



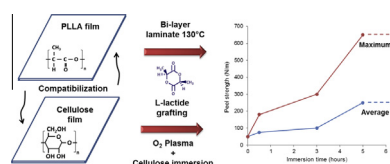
Improvement of the interfacial compatibility between cellulose and poly(L-lactide) films by plasma-induced grafting of L-lactide: The evaluation of the adhesive properties using a peel test



Benoit Couturaud, Audrey Baldo, André Mas*, Jean Jacques Robin

Institut Charles Gerhardt, Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier 2, cc1702, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 December 2014

Accepted 12 February 2015

Available online 21 February 2015

Keywords:

Plasma grafting
Interface
Cellulose
Poly(lactide)
Peel strength

ABSTRACT

Hypothesis: The interfacial compatibility between hydrophilic cellulose and hydrophobic poly(L-lactide) film surfaces is dependent on the interactions and interlocking of the macromolecular chains of the uppermost layers of both polymers. Grafting or coating the cellulose surface with molecular structures similar to the lactide monomer or oligomer is expected to improve the compatibility. Therefore, it should be possible to enhance the adhesive properties.

Experiments: Cellulose films were oxygen plasma treated and immersed in a L-lactide solution. The grafting was performed under various conditions (power, pressure, time). The treated cellulose and poly(L-lactide) films were hot-pressed, and the resulting bi-layer laminates were subjected to a peel test. Comparative experiments were performed with the bi-layer laminates prepared from the cellulose films coated with poly(L-lactide-graft-vinyl alcohol) copolymers.

Findings: X-ray photoelectron spectroscopy, infra-red analyses and wettability measurements revealed that chains bearing ester groups similar to that of lactide were covalently grafted onto the cellulose. The possible grafting mechanism that was initiated by the ionic species from the surface is discussed. As a result, the peel strength to separate the cellulose and the poly(L-lactide) films increased significantly. A comparison with data in the literature highlights the formation of entanglements inside the interfacial zone showing the efficiency of the plasma treatment.

© 2015 Elsevier Inc. All rights reserved.

1. Introduction

Environmentally-friendly materials based on natural and biodegradable polymers derived from renewable resources are intensively studied to replace polymers derived from petroleum. In this field, cellulose–poly(lactide) (PLA) is the most common

composite and is primarily investigated as a PLA matrix reinforced with cellulose fibres, powders or nanocrystals and PLA films coated on cellulose films that form bi- or multi-layer laminates. PLA was selected for its excellent mechanical properties, which is especially exemplified by its high elastic modulus and high stiffness. The interface between the highly hydrophilic cellulose and the hydrophobic PLA has to be tailored to improve the compatibility of the macromolecular chains and consequently the adhesive properties [1,2]. Many attempts to modify either the cellulose or the

* Corresponding author. Fax: +33 0467144028.

E-mail address: andre.mas02@univ-montp2.fr (A. Mas).

PLA surfaces have been performed to graft suitable functional groups. Nevertheless, it appears more appropriate to modify the cellulose as the result of its greater reactivity due to possessing hydroxyl groups as well as the availability and reasonable cost of the starting matter. Moreover, the specific treatment of PLA could further increase the price level of the resulting biodegradable polyester in certain market segments.

Chemical modification of cellulose by ring opening polymerization (ROP) of the lactide (LA) via “grafting from” and “grafting to” methods has been widely described in the literature. The most used “grafting from” method consists in performing the ROP of LA from hydroxyl groups of cellulose in the presence of stannous octoate $\text{Sn}(\text{Oct})_2$ [3]. The “grafting to” method implies that pre-formed PLA chains are coupled to the cellulose carrying suitable reactive sites. For example, the cellulose surface was ene-modified through a reaction with 9-decenoic acid and a subsequent reaction with a thiol-end group functionalized biodegradable polymer [4].

The treatment of cellulose using plasma has been investigated for a long time to confer suitable functionalities and surface properties for paper and textile applications. Recently, plasma modification was developed due as an environmentally-friendly method to improve the dispersion of cellulose fibres in polymer matrices [5]. Cellulose fibre was also treated by corona discharge resulting in oxidation and etching, i.e., chemical and physical modification. Ester functionalities similar to those of PLA and that are compatible with the PLA matrix were grafted onto the cellulose surface leading to improve Young modulus of the cellulose-PLA composites [6]. Similarly, $\text{H}_2\text{O}/\text{C}_2\text{H}_4$ and $\text{NH}_3/\text{C}_2\text{H}_4$ plasma enabled the deposition of a polymerized layer onto the cellulose fibres with various thicknesses to act as reinforcing composites. Oxygen and amine-functional layers were found to be suitable for promoting adhesion, which was measured using the interfacial shear strength [7]. Lastly, nanofibrillated cellulose films (NFC) were treated by O_2/CF_4 mixture plasma to reduce the hydrophilicity of cellulose and to confer adhesive properties between the NFC and the PLA laminated films [8].

In this work, we report the grafting of L-lactide (L-LA) onto cellulose film using O_2 plasma to improve the interfacial compatibility with poly(L-lactide) (PLLA). This new strategy for possible L-lactide polymerization from a solid surface is discussed. Treated surfaces were characterized by XPS, FTIR-ATR and wettability measurements. Cellulosic and PLLA films were hot-pressed and the adhesive properties of the resulting bi-layer laminates were evaluated using a peel test and were compared with the data in the literature.

2. Materials and methods

2.1. Materials

Eucalyptus wood pulp containing a major portion of cellulose and a low percentage (approximately 2–3 wt.%) of other constituents that were not separated from the wood by mechanical or chemical processes was supplied by Ahlstrom Research and Services (Pont-Evêque, France). Poly(vinyl alcohol) (PVA) with different degrees of hydrolysis and molecular weights, L-lactide (L-LA), N-isopropyl acrylamide (NIPAM) and solvents were supplied by Sigma Aldrich. L-LA was purified by crystallization from dried toluene then completely dried and kept under an anhydrous atmosphere. PVA and NIPAM were used as received.

Poly(L-lactide) (PLLA) in the form of films and pellets were supplied by the Goodfellow company. The thickness of the film was 80 μm . The molecular weights of the polymer pellets were determined by steric exclusion chromatography (SEC) in tetrahydrofuran with polystyrene standards that were had a M_n of 125,000 g mol^{-1} and a M_w of 198,000 g mol^{-1} . The glass transition

temperature, T_g , and the melting temperature, T_f , were 69 °C and 171 °C respectively.

2.2. Preparation of films

2.2.1. Cellulose films

Eucalyptus wood pulp was crushed and squeezed on a porous metal sheet while the liquid phase was pumped off. The material was dried at room temperature and at 50 °C under reduced pressure for 6 h. The final compressed material made up of non-oriented cellulose fibres with a thickness of approximately 2 mm is referred to as a cellulose film (CF).

2.2.2. Poly(vinyl alcohol) films

A 10 wt.% solution of PVA (97% hydrolysed, molecular weight $M_w = 31,000\text{--}50,000 \text{ g mol}^{-1}$) was prepared in water at 80 °C and was cast on a glass plate. The water was evaporated at 60 °C for 2 h at ambient atmosphere and at 40 °C under reduced pressure for 8 h. The thickness of the films was approximately 40 μm .

2.2.3. Preparation of poly(L-lactide-graft-vinyl alcohol) copolymers (PLLA-g-PVA) and coated cellulose films

Copolymers were synthesized in the melt by the ROP of L-LA via a PVA/MgH₂ macroinitiator as previously reported [9]. It was shown that the configuration of the asymmetric carbon of the L-LA was retained in the PLLA graft chains. Fully hydrolysed poly(vinyl alcohol) was used and 4 different copolymers structures were synthesized. The molecular weight of the PVA chains (M_w), the theoretical degrees of polymerization of the PLLA grafted chains (DP_n) and the theoretical degrees of substitution of the PVA backbone chains (DS) (percentage of grafted PVA units) for the copolymers were respectively 31,000 g mol^{-1} , 14 and 42%; 31,000 g mol^{-1} , 29 and 42%; 140,000 g mol^{-1} , 14 and 62%; 140,000 g mol^{-1} , 29 and 62%. The experimental values of DP_n and DS were determined by ¹H NMR and varied up to $\pm 10\%$ compared with the theoretical values. The copolymers were soluble in water. For the preparation of coated cellulose films, the cellulose films were immersed in a 10 wt.% solution of PLLA-g-PVA copolymers in toluene for 1, 5, 10 and 20 min at ambient temperature and were then rinsed with toluene and dried. Due to the slow diffusion of toluene in the hydrophilic cellulose, only a small thickness of the cellulose film was soaked with the graft copolymers.

2.3. Plasma treatment

The treatment of the cellulose films (6 × 3 × 0.2 cm) was carried out under oxygen cold plasma at room temperature. The plasma reactor consisted of two cylindrical parallel aluminium electrodes (13 cm diameter, 6 cm distance between the electrodes) placed in a cylindrical vessel coupled with a radio frequency-generator (13.56 MHz) and equipped with an efficient vacuum pump (18 m³/h flow rate, initial pressure inside the device lower than 4 Pa). Prior to plasma treatment, all samples were washed in an ultrasonic bath with acetone for 15 s and were finally dried in an oven at 60 °C. The samples were placed on the bottom electrode, the vacuum was adjusted to approximately 4 Pa, the oxygen was introduced into the reactor and was monitored with a regulated Pirani gauge to achieve the 40 Pa desired pressure and 12 sccm flow. The experiments were conducted at 10 W and 20 W for various times from 5 s to 60 min.

After oxygen plasma treatment, the L-LA grafting was conducted as follow. Oxygen flow continued for 1 min, the vacuum was then broken and ambient air was introduced within the reactor. The samples were exposed to the air for 20 min then immersed in a degassed 10% weight solution of L-LA in toluene at 80 °C for various times from 30 min to 10 h. The samples were taken out and

Download English Version:

<https://daneshyari.com/en/article/6996851>

Download Persian Version:

<https://daneshyari.com/article/6996851>

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