Colour responsive smart polymers and biopolymers films through nanodispersion of organic chromophores and metal particles

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Molecular optical brighteners incorporated into filmable polymers to a very low extent from 0.05 to 0.5 wt.% by melt-processing, provide materials which show a well-defined excimer emission by increasing dye concentration flanked by a characteristic change of the luminescent properties of the films. Then, the original colour of the film, provided by the radiative transitions of the isolated dye molecules, may be restored after polymer stretching that promotes the aggregates break-up and the alignment of the single chromophore molecules along the stretching direction thus providing an easy detectable colour change. The approach can be extended to polymer blends allowing to obtain a wide range of films with different structure and performances in colour changes determined by external stimuli. Also, nanostructured polymer films with unusual and anisotropic optical properties can be obtained through the dispersion of gold and silver nanoparticles. The metal nanoparticles can be produced directly inside the polymer matrix by a photo-reduction process. Both organic chromophores and metal particles nanostructured systems can be used to prepare “smart” coating materials with a broad type of structural characteristics and capable to detect and stores external stimuli of different origin and under different conditions.

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1. Introduction

Thermoplastic polymers for their excellent thermomechanic properties, chemical stability and low environmental impact are expanding everyday their application area, including film coating and powder coating. The above properties are largely determined by the covalent saturated structure which is not suitable for obtaining aesthetic properties, colour and response to external stimuli. These features became more and more attractive properties of coating materials and can be provided by the dispersion of conjugated organic molecules and metal derivatives thanks to their available delocalized electron system [1].

Recently, the possibility to apply the formation of excimers inside polymer matrices for the preparation of polymers with “built-in” temperature and deformation sensors has been effectively demonstrated [2–4]. Small amounts of excimer forming oligo(p-phenylene vinylene) synthetic chromophores dispersed into a ductile host polymer matrix (i.e., low density polyethylene) as very small (nano-) aggregates of dyes may be produced by guest-diffusion or by rapid quenching of the homogeneous melt blends as evidenced by the formation of excimers. On applying a mechanical deformation to the film, the shear-induced mixing between the two phases promotes the break up of the dye supramolecular structure leading to a change of the material emission properties. Another sensing mechanism may be produced on the contrary by mixing the dyes with a macroscopic structure characterized by a glass temperature above the operating temperature. In this case the sensor dyes are kinetically trapped inside the glassy amorphous phase of the host polymers and the formation of thermodynamically stable excimers occurs just after an annealing above the glass transition temperature. We have efficiently applied the photophysics of the low cost, commercial bis[benzoxazolyl]stilbene (BBS) for the detection of tensile deformation in thermoplastic films [5]. BBS chromophores belong to a well known class of stilbene derivatives generally employed as optical brighteners in many polymer objects and textiles. It is a very good additive for thermoplastic materials, but other dyes can also be used to expand application possibilities. Moreover, the combination of the optical properties of metal clusters with the mechanical ones of thermoplastic host materials has recently received remarkable attention due to the very attractive optical features of polymer nanocomposites [6]. Nanoparticles
with very small diameters (a few nm) dispersed into polymers in non-aggregated form, allow the preparation of materials with much reduced light scattering properties for applications as optical filters, linear polarisers and optical sensors. The control in nanoparticle size, shape and spatial distribution may actually provide composite materials with modulated optical properties.

In this general scenario, the present paper describes the recent work carried out in the authors laboratory aimed to provide thermoplastic polymers with attractive optical properties by nanodispersion of organic chromophores and noble metal particles. Both systems are characterized by absorption and/or emission of visible light thus providing the polymer thin films with modulated optical response to external stimuli directed to the dispersed nanophase or to the host matrix.

2. Polymers and biopolymers smart films through nanodispersion of organic chromophores

Polypropylene (PP), polyethylene (PE) and polyesters (poly(1,4-butylene succinate), PBS) films which contained different concentrations of the food-grade, luminescent dye bis(benzoazoxyl) stilbene (BBS, inset Fig. 1) were efficiently prepared by processing in the melt [5,7]. BBS has an advantage over other synthetic dyes for the low cost and higher thermal stability. Notably, it was clear that the emission characteristics of PP and PBS composite films depended on the BBS concentration and the polymer deformation. A well-defined excimer band was observed with more than 0.2 wt.% of BBS, and this conferred to the film a green luminescence. During drawing, the polymer matrix reorganization caused a break in the BBS excimer-type arrangement characterised by green emission, leading to a prevalent blue emission of the single molecules in the stretched area of the film (Fig. 1).

The orientation of the dispersed dyes along the stretching polymer matrix (i.e. the dichroic behaviour of the oriented composites), was shown to depend on the morphology of the nanostructured composite with reference to the dispersion of the stress oriented conjugated molecules. This phenomenon was particularly pronounced for low density PE/BBS blends that, owing to the absence of BBS aggregates due to the low polymer crystallinity, showed after deformation excellent dichroic properties in absorption and optical performances as linear polariser close to the pseudo-affine deformation scheme [8].

Analogous thermoplastic films sensitive to mechanical stress were prepared by using a different luminescent probe based on perylene derivatives [9]. Perylene dyes containing different peripheral alkyl chains were synthesized and efficiently dispersed at low loadings (from 0.01 to 0.1 wt.%) into linear low-density polyethylene (LLDPE) by processing in the melt. Both perylene bisimides were found to generate supramolecular aggregates promoted by π–π intermolecular interactions between the conjugated planar structure of the dyes as shown by spectroscopic investigations on heptane solutions or dispersions into the LLDPE polymer matrix. The occurrence of this phenomenon effectively changed the emission of the dyes from red (interacting dyes) to yellow-green (non-interacting dyes) (Fig. 2).

In particular, the data acquired for dyes dispersions into the polymer matrix revealed that the optical properties and responsiveness to mechanical stimuli are strongly dependent on the compactness of perylene aggregates provided by the different molecular structure of dyes.

Threshold temperature indicators based on polymers in the glassy amorphous state (that is with $T_g$ above the operating temperature) were recently realised starting from newly prepared cyclic olefin copolymers such as ethylene/norbornene copolymers (E-co-N) and BBS as thermochromic dye [10]. The use of ethylene/norbornene systems with different copolymer composition, morphology (since the prepared E-co-N copolymer was semicrystalline, N content of 15.3 mol.%) and $T_g$, allowed both the use of smaller amounts of dye (less than 0.1 wt.%) and the preparation of materials with thermochromic properties (both in absorption and in emission) in temperature regime starting from 64 °C. In detail, upon heating E-co-C/BBS blends which contain molecularly dispersed and kinetically trapped BBS chromophores at a temperature above the $T_g$, the chromophore molecules started to self-assemble into stable aggregates leading to a permanent change of the composite luminescent properties, i.e. from blue monomer emission to green aggregate emission (Fig. 3).

Thermochromic polymer blends can be also realised starting from aggregachromic dyes dispersed into semicrystalline polymers with $T_g$ below the operating temperature [7]. This was the case of BBS/poly(1,4-butylene succinate) (PBS) blends based on a thermoplastic aliphatic polyester, a polymer matrix having sim-

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**Fig. 1.** Stretched PBS films containing dispersed BBS dye.

**Fig. 2.** Emission of a LLDPE film containing the 0.1 wt.% of perylene bis-alkyl imide before and after orientation (Dr = 8). Image of the oriented film (Dr = 8) under irradiation at 366 nm.
ilar thermal transitions ($T_g = -34{\degree}C$, $T_m = 113{\degree}C$) and linearity to polyethylene but composed of more polar repeating units containing 0.02–0.2 wt.% of BBS molecules dispersed by processing in the melt. Rapid quenching from the melt at 0{\degree}C of the BBS/PBS mixtures allowed to maintain the molecular dispersion of BBS dyed provided in the melt, thus avoiding the formation of excimers. The homogeneous BBS/PBS blends appeared optically stable at room temperature for more than 2 months after preparation when the 0.05 wt.% of BBS is present. Phase separation due to BBS segregation into aggregates occurred by increasing temperature (from 50 to 80{\degree}C) or by raising dye concentration up to 0.1 wt.% (at which the thermodynamically favoured aggregation forces between dye molecules became predominant over polymer viscosity). In particular, the thermal stress applied to films led to the BBS self-assembly thus promoting the colour change of the composite material from blue (emission at about 440 nm) to green (emission at about 500 nm). What observed before for BBS/PBS blends could not be directly extended to an analogous aliphatic polyester, i.e. the poly(lactic acid) (PLA), since BBS showed within this last matrix higher solubility which prevents the generation of supramolecular dye aggregates after thermal stimuli. However, as very recently reported, the temperature responsiveness of a PLA based material was achieved by blending PLA with a minor amount (15 wt.%) of polymer having the requested BBS solubility features, such as PBS (Fig. 4) [11,12].

In detail, the blends consisting 85 wt.% of PLA and 15 wt.% of PBS (PLA85/PBS15) and containing the 0.07 wt.% of dye showed an evident change of the luminescent properties from blue monomer emission to green excimer emission when thermally solicited at temperatures higher than PLA’s $T_g$ (>60–70{\degree}C). The peculiar behaviour of the PLA/PBS blend in terms of aggregation/disaggregation of the dye with varying temperature (in the range between 60 and 100{\degree}C) seemed to be related to the effects provided by the temperature on the thermally induced mobility and change of polymer matrix thermal features. The transition of the matrix from the glassy to the viscous state promoted by thermal solicitations, induced the cold crystallization of PBS which acted as crystallization nuclei for PLA (resulting in a 23% higher PLA crystalline content in the blend), thus strongly favouring the aggregation of BBS chromophores dispersed in the amorphous phases of the blend (Fig. 5).

3. Polymer smart films through dispersion of metal nanoassemblies

Noble metal nanoparticles incorporated in polymeric matrices may confer tuneable absorption and scattering characteristics to the derived thin films which depend on particle size, shape and aggregation [13]. When dispersed into polymers as non-aggregated form, nanoparticles with very small diameters (a few nm) allow the design of materials with much reduced light scattering properties, overcoming the widely encountered problem of opacity of heterogeneous composites for optical applications. Even more interesting
is the fact that nanoparticle dispersions in a polymer matrix can be rendered macroscopically anisotropic, a feature that has allowed their use in nonlinear optical devices and linear absorbing polarizers, e.g. for display applications.

An interesting approach for the preparation of nanocomposite films containing metal nanoparticles involves the in situ formation of the nanoparticles directly within the polymer matrix. This process is simple and just requires the reduction of the metal ions precursors by a photochemical or a thermal-induced process. Recently, polymeric films based on poly(vinyl alcohol) and poly(ethylene)-co-(vinyl alcohol) matrices and nanostructured gold have been prepared by an UV photo-reduction process [14]. In this case the polymer matrix based on vinyl alcohol repeating units, acts as co-reducing agent, as protective agent against particle agglomeration and as macroscopic support. The very fast process provided gold nanoparticles with average diameters ranging from 3 to 20 nm depending on the host polymer matrix and the irradiation time. Interestingly, uniaxial stretching of the Au/polymer composites promoted anisotropic packing of the embedded gold nanoparticles along the drawing direction of the film, resulting in a shift of the absorption maximum of gold well above 30–40 nm (83 nm max.) and thus producing a well-defined colour change from blue to purple.

Recent developments have been focused in this direction in order to optimize the preparation Ag/PVA nanostructured films by using alternative “in situ” methods such as sun- (UV) or thermal-promoted reduction processes [15]. The very easy and fast methods provide dispersed Ag nanoparticles (less than 4 wt.%) with average diameters ranging from 15 to 150 nm depending on the type of preparation and efficiently stabilised by the chelating properties of the PVA hydroxyl groups (Fig. 6).

After uniaxial orientation, the Ag/PVA nanocomposites show a very pronounced dichroic behaviour thanks to the anisotropic distribution of the silver assemblies along the stretching direction. Interestingly, oriented samples when observed through a linear polarizer show colour of the films markedly deepening on the relative orientation between the polarizer and the drawing direction of the film (Fig. 7).

In the last years there has been an increasing interest towards the optical properties of elongated nanostructures, as nanorods or nanowires, because their absorption spectrum is characterised by a longitudinal and a transverse surface plasmon resonance instead the single one of isotropic spherical nanoparticles. Generally, one-dimensional structures longer than some hundreds nanometres until micrometres or having a high aspect ratio (ratio between longest and smallest structure axis) are called nanowires while smaller elongated structures will be called nanorods [16].

Ag nanorods and nanowires were prepared by a seed-mediated process: depending on surfactant (capping material), it is possible to produce shapes other than spheres during seed mediated growth. Several theories normally centre on the preferential adsorption of the surfactant to certain crystal facets on seed particles. In other words, the surfactant binds to the surface radially but not axially. This behaviour blocks crystal growth on these surfaces and the particle can only grow in the axial direction. Nanocomposite films containing metal nanostructures were prepared by mixing silver nanorods or nanowires with a water solution containing PVA and a homogeneous film was obtained after solvent evaporation. After uniaxial stretching, the elongated silver nanostructures embedded into the polymer matrix assume the direction of the drawing [17].

As expected, the oriented nanocomposite films showed strong dichroism when irradiated with a linearly polarised light (Fig. 8). The change of the relative orientation between the stretching direction of the film and the polarization vector of the incident light induced the suppression of the longitudinal surface plasmon resonance at 640 nm in favour of the transversal one at 420 nm.

Moreover, preliminary interesting results were obtained after uniaxial orientation (Dr = 5°) of the composite PVA/Ag nanowires film at 110 °C. As reported by UV–vis absorption experiments in polarized light as in Fig. 9, the mechanical drawing induced to

**Fig. 6.** Silver nanoparticle embedded in a PVA matrix; generation after sun- (UV) or thermal-promoted reduction process.

**Fig. 7.** UV–vis spectra of oriented sun-promoted Ag/PVA nanocomposite films as a function of the angle between the polarization of light and the drawing direction of the film (parallel and perpendicular configuration). Inset: images of the same films under polarized light.

**Fig. 8.** UV–vis spectra of a PVA/Ag nanorods oriented film (Dr = 5°) as a function of the angle between the polarization light and the drawing direction and images of the same film observed through a linear polarizer.
the film a pronounced dichroic behaviour. The main absorption of the oriented film pointed at about 390 nm mostly reduced its intensity when the polarization direction of the incident light shifted from the perpendicular (90°) to the parallel (0°) configuration with respect to the drawing axis. Most likely, the anisotropic behaviour was attributed to the orientation of silver nanowires and larger metal aggregates (not completely removed by the purification step) embedded in the film towards the stretching direction. As a matter of fact, the main absorption at 380–400 nm, attributed to the transverse plasmon resonance of nanowires, strongly reduced its contribution when the polarization direction of the incident light was parallel (0°) to the PVA matrix orientation.

Accordingly, those absorption features conferred the drawn films a strongly polarization-dependent colour: the colour of the transmitted light through the oriented nanocomposite film shifted from blue-gray to yellow-green when the angle between the polarization axis of an interposed polarizer and the drawing direction was varied from 0° to 90°.

4. Conclusions

The dispersion, controlled down to the nanometer dimension, of active dyes and/or noble metal nanoaggregates into thermoplastic polymer matrices is a very sustainable and very versatile route to obtain smart polymer film of different nature with detectable response to external stimuli.

Indeed, all filmable polymers with the corresponding saturated structure and well localized electrons are characterized by excellent thermomechanical properties and weatherability, but lack of any particular optical response being transparent at wavelength larger than 200 nm. However, the addition of very low amounts of properly selected molecules with an extended system of delocalized electrons as well as gold or silver nanostructures formed of few atoms has allowed to produce oriented polymer thin films showing remarkable dichroic properties in absorption and emission in the spectral range of visible light.

The concept demonstrated in our previous work [1] was further expanded with new results concerning the change of colour after mechanical or thermal stress and change of colour with orientation/temperature.

The new data reported here demonstrate that the colour response of nanodisperse dyes and metal nanoassemblies is strongly affected by the nature of polymer matrix with specific reference to interphase interactions, polymer morphology and transition temperatures.

The approach here presented and developed has then a proved general validity: indeed the preparative route and the material properties predict the possible use of different of light sensitive species in very low amount to confer a smart optical behaviour to films derived from different polymers and blends, including structures stabilized by cross-linking. On these bases the procedure can certainly be used for the obtainment of smart coating products [18] showing external stimuli response and information storing capacity.

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References

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