



ELSEVIER

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiation grafting on natural films

M. Lacroix^{a,*}, R. Khan^b, M. Senna^c, N. Sharmin^a, S. Salmieri^a, A. Safrany^d^a INRS-Institut Armand-Frappier, Canadian Irradiation Centre, Research Laboratories in Sciences Applied to Food, 531 des Prairies, Laval, Qc, Canada H7V 1B7^b Radioactivity Testing and Monitoring Laboratory (RTML), Bangladesh Atomic Energy Commission, Bangladesh^c Radiation Chemistry Department, National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt^d International Atomic Energy Agency, Vienna International Centre, P.O. Box 100, Hinterbrühl A2371, A-1400 Vienna, Austria

HIGHLIGHTS

- Irradiation of zein/PVA/acrylic acid improved the mechanical properties of films.
- Irradiation of Methylcellulose/NCC/TMPTMA improved the barrier properties of films.
- Irradiation of chitosane/Methylcellulose/HEMA/silane improved the strength of films.

ARTICLE INFO

Article history:

Received 16 November 2012

Accepted 3 April 2013

Available online 24 April 2013

Keywords:

Nanocellulose
Chitosan
Hema
Silane
Methylcellulose
Polycaprolactone

ABSTRACT

Different methods of polymer grafting using gamma irradiation are reported in the present study for the preparation of newly functionalized biodegradable films, and some important properties related to their mechanical and barrier properties are described. Biodegradable films composed of zein and poly(vinyl alcohol) (PVA) were gamma-irradiated in presence of different ratios of acrylic acid (AAC) monomer for compatibilization purpose. Resulting grafted films (zein/PVA-g-AAC) had their puncture strength ($PS=37\text{--}40\text{ N mm}^{-1}$) and puncture deformation ($PD=6.5\text{--}9.8\text{ mm}$) improved for 30% and 50% PVA in blend, with 5% AAC under 20 kGy. Methylcellulose (MC)-based films were irradiated in the presence of 2-hydroxyethyl methacrylate (HEMA) or silane, in order to determine the effect of monomer grafting on the mechanical properties of films. It was found that grafted films (MC-g-HEMA and MC-g-silane) using 35% monomer performed higher mechanical properties with PS values of $282\text{--}296\text{ N mm}^{-1}$ and PD of $5.0\text{--}5.5\text{ mm}$ under 10 kGy. Compatibilized polycaprolactone (PCL)/chitosan composites were developed via grafting silane in chitosan films. Resulting trilayer grafted composite film (PCL/chitosan-g-silane/PCL) presented superior tensile strength ($TS=22\text{ MPa}$) via possible improvement of interfacial adhesion (PCL/chitosan) when using 25% silane under 10 kGy. Finally, MC-based films containing crystalline nanocellulose (CNC) as a filling agent were prepared and irradiated in presence of trimethylolpropane trimethacrylate (TMPTMA) as a grafted plasticizer. Grafted films (MC-g-TMPTMA) presented superior mechanical properties with a TS of 47.9 MPa and a tensile modulus (TM) of 1792 MPa, possibly due to high yield formation of radicals to promote TMPTMA grafting during irradiation. The addition of CNC led to an additional improvement of the barrier properties, with a significant 25% reduction of water vapor permeability (WVP) of grafted films.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The invention of biodegradable packaging films using biopolymers is of major interest for researchers. In the market, most of the packaging materials are from petroleum-based synthetic polymers because of their excellent thermo-mechanical properties. These materials are also comparatively cheaper than biopolymers. Unfortunately, these synthetic packaging materials are not biodegradable.

Hence, research is in progress to develop alternative packaging materials that are environmentally friendly, cheap, possess good thermo-mechanical properties, and provide a good barrier to moisture and gas (Sharmin et al., 2012a). Currently, few biodegradable packaging films are being explored, developed, and marketed. In this regard, biopolymers like chitosan, alginate, cellulose, gelatin, etc. are taken into considerations. Biodegradable films made of these materials do not pose a threat to the environment and are also cost-effective. However, the disadvantages of these films include poor thermo-mechanical properties and a strongly hydrophilic nature (Sharmin et al., 2011b). Therefore, many studies are now attempting to overcome these drawbacks to approach physicochemical

* Corresponding author. Tel.: +1 450 687 5010; fax: +1 450 686 5501.
E-mail address: monique.lacroix@iaf.inrs.ca (M. Lacroix).

attributes analogous to those of petrochemical polymers (Khan et al., 2010; Salmieri and Lacroix, 2006; Le Tien et al., 2000; Ciesla et al., 2006).

Traditional food packaging has minimum interactions with food and has the function to protect the food against the environment. However, these packaging are composed of synthetic polymers and represent a threat for the environment. The new challenges are to find out alternative packaging materials which are environment-friendly, cheap and which possess good thermo-mechanical properties (Sharmin et al., 2012c). Blending compatibilization and copolymerization by polymer grafting have acquired importance in improving the performance of films based on natural materials and to create new polymers with specific physicochemical properties. The level of miscibility obtained depends on the nature of components and the blending technique. Radiation can serve as a tool for crosslinking, surface grafting and reactive compatibilization (Senna et al., 2010).

Zein is a protein that represents 80% of total proteins content in corn grains. It is considered as a by-product from corn milling and presents good thermoplasticity, hydrophobicity and impermeability to gases. Poly(vinyl alcohol) (PVA) is a versatile biodegradable polyol that is used in many industrial applications and presents an advantage to be used as a filler when blended with other polymers in order to enhance their rheological performances (Senna et al., 2010; Han et al., 2010). Cellulose is one of the most abundant polymers in the biosphere and this polymer is presently very popular in packaging materials development. It is the main constituent of plants; moreover, it is lightweight, biodegradable, and available from natural resources. The modification of this polymer by crosslinking and grafting is of important interest for commercial applications (Khan et al., 2010). Crystalline nanocellulose (CNC) is also recognized as being effective to reinforce polymers and may provide added-value materials with superior performance and extensive applications for the next generation of biodegradable materials. CNC is an interesting nanomaterial for the production of cheap, lightweight, and very strong nanocomposites. It is obtained from native cellulose sources, is composed of nanometer-sized rod like particles and is expected to show high stiffness since Young's (elastic) modulus along the axis of the cellulose nanowhiskers is 137 GPa or greater (Moon et al., 2011). Chitosan, the second most abundant natural biopolymer after cellulose, composed mainly of β -(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units. It is the major component of the shells of crustacean such as crab, shrimp, lobsters, and crawfish. Chitosan contains a large number of hydroxyl and amino groups. These two functional groups provide several possibilities for grafting of desirable bioactive groups. Chitosan could be used to prepare biodegradable packaging materials (Khan et al., 2009). Polycaprolactone (PCL) is typical aliphatic polyester, and is fully biodegradable, biocompatible, and nontoxic to living organisms. PCL has good resistance to water, oil, solvent, and chlorine (Sharmin et al., 2012a).

Generally, multifunctional monomers can be added in polymer blends to accelerate a high degree of crosslinking or functionalization during the irradiation process. Graft copolymerization of acrylic acid (AAc) on different polymer substrates has generated many researches due to highly reactive vinyl and carboxyl groups and its miscibility in water and solvents that allows many applications in modified coatings, adhesives and elastomers (Senna et al., 2010). 2-Hydroxyethyl methacrylate (HEMA) is a vinyl monomer that is soluble in water and has many applications in medical sciences. Poly-HEMA hydrogels are well known due to their biocompatibility, hydrophilicity, softness, high water content, and gas permeability (Khan et al., 2012). Alkoxysilane monomers belong to a class of organo-silane compounds having at least two reactive groups of different types bonded to silicon atom in a molecule and are consequently used as promoters, dispersing

agents, cross-linkers and surface-modifiers. They allow improving mechanical and electrical properties of polymers even under severe environmental conditions (Khan et al., 2012; Sharmin et al., 2012a, 2012b). Trimethylolpropane trimethacrylate (TMPTMA) contains three reactive methacrylic acid residues of equal reactivity and has found wide acceptance as a cross-linker and a plasticizer in various polymeric systems (Sharmin et al., 2012d).

This paper focused on the development of polymer formulations to produce "green" functionalized packaging and the use of CNC and gamma radiation technology as an innovative process to improve the functional properties of selected biopolymer-based films coupled to specific monomers.

2. Materials and methods

2.1. Materials

Chitosan (Kitomer, M_w 1600 kDa, 85–89% deacetylation degree) was obtained from Marinard Biotech Inc. (Rivière-aux-Renards, QC, Canada). Zein, PVA (87–89% hydrolyzed, M_w 85,000–146,000), MC (powder form; 400 cP for a 1% solution at 20 °C), PCL (granules form, M_w 70,000–80,000), AAc, HEMA, silane monomer (3-amino-propyl trimethoxy silane) and TMPTMA were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). CNC was produced by FPIInnovations pilot plant CNC reactor from a commercial bleached softwood kraft pulp (Pointe-Claire, QC, Canada). Glycerol (99.5%) was obtained from Laboratoire Mat (Beauport, QC, Canada).

2.2. Films preparation

The required blend compositions were continuously stirred and degassed under vacuum. Required amounts of monomer were added to the polymer blend in bottles under flow of nitrogen atmosphere prior to irradiation. Bottles were exposed to gamma-rays using a Co^{60} source (Gamma Cell 220; Nordion Inc., Kanata, ON, Canada) at a mean dose rate of 20 kGy/h. Films were then cast by pipetting 5–8 mL of polymer solution at 1–5% (w/w) onto polystyrene or polymethacrylate (Plexiglass®) plates (100 mm \times 15 mm), and placed on a horizontal-levelled surface. Solutions were allowed to dry overnight in a ventilated oven at 60 ± 2 °C. Dried films (thickness \sim 30–80 μ m) were peeled intact from the casting surface. Preparation of zein/PVA-g-AAc films was performed according to a procedure from Senna et al. (2010). MC-g-HEMA films and MC-g-silane films were synthesized via a method from Khan et al. (2012). Preparation of chitosan-g-silane films and their incorporation for the formation of trilayer composite films (namely PCL/chitosan-g-silane/PCL) was performed according to a method by Sharmin et al. (2012a). CNC-reinforced MC-g-TMPTMA films were prepared by following a method from Sharmin et al. (2012d).

2.3. Measurement of the mechanical properties

Puncture strength (PS) and puncture deformation (PD) were measured using a Stevens-LFRA texture analyzer (model TA-1000; Texture Technologies Corp., Scarsdale, NY, USA), according to a method by Khan et al. (2010). Tensile strength (TS) and tensile modulus (TM) of the films were measured using a Universal Testing Machine (model H5KT; Tinius Olsen Testing Machine Co., Inc., Horsham, PA, USA), equipped with a 100 N-load cell (type FBB) and 1.5 kN-specimen grips. Measurements were carried out following an ASTM D638-99 method (1999) with a crosshead speed of 1 mm/s at a span distance of 25 mm.

Download English Version:

<https://daneshyari.com/en/article/1891360>

Download Persian Version:

<https://daneshyari.com/article/1891360>

[Daneshyari.com](https://daneshyari.com)