite without having unbound POA was prepared.

Elemental Microanalysis

Elemental microanalysis (C, H and N) was carried out using Heraeus CHN-Rapid analyzer (Germany). From the percentage of the elements, POA content in the composite film was determined.

Conductivity Measurements

Conductivity of PET and composite films in the doped state were determined by standard four-probe method using Concord Instruments, India. A film of 125 µm thickness was used to measure conductivity of the doped POA-PET film.

FT-IR Spectroscopy

POA and the composite film were pressed as a disk with KBr and FT-IR spectra were recorded using PerkinElmer-FTIR Rx 1(UK) at a resolution of 4 cm⁻¹ at a minimum of 32 scans and were signal-averaged at room temperature.

Figure 1. Visible spectra of POA in NMP at different Soxhlet-extraction time (Inset: UV-vis spectrum of neutral POA).

UV-vis Spectroscopy

The UV-vis spectra of the POA powder and the composite films were recorded using Shimadzu UVPC-2401 PC spectrophotometer.

Thermo Gravimetric Analysis

Thermogram of POA, PET and composite film were recorded with a DuPont TA Instrument 2050 Thermo gravimetric Analyzer using platinum crucibles with *ca.* 2 mg of the samples, under dynamic air atmosphere (30 mL/min) at a heating rate of $10^{\circ}\text{C min}^{-1}$.

X-Ray Diffraction Studies

X-Ray diffraction patterns of PET and composite films were recorded with Shimadzu XRD-6000 diffractometer at room temperature using Cu K_{α} radiation and Ni filter. Diffraction intensity data from 5° to 80° (2θ) were obtained at a scan rate of $1^{\circ}\text{ min}^{-1}$.

Tensile Strength Measurement

Tensile strength of the PET and the composite film were measured by using Tensometer (Type 'W' 10241-Monsanto, England). A specimen length of 10 cm and a width of 0.5 inch were used to measure the tensile strength of PET and the composite film.

AFM Topography

AFM observations were carried out for PET and the composite film using Nanoscope III instrument (version 3.2), Digital Instrument Corporation.

RESULTS AND DISCUSSION

Isolation of POA-PET Film from Homopolymer

Soxhlet-extraction was performed to remove the unbound POA from the composite film. Figure 1 shows the visible spectra of POA in NMP solution for different Soxhlet-extraction time intervals. The spectrum shows a broad band at 650 nm and the absorbance decreased with increase in the Soxhlet-extraction time. After 15 h of Soxhlet-extraction, the visible spectrum showed no absorbance value informing the complete removal of physisorbed POA from the mixture. For comparison, UV-vis spectrum of neutral POA in NMP (Figure 1, inset) is presented. Two absorption peaks, one at 320 nm and other around 650 nm, were noticed. The peak at 320 nm corresponds to $\pi-\pi^*$ transition of the benzenoid ring and the broad band at 650 nm corresponds to the excitation band of quinoid ring of the polymer.

The thickness of the POA-PET film was about

Figure 2. Variation of POA content with polymerization time.

125 μm . Elemental analysis (C, H and N) was carried out for the composite films prepared at various time of polymerization of OA. From the percentage of the elements, POA content in the composites was determined. Figure 2 shows the effect of polymerization time on the content of HCl-doped POA in the composite film. POA content of the composite film increases with increasing polymerization time initially and level off after 7 h. The initial increase in the % POA content in the composite film may be due the possible spreading of the oxidant solution to the surface and as well as to the bulk of PET film through diffusion. Once a layer of POA is formed on the surface of PET, diffusion of the oxidant solution to the interior layer gets hindered. Hence, no change in the wt. % of POA was witnessed after 7 h.

Most of the conducting polymers are doped through the partial or total oxidation of the π bond conjugated system. In the case of the POA–PET composite, the film is oxidized by insertion of dopant (HCl). Removal of dopant (HCl) makes the composite film to an insulating state. The presence of electron donating group, $-\text{OCH}_3$ on the ring in the repeat units of POA provides easier environment for oxidation from benzenoid form to semi-quinone configuration. Conductivity of the composite film is higher when the repeat units of POA exist in the quinoid form due to doping with HCl.

The conductivity of the composite film showed an increase with POA content (Figure 3). It is inferred that conductivity of the composite increases sharply with POA content. The conductivity of the composite reaches a maximum of about $15.6 \text{ K } \Omega^{-1} \text{ cm}^{-1}$ at 3.5 wt. % of POA. A low percolation threshold of about 3.5 wt. % was noticed.²⁰ This infers that a small amount of POA can generate interconnected net work frame with PET matrix. It is to be noted that the conductivity of the POA prepared under the same experimental condition was in the order of $0.5 \text{ } \Omega^{-1} \text{ cm}^{-1}$.

Figure 3. Variation of conductivity with POA content in HCl-doped POA–PET.

FT-IR Spectroscopy

Figure 4 shows the FT-IR spectra recorded for HCl-doped POA powder and HCl-doped POA–PET composite film. In the case of POA powder, the characteristics absorption band at 1571 cm^{-1} is assigned for $\text{C}=\text{C}$ stretching frequency mode of benzene ring.²¹ The strong absorption band at 1501 cm^{-1} is assigned for the bending mode of aromatic secondary amine.²² The band around 1393 cm^{-1} may be due to the stretching vibration of $\text{C}-\text{N}$ groups with partially double bond characteristics. The band at 1214 cm^{-1} is due to the vibrational mode of the imino-1,4 phenylene units.²³ The vibrational bands of POA noticed around 1571 , 1501 , 1393 and 1214 cm^{-1} were shifted to 1536 , 1446 , 1374 and 1178 cm^{-1} respectively for the composite film. A comparison of the spectrum of the composite film with POA powder shows that the peak positions of POA are shifted towards lower wave numbers. The shift of frequencies towards the lower wavelength may be due to the formation of hydrogen bonding between POA and PET film, which results in the weakening of bond strength of POA. This kind of observation was noticed earlier by others for polyaniline–poly(vinyl alcohol) and polypyrrole–poly(vinyl alcohol).^{24,25} Besides these, the FT-IR spectrum of POA–PET composite film (Figure 4b) shows distinctive absorptions peaks at 1724 cm^{-1} and $1400\text{--}1500 \text{ cm}^{-1}$ characteristics of $\text{C}=\text{O}$, $\text{C}=\text{C}$ stretching in PET film.

UV–vis Spectroscopy

UV–vis spectra of HCl-doped POA powder and HCl doped POA–PET are presented in Figure 5. For HCl-doped POA powder UV–vis spectrum shows two bands. The band at 305 nm is assigned for the $\pi-\pi^*$ transition of the benzenoid ring²⁶ in the polymer backbone. A broad band $>600 \text{ nm}$ is assigned to the excitation transition of the quinonoid rings.²⁷ However, the composite film shows three transitions at 350 , 420 and $>600 \text{ nm}$. The bathochromic shift of $\pi-\pi^*$

Figure 4. FT-IR spectra of (a) HCl-doped POA powder and (b) HCl-doped POA-PET.

Figure 5. UV-vis spectra of (a) HCl-doped POA powder and (b) HCl doped POA-PET.

Figure 6. TGA curves of (a) HCl doped POA-PET, (b) PET and (c) HCl doped POA powder.

transition from 305 to 350 nm for the composite film also favor that there can be molecular level (hydrogen bonding type) interactions between PET and POA.

Thermal Analysis

Figure 6 shows the thermogram of HCl doped POA-PET, PET and HCl doped POA powder. The thermogram of POA powder shows two stages weight losses. The weight loss at lower temperature 115 °C may be due to the loss of the counter-anion.²⁸ The first weight loss is about 10%, which begins from 115 °C and continues up to 350 °C. The second stage weight loss starts from 465 °C corresponds to the decomposition of the polymer backbone.²⁹ PET film shows only one major weight loss at 325 °C, which is attributed to the structural decomposition. Only 10% of residue is left over after 440 °C. The composite film exhibits the lower decomposition temperature than that of pure PET. Hence, the composite does not show any improvement in thermal characteristics over the PET film.

XRD Analysis

Figure 7 shows the scans of relative intensity versus 2θ , recorded during X-ray diffraction analysis of PET,

and the composite film with different proportion of POA (1.6 and 7.9 wt. %). PET film shows a prominent peak at $2\theta = 25.18^\circ$ is assigned to as the (100) plane of the crystallites.³⁰ The peak at 12.28° is assigned for the amorphous phase in PET film. Generally commercial PET films are fabricated by a biaxial stretching process in a sequential way. Due to stretching process, both the crystallites and the amorphous chains of the polymer become aligned with the drawing axis. Also, the molecular orientation changes the internal morphological structure of the polymer. A less intense peak is observed at $2\theta = 11.68^\circ$. Aiji *et al.*³¹ assigned the peak at $2\theta = 11.68^\circ$ for the in-plane orientation of amorphous phase in the polymer.

In the case of the composite film having different proportions of POA, peaks representing PET are predominantly noticed. A perusal at the 2θ for the composite film shows that there is no change in the position of peak at 22.24 and 25.18. However, the peak, which is assigned for the in-plane orientation of the amorphous phase of PET was completely disappeared with POA content of about 7.9 wt. % (Figure 7(c)). The XRD pattern of the composite films clearly informs that the incorporation of POA into the PET matrix destroys the amorphous nature of PET.

Figure 7. X-Ray diffraction patterns of (a) PET, (b) POA-PET (POA 1.6 wt. %) and (c) POA-PET (POA 7.9 wt. %).

Reversibility of the Composite Film

The composite film was converted into its base form (dedoping) by treating it with 1 M aqueous ammonia. Figure 8(i) represents the UV-vis spectra recorded for the dedoped composite film. An absorption peak at 310 nm and another broad band around 500 nm were noticed. The peak at 310 nm corresponds to $\pi-\pi^*$ transition and the peak at 500 nm corresponds to the excitation band of quinoid ring of the polymer.³² On thermal treatment of the film at 150 °C for 2 h (Figure 8(ii)), the peak observed at 500 nm, which is assigned for the excitronic transition was completely disappeared. The absence of this peak may be due to the cross-linking between imine and amine group of POA by thermal treatment.²⁴ However, no change in the band for $\pi-\pi^*$ transition is observed after thermal treatment. At the same time, the thermally treated HCl doped composite film shows three absorption bands (Figure 8(iii)). A new band at 410 nm was observed. The new band at 410 nm is due to the polaroic form of the polymer.³³ Interestingly, a broad band at >650 nm was observed after the thermal treatment of the composite film at 150 °C for 2 h (Figure 8(iii)). The band may be due to the transformation to oxidized form by the action of doping. At the same time, a drop in the conductivity value is also observed for the same.

Figure 8. UV-vis spectra of (i) undoped POA-PET, (ii) thermally treated undoped POA-PET, (iii) thermally treated HCl doped POA-PET, (iv) HCl doped POA-PET after heat treatment and (v) dedoped POA-PET after heat treatment.

Table I. Tearing strength for PET and composite film

Polymer	Max. Load Applied (kg)	Tearing strength from graph (cm)	True Extension (cm)	Elongation Percent	% Stress	% Strain
PET	17.0	9.2	2.375	25.0	617.05	43.7
POA–PET (POA 7.9 wt. %)	17.0	7.9	1.975	25.0	581.18	39.9

Figure 9. Stress–Strain curve for PET and POA–PET (POA 7.9 wt. %).

Figure 8(iv) represents the UV–vis spectrum of HCl doped composite film after heat treatment. After redoping the thermally treated composite film, the peak at 410 nm completely disappeared. However, other two-peak positions were similar to the composite film before thermal treatment. Also, the spectrum of dedoped composite film after heat treatment shows two absorption bands at 310 and 500 nm. The above results reveal that reversible molecular level interactions (hydrogen bonding type) between the components of the composite may occur during doping–dedoping process.

Tensile Strength Measurements

The results of tensile strength measurement of POA–PET (7.9 wt. % POA) and PET are presented in Table I. There is no significant difference in the physical property particularly tensile strength between the composite film and PET. And further it is confirmed by the stress–strain curve (Figure 9).

AFM Morphology

AFM topographical images (3D) of PET film and the composite film under same magnification are presented (Figure 10). The PET film shows an overall smooth surface. It contains flatness distributed randomly. Mean roughness is of 3 nm. The mean roughness is the average of roughness, R_a obtained at five different locations. R_a was calculated from the elevation of the roughness curve (z) values relative to the center plane.³⁴ The composite film (Figure 10(b))

Figure 10. AFM topographical images of (a) PET and (b) POA–PET.

has the roughness value of about 80 nm. The polymer, POA was observed all over the film as humps with R_a around 80 nm.

CONCLUSIONS

Composite film of poly(ethylene terephthalate) with poly(*o*-anisidine) has a low perchloration-threshold with a conductivity of about $15.6 \text{ K } \Omega^{-1} \text{ cm}^{-1}$ for the film for 3.5 wt. % of POA. There exists hydrogen bond between the groups of PET and POA. The cross-linking between the groups of POA and PET influences the amorphous region of the PET. The cross-linking between the groups of POA with PET can be reversibly altered by doping–dedoping of POA. AFM photographs reveal the formation of a genuine composite between POA and PET.

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