Optical absorption coefficient measurements in nanostructures embedded in UHMWPE

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Abstract

Light absorption coefficients in Ultra High Molecular Weight Polyethylene have been determined in the range between 200 nm and 1200 nm wavelength by means of optical spectroscopy. The absorption investigations have been carried out by evaluating the absorption of characteristic peaks emitted from a Hg-Ar lamp and detected by at high sensitivity optical spectrometer. Measurements have been performed in pure and doped polyethylene. As doping agent at different concentrations, have been employed nanostructures of carbon-nanotubes, iron oxide and methylene-blue. The aim of these analyses is to modify the absorption coefficients of polyethylene-based polymers in a large range of wavelength in order to obtain special polymers for optical applications in different scientific fields, such as physics, medicine, chemistry and engineering.

Introduction

The interest on modified specimens such as nanocomposites or nanotubes has increased in several branch of science as a result of their numerous applications: medical, thermoplastical material, electric insulator, lens,… By using microstructures embedded in polymeric materials it is possible to improve the optical absorbing properties [1]. As an example, it is well-known as the Through Transmission Visible Laser Welding (TTVLW) method, requires two plastic materials which will be joined by localized heating at this two interfaces. This process needs an optically transparent plastic layer and another absorbent [2]. The localized heating at these two interfaces, produces a strong weld. Another interesting application is related to the employing of modified polymers in order to be irradiated by high intense lasers to generate plasmas in vacuum [3]. Moreover, special polymers characterized by roughness or containing nanostructures with dimensions comparable with the laser wavelength, enhances strongly their energy absorption through mechanisms of resonant absorption of the laser light [4]. For these reasons, it is very interesting the study of absorbing materials or combinations of materials such as nanofibers and nanostructures embedded in polymers which have high absorption coefficient at particular wavelengths. Additives such as carbon nanotubes (CNTs), nanostructures of Fe_2O_3, and a pigment of $C_{16}H_{18}N_3SCl$ (Methylene Blue), can be utilized to color black, red or blue, respectively, because the polymer's absorbance is sensitive to the presence of colorant (chromophores) pigments [5].

In order to study physical properties of nanostructures embedded in UHMWPE (Ultra High Molecular Weight Polyethylene), the

interactions with modified samples, optical parameters, such as the absorption coefficient and the attenuation length have been investigated

Materials and methods

Several kind of targets have been employed, all with a common matrix of Ultra High Molecular Weight Polyethylene, $3x\ 10^6$ g/mol molecular weight, 50% crystalline and 50% amorphous. Targets contain Fe_2O_3, $C_{16}H_{18}N_3SCl$ and CNT nanostructures in different concentrations, ranging between 0.01 wt% and 10 wt%, were used for experiments. As can been seen in Fig. 1, these fillers color the polymer red, blue, and black, respectively.
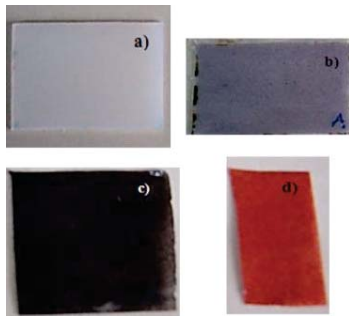

Fig.1 Pure polyethylene (a), Polyethylene + C16H18N3SCl (b), Polyethylene + CNT (c), Polyethylene +Fe2O3, (d)

The particles size for iron oxide and the diameter of carbon nanotubes is about 100 nm, instead Methylene Blue is entrapped in a silica matrix with particles size lower than 50 μm.
Plastic samples with thickness ranging between 10 μm and 1mm have been used for the optical measurements.
The optical properties of polymers have been analyzed considering the effects of thickness of these films on their physical, electric and mechanical properties. An incident radiation produced by a Hg-Ar lamp impinges a sample placed into a holder-target with a tilt angle of 90°, and a fraction of the wave is absorbed when a radiation passes through the infinitesimal thickness dx.

The difference in intensity dI, due to the slice of absorbing material dx is given by:

$$dI = I \mu\, dx \qquad (1)$$

where μ is the absorption coefficient.
The Beer-Lambert's law [6] has the form:

$$I = I_0\, e^{-\mu x} \qquad (2)$$

from which :

$$\mu = (1/x)ln(I_0/I) \quad (cm^{-1}) \qquad (3)$$

Where the absorbance μ of electromagnetic wave, is expressed in terms of incident light I_0, transmitted light I and thickness x of the sample used. Fig. 2 shows the sketch for the optical spectroscopy configuration.
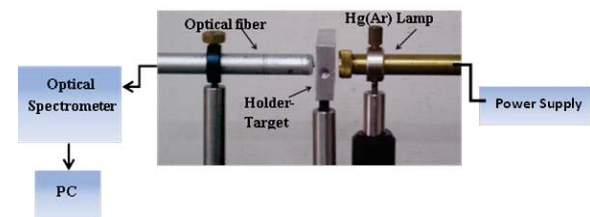

Fig.2 Optical Spectroscopy set-up

The beam of light is captured by an optical Fiber interfaced to Horiba Jobin Yvon Spectrograph instrument covering the 220-1100 nm wavelength range. A Lynear spectroscopy software acquires up to 160 full spectra per second, those are stored on a PC. Subsequently, a sample is placed on a holder target, the wave impinges perpendicularly into a target and then, emerges across the sample with an intensity lower than the entered light. The Hg(Ar) lamp contains a small amount of mercury which dominates the output spectrum as showed in Fig.3 and argon as a started gas.
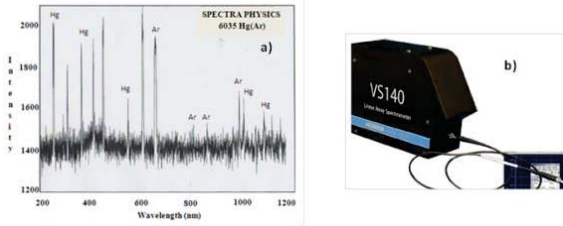
Fig.3 Hg(Ar) lamp spectrum (a) measured by Horiba Jobin Yvon Spectrograph (b)

It is well-known that after a beam light impinges on a target a fraction of it is reflected, part of it undergoes absorption and scattering processes and part of it is transmitted. In order to reduce the absorption and the scattering effects, the thickness of samples employed ware ranged between 10 μm and 1 mm. The optical response of the specimens, is given by the Beer-Lambert law, which describes in general the exponential decrease of light intensity E(z) as a function of the material depth z due to the absorption. The transmission yield was investigated at different operation wavelengths, by evaluating different characteristic peaks of the lamp, particularly the lines at 240 nm, 600 nm and 1080 nm wavelength that have been chosen to calculate the absorption in the doped materials having concentrations of 0.1%, 0.3%, 0.5% and 1%, for different thickness, 10μm, 100μm, 600μm, and 1000μm employed for these measurements. It has been useful to consider the penetration depth of the radiation defined as the depth at which the intensity of collimated beam is attenuated by a factor 1/e. The attenuation length or to be more exact, penetration depth of the beam radiation can be expressed as:

$$L=1/\mu \ (cm) \qquad (4)$$

where μ is the absorption coefficient for the treated material.

Results

Fig. 4 indicates the fraction of transmitted intensity of the incident light on UHMWPE 1mm in thickness and in the regions of near UV, Visible and near IR.
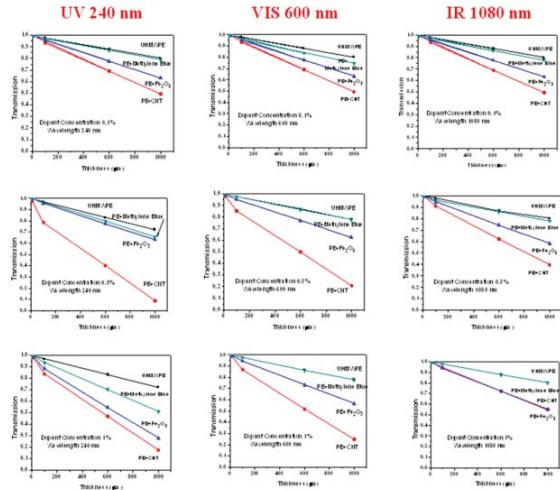

Fig. 4 Spectra comparison showing transmission as a function of thickness, concentration of dopants and wavelengths

Pure UHMWPE has high transmittivity at UV, VIS, and IR, which is about 85% for 1mm in thickness. UHMWPE + CNT (1%) presents the minor transmittivity at UV,VIS and IR which is 15%, 25%, and 55% respectively, for the three used wavelengths (240 nm, 600 nm and 1080 nm). UHMWPE +Methylene Blue has higher transmittivity of the doped polymer and it shows values comparable to pure UHMWPE for VIS and IR, while values of about 60% for 1% in concentration. Higher percentage of filler, of the order from 5% to 10%, show lowest transmittance than other for blue polymers. UHMWPE+ Fe_2O_3 (1%) has a significant transmittance that is roughly 30%, 60% and 55% for UV, VIS and IR respectively. In general, in the UV region the transmission decreases as a consequence of an increment of the absorption coefficient. By way of polyethylene with CNTs embedded at the same conditions considered

previously, and at 240 nm view as for concentration of 0.1wt% and 1 wt%, the percentage of transmitted light goes from 60% to 15% respectively. Moreover, evaluating different wavelengths, it has been observed the increase of transmitted light, from 25% at 600nm, up to 70% at 1080 nm. It is common knowledge that molecules absorb specific frequencies that are characteristics of its own structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. However at the employed wavelengths region, in the near IR and visible, the absorption peaks are due mainly to de-excitation of molecules of the chromophores embedded in the UHMWPE. The interpretation of the absorption coefficient vs. wavelength spectrum for polyethylene it is possible by knowing the molecular structure. Although to a first approximation, polyethylene may be considered as an infinite chain of CH_2 groups, the chains are found in the planar zig-zag configuration. By the comparison between experimental data and literature, Fig. 5 (a), (b), presents high absorption with the peak position near 290nm, 510nm, 550nm, due to C-H* de-excitation modes. Fig.5 (c) (d) show absorption peaks at 246nm, 292 nm, 664nm [7]. The absorption bands with maxima at 610nm and 664nm are assigned to C-C* transition de-excitation of dimmers (C_2H_4) and monomers(CH_2), respectively [8].
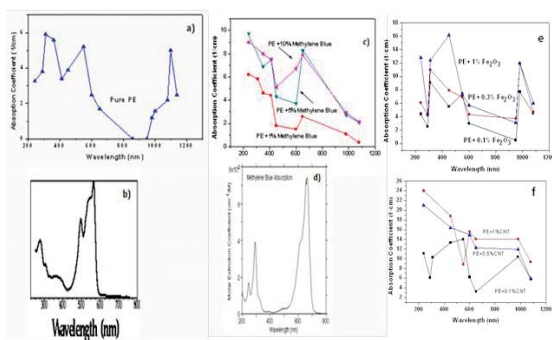

Fig. 5 Absorption coefficient vs Wavelength for a)UHMWPE, c) PE+Methylene Blue, e) PE+Iron Oxide

The absorption spectra of polyethylene with Fe_2O_3, $C_{16}H_{18}N_3SCl$ and CNTs, at concentration of 0.01, 0.1, 0.5, 1 wt% embedded showed in Fig. 5 indicate the increase of the absorption coefficient with the concentration of dopants and its decreasing with the wavelength.

In Fig. 6 are presented the values of measured absorption coefficients, μ achieved by using the expression (4) for targets manufactured by using UHWPE as matrix for samples where micro and nano structures have been embedded.
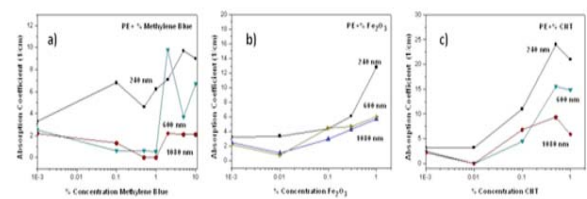

Fig. 6 Graphics relating absorption coefficient as a function of dopant concentration

The absorption coefficient increased linearly with increasing of concentration of nanostructures.

In Fig.7 reporting the attenuation length vs. the wavelength and doping concentration.
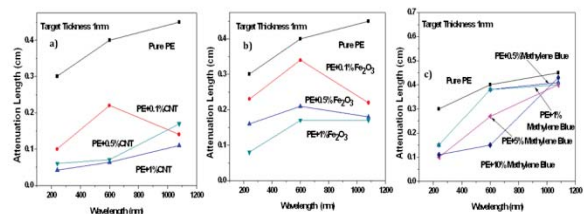

Fig. 7 Graphics regarding attenuation coefficient as a function of the wavelength for samples with same thickness

The attenuation length for 1mm PE from 0.1% to 1% CNT is of about 500 μm at 240 nm and increments to about 0.15 cm for 1080 nm. For comparison, in pure PE the attenuation length assumes the value of 0.3 cm, 0.4 cm and 0.46 cm for 240 nm, 600 nm and 1080 nm respectively (a). The attenuation length for visible radiation generally is intermediate with respect to near UV and IR regions.

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The length of extinction is 400 μm for polyethylene with CNTs filler embedded in concentration of 1%, and 0.1 cm for Methylene Blue in concentration of 10%. The reason of this difference is due to the carbon nanotubes that are highly absorbent, and have a size of the order of 100 nm. On the contrary, Methylene Blue is entrapped in a silica matrix with about 50 μm particles of size. The measurements performed, have been repeated with different concentrations, thickness and confirm, as presented in Fig.8, that the absorption in UV range is higher than VIS and near IR regions, and that pure polymers transmit light more than plastic materials doped with Methylene Blue, Iron oxide and carbon nanotubes respectively.
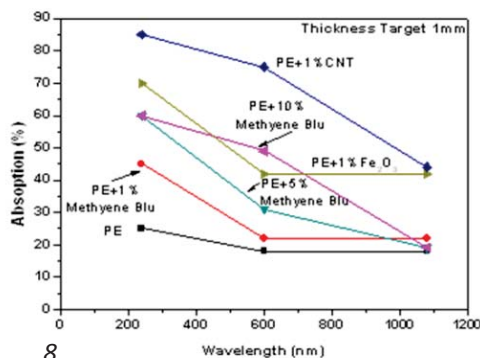

Fig. 8
Absorption percentage as a function of wavelength and dopant concentration

Discussion and conclusions

The absorbance measurements of nanostructures embedded in UHMWPE, were obtained by using a single and simple set up consisting in an optical spectrometer and the characteristic lines of the Hg-Ar lamp. They put in evidence the relation between attenuation coefficient and concentration of embedded nanostructures.

It has been observed that the absorbance depends on the thickness of the specimens, on the radiation wavelength and on the nature of filler employed.

CNT, Fe_3O_2, Methylene Blue, are responsible for interesting effects because by changing their concentration change important parameters of the treated samples.

In this context, in the field of polymer welding have been investigated the better conditions to produce high absorption and consequently a good joint [10] for mechanical or biomedical applications. Moreover, the prepared polymers find interesting applications in the use of special thin targets to be laser irradiated at high laser intensity in order to obtain high hydrogenated plasmas in vacuum [11].

The use of modified targets and the investigation of their optical properties have some advantages, from laser irradiations such as to treat surfaces in order to modify the roughness of the specimen and their physical and chemical properties (mechanical resistance, electric conductivity, thermal conductivity, chemical reactivity, wetting ability, etc.) and to control the absorption of laser light.

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