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Influence of poly(vinyl alcohol) on cellulose photochemical stability in cryogels during UV irradiation

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ABSTRACT

The paper deals with surface properties modifications of cryogels based on poly(vinyl alcohol) and cellulose during exposure to several doses of ultraviolet (UV) irradiation. Significant color changes were observed during UV exposure. The cryogels exhibited a fading trend with irradiation dose increase. Structures accumulated instable red chromophores and exhibited a yellowing tendency. The ultraviolet–visible (UV–vis), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectra indicated important structural modifications during irradiation. The cryogels followed a complex photodecomposition mechanism through random macromolecular chain scissions accompanied by decarbonylation and photooxidation with carbonyl and carboxyl groups accumulation. Hydroperoxides, which were confirmed by an iodometric method, acted as important initiating sites. Cellulose chains were photochemically protected by poly(vinyl alcohol) up to a concentration of 70% in the cryogels, after which phase separation phenomena occurred as demonstrated by scanning electron microscopy technique (SEM), thus ending the protective effect of PVA. The major evolved volatile compounds during cryogels photodecomposition were identified by means of mass spectrometry (MS) and were the following: acetic acid, acetone, 2-propenal, propanoic acid, butanoic acid and ethyl methyl ketone.

1. Introduction

Cryogels are three-dimensional physically or chemically crosslinked polymer networks formed in frozen solutions of polymeric or monomeric precursors which are capable of absorbing high quantities of water and biological fluids, allowing safe diffusion of solutes and mass transport of nano- and microparticles. In addition, polymeric cryogels are excellent carriers designed for immobilization of different cells and biomolecules [1,2]. In contrast to chemically crosslinked hydrogels, the physically crosslinked ones exhibit increased strength due to their crystalline regions and possess superior elasticity [3,4].

Poly(vinyl alcohol) (PVA) has a strong hydrogen bonding capacity, is water soluble, biocompatible and biodegradable, thus being a good material for obtaining blends with natural polymers [5]. Natural polymers are used due to their wide properties range and also from ecological and economical perspectives. PVA cryogels encompass a wide palette of applications including membranes for biosensors, drug and aroma controlled release carriers, scaffolds in tissue engineering, biodegradable packaging materials in food industry, etc. [6–11]. PVA and polysaccharides based cryogels are reported as good candidates for wound dressings, creating appropriate conditions for healing processes whilst assuring a shield against infections [12,13]. A moist environment promotes wound healing enhancement, making PVA/polysaccharides hydrogels suitable as dressings for such purposes, by assuring an appropriate moisture level at the wound-dressing interface. Such materials possess exudates absorbance capacities, are excellent wound desiccation retardants and non-adhesive, may incorporate and deliver bioactive principles and assure a barrier against microorganisms. Paduraru et al. [14] synthesized PVA/cellulose cryogels, which make the subject of the present study, and tested them "*in vitro*" as carriers for the delivery of vanillin, which is an antioxidant and antimicrobial agent. The strength and the swelling performances of these cryogels were improved by the cellulose content. Also, the increased cellulose content in the cryogels enhanced the released percentage of vanillin from their structures and shortened the half time and maximum release time. Varganici et al. reported a pyrolysis study on the same structures [15]. Decomposition studies in different

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conditions of pure cellulose and PVA have been published [16,17]. However, no literature studies have been reported on the photochemical behavior of PVA/cellulose cryogels. UV radiation may cause significant changes in polymer structure influencing both the physico-mechanical strength as well as the surface properties [18–20]. The scission of macromolecular chains, cross-linking, branching, oxidation and loss of side groups are the main effects of the UV radiation action on organic polymers.

Because UV radiation induces damages to materials containing polymers and modifies their surface properties, the investigation of photochemical reactions that occur in complex polymer systems shows a great practical importance [21]. UV irradiation may also be used for surface properties modification, thus knowledge on the photochemical decomposition mechanism must be accumulated.

The aim of this paper is to study the UV radiation induced reactions on PVA/cellulose cryogels and to explain the stabilization effect between the two components of the cryogels with establishment of photodecomposition mechanisms.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose Avicel PH-101 was obtained from Fluka. PVA with an average molecular weight of 147,000–186,000 and a hydrolysis degree of 99% was purchased from Aldrich.

2.2. Synthesis

Three cryogels were obtained with PVA as scaffold and increasing cellulose content, according to Table 1. The cryogels synthesis and structural characterization was described in a previous paper [14].

2.3. Irradiation

30 mm^2 (6×5 mm) of samples, 100 ± 2 μm thick, were irradiated with a medium pressure OSRAM HQE-40 lamp, as artificial light source and in the range 240–400 nm with a power of 100 W. Irradiation of the samples was performed in air. A rotating hexagonal prism shaped device, as sample carrier, with the light source positioned on the central axis of the prism was used. Structures were protected from thermal degradation using a distilled water filter and a fan. Radiations with $\lambda < 300$ nm, absent in the natural light spectrum, were hindered with an incorporated quartz/borosilicate filter having a maximum transparency at 365 nm. The irradiance value, measured at a distance of 60 mm from the source was 9.7 mW cm^{-2}. This value was about 4.4 times higher than the average UV irradiance measured outdoors at zenith on a clear summer day (2.2 mW cm^{-2}), which is lower than the medium value in Japan (3.5 mW cm^{-2}) [22]. Measurements of irradiance and of radiance exposure, dependent on the irradiation time, were carried out with a PMA 2100 radiometer provided with a UVA detector, type PMA 2110 (Solar Light Co., USA). The temperature inside of the irradiation device was 20–22 °C. The relative air humidity (RH) was varied between 50% and 55%. The temperature and RH values during irradiation were controlled with a thermo-hygrometer model JK-HTM-3 (Shanghai Jingke Scientific Instrument Co., China). The structures were removed from the irradiation device every 20 h and analysed.

Table 1
Cryogels composition.

Sample code	Composition (%)	
	PVA	Cellulose
PVA	100	0
90/10	90	10
70/30	70	30
50/50	50	50
Cellulose	0	100

2.4. Analytical methods

Samples thickness was measured with a PosiTector 200 instrument from DeFelsko USA. Color analyses were conducted with a PocketSpec apparatus purchased from Color QA SUA having a sensor head of 6 mm in diameter. The device was calibrated with a super white sulphate barium pellet. Measurements were conducted under reflectance mode using D_{65} illuminant at 10° standard observer. Results were extracted in the CIELAB system. The color parameters of this system are the following: the L^* axis is the lightness (ranging from 0 (black) to 100 (white)), whilst a^* and b^* axes represent the chromaticity coordinates (a positive a^* value corresponding to red and a negative a^* value to green, whilst $+b^*$ and $-b^*$ denote yellow and blue, respectively). The FTIR spectra were recorded using a Bruker Vertex 70 device equipped with a MIRacle accessory designed for single or multi-reflection attenua-ted total reflectance (ATR). The ATR crystal plate was made from diamond and the solid material was put in physical contact with the sampling area through high pressure clamping in order to record high-quality and reproducible spectra. The spectra were recorded in the range 4000–600 cm^{-1} at a spectral resolution of 4 cm^{-1} and 64 scans. FTIR spectra signals were assigned using the literature data [23]. The FTIR spectra were recorded in mostly the same point of each same sample. In order to eliminate eventual thickness variation errors during photoirradiation, normalization of spectra was conducted. This was done through dividing the whole spectrum surface by sample thickness after each irradiation time, which is a common procedure in such cases. Changes in UV–vis spectra were monitored with a SPECORD 200 Analytik Jena spectrophotometer equipped with an integrated Industries sphere. The device was used in reflectance mode. Spectra were recorded in the range 400–800 nm and samples were used as non-transparent pellets, except PVA which was used as film. X-ray photoelectron spectroscopy (XPS) experiments were performed on a KRATOS Axis Nova (Kratos Analytical, Manchester, UK) spectrometer, using a monochromatic AlKa source (1486.6 eV), with 10 mA current and 15 kV, and base pressure of 10^{-8}–10^{-9} Torr in the sample chamber. The incident mono–chromic X-ray beam was focused on a 0.7×0.3 mm^2 area of the surface. The XPS survey spectra of the samples were collected in the range of −10 to 1200 eV with a resolution of 1 eV and a pass energy of 160 eV. The high-resolution spectra for all the elements identified from the survey spectra were collected using pass energy of 20 eV and a step size of 0.1 eV. The binding energy of the C_{1s} peak was normalized to 285 eV. To determine the type of O—C bonds present, a chemical bond analysis of carbon was accomplished by the deconvolution of the curve into corresponding peaks. Data were analyzed using the Vision software from Kratos (Vision 2.2.10). Scanning electron micrographs were taken on liquid nitrogen fractured samples, with a Quanta 200 instrument. The fractured surface was coated with a gold layer. Hydroperoxides determination was undertaken by applying an iodometric method described in the literature [24]. According to the method 0.1 g of irradiated sample was immersed in 15 mL chloroform in a round bottom flask in nitrogen atmosphere. To this solution was added a 10 mL mixture of acetic acid:chloroform (2:1). 1 mL potassium iodide solution was added to the mixture after 10 min. The flask was sealed after 2 min and left in the dark for 1 h under stirring. Hydroperoxide concentration was determined by measuring the absorbance at 362 nm with the help of a calibration curve obtained from known quantities of