On the hydrogen bond increasing in polyethylene oxide aqueous solution induced by exposure to electromagnetic fields

Emanuele Calabrò*, Salvatore Magazù
Department of Physics, University of Messina, (ITALY)
E-mail: e.calabro@yahoo.com

ABSTRACT

The objective of the present article is to study the behaviour of Polyethylene oxide in aqueous solution exposed separately to a 50 Hz electromagnetic field (EMF) at the intensity of 1 mT and to 900 MHz microwaves at the average magnetic flux density of 16 mA/m.

Fourier transform infrared spectroscopy was used to investigate the alterations of the vibration bands in PEO induced by exposures to EMFs. The 3000–1000 cm^{-1} region was investigated, involving the stretching vibrations of ether band, C–H symmetric-antisymmetric and wagging vibrations of methylene groups, and in particular the C–O–C stretching band.

A decrease in intensity of symmetric and asymmetric stretching CH_2 vibration bands was observed after exposures to 50 Hz EMF and MWs.

The C–O–C stretching band around 1080 cm^{-1} resulted to increase in intensity after exposures. This result can be attributed to the increase of formation of the intermolecular hydrogen bonding occurred in PEO aqueous solution after exposure.

In addition, an increase of the methylene wagging vibration at 1349 cm^{-1} band was observed in exposed sample spectra, that can be related to a decrease of the PEO crystallization process induced by exposure to EMFs, which is in well accordance with the conclusion that hydrogen bond increases in PEO aqueous solution under exposure to EMFs.

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INTRODUCTION

Polyethylene oxide (PEO) is one of the most extensively studied water soluble polymers which can be considered the simplest structure of water-soluble polymers, because the simplicity of its macromolecule's basic forming unit, the monomer CH_2CH_2O.

Some vantages of water-soluble polymers are represented by their use in a variety of industrial and consumer products such as polymeric surfactant, pigment dispersants or detergents.

Indeed, a significant interest in the development of drug delivery vehicles based on polymer assemblies such as spherical micelles and vesicles increased in the last decades[1-3]

In particular, these specific features makes poly-

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meric micelles as aggregates of PEO that are good candidates for drug delivery purposes[4,5].

Furthermore, the interest of researcher focused on their use in biomedical applications[6,7].

In particular, PEO is biocompatible and can inhibit protein adsorption[8,9]. Also, it can replace some biopolymers and provides an insight to their behavior and functions[10].

The structure of PEO micelles is well described by the core-corona model[11-14].

Previous experimental and theoretical research highlighted that hydrogen bonding taking place in aqueous solutions of PEO is important to understand the behavior of PEO in water[15-18].

The presence of an oxygen atom changes entirely the nature of the interactions and therefore the thermodynamics of PEO when dissolved in various solvents.

When dissolved in water, PEO is characterized by hydrophobic interactions as the CH_2 groups repel water, and by hydrophilic interactions represented by hydrogen bonding of water molecules to the oxygen atoms on the polymer. PEO can dissolve in water only because water molecules form a sheath around the PEO macromolecule.

Indeed, the hydrogen bond model has been extensively used to interpret the mechanism of the solubility of PEO in water[19-21].

Hydrogen bonding plays a large role in most biological studies due to the prevalence of water itself and O-H, N-H, S-H and P-H groups in most systems. Hydrogen bonding weakens chemical bonds between atoms and therefore is responsible for shifts to lower frequencies and broadening in absorption bands. Compared with the peak position of the free-water, the bending vibration band of water would shift to the higher wave-number after the formation of the hydrogen bonds[22].

Polymers structure have been accurately studied using neutron scattering techniques[23-25].

Furthermore, it is only recently that the electrical characteristics of polymers have begun to be studied in detail.

Despite polymers have low electronic conductivity, more subtle effects can be observed such as space charge, and some experimental techniques have been developed to evaluate electrical breakdown strength,

dielectric loss and permittivity[26].

This research led us to study the effects of external electromagnetic fields (EMFs) on the vibration bands of PEO using Fourier Transform Infrared (FTIR) spectroscopy. Indeed, infrared spectroscopy have already been proved to be a powerful tool in the investigation of the water structures inside polymeric materials[27]. Vibration spectroscopy was successful used to observe the self-association of surfactants and the coil-globule transition of water soluble polymers[28-30].

Hence, FTIR spectroscopic techniques were chosen to investigate the alterations induced in the vibration bands in PEO in aqueous solutions after separated exposures to a 50 Hz EMF and to microwaves (MWs).

MATERIALS AND METHODS

Materials

Polyethylene oxide with Mw = 600000 was purchased from Sigma Aldrich (Milan, IT).

The polymer was dissolved at 20 mg/ml concentration in bi-distilled H_2O with gentle agitation at the room temperature of 20°C.

Samples of 250 μL of PEO aqueous solution were constituted at this concentration and immediately subjected to the following assays.

Experimental design

Part I: Exposure to 50 Hz EMF

The exposure system consisted of a couple of Helmholtz coils, with pole pieces of round parallel polar faces to produce a uniform magnetic field at the center of the coils distance, where the samples were placed, as described in[31].

A couple of Helmholtz coils was used also to generate time-varying electromagnetic fields at the frequency of 50 Hz by means of a AC voltage regulating up to 230 volt, following the experimental design used in[32].

This enabled to change the magnetic flux density up to 1 mT between the polar faces of the coils. Samples of PEO aqueous solution were placed at the centre of a uniform field area between the coils.

The magnetic field was continuously monitored by a magnetic field probe (GM07 Gaussmeter of HIRST-Magnetic Instruments Ltd - UK) in the I and II part of the experimental design.

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Part II: Exposure to MWs

MWs were produced by an operational mobile phone to which a sound was transmitted such as accurately described in[33,34].

The relative sound spectrum analysis (at 1/3 octave band) of the energy average sound level Leq was acquired by a precision integrating sound level meter, the Larson Davis LxT.

Samples of PEO aqueous solution were placed at three centimeters from the mobile phone, and exposed to the relative GSM 900 MHz microwaves.

The intensity levels of the EMF components produced by the exposure system were monitored by a SRM-3000 instrument of Narda Safety Test Solutions.

The Spectrum Analysis mode of the device was chosen as preliminary analysis to detect the MWs frequencies values impinging the three axis antenna, and the intensities of the electromagnetic components of MWs were continuously monitored by Time Analysis mode, as explained in[35].

The average intensity of the magnetic component produced by the exposure system was 16 mA/m during exposure.

Analogue unexposed samples were located in the same room at the temperature at 20° C and were used as the control for the three experimental design.

Infrared spectroscopy

FTIR absorption spectra were recorded at room temperature by a spectrometer Vertex 80v of Bruker Optics and the attenuated total reflection (ATR) method has been chosen for spectrum collection.

PEO aqueous solution (20 mg/ml) samples were placed between a pair of CaF_2 windows separated with a 25 μm Teflon spacer. For each spectrum 64 interferograms were collected and co-added by Fourier transformed employing a Happ-Genzel apodization function to generate a spectrum with a spectral resolution of 4 cm^{-1} in the range from 4000 cm^{-1} to 1000 cm^{-1}. IR spectra of water solution were subtracted from the spectra of PEO solution at the corresponding temperature.

Each measure was performed under vacuum to eliminated minor spectral contributions due to residual water vapor and smoothing correction for atmospheric water background was performed. IR spectra were baseline corrected and area normalized for exposed and control samples, using vector normalization, calculating the average value of the spectrum and subtracting from the spectrum decreasing the mid-spectrum. The sum of the squares of all values was calculated and the spectrum divided by the square root of this sum.

Interactive baseline rubberband correction was used to subtract baselines from spectra. This method also uses a rubberband which is stretched from one spectrum end to the other, and the band is pressed onto the spectrum from the bottom up with varying intensity. This method performs iteratively, depending on the number of iterations in the algorithm and the baseline as a frequency polygon consisting of n baseline points. The result spectrum will be the original spectrum less the baselines points manually set and a subsequent concave rubberband correction. The values of n = 50 baseline points and 50 iterations were used.

Statistical analysis

Statistical analysis was carried out using Student's t-test for comparisons between two groups, with P-values less than 0.05 considered significant.

RESULTS AND DISCUSSION

This investigation is based upon the study of the interaction between an applied electric field and the dipole moments of PEO in aqueous solution. Indeed polymers are popular dielectric insulators.

Different samples of 250 μl of PEO in bi-distilled water aqueous solution, prepared as described in the preceding section, were exposed for 2 hours to a 50 Hz EMF of 1 mT, and to 900 MHz MWs at the average intensity of 16 mA/m, at the room temperature of 20°C.

Analogue unexposed samples were used as control, at the same temperature.

Exposures were repeated twelve times to ensure statistical significance of the results.

Representative exposed and not exposed FTIR spectra in the region 2800-3000 cm^{-1} obtained after 2 hours of exposure are showed in Figure 1.

Two relevant vibration bands appeared to change in that range: the band around 2850 cm^{-1} and the peak at 2925 cm^{-1} that are due to the symmetric stretching

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($^sCH_2$) and to the asymmetric stretching ($^{as}CH_2$) of the methylene group, respectively[36-38].
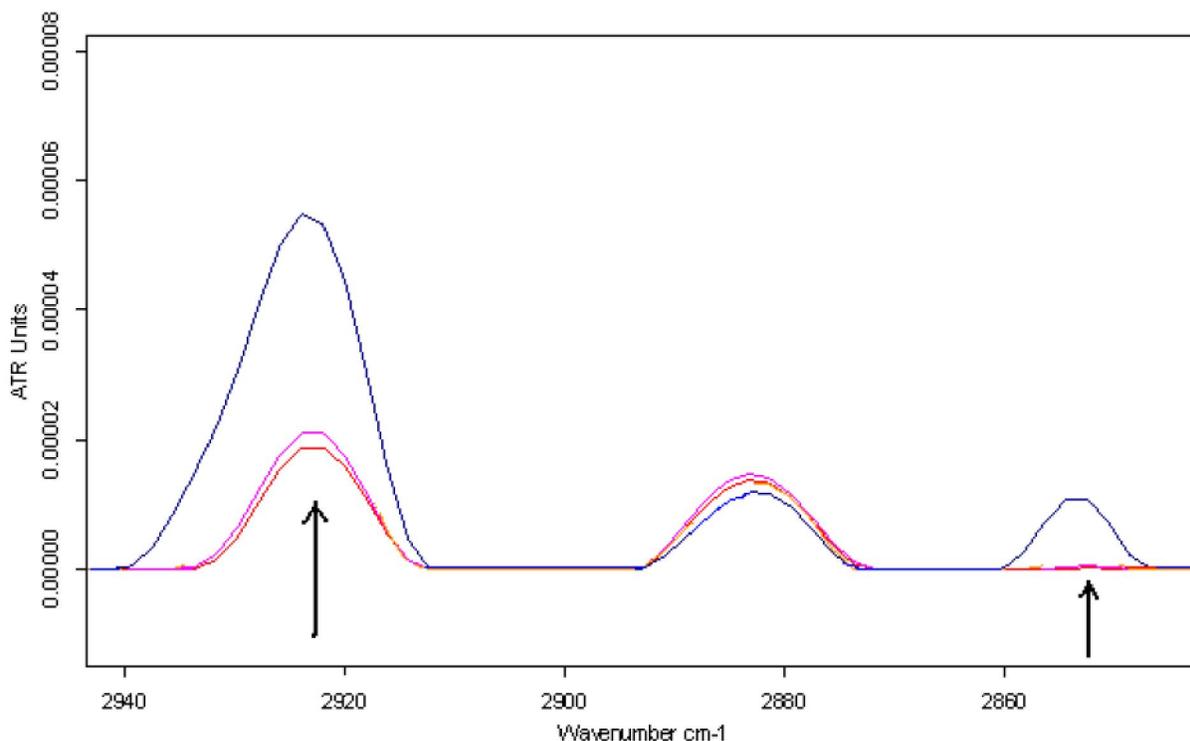

Figure 1:　A representative spectrum in the region 3000–2800 cm^{-1} of PEO in bi-distilled water solution. The vibration band around 2850 and 2925 cm^{-1} (indicated by arrows) are due to the symmetric stretching and asymmetric stretching of the methylene group, respectively. Their intensity decreased significantly after exposures to 50 Hz EMF and to 900 MHz MWs, whose spectral lines are represented by red and purple curves, respectively. The control spectrum is represented by the blue line.

There appears as the intensity of CH_2 bands decreased strongly for PEO in bi-distilled water solution after exposures to 50 Hz EMF and to MWs, whose spectral lines are represented by red and purple curves, respectively (the control spectrum is represented by the blue line).

The decrease in intensity of CH_2 bands after exposure was significantly different in comparison to controls ($p < 0.05$).

Vibration bands of CH_2 group are foreseen at higher wavelength, where the decrease of CH_2 groups after 2 h of exposure to 50 Hz EMF and to MWs was observed, as well.

The strong vibration bands around 1465 cm^{-1}, represented in Figure 2, appears splitted into two bands and can be assigned at CH_2 scissoring vibration bands[39,40].

Spectral changes occurred also in the domain of 1200–1000 cm^{-1}, where a strong band around 1080 cm^{-1} was observed, which can be assigned to the C–

O–C stretching vibration[41,42].

The formation of a hydrogen bond produces that lone pair electrons on the oxygen atom are withdrawn by the hydrogen atom of water, inducing a reduction of electron density on the C–O bond which generates a red shift of the C–O–C stretching band from 1113 to about 1080 cm^{-1}[43].

It represents the strongest band of the C–O–C linkages and its bandwidth broadening indicates that polymers in aqueous solution have higher mobility[44].

Moreover, the band around 1140 cm^{-1} can be assigned to the dehydrated C–O–C bonds at 1130 cm^{-1}[45,46].

In fact, the assignment of bands for PEO was carried out by[47,48] that used their FTIR apparatus to show that increasing molecular weight caused the peaks to shift to slightly higher wavenumbers.

C–O–C stretching band resulted to increase in intensity after exposures to the 50 Hz EMF and MWs, as can be observed in the representative spectrum in

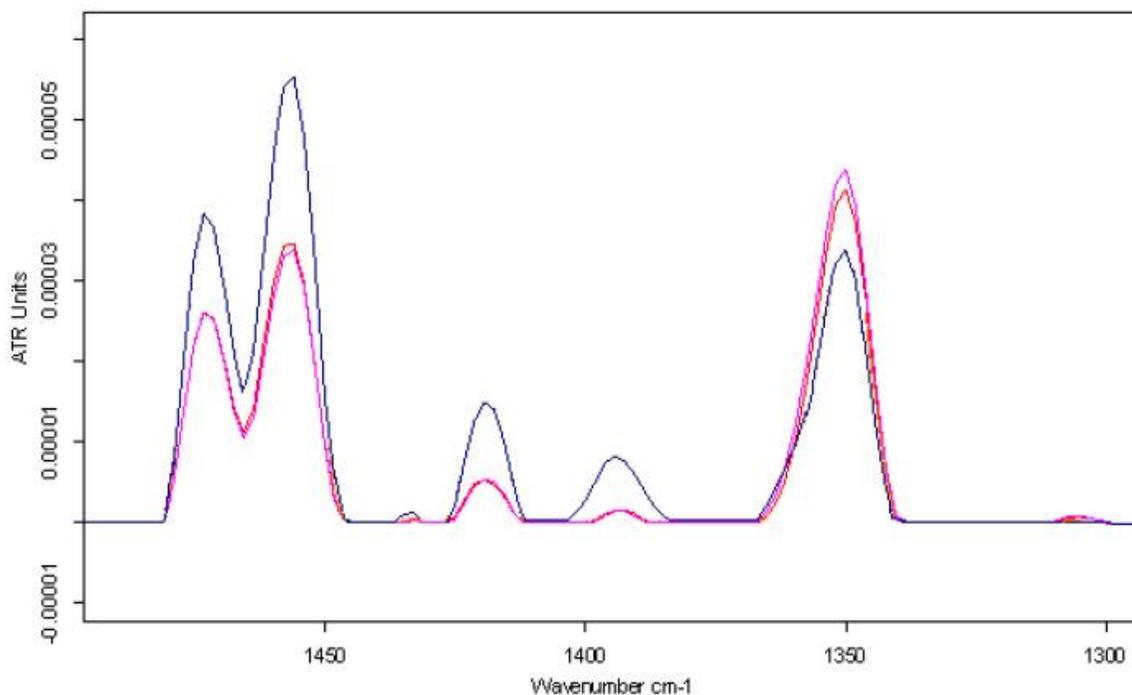Figure 3; this change was significantly different in comparison to controls (p < 0.01).

Figure 2 : A representative spectrum in the region 1500–1300 cm⁻¹ of PEO in water solution. The strong vibration band around 1465 cm⁻¹ is splitted in two bands and can be assigned at CH₂ scissoring vibration bands. The 1349 cm⁻¹ peak is related to the EO methylene wagging vibrations of the gauche conformation. Red and purple curves refer to sample exposed to 50 Hz EMF and 900 MHz MWs, respectively. The control spectrum is represented by the blue line.

Figure 3 : A representative spectrum in the region 1200–1000 cm⁻¹ of PEO in water solution. The band around 1140 cm⁻¹ can be assigned to the dehydrated C–O–C bond and the strong band around 1080 cm⁻¹ can be assigned to the C–O–C stretching hydrated bond. Red and purple curves refer to sample exposed to 50 Hz EMF and 900 MHz MW, respectively. The control spectrum is represented by the blue line.
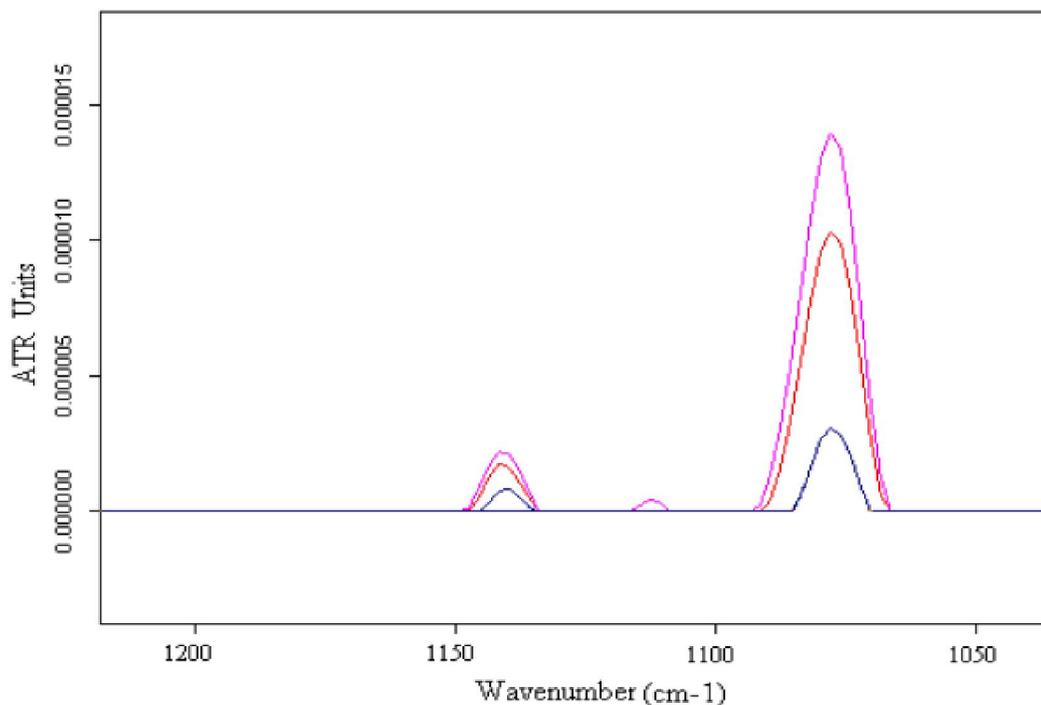
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These results, were observed after exposure up to 4 hours, as well.

As water is added to form PEO aqueous solution, the hydrophobic block CH_2 is insoluble and collapses to form the micelle core and it is encapsulated into the micelles.

In contrast, the dehydration in the micellization process could be inferred by the FTIR spectral analysis from a low shift of the frequency of the C–O–C stretching band toward higher wavenumbers.

The observed increase of the carbonyl stretching vibration C–O–C around 1080 cm^{-1} after exposure to EMFs can be attributed to the increase of formation of the intermolecular hydrogen bonding occurred in PEO aqueous solution after exposure.

The vibration bands at 1359 and 1342 cm^{-1} did not appear in the spectra; these bands are associated with CH_2 wagging motion and are characteristic for crystalline state of PEO[49].

The 1359 and 1342 cm^{-1} doublet in PEO spectrum is replaced by the single 1349 cm^{-1} band in PEO aqueous solution, as can be observed in Figure 2.

The 1349 cm^{-1} peak is related to the EO methylene wagging vibrations of the gauche conformation, whereas those at 1362 and 1340 cm^{-1} provides information about the trans conformation of EO segments[45,47,50]. These changes in intensity indicate that the proportion of trans conformation of EO segments decreases, while gauche conformation of EO segments increases.

The increase of 1349 cm^{-1} band after exposure to 50 Hz EMF and MWs can be observed in the typical spectrum represented in Figure 2; it suggests a decrease of the PEO crystallization process during EMFs exposure. Hydrogen bonded C–O groups changed accordingly with methylene groups of gauche conformation, following Noda's rule[51,52].

This result is in well accordance with the conclusion that hydrogen bonding in PEO aqueous solution increases during exposure to EMFs.

Hydrogen bonds are the results of a delicate balance between electrostatic interactions, exchange and dispersion forces, that can be altered by an external EMF.

Indeed, a simulation showed as the attractive electrostatic interactions between the positive water O-H bond and the negative PEO lone pairs is the driving force for the hydrogen bonding on PEO-water[53].

CONCLUSION

FTIR spectroscopy evidenced the alterations of the vibration bands in PEO in aqueous solution induced by separated exposures to a 50 Hz EMF at the intensity of 1 mT and to 900 MHz MWs at the average magnetic flux density of 16 mA/m.

The infrared region in the range 3000–1000 cm^{-1} was investigated, giving more attention to the 1400–1000 cm^{-1} region, involving the stretching vibrations of ether band, C–H wagging vibrations of EO methylene groups and C–H symmetric deformation vibrations of PO methyl groups.

A decrease in intensity of symmetric and asymmetric stretching CH_2 vibration bands around 2925 and 2850 cm^{-1}, respectively, was observed after exposures.

The C–O–C stretching band around 1080 cm^{-1} increased in intensity after exposures to the 50 Hz EMF and MWs. This result can be attributed to the increase of formation of the intermolecular hydrogen bonding occurred in PEO aqueous solution after exposure.

In addition, an increase of the methylene wagging vibration at 1349 cm^{-1} band was observed after exposure to EMFs, that can be related to a decrease of the PEO crystallization process during exposure, showing as hydrogen bonded C–O groups changed accordingly with methylene groups of gauche conformation.

This results led to the conclusion that hydrogen bonding in PEO aqueous solution increases during exposure to EMFs.

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