



## Macromolecular Nanotechnology

# Influence of nanoparticles on elastic and optical properties of a polymeric matrix: Hypersonic studies on ethylene–vinyl alcohol copolymer–titania nanocomposites

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## ABSTRACT

High resolution Brillouin spectroscopy (HRBS) backscattering elastic data in nanocomposites of ethylene–vinyl alcohol copolymer (EVOH) and TiO<sub>2</sub> nanoparticles present anomalous dependence with concentration, while Young's modulus and microhardness data show the expected behaviour. When performing HRBS with the 90A scattering geometry to assess the effective elastic constant, the expected behaviour for low concentration of TiO<sub>2</sub> nanoparticles is again obtained. This unusual disagreement can be solved assuming that the inclusion of TiO<sub>2</sub> nanoparticles induces anomalous refractive index behaviour at the applied laser wavelength for the different EVOH–TiO<sub>2</sub> nanocomposites. Comparison with experimental elastic and optical data obtained in isotactic-polypropylene–TiO<sub>2</sub> nanocomposites proves that EVOH–TiO<sub>2</sub> nanocomposites show an unusual optical behaviour at the laser wavelength, possibly due to a singular bonding between the EVOH polymer and the TiO<sub>2</sub> nanoparticles.

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## 1. Introduction

Hybrid or nanocomposite organo–inorganic materials that combine attractive qualities of dissimilar components have received immense interest for a wide range of mechanical, electronic, magnetic, biological, and optical properties. The control of nature and properties from surface/interface interactions between components appears of prime importance in the development of advanced materials having novel functionalities out of those characteristic of the components [1].

Modification of food packaging polymeric matrices to prevent growth or reduce adhesion of detrimental microorganisms is a highly desired objective. Hence, there is a significant interest in the development of antimicrobial

materials for application in the health and biomedical devices, food and personal hygiene industries [2]. TiO<sub>2</sub> is an inert, non-toxic and cheap material with a potential activity against all kind of microbes. Anatase and rutile are the two main crystalline structures of TiO<sub>2</sub>. A crystallographic research [3] demonstrated that anatase-type TiO<sub>2</sub> has {0 1 1} and {1 1 0} crystal faces, and that rutile-type one has {0 0 1} and {0 1 1} faces. It was suggested that the different crystal faces make varied roles as oxidation and reduction sites. Concerning the photocatalytic reactivity, it was reported that anatase-type TiO<sub>2</sub> exerts higher activity than rutile-type one in many photocatalytic reactions in air and water [4–7]. Moreover, under light excitation, with energy above the TiO<sub>2</sub> band gap (3.2 eV), the formation of energy rich electron–hole pairs is produced. Once at the surface of the material, such charge carriers are able to interact with microorganisms rendering biocidal properties to the TiO<sub>2</sub>-containing nanocomposite materials. The

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control of the TiO<sub>2</sub> polymorphism (i.e. to ensure the presence of the anatase phase) and primary particle size of these inorganic nanoparticles, yields to a correct handling of the UV-light matter interaction, ultimately leading to an optimized photo-activity in the elimination of microorganisms [8].

The influence of TiO<sub>2</sub> nanoinclusions on the acoustic and optical phonons in ethylene–vinyl alcohol copolymer EVOH–TiO<sub>2</sub> nanoparticle composites (from now on nanocomposites) for their application in the food packaging industry, previously studied [9,10], can deliver hints on the interactions between polymeric matrix and inorganic nanoparticles. In this work, a combination of different experimental techniques delivering elastic, optical and mechanical information has been used in order to clarify whether the anomalous optical behaviour already observed in EVOH–TiO<sub>2</sub> nanocomposites [10] is either real or only a possible artifact of the applied experimental techniques. Moreover, comparison to isotactic-polypropylene i-PP–TiO<sub>2</sub> nanocomposites will be drawn, reinforcing the anomalous optical behaviour of EVOH–TiO<sub>2</sub> nanocomposites.

## 2. Experimental

The TiO<sub>2</sub> component was prepared using a microemulsion synthetic route by addition of titanium (IV) isopropoxide (Aldrich) to an inverse emulsion containing an aqueous phase dispersed in *n*-heptane (Panreac), using Triton X-100 (Aldrich) as surfactant and 1-hexanol (Aldrich) as cosurfactant [1]. A commercially available ethylene–vinyl alcohol copolymer (EVOH; Kuraray), containing a nominal 71 mol% vinyl alcohol content, was used as polymeric matrix in the preparation of EVOH–TiO<sub>2</sub> nanocomposites with different TiO<sub>2</sub> nanoparticle contents: 0.25, 0.5, 1, 2, 5, 10 and 13 wt.%. These novel materials were prepared through melt processing in a shear mixer prototype with a volumetric capacity of 3 cm<sup>3</sup> at 195 °C and at 60 rpm for 5 min. Films of the nanocomposites were prepared by compression moulding at a pressure of 1.5 MPa for 5 min in a Collin Press (Model 3912) between hot plates at 210 °C for dynamic mechanical thermal analysis and microhardness measurements. A quench was applied to the different films from the melt to room temperature. The question about the dispersion of the TiO<sub>2</sub> nanoparticles in the EVOH matrix has been already discussed [9].

In the case of isotactic-polypropylene–TiO<sub>2</sub> nanocomposites, a commercially available metallocene-catalysed isotactic-polypropylene, i-PP (Basell Metocene X50081: melt flow index of 60 g/10 min at 230 °C/2.16 kg, ASTM D1238), meeting FDA requirements for food contact (Federal Regulations, 21 CFR 177.1520), is used as polymeric matrix. A polypropylene wax partially grafted with maleic anhydride, PP-g-MAH, is used as interfacial agent (Licomont® AR 504 fine grain supplied from Clariant). The compatibiliser composition added is of 80 wt.% with respect to the content in TiO<sub>2</sub> nanoparticles. These biocidal nanocomposites are prepared at 160 °C and at 60 rpm for 5 min and later moulded at 175 °C. The TiO<sub>2</sub> nanoparticle contents studied were: 0.5, 1, 2 and 5 wt.%.

Raman spectroscopy and X-ray diffraction data confirmed that the nanoparticles were exclusively of the anatase-type (a polymorph of Rutile and Brookite, other forms for TiO<sub>2</sub> to be found in nature, and showing tetragonal symmetry) and had a primary particle size of 10 nm [9]. Absorption spectra were recorded in transmission with a Cary 4000 UV–vis spectrophotometer from Varian. Photoluminescence measurements were performed at room temperature with different laser lines of an Ar<sup>+</sup>–Kr<sup>+</sup> laser, a Jobin–Yvon HR 460 monochromator and a N<sub>2</sub> cooled CCD. The excitation light was focused on the sample with an Olympus microscope (except for UV laser lines) which was also used to collect the scattered light. Spectra are corrected by the instrumental function recorded with a calibrated white source and a CaF<sub>2</sub> pellet.

High resolution Brillouin spectroscopy (HRBS) is used to study the acoustic phonons' behaviour. HRBS is a very suitable experimental technique to evaluate elastic properties in polymer systems [11]. The Brillouin scattering (HRBS) experiment is performed using as light source a 2060 Beamlok Spectra Physics Ar<sup>+</sup> ion laser ( $\lambda_0 = 514.5$  nm). The scattered light was analysed using a Sandercock-type 3 + 3 tandem Fabry–Pérot interferometer [12]. No polarization analysis of the scattered light was made.

The inclusion of TiO<sub>2</sub> nanoparticles in the EVOH copolymer or i-PP homopolymer matrices results in certain opacity since the samples thickness is ca. 200  $\mu$ m. In this context the backscattering geometry is the one suitable methodology to obtain information about the acoustic phonons using high resolution Brillouin spectroscopy. The propagation velocity of an acoustic wave ( $v$ ) can be obtained from the acoustic phonon frequency ( $f$ ) provided the acoustic wave vector ( $q$ ) [11]:

$$v = 2\pi f / q \quad (1)$$

The magnitude and direction of the acoustic wave vector is fixed by the scattering geometry used. In the case of backscattering geometry,

$$q = 4\pi n / \lambda_0 \quad (2)$$

where  $n$  is the refractive index of the sample and  $\lambda_0$  is the laser wavelength in vacuum. In order to avoid the direct reflection entering the spectrometer in the backscattering measurements, the sample was inclined so that the incident beam was tilted some degrees off the surface normal.

In the case of transparent samples the 90A scattering geometry is the one usually applied, being

$$q = 4\pi \sin(\pi/4) / \lambda_0 \quad (3)$$

and the wave vector lies within the sample plane [11]. It is very important to notice that the first one is refractive index ( $n$ ) dependent while the second one is not. One step further is to obtain the value of the related elastic constant:

$$c = \rho \cdot v^2 \quad (4)$$

where  $\rho$  is the mass density of the sample. If the system studied can be assumed to be elastically isotropic this elastic constant corresponds either to  $c_{11}$  or to  $c_{44}$  depending on the light polarization state. Moreover the combination of the two scattering geometries lead, in the absence of acoustic dispersion, to the determination of the refractive

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