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Surface modification of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) by direct plasma-radiation-induced graft polymerization of N-hydroxyethyl-acrylamide

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ABSTRACT

A new type of cell-carrier-scaffold based on the surface modification of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) by direct plasma-radiation-induced graft polymerization of N-hydroxyethyl-acrylamide was prepared. Parameters such as the membrane position for plasma treatment, delivering power and exposure time were varied. The yields over the film surfaces, chemical changes, morphology and roughness were surveyed. The results indicate that the tailoring is more favorable at 10 W for 10 minutes because at lower values, low degrees of grafting are obtained, whereas at higher values, there is an increase in the degradation of the film. It was found that the use of 30% v/v of HEAA/ethanol (etching agent) led to the formation of a coral-like structure with a greater average roughness than the pristine biomaterial. Hydrophilicity was slightly increased in the modified surface.

1. Introduction

Polyhydroxyalkanoates (PHAs) have widespread applications in biomedical engineering [1]. This is attributed to their appropriate properties for the preparation of three-dimensional scaffolds [2]. Most of the research on PHAs is based on the fact that their original molecular structure can be modified to generate novel applications [3]. Poly(3-hydroxybutyric acid-*co*-hydroxy valeric acid) P(3HB-*co*-3HV) is one of the most important PHAs; it can be used in biomedicine [4] and in the preparation of long-term drug release systems [5]. However, their practical applications are limited by their relatively high degree of crystallinity and hydrophobicity [6]. Considerable efforts have been carried out to develop new materials from P(3HB-*co*-3HV) with improved properties [7]. For instance, the UV radiation-induced graft polymerization of polyacrylamide onto a P(3HB-*co*-3HV) surface was recently carried out [8].

Plasma treatment has also been used to modify the PHA surface to prepare bio-interfaces [9]. Recently, a non-thermal plasma has been used for the surface modification of P(3HB-*co*-4HV) and P(3HB) with acrylic acid [10]. On the other hand, amine functionalization of PHA has gained increasing attention due to its potential as a scaffold protein linker [11,12]. Luk has affirmed that both carbonyl and amine groups have the potential to be used as a chemical linker to immobilize macromolecules [12], while Guan mentioned that "ideal scaffolds should approximately mimic the structural morphology of the extracellular matrix and present appropriate porosity, sufficient surface area and suitable surface chemistries that encourage cell adhesion, proliferation, and differentiation [sic]" [13]. The plasma-treatment surface modification of P(3HB-*co*-3HV) with N-hydroxyethyl-acrylamide (HEAA) has not been reported yet. This study aimed to investigate the surface modification of P(3HB-*co*-3HV) with HEAA by direct plasma-radiation-induced graft polymerization. The effect of an ethanol/HEAA solution as an etching agent, the position of the P(3HB-*co*-3HV) membrane in the plasma chamber, the exposure time and the delivering power were also evaluated. Additionally, the morphology of the novel scaffold was surveyed by scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM).

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2. Experimental

2.1. Materials and methods

P(3HB-*co*-3HV) films that were approximately 1 cm^2 in area and 20 μm in thickness with an average molecular weight of 6×10^5 g/mol and containing 8% 3-hydroxyvalerate (Sigma-Aldrich, St. Louis, MO, USA) were used as received. N-Hydroxyethyl acrylamide and ethanol (99.9%) (Sigma-Aldrich) were dissolved (30% v/v of HEAA/ethanol). The polymer films were immersed in the etching agent for two days for complete swelling and were dried before being placed in the reactor. The reactor was a sputtering chamber under a 10 Pa Ar atmosphere. We placed P(3HB-*co*-3HV) (hereafter called S2) swollen samples, after drying with a disposable paper towel, at two positions using masking tape, that is, at the top of the chamber (called B) and at the bottom of the chamber (called D). The RF-Plasma was operated at 13.56 MHz. The exposure times were T1 = 1 min, T2 = 5 min, and T3 = 10 min, and the delivering powers were P1 = 5 W, P2 = 10 W, and P3 = 15 W. However, important results (such as the graft ratio and morphology) were only observed in samples at a higher exposure time (T3). The modified membranes were Sohxlet-extracted with acetone for 48 h to eliminate excess HEAA and ungrafted poly (hydroxyethyl acrylamide) and then dried in a vacuum oven at 40 °C. Herein, we report the results obtained for membranes exposed for 10 min at various delivery powers.

2.2. Characterization

The graft ratio (GR) of HEMA on P(3HB-*co*-3HV) films was determined using the following equation $\boldsymbol{GR}(\%)=\frac{(\boldsymbol{m_g}-\boldsymbol{m_o})}{\boldsymbol{m_o}}*100$, where m_o(g) is the initial weight of the polyester and m_g(g) is the grafted copolymer weight. GR was estimated in a thermo-gravimetric (TG) analyzer of Netzsch (STA Jupiter® 449) under nitrogen atmosphere at a heating rate of 10 °C /min. A micro-Raman spectrometer (Bruker Senterra, model 910, MA, USA) equipped with a 785-nm laser light source was used to characterize the surfaces of neat and modified P(3HB-*co*-3HV) membranes under similar previously reported conditions [6]. The morphology of plasma-treated membranes, previously coated with gold, was surveyed with SEM (JEOL-JSM-6060LV) operated at 20 kV. The image magnification ranged from 1000 to 5000 ×. The morphologies of untreated and plasma-treated membranes (uncoated samples) were also observed in tapping mode with a JEOL JSPM 5200 AFM equipped with a silicon nitride cantilever (Micromash). The value of the peak frequency was established at 349.3 kHz, and the quality factor was 1031,003. The scanning speed and loop gain were varied depending on the particular conditions of each sample. The swelling percentage was calculated using the equation: $\boldsymbol{S}(\%)=\frac{(\boldsymbol{m}-\boldsymbol{mo})}{\boldsymbol{m}}*100$, where m_o is the initial mass and m is the mass of the swelled film; excess water was removed by filtration, as described in the Active Standard ASTM D570.

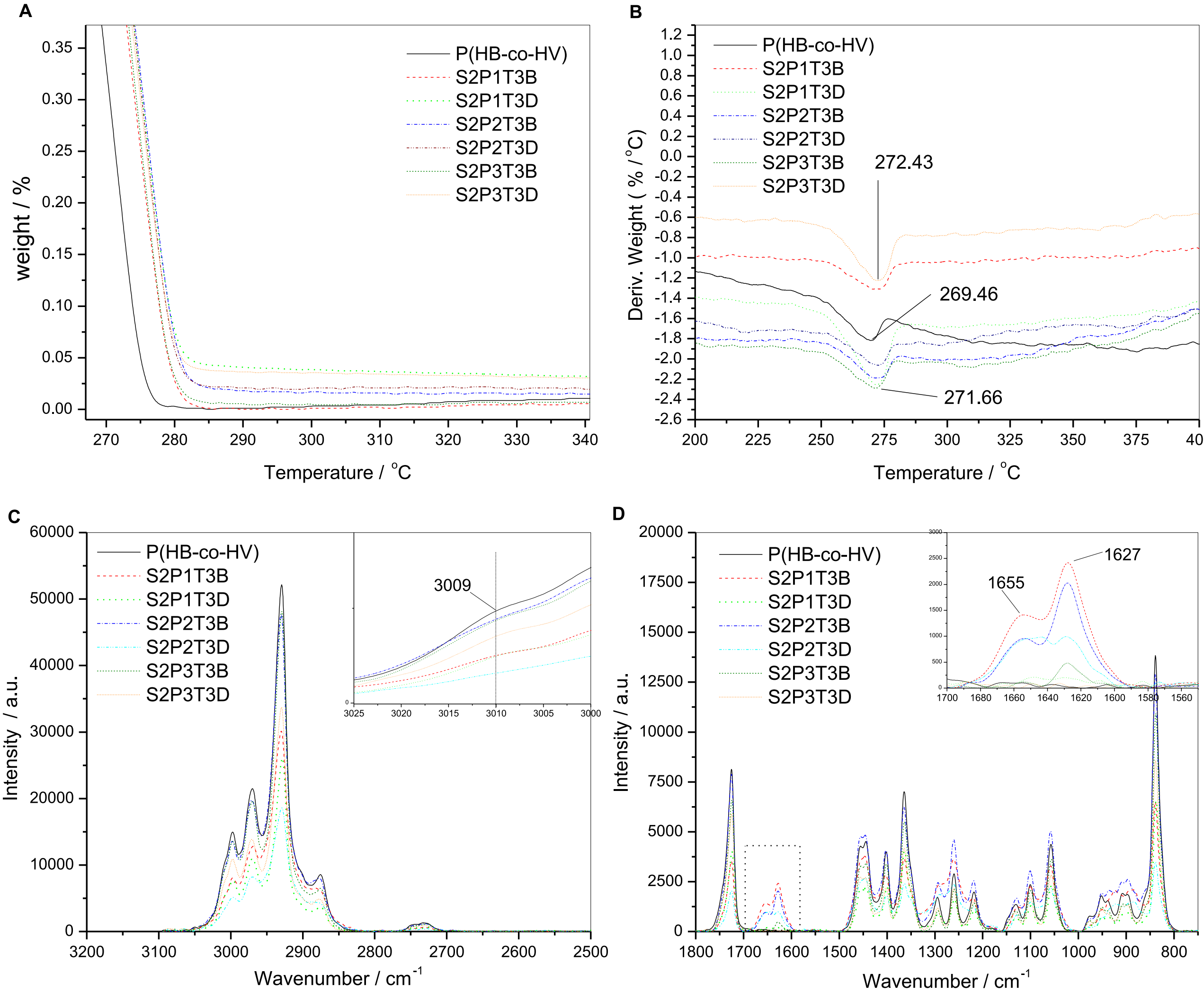

Fig. 1. (A) Thermal gravimetric analysis (TGA); (B) thermograms (DTGA); (C) Raman in the 3200–2500 cm^{-1} region; (D) Raman in the 1800–750 cm^{-1} region.