D-Glucose-based polymer chains investigated by Delayed Luminescence

R. Grasso[1,2], F. Musumeci[1,2], A. Triglia[1,2], L. Brizhik[3], A. Scordino[1,2]

1) Dept.of Physics and Astronomy, University of Catania, via S. Sofia 64, Catania, Italy
2) Istituto Nazionale di Fisica Nucleare - Laboratori Nazionali del Sud, via S. Sofia 62, Catania, Italy
3) Bogolyubov Institute for Theoretical Physics, Kyiv, Ukraine

Abstract - Worth to note the relevance of glucose in biological systems, being the most important source of energy in all organisms. In this work we studied the different Glucose based polymers, Amylose and Cellulose, by means of Delayed Luminescence (DL) spectroscopy, with the aim to acquire new knowledge on the mechanisms responsible for the DL phenomenon and check the possibility to give in-depth analysis of possible collective states present in Glucose-based structures. Indeed, the experimental results qualitatively agree with the soliton mechanism of the Delayed Luminescence.

INTRODUCTION

Numerous studies have demonstrated that Delayed Luminescence (DL) emitted from both condensed matter [1] and biological [2] systems is correlated to topologic coherence such as the size of an ordered structure. Based on these results a theoretical model hypothesized that the DL is connected with the formation and dissociation of non-linear coherent self-trapped (localized) electron states (solitons and electrosolitons) which are much more stable (in view of long duration of DL) than the corresponding delocalized states, and can be created, in low-dimensional macromolecular structures during the charge and energy transfer processes, by the pre-illumination of the sample [3]. Moreover, DL has been proved to be able in providing valuable information, quickly and non-invasively, on the state of the systems.

So in order to acquire new knowledge on the mechanisms responsible for DL, we studied the DL of an important organic molecule, Glucose, that is the main product of photosynthesis and provides energy for respiratory processes, and of its polymers Cellulose and Amylose.

As a matter of fact, the structures of glucose polymers have been well described in Literature. In Amylose, all glucose repetition units (Fig.1a) are oriented in the same direction by α(1→4) glycoside bonds (fig. 1b), while in Celluloses each monomeric unit of glucose is "upside down" compared to its neighbours, showing an alternating orientation (Fig 1c), that is linked by β(1→4) glycoside bond. In addition, the knowledge of collective states present in such structures need further in-depth analysis.

Moreover, considering the influence of water on biological systems, we compared the response of wet polymers with the one of water solution of Glucose.

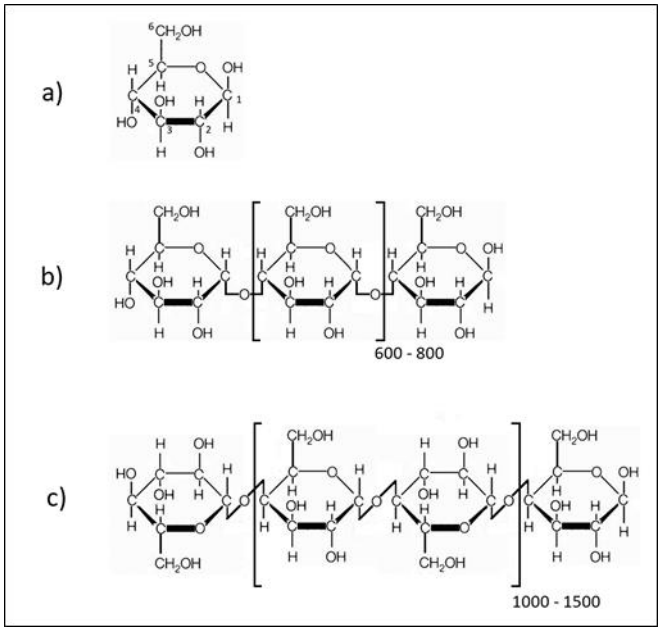

Figure 1: Chemical structure of studied materials: a) D-Glucose, b) amylose, c) Cellulose. *(from Ref .6)*

MATERIALS & METHODS

We used α-D-glucose powder (Sigma-Aldrich, 158968, anhydrous, 96%) composed by α-D-glucose molecules organized in a hydrogen bonded molecular solid belonging to orthorhombic system with the space group P212121.

The used amylose sample (Sigma-Aldrich, A0512, from potato) contained a number of glucose units of the order of one thousand.

We considered two cellulose samples characterized by different grain sizes: sigma-cell cellulose microcrystalline type 20 (Sigma-Aldrich, S3504) with 20 μm grain size and sigma-cell cellulose microcrystalline type 50 (Sigma-Aldrich, S5504) with 50 μm grain size.

We also measured DL emitted by sample of cellulose type 50, imbibed by ultrapure water (Panreac Hiperpur-plus (TMA), MW 18.016). Imbibition was performed in such a way that the same number of water molecules per glucose molecule were present in the cellulose sample and in the water solution of glucose prepared for comparison.

The Delayed Luminescence was measured by using the ARETUSA set-up developed at LNS-INFN [4], suitably adapted to the samples in studying.

The samples were excited by a Nitrogen Laser source (Laser Photonics LN 230C) whose specification was: wavelength 337 nm, pulse-width 0.6 ns, energy 100±5 μJ/pulse.

DL was detected in the wavelength range 400-850 nm by using a photomultiplier (PMT) working in single photon count regime and cooled down to -10°C.

The spectral analysis of DL signal was performed by using three Broadband Bandpass Interference Filters (Edmund Optics; centred at 450 nm, 550 nm and 650 nm; 50 nm FWHM).

To increase the time window of measurement, every trial included two successive illuminations of the same sample, using a dwell time of 2 μs in the first run and a dwell time of 20 μs in the second one. The two data series, after normalization, were melted in only one temporal trend ranging from 9 μs up to 1.0 s.

RESULTS & DISCUSSION

We examined seven different types of sample, namely α-D-Glucose, Amylose, Cellulose type 20, Cellulose type 50, wet Cellulose type 50 (soaked by water) and D-Glucose aqueous solution. Starting from the experimental DL data from the samples, we examined: (i) the relation between total number of measured counts and the laser intensity; (ii) the DL quantum yield (QY); (iii) the emission spectra; (iv) the DL time trends after a normalization procedure in order to have a fixed arbitrary value as the first point.

Detailed results are reported n Ref.6. Here we report some of them.

The DL time trend *I(t)* can be described as a convolution of a suitable distribution of exponential decays [5]:

$$I(t) = I_0 \int_0^\infty h(\tau) e^{-t/\tau}\, d\tau \qquad (1)$$

Figure 2 reports the lifetimes probability density function *h(τ)* Eq.(1), as analytically evaluated after having accorded the time trends to the convolution of three hyperbolic decays. Different lifetimes τ_{max} characterized the maximum value of *h(τ)*, suggesting again a correlation with the arrangement of α-D-Glucose molecules.

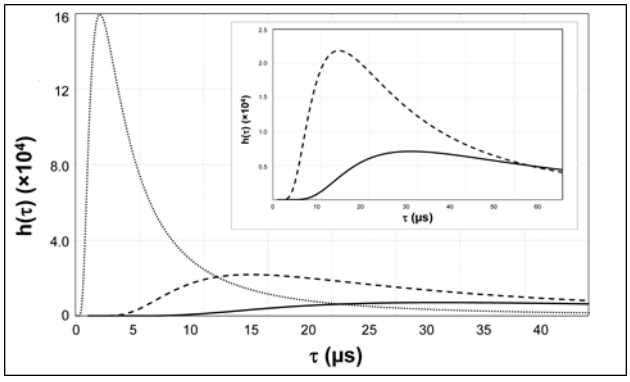

Figure 2: Lifetime probability density function: (solid line) Cellulose type 20, (dashed line) Amylose, (dotted line) α-D-Glucose. Inset enlarges the y-axis scale. *(from Ref .6)*

Comparing wet and dry Cellulose samples it appears that the lifetime distribution *h(τ)* (data not shown) moves to shorter lifetimes, going from dry to wet condition, so indicating that water is able, and indeed does, to interfere with the hydrogen bonds, the ones that stabilize the long and straight chains constituting the dry cellulose structure, causing the softening of the structure. So, DL is able to reveal these structural changes

Figure 3 summarizes DL results in a unique image. It compares two parameters that characterize the DL of every samples, the Yield, linked to the number of states excited during the initial illumination that radiatively decay, and the most probable value among the decay lifetimes τ_{max}, linked to the capacity of the excited states to survive within the structure.

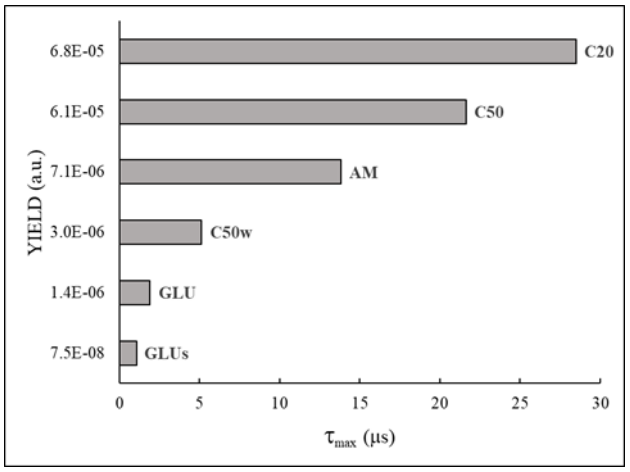

Figure 3: DL Yield as a function of τ_{max}. Legend: (C50) Cellulose type 50, (C20) Cellulose type 20, (AM) Amylose, (C50w) Wet Cellulose type 50, (GLU) α-D-glucose power, (GLUs) D-Glucose water solution)

Moreover, the results accord our previously developed soliton model [3]. The different conformations of glucose monomers in Amylose and Cellulose, which in turn give raise to different dipole moments and dipole-dipole interactions, allow to qualitatively explain the different DL response from the two glucose polymers.

In conclusion these results could be potentially important for the applications of DL based methods in studying changes of glucose-related processes, as for instance diabetes.

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