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Plasma-polymer coatings onto different biodegradable polyesters surfaces

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ABSTRACT

Hydrocarbon-like coatings were deposited on different biodegradable polyesters from renewable (bio-based) and non-renewable (fossil-based) resources, such as homopolymers (polylactic acid – PLA, polycaprolactone – PCL) and copolymers (Polyhydroxybutyrate-co-hydroxyvalerate – PHBV, polybutylene adipate-co-terephthalate – PBAT), respectively. The coated samples were tested in terms of adhesion and barrier properties, fragmentation tests, roughness, surface composition and water contact angle measurements. Depending on the substrate, these properties exhibit different behaviours. The coating adhesion of PCL or PHBV is twice higher than the adhesion of coated PLA or PBAT, and depends on the substrate. Barrier performances were mainly improved for both coated PCL and PHBV. Different behaviours are assigned to the change of substrate nature, which induces different interface structure and composition.

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1. Introduction

An increased concern exists today about the preservation of our ecological systems. Since most of today's polymers are not biodegradable, persistent thermoplastics generate significant sources of environmental pollution, harming wildlife when they are dispersed in nature. It is widely accepted that the use of long-lasting polymers in products with a short life-span, such as engineering applications, packaging, agriculture, catering, leisure, surgery, and hygiene, is not adequate. As plastics represent a large part of the waste collection at the local, regional, and national levels, institutions are now aware of the significant savings that compostable or biodegradable materials would generate. According to ASTM standard D-5488-94d and European norm EN 13432, biodegradable means capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, and biomass. The predominant mechanism is the enzymatic action of micro-organisms (biotic degradation), which can be measured by standard tests over a specific period of time, reflecting available disposal conditions [1].

Reaching the conditions of conventional plastic replacements by degradable polymers, particularly for short term applications is of major interest for society as a whole, from the plastic industry to the citizen. That the reason why the high potential of development of the biodegradable polymers has attracted several companies and generates huge investments [2]. These polymers can be classified into two main families, agro-polymers and biodegradable polyesters. Biodegradable polyesters, or "biopolyesters" are (i) synthesized from monomers obtained from agro-resources e.g., polylactic acid (PLA), (ii) obtained by microbial production e.g., the polyhydroxyalkanoates (PHA), or (iii) by conventional petrochemical synthesis, e.g., polycaprolactone (PCL) or poly(butylene adipate-co-terephthalate) (PBAT) [2].

However and untill now, biodegradable polymers have not found extensive applications in the industries to

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largely replace conventional materials, reasons being their rather high costs and some limited properties. For instance, for some applications such as packaging, a key property is the barrier performances. The oxygen transmission rate of these biodegradable materials is generally moderate compared to traditional thermoplastics [3–5]. But, according to Shogren [6] the water vapour transmission rate is rather high compared for instance to the conventional polyolefins. To overcome these issues, different multiphase systems have been tested, such as nano-biocomposites [7] or co-extrudated multilayers [8], without a full success. Then, one solution could consist in the deposition of a dense plasma-coating onto the surface of the polyesters.

Amorphous hydrogenated carbon (a-C:H) plasma-coatings are known to reduce gas permeabilities. They can be used for example as protective barriers for PET bottles and extend the shelf-life of packed products [9]. The improvement is assigned to the high density of the coatings [9,10] which is affected by several factors such as deposition techniques and parameters, coating structure, composition or thickness [11,12]. However, gas transport properties through thin films are mainly dominated by density and defects size [12]. The coating will retain its properties as long as stress cracking does not occur. In the case of multilayer systems such as plasma-coated polymers, the stress undergone by the plasma-deposit when the system is strained depends on the interfacial adhesion strength between the two layers.

During the last decade, a promising method, the fragmentation test, has been developed to characterize the coating adhesion strength. This technique consists in the monitoring of a surface crack pattern of coated materials undergoing uniaxial tension [13]. The crack density is a function of the stress transfer at the interface between two layers. This density at saturation, i.e. when no additional cracks are formed with increasing strain, is evaluated by microscopy and allows determination of the interfacial shear strength, and is related to interlayer adhesion. This technique has been successfully used for determination of adhesion between SiO_x coatings and polymer substrates [13], or DLC (Diamond-Like Carbon) coatings onto metallic substrates [14]. Adhesion is strongly dependant on the substrate chemical structure, which plays a key role in the composition of the plasma-film/polymer interface [13], and on the substrate mechanical properties [15,16].

Plasma deposition is becoming more and more important, for instance in biomedical surface modification. According to a recent review [17], surface engineering of biodegradable polymers is of interest for many studies and has seen an increased interest in the field of tissue engineering, with different biodegradable supports. In tissue engineering the aim is mainly to increase the acceptance of the implant by the body or to avoid foreign-body reactions in general. Consequently, within this field, the aim is to increase the wettability of the surface. In this domain, biodegradable polymers such as PLA have already been widely subjected to non-thermal plasma techniques [17,18]. However and more recently, a shift to more advanced biodegradable polymers, such as PCL or PHBV, can be noted [17,19].

Plasma deposition is also commonly used to improve barrier properties for packaging applications. Bichler et al. [20] reported a barrier improvement factor of 2 for water vapour or oxygen transmission rates, in case of SiO_x-coated PCL or PHA. An unpublished internal report (P2029-1997) of Nutek project (Sweden) from K.S. Johansson showed that SiO_x-coatings on PLA exhibited promising improvements [21]. When optimized, plasma-coatings may then be efficient in improving gas barrier properties of biodegradable polyesters.

In this study, different biodegradable polyesters from renewable (biobased) and non-renewable (fossil-based) resources, such as homopolymers (PLA, PCL) and copolymers (PBAT, PHBV), are tested, respectively. To our knowledge, no equivalent report has been published with different coated biodegradable polyesters. The aim of this work is to evaluate the adhesion and the gas barrier properties of these plasma-coated biopolyesters to investigate the influence of the substrate nature on coating properties, with fragmentation tests and oxygen or water vapour permeability measurements. The adhesion between both layers is characterized by fragmentation tests. The surface roughness is evaluated by AFM experiments, while the coating composition is analyzed by XPS analyses and contact angle measurements.

2. Experimental part

2.1. Materials

Polylactic acid (PLA), polycaprolactone (PCL), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and polybutylene adipate-co-terephthalate (PBAT), i.e., four different biodegradable polyesters are used in this study, as representative of the different types of biopolyesters. An aliphatic and non-renewable polyester, PCL (CAPA 6250) was purchased from Solvay (United Kingdom). An aromatic and non-renewable copolyester PBAT (Eastar Bio 14766), was purchased from Eastman (USA). A biobased and aliphatic polyester, PLA (92% L-lactide and 8% meso-lactide) was obtained from Cargill-Natureworks (USA). Finally a copolymer of PHA (Biopol D400G), PHBV with 8% of hydroxy valerate (HV), was obtained by bacterial fermentation from biomass, and kindly supplied by Monsanto (USA).

The chemical structures and properties of these polyesters are presented in Fig. 1 and Table 1, respectively. Thermal properties of the four biopolyesters were previously given by Avérous [2]. PHBV and PLA molecular weights were determined in another paper [22]. PCL molecular weight was determined in THF at 25 °C and a flow rate of 1 mL min^{-1}, using a PL Gel Mixed D Shodex column (Japan). The elution volume was monitored by an IR differential refractometer (Waters 410, USA) and a multi-angle laser light scattering detector (MALLS, Wyatt Dawn DSP, USA). Data were analyzed using the Millenium software (Waters, USA) and the result is expressed in polystyrene equivalents.

2.2. Films preparation

According to the rheological and thermal behaviours of each polyester [23], different protocols are used to obtained the films.

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