Preparation and Optical Properties of New Metal/Macromolecule Architectures

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Summary: Polymer nanocomposite films with unusual and anisotropic optical properties were obtained by the controlled in-situ generation of noble metal nanoparticles (NPs). Poly(vinyl alcohol) (PVA) and poly(ethylene-*co*-vinylalcohol) (EVAl) nanocomposites containing gold and silver NPs were efficiently produced by a photo-reduction or thermal process both operating directly in the solid state and resulted efficiently stabilized by the presence of polymer hydroxyl groups, which prevent particles agglomeration. Uniaxial drawing of the NPs/polymer composites promoted anisotropic packing of the embedded particles along the stretching direction of the film, resulting in a shift of the surface plasmon resonance well above 40 nm and thus producing a well-defined polarization-dependent colour change. Such nanostructured materials when are obtained in the form of thin films can be applied to several fields, from sensor to photonics (i.e., macromolecular strain sensor, linear absorbing polarizer).

Keywords: linear polarizers; optical properties; polymer nanocomposite: metal nanoparticles

Introduction

Polymer film with field responsive optical properties can be produced by dispersing into oriented polymers, light absorbing low molecular weight species such as highly conjugated organic molecules (organic metals) or metal clusters and complexes.[1–3]

Interestingly, 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.[4–8] When dispersed into polymers in non-aggregated form, metal complexes or nanoparticles with very small diameters (a few nm) allow the preparation of materials with much reduced light scattering properties for applications as optical filters,[9] linear polarizers[5,6,10,11] and optical sensors.[12]

The efficient strategy based on coupling the optical and tailored structural properties of the organic moiety and the metal properties of the inorganic core with extremely high dispersion in polymer matrices are used to develop materials combining the excellent thermomechanical properties of polymers from 1-alkenes with the electro-optical properties of metal nanoparticles. Moreover, the development of methods to control size, morphology and aggregation of inorganic nanoparticles is a subject of particular interest, since these variables dramatically influence their optical properties, and therefore offer ideal means for controlling them.[13–15] Differently from smooth metal surfaces or metal powders, clusters of noble metals, such as gold, silver or copper, assume a real and natural colour due to the absorption of visible light at the surface plasmon resonance frequency, and this, as described by the Drude–Lorentz–Sommerfeld[13,14]

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theory is much affected by cluster size. In particular, the decrease in metal particle size leads to broadening of the absorption band, decrease of the maximum intensity and often to a hypsochromic (blue) shift of the peak, and these effects depend also on cluster topology and packing. For example, the anisotropic orientation of dipoles in nanoparticles by a uniaxially oriented host polymer matrix,[5,6,9–11] generates two different excitation modes: with photons polarized along the aggregation direction, leading to a bathochromic (red) shift of the surface plasmon resonance, or orthogonally to it, resulting in a hypsochromic (blue) shift.[13]

Among the large number of hybrid organic-inorganic system the nanocomposites based on Poly(vinyl alcohol) (PVA) and silver are attracting great interest because of their specific optical, catalytic, electronic, magnetic and antimicrobial properties. In fact, silver exhibits the highest electrical and thermal conductivities among all the metal and PVA is widely used for its easy processability and high trasmittance resulting a very useful host matrix for silver particles.

In the last decade a lot of efforts were focused on the preparation of silver ‘‘nanodispertion’’ directly in the PVA matrix by a one-step method based on the reduction of the inorganic precursor through a solid state synthesis. Thermal annealing[16] and UV irradiation[17–19] result very efficient methodologies because they take advantage on the formation of a complex between the PVA matrix and the silver nitrate: Ag^+ ions can be easily chelated by the hydroxyl groups of the polymer[20] and then reduced directly in the host matrix.

The present paper describes work carried out in the authors Laboratory aimed to provide ethylene and vinyl alcohol polymers and copolymers with new optical properties by dispersion of noble metal nanoparticles. The dispersed systems are characterized by absorbing visible light thus providing polyolefin thin films with unique optical response which can be modulated by external stimuli directed to the dispersed nanophase or to the host matrix.

Experimental Part

Materials

Poly(vinyl alcohol) (PVA, 99+ % hydrolyzed, Mw = 146,000–186,000), Silver nitrate (99+ % A.C.S. reagent) and Ethylene Glycole (99+ %, spectrophotometric grade) were supplied by Aldrich and were used without further purification.

Sample Nomenclature

The samples were named by listing the metal, the polymer, the synthetic method (A for the irradiation and B for thermal treatment) and the reaction time (in minutes), e.g. Ag/PVA-B120 is a Silver/PVA nanocomposite obtained by thermal treatment for 120 minutes.

Nanocomposites Preparation

Polymeric film nanocomposites containing silver nanoparticles were prepared by using a photochemical and a thermal process, method A and B respectively, both operating directly in the solid state.

The typical procedure for the preparation of Ag/PVA nanocomposites by method A is reported as follow: 300 mg of PVA was dissolved in 20 mL of deionised water under stirring and after complete dissolution of the polymer, 12 mg of $AgNO_3$ and 90 mg of Ethylene Glycol were added (2 wt. % and 30 wt. % respectively). The solution was then casted into a Polytetrafluoroethylene (PTFE) Petri dish and the film was obtained after complete water evaporation at room temperature and in the dark, in order to prevent any possible Ag^+ reduction during film preparation.

The film Ag/PVA-A was then exposed to sun light (density power of radiation: 1250 and 10 $\mu W/cm^2$ at 365 and 254 nm respectively) at room temperature.

The typical procedure for the preparation of polymeric silver nanocomposites by the method B is reported as follow: 300 mg of PVA was dissolved in 20 mL of deionised water under stirring and after complete dissolution of the polymer 6 mg of $AgNO_3$ was added (2 wt. %).

Analogously at procedure A, the solution was then casted into Polytetrafluoroethylene (PTFE) Petri dish and the film was obtained after complete evaporation of water at room temperature and in the dark.

Portions of dried Ag/PVA-A and Ag/PVA-B films with a thickness of about 90 μm and 1 × 3 cm size were placed in a Binder® oven and heated for different times.

The Ag/PVA (films type A and B) nanodispersions obtained by the two previous methods were successively stretched by uniaxial tensile drawing of the samples on a thermostatically controlled hot stage at the constant temperature of 110 °C at draw ratios (D_R, defined as the ratio between the final and the initial length of the sample respectively) higher than 3.

Physical-Chemical Characterization

Attenuated Total Reflectance Fourier Transform Infrared (ATR/FTIR) spectra were recorded on polymer films with the help of a Perkin-Elmer Spectrum One spectrometer fitted with Universal ATR (UATR, DiCompTM crystal) accessories.

X-ray diffraction (XRD) patterns were obtained in Bragg-Brentano geometry with a Siemens D500 KRISTALLOFLEX 810 (CT: 1.0 s; SS: 0.050 dg and CuKα, $\lambda = 1.541$ Å) diffractometer. Data were acquired at room temperature.

Atomic force microscopy was performed in Tapping Mode under ambient conditions using a Digital Instruments Multimode AFM, equipped with the Nanoscope IIIa controller. The tapping tips were mounted on 115–135 mm long, single beam silicon cantilevers, with resonant frequencies in the range of 230–300 kHz and a spring constant of 20–80 N/m.

Particle analysis was performed using the public domain Image Tool 3.00 version image analyzer program developed at the University of Texas Health Science Center in San Antonio and available on Internet at http://ddsdx.uthscsa.edu/dig/itdesc.html.

UV-Vis absorption spectra of polymer films were recorded under isotropic conditions with a Perkin-Elmer Lambda 650, and in linearly polarized light by mounting motor-driven Glan-Taylor linear polarizers.

The film roughness was diminished using ultra-pure silicon oil (Poly(methyl phenylsiloxane), 710® fluid, Aldrich) to reduce surface scattering between the polymeric films and the quartz slides used to keep them planar.

Origin 7.5, software by Microcal Origin®, was used in the analysis of the XRD and absorption data.

Results and Discussion

Metal/Polymer Dispersions: Gold Nanocomposites

Noble metal nanoparticles incorporated in polymeric matrices, depending on particle size, shape and aggregation, may confer tuneable absorption and scattering characteristics to the derived thin films.[32] For example, PVA[5] and high density polyethylene (HDPE) film composites with alkyl thiol coated gold and silver particles, once uniaxially oriented by stretching, present angular dependencies of the absorption intensity and the colour of the transmitted light. The absorption of photons is dominated by the excitation of surface plasmons in the metal particles and their (nano-)aggregates.[6,7]

The optical response of metal nanoparticles can be modulated and enhanced through the introduction of photoactive organic molecules, possibly combined with control of the nanoparticle dimensions.[33] The presence of direct electronic interactions between gold and gold-bound terthiophene chromophores allowed a fine modulation of the optical properties by inducing an energy transfer from the excited state of the chromophore to the surface plasmon resonance of the metal.[21]

Field-responsive gold nanoparticles can be produced directly inside a polymer matrix by a photo-reduction process.[11] Dispersions of $HAuCl_4$ and ethylene glycol in polymer films, such as poly(ethylene-co-vinylalcohol) (EVAl copolymers with 0.27 and 0.44 ethylene molar fraction) and of

PVA, were irradiated with a strong UV source (400 W high pressure mercury lamp) providing gold nanoparticles already after a short time (~5 minutes).[34–36] The resulting gold particles were efficiently stabilized by the presence of electron-donor hydroxyl groups composing the polymer matrices, which prevented agglomeration and formation of micro-sized phase separated metal aggregates. By increasing the irradiation time to 30 min the average diameter of gold nanoparticles was reduced from 12–23 nm to 3–4 nm (Figure 1).

During nanoparticles preparation the solid-state photo-induced reaction ($Au^{3+} \rightarrow Au^0$) was monitored by analysing the film with different spectroscopic techniques such as FT-IR (evolution of the typical carbonyl band at about 1740–1720 cm^{-1} proofing the oxidation of the ethylene glycol during the process), UV-vis (disappearing of the Au^{3+} absorption band at 300 nm and evolution of the surface plasmon absorption band attributed to nanostructured Au^0 and XRD (evolution of diffraction peaks assigned to the face-centred cubic (fcc) unit cell of gold).[37]

The irradiated samples oriented via mechanical stretching, showed a highly pronounced anisotropic absorption (~70 nm band shift, $D_R = 5$) when analyzed with polarized light according to the alignment of the gold nanoparticles along the oriented polymer matrix.

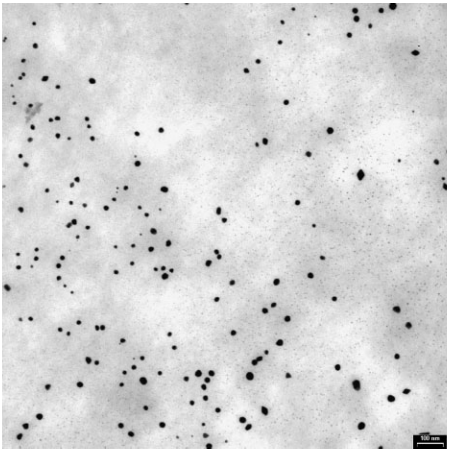

Figure 1.
Bright-field transmission electron micrograph and particles size distribution of $Au/EVAl_{27}$ film irradiated for 30 min (scale bar = 100 nm).

Generally, more the polymer matrix is uniaxially drawn and more the dispersed particles resulted aligned along the stretching direction.[3,12] However, considering the nanosized spherical shape of the noble NPs and the general principle that small particles should be more sensitive to mechanical orientation in a highly viscous matrix, moderate drawing ratios (i.e., $D_R \geq 3$) are considered sufficient to provide anisotropic nanocomposites.[5,12]

The anisotropically distributed and interacting gold particles are known to display a bathochromically (i.e., red-) shifted absorption band, when the polarization vector of the photons is aligned with the stretching direction of the film, and a hypsochromic (blue-) shift for the cross-polarized absorption.[5,7]

Metal/Polymer Dispersions: Silver Nanocomposites

Preparation and Structural Characterization

In order to obtain metal/polymer nanodispersions the bottom-up approach (method A), consisting of irradiation with UV-Visible light a polymer matrix containing an inorganic salt as precursor and an organic compound sensitive to light able to generate electrons necessary for the metal salt reduction, was successfully applied.

The polymer and the precursor used in this work were PVA and $AgNO_3$ respectively and ethylene glycol was used as electron source because it rapidly oxidised by UV light to aldehyde giving the electrons necessary for the metal salt reduction[22,11].

Five samples of the Ag/PVA film prepared with method A (see experimental part) were fixed upon an inert support and than placed under sunlight at room temperature for different exposure times (5, 15, 30, 60 and 120 minutes).

Before the sunlight exposition the samples appeared totally colourless but they became yellowish just after 5 minutes of irradiation turning gradually more intense and grey-reddish with the irradiation reaching the maximum colour intensity after about two hours.

This colour change of the film with the UV exposure time is due to the formation of Ag particles with nanometric dimensions generated in the polymeric matrix and characterised by the typical surface plasmon absorption band at about 430 nm[23] (Figure 2).

The continuous increasing of the 430 nm band intensity indicates that the reduction of Ag^+ ions started immediately and progressively continued for 120 minutes until the irradiation was stopped.

The photo-oxidation of alcohols with available hydrogen atoms of ethylene glycol[11,24,25] promotes actually the metal precursor reduction according to the scheme reported as follow:

$$HOCH_2CH_2OH \xrightarrow{h\nu} H^+ + e^- + HOCH_2CHOH$$

$$HOCH_2CHOH + Ag^+ \xrightarrow{h\nu} HOCH_2CH{=}O + Ag$$

A partial confirmation of this reaction mechanism is given by the presence in the FT-IR spectrum of the irradiated film of absorption bands typical of aldehyde groups in the carbonyl spectral region at about 1740–1720 cm^{-1} that are absent before sunlight exposition.

Another similar approach (method B) to generate silver nanoparticles directly in a solid polymeric matrix like PVA is based on a fast one-step method consisting on a thermal treatment of the host matrix containing silver nitrate salt.

Vinyl polymers having high density of polar groups in side chain can easy stabilise metal nanoparticles grown in the matrix at nanometric dimension because they wrap the particles avoiding their agglomeration.

Accordingly, PVA films containing Ag nanoparticles were prepared by method B (as reported in the experimental part) and also in this case the formation of metal particles in the solid matrix is well evidenced by a colour change of the samples that become yellow from colourless.

In this case the samples annealed for two hours were clearer with respect to the analogous film obtained with the method A because the Ag^+ reduction is promoted only by the relatively slow oxidation of polymeric matrix without the aid of a specific reducing agent.

This mechanism probably generated well-defined spherical shaped Ag nanoparticles whereas the faster light induced reduction process promoted the formation

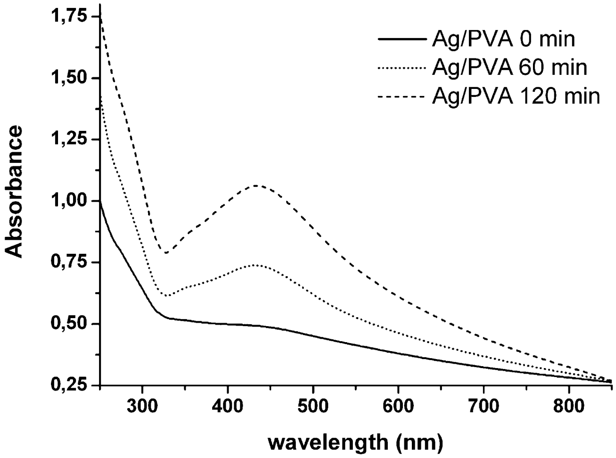

Figure 2.
UV-Vis spectra of Ag/PVA-A samples irradiated for 0, 60 and 120 min respectively.

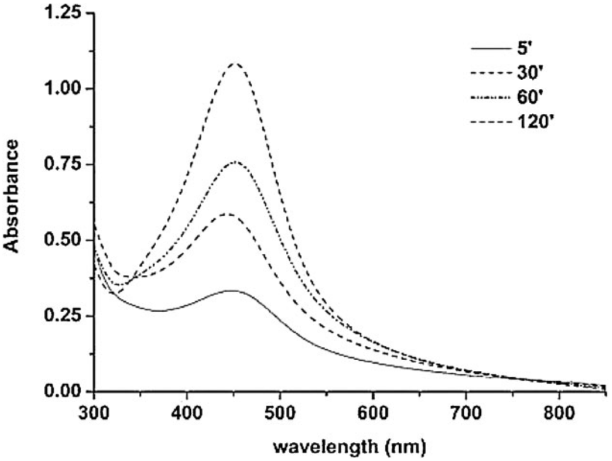

Figure 3.
UV-Vis spectra of Ag/PVA-A film heated for 5, 30, 60 and 120 min respectively.

of less-spherical (or bigger) metal cluster according to negligible absorption at wavelengths higher than 500–600 nm.[11,26] The UV-Vis spectra of the sample after thermal treatment show the emersion of a band at about 420 nm due to the surface plasmon resonance that increased with the exposure time (Figure 3).

The thermal treatment of the host matrix gave rise to a partial oxidation of the polymer that promotes the reduction of the colourless Ag(I) ions to characteristic yellow metallic silver nanoparticles that result efficiently stabilized by the electron donor OH groups of the PVA.

The formation of Ag(0) particles after thermal treatment in the PVA matrix is also confirmed by X-ray diffraction analysis (XRD, Figure 4) that shows the characteristic reflections of silver nanoparticles with

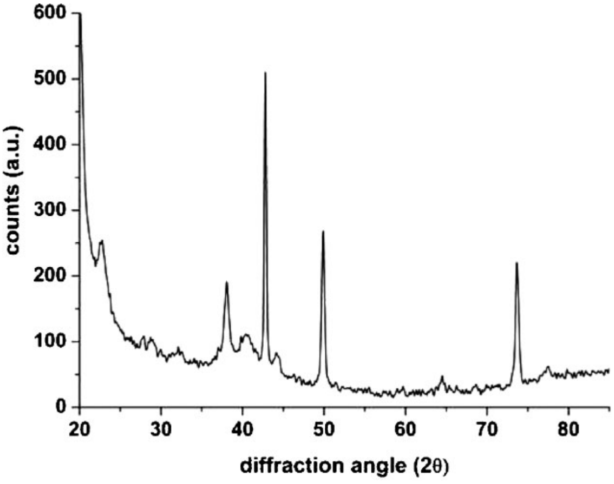

Figure 4.
XRD diffractogram of Ag/PVA-A120 film.

face centred cubic geometry[27] ($2\theta = 38.1°$, 44.3°, 64.5°, 77.4° for planes 111, 200, 220 and 311 respectively).

According to literature16, the silver nitrate reduction with formation of Ag(0) in the polymeric film was promoted by the thermal induced degradation of the PVA host matrix occurred through the mechanism reported as follow[28]:

$$> R - OH + Ag^{+} \rightarrow > R - O - Ag + H^{+},$$

$$> R - O - Ag \rightarrow -R = O + Ag^{0}$$

As partial evidence of this mechanism the FT-IR analysis of the sample shows the presence of a band in the range between 1710 and 1740 cm^{-1} that increases in intensity with the exposure time due to the formation of carbonyl groups in the polymer by the PVA hydroxyl groups oxidation.

In addition the FT-IR analysis of pure PVA and Ag/PVA mixture (Figure 5) suggests the presence of a chemical interaction between OH groups of the polymer and Ag particles.

In fact, in the spectrum of Ag/PVA the band at 1327 cm^{-1}, generated by the coupling of O–H vibrations at 1420 cm^{-1} and C–H wagging, results increased with respect to pure PVA in which the band at 1420 cm^{-1} appears stronger.

The increasing in the trasmittance of the band at 1327 cm^{-1} in comparison with the band at 1420 cm^{-1} is due to the decoupling of O–H and C–H vibrations as a consequence of the bonding interaction between OH groups and Ag nanoparticles.[29,30]

As reported by authors, the thermal treatment for longer time gives rise to a new at 1140 cm^{-1} attributed to C–O–C vibrations of cross-linked PVA.[31]

The morphology of the Ag/PVA nanocomposites was analysed by Atomic Force Microscopy (AFM). In the film surface it is well evident that dispersed phase is constituted by the silver nanoparticles that are homogeneously distributed on the overall surface of the film and having a simple spherical morphology (Figure 6).

An evaluation of their average diameter, that results of about 130 ± 90 nm, did not reflect the real average dimensions of all the particles dispersed in PVA because the particles generated in the inner matrix have probably smaller dimensions thanks to a more efficient stabilization by the polymer with respect to the particles generated in the surface where there is a less number of hydroxyl groups are present[11].

Optical Properties

It is well known that uniaxial tensile drawing of a polymeric matrix induces a reorganization of polymeric macromolecules with the consequent alignment of the particles, along the stretching direction.[1,5,10]

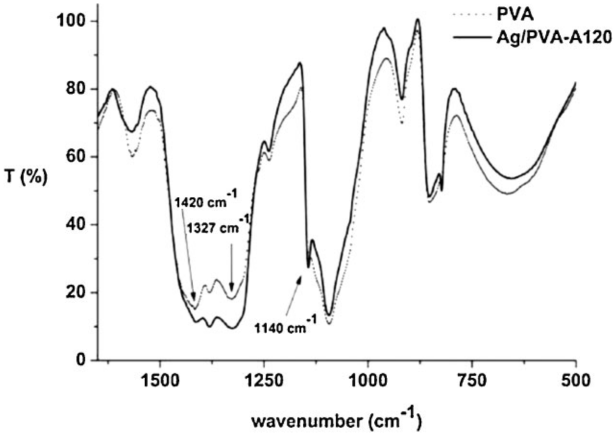

Figure 5.
FT-IR spectrum of Ag/PVAA-120 and pure PVA films.

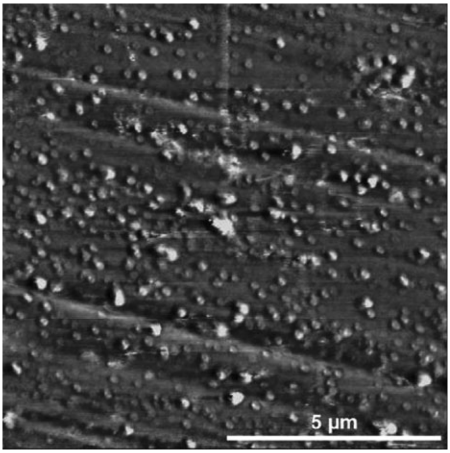

Figure 6.
AFM image of a Ag/PVA-B120 film.

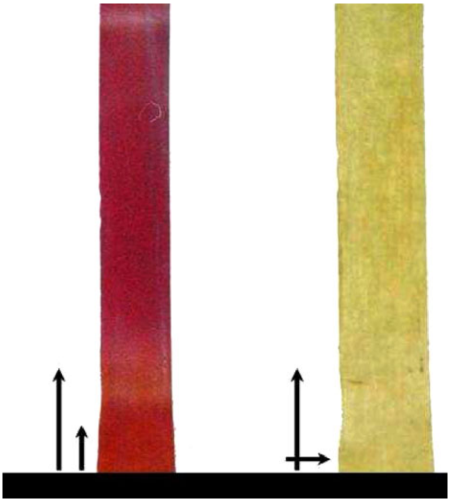

Figure 7.
Images of oriented Ag/PVA-A120 film (Dr = 4) with polarization direction of the incident light parallel (left) and perpendicular (right) to the drawing direction.

The optical behaviour of anisotropically oriented particles strongly depends on the mutual interaction of the nanoparticles and their relative orientation.

In facts, if the polarization of the incident light is parallel or perpendicular to the particles orientation the radiation absorption is shifted to lower or higher energies respectively, giving rise to a dichroic assembly.[7,5]

The polymeric nanodispersions obtained with both the two methods (A and B), and characterised by a surface plasmon resonance band in the visible region of the UV spectrum, were then stretched at D_R higher than 3 in order to promote an anisotropic orientation of the particles dispersed into the host polymeric matrix.

In uniaxially oriented samples ($D_R \geq 3$), the light absorption strongly depends on the angle between the polarization direction of the incident light and the orientation of the particles embedded onto the host polymeric matrix. Simply by observing oriented samples with a linear polarizer it is possible to observe that the colour of the tapes dramatically depends on the relative orientation between the polarizer and the sample (Figure 7).

The dichroic behaviour of oriented Ag/PVA composites ($D_R = 5$ in both cases) was even better evidenced by UV-Vis spectroscopy in polarized light at different angles between the polarization of light and the drawing direction of the film (Figure 8a and 8b).

The maximum shift measured for the Ag/PVA-A and Ag/PVA-B films were 113 and 20 nm respectively and all the spectra showed a well-defined isosbestic point confirming the existence of two different populations of absorbing nanoparticles.[11]

The remarkable difference between the two samples of the shifts in wavelength and in absorbance between the absorption at 0° and 90° ($\Delta\lambda$ and ΔA, respectively) values is probably attributed to the different shape and size between the metal clusters obtained by the two different methods (considering that both films were oriented at the same drawing ratio, i.e. $D_R = 5$). In fact, the particles obtained by the photo-induced reduction process (method A) have probably higher dimension and less symmetry with respect to the spherical ones obtained by method B. This reduced symmetry might induce a more favoured orientation of the particles into the uniaxially stretched macromolecular matrix as recently reported for Au nanorods, thus

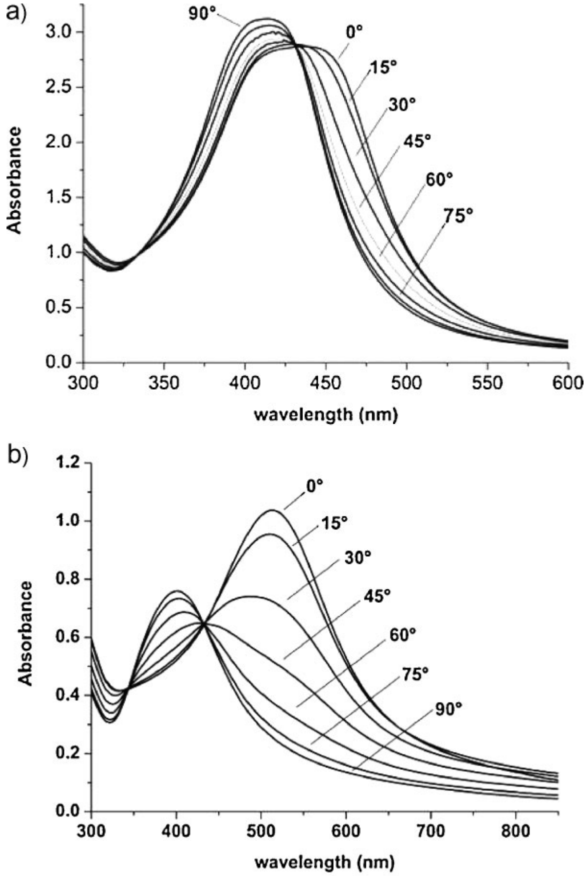

Figure 8.
UV-Vis spectra of stretched ($D_R = 5$) Ag/PVA-A120 (a) and Ag/PVA-B120 (b) films as a function of the angle (φ) between the polarization of light and the drawing direction of the film. In both cases, $D_R = 5$.

providing a remarkable dichroic behaviour with absorption shifts as high as 100 nm.[38]

Trasmission Electron Microscopy analyses are still in progress in order to gain a complete understanding of the phenomenon reported.

Conclusions

The results presented and discussed in the present paper provide a clear demonstration about the potentiality offered by the dispersion, controlled down to the nanometer dimension, of noble metal nanoaggregates into thermoplastic polymer matrices.

Indeed monoalkene polymers, commercially known with the broad name of polyolefins, are characterized by excellent thermomechanical properties and weatherability but lack of any particular optical response being transparent at wavelength larger than 200 nm. On the other side the addition of very low (less than 4 wt.%) amount of gold or silver nanoparticles has allowed to produce oriented polyolefin thin films showing remarkable dichroic properties in absorption in the spectral range of visible light. Additional peculiar optical response was observed connected to the change of colour after mechanical stress and change of colour with orientation.

The key factors in determining this behaviour are the interface interaction between the polymer matrix and the dispersed nanophase, the method of preparation of the composite and the order parameters and aspect ration of the dispersed phase molecules or particles.

Considering the general validity of the approach and methods used and the enormous number of nanoparticles available as of man-made and natural polymers known, unlimited possibilities can be predicted.

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