Comparative study on gamma irradiation and cold plasma pretreatment for a cellulosic substrate modification with phenolic compounds

Anamaria Irimia\textsuperscript{a}, Ghiocel Emil Ioanid\textsuperscript{b}, Traian Zaharescu\textsuperscript{b}, Adina Coroab\textsuperscript{a}, Florica Doroftei\textsuperscript{a}, Agnes Safrany\textsuperscript{c}, Cornelia Vasile\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Romanian Academy, "P. Poni" Institute of Macromolecular Chemistry, Iaşi, Romania
\textsuperscript{b} National Institute of Research and Development for Electrical Engineering, ICPE CA, Bucharest, Romania
\textsuperscript{c} Section of Radioisotope Products and Radiation Technology, Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna, Austria

HIGHLIGHTS

- A two steps procedure was applied to bond phenolic compounds onto cellulose/chitin substrate.
- \(\gamma\)-irradiation or cold plasma were used to activate a cellulose/chitin mix substrate.
- Some vegetable oils containing phenolic compounds were reacted with pre-activated substrate.
- By bonding of phenolic compounds antimicrobial/antioxidant materials were obtained.

ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 22 July 2016
Accepted 25 July 2016
Available online 27 July 2016

Keywords:
Cellulose
Chitin
\(\gamma\)-Irradiation
Plasma
Phenolic compounds

ABSTRACT

The efficiency of the activation of the cellulose/chitin mix substrate by cold plasma or \(\gamma\)-radiation exposure in order to modify it with bioactive compounds was studied. The eugenol or vegetable oils such as grape seed oil and rosehip seed oil have been grafted onto activated substrate. The examination of modified cellulose/chitin mix substrate by ATR-FTIR spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy confirms that the structural and morphological changes took place in both cases.

The grafting degrees of the surface layer estimated from XPS data varied from 31.1\% to 58.7\% for air cold plasma activation and from 9.7\% to 22.8\% for \(\gamma\)-irradiation treatment. They depend both on bioactive compound used and procedure of substrate activation. Higher grafting degree are obtain by using vegetable oils than in the case of modification with eugenol and the air cold plasma activation seems to be much efficient than \(\gamma\)-irradiation.

By grafting the polymeric substrate with bioactive compounds, antimicrobial and antioxidant properties have been conferred. Such materials can be considered promising for food packaging applications and medical textiles and also the applied procedures are environmental friendly ones.

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1. Introduction

Composite fiber of chitin and cellulose attract a lot of attention in the field of medicine and food for improving human health (Zhang et al., 2009). Both chitin and cellulose are 100\% natural and safe substances. Safety of chitin has been well verified through oral intake and dermal absorption tests. The textile and packaging industry is concerned about the development and production of raw materials, converting them into finished products, meeting customer expectations with human health and environmental safety, and making a profit. Finding new products, alternative raw materials, and processing technologies more "environmentally friendly", obtained with new natural processes and conditions, is central for further developments of industry. It is a great interest in obtaining antibacterial products. Cellulose fibers are moisture-absorbent, comfortable, while chitin fibers are biostatic, inflammation diminishing, odor-resistant, odor-preventing and itch-resistant. (Mikhailov and Lebedeva, 2007) Therefore, the...
combination of cellulose with chitin seems to be an attractive task. The biodegradable cellulose/chitin blend fibers with good mechanical properties and compatibility combine the beneficial characteristics of the individual components, which makes them available for biomedical applications. Furthermore, some procedures have been applied to modify the properties of these mix fibers gave interesting results. Modification with N-isopropylamide offers temperature and pH responsiveness (Sdrobiş et al., 2012, 2015; Irimia et al., 2015a), with acrylic acid and oleic acid (Sdrobiş et al., 2013) enhanced compatibility with other polymers (Sdrobiş et al., 2012) while modification with p-hydroxybenzoic acid (HBA), gallic acid(GA) and eugenol (Eu) can be widely applied in the dermo-cosmetic field to protect the skin from oxidative stress, as transdermal patches which could be effectively used as a material in wound dressings (Irimia et al., 2015b). The possibilities of modification are unlimited both in respect with procedure applied and compounds used in order to obtain materials with new functionalities and properties.

**Phenolic compounds** are well known as antioxidants against superoxide radical. Phenols are known to reduce the rates of oxidation of organic mater by transferring an H atom (from their OH group) to the chain-carrying RO· radicals. Eugenol (4-allyl-2-methoxyphenol) is a naturally occurring phenol essential oil extracted from cloves, is known to be a monoamine oxidase (MAO) inhibitor and known to have neuroprotective effects. In addition eugenol exhibits an excellent bactericidal activity against a wide range of organisms like *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* (Walsh et al., 2003), *Listeria monocytogenes* (Figuereas and Vanetti, 2006).

**Essential oil compounds** which have a well documented antimicrobial activity against spoilage microorganisms, foodborne and postharvest pathogens, are of great potential use in bioactive coatings (Sanchez-Gonzalez et al., 2009; Bakkali et al., 2008).

Cold plasma technology is an emerging, green process offering many potential applications for food packaging. While it was originally developed to increase the surface energy of polymers, enhancing adhesion and printability, it has recently emerged as a powerful tool for surface decontamination of both foodstuffs and food packaging materials (Pankaj et al., 2014). New trends aim to develop in-pack decontamination, offering nonthermal treatment of foods post-packing.

In the context of food packaging, cold plasma is specifically an antimicrobial treatment being investigated for application to fruits, vegetables and other foods with fragile surfaces (Misra et al., 2011). These foods could be either not adequately sanitized or are otherwise unsuitable for treatment with chemicals, heat or other conventional food processing tools.

The exposure of polymers to the action of **high energy radiation** causes bulk modification of properties and even the backbone scissions depending on radiation dose applied (Spinks and Wood, 1990). The most important feature of irradiated polymers at low doses is the possibility of grafting for certain structures, because the radical sites are available for coupling. This process can be conducted by the initiation of scissions and the attachment of other structure onto gamma-irradiated material. Radiation induced grafting runs efficiently for several polymeric supports (Jianqin et al., 1999). The concentration of the active points available for grafting becomes an important parameter that determines the evolution in the yield of grafting. These centers are consumed predominantly on the first stage of process, which trends asymptotically to a pseudo-plateau depicting the maximum degree of grafting (Pierpoint et al., 2001). It is evident that the irradiation dose decides the profile of grafting progress by the growth slope on the early phase of process on which the most amount of grafting structure is consumed. The modifications induced by high energy exposure of cellulose were previously analyzed (Wojnarovits et al., 2010) and the mechanism of radiation grafting has been discussed in details by Chapiro (Chapiro, 1962). The carbon reactive centers as well as the peroxy sites are simultaneously formed during the radiolysis of polymers contribute to grafting, if this process is accomplished under irradiation or on post-irradiation stages. The formation of radiolytic peroxides may be similar with peroxidation pre-processing which allows the increase in the grafting degree (Moura et al., 2011; Ferraz et al., 2014). Of course, the stability of polymer matrix influences the modification in the concentration of peroxy groups, but the contribution of these structures must not be discarded, especially at low exposure doses.

Gamma irradiation represents the most widely used cold sterilization method for foods, food packaging, and medical products. The procedure is simple, cheap and effective with high penetration power. In the case of polymers, irradiation can cause increase (cross-linking) or decrease (chain scission, degradation) of molecular weight. These undesirable effects depend on the structure of the polymers, the dose applied, the testing conditions or the presence of additives (Jipa et al., 2012).

One of the current trends in the food industry consists of the substitution of chemical additives with natural compounds, especially in the area of food preservation. In response to this consumer requirement, the innovative concept of active packaging appears to be an interesting strategy. Recently, the exploitation of natural products of plant origin has been receiving more and more attention.

The aim of the study is to establish the efficiency of the plasma and gamma irradiation treatment, the optimal conditions of modification and to obtain new materials with multifunctional properties offered both by the activated substrate and also by the monomers grafted.

For this purpose, in this paper we present the modification of cellulose/chitin mix substrate (CC) with a phenolic compound, eugenol (Eu), and vegetable oils such as grape seed oil (GO) and rosehip seed oil (RO) in order to improve the surface properties of material useful as medical textiles, food packaging or in pharmaceutical and biomedical fields.

2. Experimental

2.1. Materials

The cellulose/chitin mix substrate (CC) was delivered under the trade name of CHITCEL by Shandong (China), and contains 9–11 wt% chitin.

Eugenol was purchased from Sigma-Aldrich. The purity was of 99% and it was used without further purification. It was used as model antioxidant compound to be compared with two vegetable oils obtained by cold press method namely grape seeds oil and rosehip seed oil.

Grape seeds oil (*Vitis vinifera*) was purchased from S.C. Manicos S.R.L. (Romania) and rosehip seed oil (*Rosa rubiginosa*) was purchased from S.C. HerbaVit S.R.L. (Romania). Grape seeds oil contains about 86% unsaturated fats (~70% linoleic acid and ~16% oleic acid), 0.8–1.5% unsaponifiables rich in phenols (tocopherols) and steroids (campesterol, beta-sitosterol, stigmasterol) (Oomah et al., 1998).

Rosehip seed oil contains a high percentage of unsaturated essential fatty acids (~48% linoleic acid, ~15% oleic acid, ~26% linolenic acid) and other substances such as trans retinoic acid, tannins, flavonoids, vitamin C and β-carotene (Concha et al., 2006).

Polyphenols in plant extracts react with specific redox reagents (Folin-Ciocalteu reagent) to form a blue complex that can be quantified by visible-light spectrophotometry. The reaction forms...
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