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High-performance oxygen barrier inorganic–organic coating for polymeric substrates

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ABSTRACT

Aqueous-based inorganic–organic hybrid coating materials comprising self-assembled silica nanophase (SNAP) particles and the sodium salt of 9,10-anthraquinone-2,6-disulfonate (AQDS), an oxygen-scavenging precursor molecule, were coated onto PET films under ambient laboratory conditions using a spiral-bar coating technique. Active SNAP-based coatings containing 0.08% w/w AQDS displayed an oxygen transmission rate of 0.04 ± 0.01 cm^3 mil m^{-2} day^{-1} atm^{-1}; an improvement in oxygen barrier by an order of magnitude compared with comparable coatings produced using dip-coating. The spiral-bar coating technique also provided other important technical advantages over the previously used dip-coating method, including a reduction in the AQDS concentration required in the coating solution by almost an order of magnitude. The oxygen barrier performance provided by these single-layer active SNAP-based coatings approaches that provided by other far more sophisticated multi-layer plastic barrier materials produced using vacuum-deposition methods.

1. Introduction

The integration of organic semiconducting materials into thin-film electronic devices such as organic photovoltaic (OPV) modules is currently the focus of substantial research effort globally [1,2]. Among the potential benefits associated with the use of organic semiconductors is their suitability for device fabrication via conventional roll-to-roll printing onto flexible plastic substrates [3,4] leading to more cost-efficient production and greater product versatility. However, the performance of OPV modules is highly susceptible to degradation on exposure to ambient oxygen and moisture [5,6], so it is imperative that these devices be encapsulated in materials that can provide a sufficiently high barrier to the transmission of oxygen and water vapour whilst enabling the printed modules to retain their inherent flexibility. In the case of OPV modules, high transmittance of sunlight is a further requirement for the encapsulation layer on the irradiated side of the device. Several flexible plastic barrier materials that meet these requirements have been reported [9], although these typically comprise sophisticated multilayer structures deposited using capital-intensive vacuum-based techniques [7,8]. The realisation of barrier films compatible with low-cost manufacturing methods such as printing will represent an important milestone in the development of flexible electronics including the next generation of solar cells.

Previously we reported [10] that the application of single-layer silica nano-phase (SNAP)-based coatings on a polypropylene (PP) film substrate using a dip-coating technique under ambient atmospheric conditions can provide a substantial increase in oxygen barrier performance. The oxygen barrier performance of spin-coated PP films displayed an enhancement in barrier performance of around four orders of magnitude compared with uncoated PP films. In this previous work we also reported preliminary oxygen barrier results for active SNAP-based coatings containing the sodium salt of 9,10-anthraquinone-2,6-disulfonate (AQDS) as the oxygen-reactive agent at concentrations in the range 1–4% w/w where, again, the coatings were deposited using a dip-coating technique. Our aim in that work was to produce coatings containing a sufficiently high concentration of AQDS to evaluate the technical feasibility of the active SNAP-based barrier coating approach, and little effort was made to optimise the barrier performance.

We demonstrated in this earlier work that a further improvement in oxygen barrier performance for these active SNAP-based coatings could be achieved compared with passive SNAP-based coatings, however several difficulties were encountered in producing the active coatings. For instance, in order to achieve reasonably high loadings of AQDS in the coatings, the use of AQDS concentrations in the coating solutions approaching the saturation limit was necessary due to the relatively low efficiency of transfer of the AQDS molecules from the coating solution to the substrate surface in the dip-coating process. The use of such high AQDS concentrations in the coating solutions also resulted in the immediate production of an intense red colouration upon addition of the diethylene

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triamine (DETA) cross-linking agent. This is attributed to a redox reaction between DETA and AQDS resulting in the formation of a small amount of the anthrahydroquinone form of AQDS followed by de-protonation of the phenolic groups resulting in the formation of the characteristically strongly red-coloured anionic forms of the anthrahydroquinone [11]. This residual red colour persisted through the coating process, but slowly disappeared during drying of the coating. The active coatings again developed a red colour on irradiation by the ultra-violet lamps which was attributed to the photo-reduction of AQDS by DETA residues in the organic phase of the cross-linked SNAP-based coating to form the semi-quinone radical anion oxygen-scavenging species, which disappears on exposure to air. This colouration of the coating would negatively impact the performance of photovoltaic devices if such high concentrations of AQDS were actually necessary in practice. Furthermore, we found that the active SNAP-based coatings could be susceptible to cracking on exposure to the UV light, and that this seemed to be dependent on the AQDS concentration in the coating.

Since the spiral-bar application technique can, in principle, enable better control of the active SNAP-based coating composition deposited on the substrate, it was recognised that its use could potentially provide an opportunity to substantially decrease the AQDS concentrations required in the coating solution. Furthermore, the spiral-bar coating method also more closely replicates a conventional roll-to-roll coating process than dip-coating. Consequently, a primary motivation for the present work was to investigate the use of the spiral-bar technique as a possible means for overcoming the significant technical shortcomings associated with using the dip-coating technique for SNAP-based coatings.

2. Experimental section

2.1. Preparation of the coating solution

(3-Glycidyloxypropyl) trimethoxysilane (GPTMS), tetraethoxysilane (TEOS) and diethylene-triamine (DETA) were obtained from Aldrich and used as received. The method used to prepare sols containing the self-assembled nanophase particles (SNAP) was the same as that described previously [10], with the molar ratios of GPTMS to TEOS, r_{GT}, and of DETA to GPTMS, r_{DG}, being 6.0 and 1.0, respectively, as these values were found in our earlier work to provide SNAP-based coatings having optimal passive oxygen barrier. The coating solutions were prepared by combining the SNAP sol, de-ionised water (Millipore), and the cross-linking agent DETA as described previously [10].

A typical synthesis of the coating solution proceeded as follows: GPTMS (26.0 ml, 0.12 mol) and TEOS (4.5 ml, 0.02 mol) were added drop-wise simultaneously, but separately, through two necks of a 3-neck round-bottom flask to a dilute aqueous solution of acetic acid (37.8 ml, 0.05 mol dm^{-3}) whilst stirring at approximately 400 rpm. The mixture was then stirred at 700–800 rpm for a further 1 h under ambient conditions with the flask open to air. The flask was then closed using stoppers and the mixture was allowed to age for 3 days in the closed flask whilst being stirred at this same rate.

After completion of the ageing period, and immediately prior to coating of the substrate, an aliquot of the SNAP sol (typically 10 g) was diluted by the addition of de-ionised water (7.5 g), followed by the drop-wise addition of DETA (1.9 ml). For the active barrier coatings, 9,10-anthraquinone-2,6-disulfonic acid (AQDS; Acros) was used as the oxygen scavenger, with the required weight of AQDS being dissolved in the diluted SNAP sol (17.5 g) followed by the addition of the DETA.

2.2. Coating the polymer substrate

Substrates were prepared by cutting 75 μm-thick poly(ethylene terephthalate) (PET) film into 20 cm × 10 cm pieces and then activating one side using a corona treater (Tantec, HV 05-2) prior to coating. Corona treatment was found to increase the surface energy of the PET substrate from less than 30 mN cm^{-1} to greater than 60 mN cm^{-1}, as indicated by Dyne pens (ICE Equipment). This increased surface energy persisted for at least 24 h, during which time the coatings were applied.

The coating solutions eventually become a viscous gel after addition of the DETA, and the time at which this occurs is referred to in the present work as the gelation time, $t_{\rm gel}$, which is dependent on the magnitudes of the composition ratios $r_{\rm GT}$ and $r_{\rm DG}$ [10]. For the coating solutions used in the present work $t_{\rm gel}$ was around 30 min. The time after DETA addition at which the coating of the PET substrate was commenced with respect to $t_{\rm gel}$ determines the degree of cross-linking in the bulk coating solution and is referred to as $t_{\rm coat}$, and two values of $t_{\rm coat}/t_{\rm gel}$ were investigated in the present work, namely 0.3 and 0.5.

An aliquot of the coating solution (3.0 g) was applied evenly across the full width of one edge of the PET film using a pasteur pipette and then spread over the corona-treated PET substrate surface using a spiral-bar coater (K Control Coater; RK Print-Coat Instruments Ltd.; Model 101) fitted with a close-wound metering bar (wire diameter 1.27 mm) at a speed of 2.2 cm s^{-1}. The coated PET films were then air-dried in an oven at 60 °C for 30 min. The coating weight on each PET substrate was measured gravimetrically and was used to estimate the coating thickness by using an estimated density for the dried SNAP-based coating of 1 g cm^{-3}. This estimate is based on the known weight fraction of Si in the coating formulation where it was assumed that this is present in the final coating in colloidal SiO_2 form having a density of 2.2 g cm^{-3} [12], and values of 1.2 g cm^{-3} and 16% for the density of the cross-linked organic phase [13] and coating porosity [14], respectively.

For a uniform polymeric layer containing immobile oxygen-scavenging molecules distributed homogeneously, where the outer surface of the layer is exposed to air and the inner surface is exposed to a medium that is essentially devoid of oxygen, and where the bimolecular scavenging reaction is much faster than diffusion and is irreversible, the time required for oxygen molecules to permeate across the layer from the air-exposed surface to reach the opposite surface, t_L, can be estimated using Eq. (1) [15–17].

$$t_L = \frac{l^2[A]_0}{2\upsilon DSp_{out}} \tag{1}$$

In this equation, l is the thickness of the barrier layer, $[A]_0$ is the initial concentration of scavenger in the barrier layer, ν is the number of oxygen molecules scavenged per scavenger molecule, D and S are the coefficients of diffusion and solubility, respectively, of oxygen in the barrier layer, and p_{out} is the partial pressure of oxygen to which the outer surface is exposed. The product DS appearing in the denominator of Eq. (1) is the oxygen permeability of the barrier layer in the absence of active scavenger, which in the present work is taken to be the same as the permeability of the passive SNAP-based coating.

Eq. (1) is expected to under-estimate the actual oxygen breakthrough time in the present work because the structure under test is not a single layer of the SNAP coating but a bi-layer in which the ‘outer’ surface of the SNAP coating forms an interface with the PET layer rather than air (i.e. structure tested was glass/rubrene//SNAP coating/PET/air). However, the high oxygen permeability of the outer PET layer relative to the SNAP-based coating means that the effect of this on the value of t_L calculated using Eq. (1) is expected to be negligibly small. Furthermore, Eq. (1) ignores the time lag associated with the equivalent passive SNAP-based coating which is assumed to be negligibly small relative to that associated with the active SNAP-based coating.

Using Eq. (1), a concentration of AQDS in the coating layer of around 1 mol m^{-3} (about 0.04% w/w) is expected to produce a time lag of slightly more than 12 h (i.e. the length of the dark cycle used in the present work) under the following assumptions; (i) a value for the oxygen permeability of the passive SNAP-based coating of 0.87 cm^3 mil m^{-2} day^{-1} atm^{-1} based on our previous work [10], (ii) a target barrier coating thickness of 15 μm, (iii) the concentration of the photo-reduced