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Photochromic dynamics of organic–inorganic hybrids supported on transparent and flexible recycled PET

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Organic–inorganic hybrids (OIH) synthesized by sol gel process containing phosphotungstic acid (PWA) entrapped have been attracted much attention for ultraviolet sensitive materials. However, the limitations for practical photochromic application of these materials are the poor interaction with flexible polymer substrates such as Poly(ethyleneterephthalate) (PET) and also photo response under ultraviolet radiation. This paper describes the use of the d-ureasil HOI, based on siliceous network grafted through linkages to both ends of polymer chain containing 2.5 poly(oxyethylene) units with PWA entrapped prepared as films on recycled PET. Films were characterized by IR-ATR, XRD, TG/DTG, UV–Vis and Contact angle. XRD patterns showed that both pristine hybrid matrix and those containing PWA are amorphous. IR showed that PWA structure is preserved in the matrix and interactions between them occur by intermolecular forces. Films are thermally stable up to 325 °C and contact angle of 25.1° showed a good wettability between substrate and hybrid matrix. Furthermore, films showed fast photochromic response after 1 min of ultraviolet exposure time. The bleaching process revealed that the relaxation process is dependent of the temperature and the activation energy of 47.2 kJ mol^{-1} was determined. The properties of these films make them potential candidates for applications in flexible photochromic materials.

1. Introduction

Organic Inorganic Hybrid (OIH) materials containing polyoxometalates (POMs) entrapped have attracted enormous attentions which make them suitable for photochromic applications [1–9]. Phosphotungstic acid (PWA), a Keggin structure, represented by $H_3PW_{12}O_{40}$ formula is one of the most important POM used due to its solubility in many solvents, defined size and structure and mainly due to the photoreduction of its W^{6+} species under ultraviolet irradiation which promotes change of color [10]. d-ureasil is an interesting class II hybrid material, synthesized by sol gel process, composed by variable polyethylene oxide units covalently bonded to silicon atoms at both sides through urea groups [11]. The molecular weight of the polymer chain can be tuned which affects the photochromic behavior [12]. Usually, photochromic materials are employed in films deposited on rigid substrate like glass. However, for flexible polymeric substrates more investigation becomes necessary. Poly(ethylene terephthalate) (PET) has been widely applied in many different fields such as food packages, drink bottles, displays, etc. It has advantages such as flexibility, high transparency in the visible range, dimensional stability, solvent resistance and thermal stability [13]. Tricot et al. have obtained photochromic Ag:TiO_2 thin films on PET substrate in two steps by sol gel process and evaporation induced by self-assembly method [14]. Filpo et al. have obtained photoelectrochromic (PET)-TiO_2 –PO_4 – Methylene blue by the deposition of TiO_2 nanoparticles on PET conductive substrate [15]. Bessière et al. have deposited electrochromic tungsten oxide films on PET covered with ITO [16]. A common drawback to use flexible PET for optical application is the price and commercial availability. According to the principles of the green chemistry, challenges that should be taken into account are recycling and designing of materials, considering a sustainable approach [17]. Recycled PET (RPET) has been applied, for example, in nanocomposites to improve mechanical, thermal and optical properties [18]. Moreover, RPET in sheets dimension (thickness in microns) transparent in a visible range can be considered as a cheaper and alternative

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substrate [19]. In this investigation, to our best knowledge, it is the first study done by using OIH based on d-ureasil deposited on transparent recycled sheet PET substrate which has potential application for photochromic flexible devices.

2. Experimental

2.1. Chemicals and materials

All chemicals were used as received. They were purchased from Huntsman (Jeffamine-D230®), Aldrich (3-isocyanatepropyltriethoxysilane, ICPTES) and phosphotungstic acid (PWA). Recycled PET (RPET) sheets with a thickness of 250 μm were supplied by KGM®.

2.2. Synthesis of the precursor d-UPTES230

The precursor d-UPTES230 (termed d-UreaPropylTriethoxySilane, d-UPTES), where U represents urea groups and 230 g mol^{-1} the average molecular weight of the organic chain, was synthesized grafting the polymer chains to a siliceous network by means of urea linkages. The cross-links between the organic and the inorganic parts were formed by reacting the NH$_2$ groups of a diamine commercially named as Jeffamine-D230®, where 230 containing approximately 2.5 CH$_3$CHCH$_2$O units with the -N=C=O group of 3-isocyanatepropyltriethoxysilane, ICPTES in a molar ratio ICPTES: Jeffamine 2:1 in tetrahydrofuran, THF, under reflux and magnetic stirring at 80 °C for 24 h. Precursor was isolated after evaporating the solvent [11].

2.3. Synthesis of the hybrids U(230) and U(230)PWA

d-UPTES230 precursor was diluted in methanol in w:v ratio (d-UPTES230: methanol (1:6)), stirred for 15 min and then deionised water was added in a molar ratio (d-UPTES230: H$_2$O (1:3)) and the final sol was stirred for more 2 h. For the photochromic hybrids, the same procedure described above was used, and PWA diluted in methanol was added in a molar ratio (n = 50) where n means the molar ratio [CH$_3$CHCH$_2$O]/PWA.

2.4. Films on flexible recycled PET

Recycled PET (RPET) sheets with 250 μm of thickness as substrates were previously cleaned with isopropanol at 60 °C for 15 min, rinsed with deionised water and dried in nitrogen flow. Films were obtained by spin coating technique using rotation of 1000 rpm during 20 s for both films with PWA RPETU(230)PWA and without RPETU(230).

IR spectra were collected at room temperature using an IR Prestige 12 Shimadzu spectrometer over the range of 2000-600 cm^{-1} in ATR (Attenuated Total Reflectance) mode by averaging 200 scans to the films and using KBr pellets to PWA.

XRD measurements were carried out using a Rigaku (Ultima+) diffractometer with CuKα (1.54 Å) over the 2θ range of 5-70° and resolution of 0.05°, operating at 20 mA, V = 40 kV.

Thermal analysis was performed by using a DTG-60H Shimadzu under nitrogen flux of 50 mL min^{-1} and heating rate of 10 °C. min^{-1} from 25 to 800 °C.

Absorption spectra were obtained using a UV–Vis Varian 5000 Cary NIR spectrophotometer and the spectra were recorded from 200 to 2000 nm. Kinetic measurements were performed in-situ by using an oven coupled to the spectrophotometer.

UV mercury lamp was used to irradiate films for photocoloration and kinetic measurements. All samples were maintained at the same distance (15 cm) to the lamp in a constant irradiance of the 9.55 mW cm^{-2} for 20 min.

Contact Angle and surface tension measurements were carried out by using a System OCA 15 plus apparatus on sessile and pendant drop configurations.

3. Results and discussion

Fig. 1(a–d) shows IR spectra of the recycled RPET substrate, PWA, RPETU(230) and RPETU(230)PWA films, respectively. In the case of the RPET substrate (Fig. 1a), bands at 721 cm^{-1}are attributed to ν(C-H) of the aromatic ring; at 1089 cm^{-1} to $_{ass}\nu$(O-CH$_2$-CH$_2$); at 1236 cm^{-1} to $_{ass}\nu$(C-C) and at 1710 cm^{-1} to ν(C=O) [20,21]. The main band of the PWA (Fig. 1b) at 1080 cm^{-1} is assigned to ν(P-O$_a$); at 987 cm^{-1} to ν(W-O$_d$); at 894 cm^{-1} to ν(W-O$_b$-W) and at 802 cm^{-1} to ν(W-O$_c$-W) [1–3,10]. The film RPETU(230) hybrid matrix (Fig. 1c), so-called d-ureasil which is based on polyether chain grafted to the silica networks by means of urea groups, present the main bands attributed to amide I and II regions. According to *Bermudez* et al. amide I broad band at 1642 cm^{-1} is attributed to a complex vibration mode of N-H and C-N stretching, νC-C, $_{\delta}$C-C-N and νC=O which is sensitive to the hydrogen bonding inter polymer chain. For the amide II region, the band at 1565 cm^{-1} involves contribution of νC-N, N-H in plane bending and νC-C. Moreover, an intense and broad band found at 1110 cm^{-1} is attributed to νC-O from the polyether chain and ν(Si-O) from inorganic network [11]. Besides, the spectrum of the RPETU(230) pristine film without PWA, deposited on RPET, shows RPET substrate bands as reported in Fig. 1b. Amide I, II and C-O of polyether chain of the d-ureasil hybrid U(230) are sensitive to the interaction with the RPET substrate through hydrogen bonding by O-CH$_2$-CH$_2$ and C=O groups of the recycled PET structure. Bands at 1634 cm^{-1} assigned to amide I

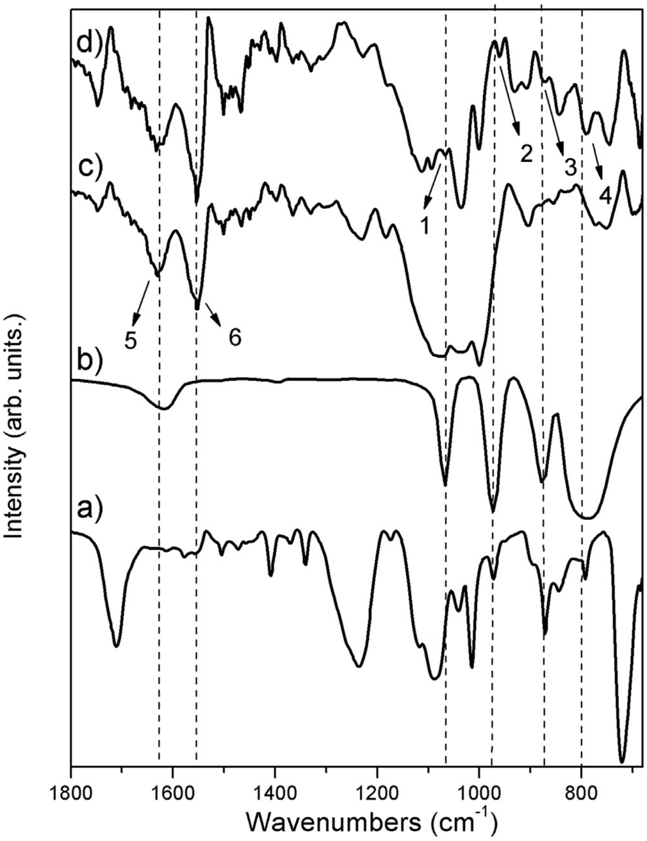

Fig. 1. IR spectra of RPET (a); PWA (b); RPETU(230) (c); and RPETU(230)PWA (d).