Polymer Degradation and Stability 131 (2016) 71–81

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Surface properties of poly(lactic acid)/polyacrylate semi-interpenetrating networks – Effect of UVC radiation

Jolanta Kowalonek [a], Irena Vuković-Kwiatkowska [a], Dariusz Moszyński [b], Halina Kaczmarek [a, *]

[a] Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Department of Chemistry and Photochemistry of Polymers, Gagarina 7, 87-100, Toruń, Poland
[b] West Pomeranian University of Technology, Szczecin, Institute of Inorganic Chemical Technology and Environment Engineering, Pułaskiego 10, 70-251, Szczecin, Poland

ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form
13 June 2016
Accepted 8 July 2016
Available online 9 July 2016

Keywords:
Poly (lactic acid)
Polyacrylate
Semi-interpenetrating networks
UVC-irradiation
Contact angle measurements
XPS
AFM

ABSTRACT

Poly(lactic acid), PLA, was blended with multifunctional acrylate monomer (dipentaerythritol pentaacrylate) in various weight ratios (1:1 and 9:1). The reaction of photopolymerization of the acrylate monomer in poly(lactic acid) matrix was conducted to obtain semi-interpenetrating networks in the form of films dedicated for use in the packaging industry. Next, the PLA/polyacrylate films were exposed to UVC radiation in order to examine their photostability under the influence of high energy radiation, which can be used as sterilizing factor. In these studies, the following methods have been applied: contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). These methods made it possible to determine the influence of sample composition on the surface properties and photochemical resistance. It was found that PLA was the most susceptible to UVC-irradiation among the studied samples. In PLA/polyacrylate films UV light induced a slight increase in surface roughness and only negligible changes in surface polarity and chemical composition. The mechanism of photodegradation in the tested specimens was also discussed.

1. Introduction

Poly (lactic acid), PLA, is a synthetic thermoplastic polymer that belongs to the group of polyesters. This polymer can be obtained by fermentation of starch derived from renewable resources such as corn, potatoes, etc., which means that it may constitute an ecological alternative to polyolefins obtained from fossil fuels [1]. Direct condensation of lactic acid monomer leads to the obtaining relatively low molecular weight PLA due to undesirable chain-transfer reactions. The method of preparing high molecular weight PLA involves the ring-opening polymerization of lactide which is a cyclic di-ester of lactic acid [2]. PLA is a valuable material in the packaging industry due to its good mechanical and optical properties (stiffness, mechanical resistance, transparency) [3]. It can be processed by standard methods such as extrusion, injection molding, casting, thermoforming, fiber spinning and blow molding [4]. PLA is also widely used in medicine as a drug carrier or scaffolds in tissue engineering owing to its biodegradability and biocompatibility [3,5,6]. However, this polyester has also drawbacks such as rather poor barrier properties, brittleness and a low resistance to UVC radiation. Various methods of PLA modification have been proposed to tailor the polymer with appropriate physicochemical properties to control the rate of biodegradation of PLA, for example, copolymerization, crosslinking, physical blending with other polymers, introduction of fillers (e.g. nanoclays, natural or synthetic fibers), plasticizers, nucleation agents, film orientation [7,8]. Surface properties of PLA can be successfully modified by electron beam, laser action, corona discharge or plasma treatment [9–11].

Our previous works concerned modification of poly(lactic acid) by conducting the reaction of the photopolymerizable multifunctional acrylate monomers in PLA matrix in the presence of selected photoinitiators [12–15]. Such PLA modification significantly improved the resistance of the polymer blends to diffusion of gas molecules (water vapor and CO_2), decreased PLA crystallinity and increased the stability to simulated sunlight, which can broaden PLA application in the packaging industry. Moreover, such blends exhibited good mechanical properties at low temperatures (even at

---

* Corresponding author.
E-mail address: halina@chem.umk.pl (H. Kaczmarek).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.07.008
0141-3910/© 2016 Elsevier Ltd. All rights reserved.

−18 °C), which makes them useful as packaging materials for storage of food in a frozen state.

However, surface properties of PLA modified with acrylate monomer, important from a practical point of view, have not been investigated yet. Also, in the scientific literature there are few reports about the surface properties of modified PLA [16–18].

The purpose of this work was to study the surface properties of the obtained PLA/polyacrylate semi-interpenetrating networks (semi-IPNs) before and after exposure to UVC-radiation which is a cheap and effective method of destroying bacteria, viruses, algae and mildew.

Three complementary techniques: contact angle measurements, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) have been used to monitor the photochemical changes at the polymer surface.

2. Experimental part

2.1. Materials and sample preparation

Poly (lactic acid), PLA, 2002D, an average molecular weight ~ 200 000, was supplied by Nature-Works, USA. The monomer, dipentaerythritol pentaacrylate (DPEPA, M = 524 g/mol), was produced by Polyscience Inc., Warrington, PA, USA, and photoinitiator, 2-hydroxy-2-methyl-2-phenyl-propan-1-one (DAROCUR 1173), - by Ciba, Switzerland. The chemical structures of polymers are shown in Fig. 1.

Chloroform (Avantor Performance Materials Poland SA, Poland) was a solvent for PLA. High purity of diiodomethane, CH_2I_2 (Aldrich), and glycerol, $C_3H_8O_3$ (Avantor Performance Materials Poland SA, Poland), was applied for contact angle measurements.

Films were prepared by mixing an acrylic monomer with the solution of PLA in chloroform yielding systems containing 50 wt% and 10 wt% of monomer. 5 wt% of photoinitiator (relative to the monomer amount) has been added to each formulation. The solutions were cast on glass plates. Solvent has been evaporated in ambient conditions in dark. The obtained films were quickly photopolymerized (during 5 min) using high-pressure mercury lamp (HPK 125 W Philips), emitting polychromatic radiation in the range of 248–578 nm. Simultaneously, films of pure PLA and polymerized acrylate monomer (denoted further in the text as polyDPEPA) were prepared as comparative samples.

In the next stage of the studies, all films were treated with UVC radiation at various time intervals for evaluation of their photostability. For this purpose we used germicidal lamp TUV-30 W (Philips, The Netherlands), emitting radiation with a wavelength of 254 nm and intensity of 3.43 mW/cm^2. All experiments have been done at room temperature and in air atmosphere. The distance between sample and UV source was 10 cm.

2.2. Methods

2.2.1. Contact angle measurements

Contact angle (Θ) measurements for non-radiated and UVC-irradiated samples were performed by sessile drop method using DSA10 goniometer (Krüss GmbH, Germany) at room temperature. The drop of test liquid was placed on the film surface and the image of the drop was recorded and digitalized by camera. The reported Θ value is an average of at least 8 measurements for each specimen. The deviation from the average Θ was lower than 2°. Obtained contact angles for two different liquids (polar – glycerol and non-polar – diiodomethane) were used for calculation of surface free energy using Owens-Wendt's method [19]. Glycerol is polar liquid, its dielectric constant (ε_r) and dipole moment is 42.5 and 2.56 D, respectively, while diiodomethane is nonpolar liquid (($\varepsilon_r = 5.32$), dipole moment = 1.08 D) [20] but very sensitive to light.

2.2.2. X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectra were obtained using Al $K\alpha$ ($h\nu = 1486.6$ eV) radiation with a Prevac system equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy (Ep = 50 eV). The spectrometer was calibrated using the following photoemission lines (with reference to the Fermi level): EB Cu $2p_{3/2} = 932.8$ eV, EB Ag $3d_{5/2} = 368.3$ eV and EB Au $4f_{7/2} = 84.0$ eV. The instrumental resolution, as evaluated by the full-width at half maximum (FWHM) of the Ag $3d_{5/2}$ peak, was 1.0 eV.

The samples were attached to a molybdenum sample holder with use of carbon conductive double-sided adhesive discs. Charging effects were corrected by using the C 1s peak ascribed to the aliphatic carbon bindings (CH_x) and set to 285.0 eV. The XPS lines of other observed elements were shifted correspondingly. The reproducibility of the peak positions was ±0.1 eV.

The surface composition of the samples was obtained on the basis of the peak areas using the sensitivity factor approach and assuming homogeneous composition of the surface layer.

2.2.3. Atomic force microscopy(AFM)

AFM images have been obtained in ambient conditions using MultiMode Nanoscope IIIA, Veeco Metrology and silicon nitride tips. The intermittent (also called tapping) mode has been used. The results were analyzed using Nanoscope v.6.13R1 software supplied

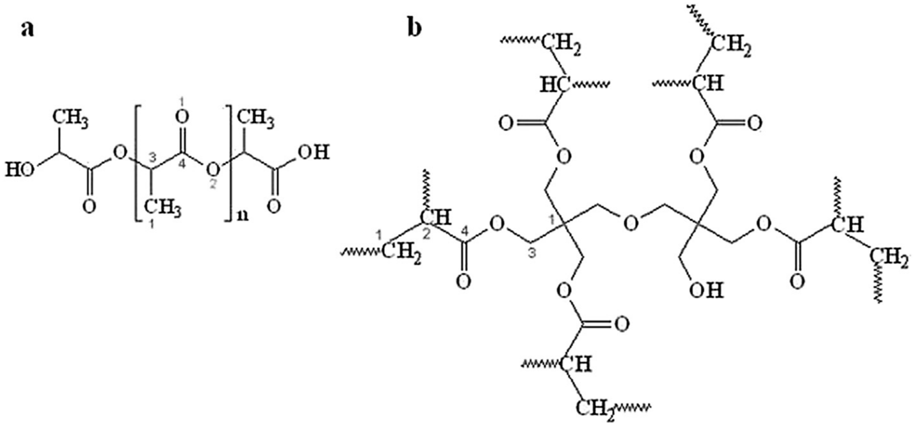

Fig. 1. Chemical structure of PLA (a) and polyDPEPA (b). The numbers indicate the assignment of a given atom to a signal component of XPS spectrum.