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Texturing of polypropylene (PP) with nanosecond lasers

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ABSTRACT

Polypropylene (PP) is a biocompatible and biostable polymer, showing good mechanical properties that has been recently introduced in the biomedical field for bone repairing applications; however, its poor surface properties due to its low surface energy limit their use in biomedical applications. In this work, we have studied the topographical modification of polypropylene (PP) laser textured with Nd:YVO_4 nanosecond lasers emitting at $\lambda = 1064$ nm, 532 nm, and 355 nm. First, optical response of this material under these laser wavelengths was determined. The application of an absorbing coating was also studied. The influence of the laser processing parameters on the surface modification of PP was investigated by means of statistically designed experiments. Processing maps to tailor the roughness, and wettability, the main parameters affecting cell adhesion characteristics of implants, were also determined. Microhardness measurements were performed to discern the impact of laser treatment on the final mechanical properties of PP.

1. Introduction

Millions of people worldwide suffer from bone, and joint degenerative and inflammatory problems [1]. Despite bone is a tissue with the capability to heal and regenerate, if the defect site has dimensions exceeding the so called critical diameter, this tissue is not able to heal. In these cases, biomaterials to substitute or repair different tissues (e.g. bone, cartilage, ligaments, or tendons) are required. Among them, polymers have been extensively used as biomaterials, and in particular, polypropylene (PP) is of great interest. It is biocompatible, biostable, and shows good mechanical properties; furthermore, it experiences a less drastic reduction in mechanical properties at elevated temperatures. These properties make them adequate as a bone replacement material; however, its poor surface properties due to its low surface energy limit their use in biomedical applications. It is reported that the interactions between the biological environment and artificial materials are most likely dominated by the materials' surface properties, including wettability, roughness, and morphology, among others [2–5]. Some authors have investigated the potential application of hydroxyapatite (HA) reinforced PP composites as a bone analog biomaterial [6,7]; excellent biocompatibility of HA improves the biological performance of the polymer, but the mechanical properties are affected. Hence, surface modification arises as a good option with the aim to improve the biocompatibility of PP samples without compromising its mechanical performance. At present, these studies have only focused on the utilization of plasma treatment [8,9] showing a better cell adhesion due to the creation of hydroxyl groups in the surface which improves wettability; however, no studies of surface treatment of PP using laser beams are found in the literature.

Lasers have a great potential to precisely modify the surface characteristics of biomaterials, especially in the case of polymers [10,11]. These can effectively modify the implant surface from the macro- to the nano-sized topography without direct contact (avoiding undesirable contamination); moreover, laser treatments are clean, and easily performed on different materials with different geometry. This process relies on the absorption of a laser beam in the surface of a material and the generation of a topographical or chemical alteration due to subsequent processes (thermal, or photochemical processes) in the interaction region [12]. The main problem of using lasers to modify the surface topography and chemistry of PP is the low absorptivity of this material to the laser radiation emitted by conventional laser sources [13]. The pure material exhibits a large transparency for laser wavelengths in a range of 400–1600 nm [14]. This prevents any substantial modification of the surface of PP using lasers in the visible and near-IR part of the spectrum.

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The optical properties of polymers are determined to a considerable extent by their molecular structure. In order to achieve a sufficient absorption of the laser radiation to modify the surface of the PP, suitable additives have to be added to the plastic. Filler materials, organic and inorganic pigments, and dyes have been used for this purpose in laser transmission welding of plastics [15]. Increment of the absorption can occur due to their higher laser absorptivity (e.g. when using organic dyes like azo, or perylene dyes), or because they promotes the scattering of the laser light (e.g. when using filler materials as talcum, or glass fibers) [16]. Carbon black pigments are widely used to increase the absorptivity of polymers for laser transmission welding applications since it is an inexpensive material with good absorbing properties of near-IR radiation [17]. These pigments consist of carbon particles.

In the present work, texturing of PP using nanosecond lasers was investigated. The potential application of nanosecond lasers in order to tailor the wettability and surface structure of this material for biomedical applications was studied for different laser wavelengths (λ = 1064 nm, 532 nm, and 355 nm). The observed large transparency of this material to these laser wavelengths, imposed the requirement of using an absorbing coating (carbon particles) prior to all laser treatments. The laser beam interaction with the carbon particles deposited onto PP samples was investigated using high speed imaging. Influence of laser processing parameters (irradiance, pulse frequency, scanning speed, and spot overlapping) on the final surface properties of this material was determined by using an advanced statistical planning of experiments. Furthermore, microhardness measurements on the treated areas and infrared spectroscopy were used to determine possible structural or chemical modifications induced by the laser radiation.

2. Materials and methods

2.1. Materials

The present study was carried out on flat samples of PP. This polymer is a thermoplastic material composed by polymeric chains of propylene monomers. This polymer has a good impact strength, surface hardness, dimensional stability, and excellent abrasion resistance. It is resistant to a wide variety of chemicals, and has a good corrosion resistance. Sheets of 80 mm × 80 mm × 3 mm and an initial average surface roughness of R_a = 0.06 μm were used in the experiments.

After the laser treatments, the surface of the samples was cleaned by ultrasonic treatment in ethanol in order to remove the unstuck carbon powder.

2.2. Experimental procedures

The experiments were performed using diode end-pumped Nd:YVO_4 laser sources (Rofin-Sinar PowerLine E) emitting a TEM_{00} pulsed laser beam ($M^2 < 1.2$) at 1064 nm, 532 nm, and 355 nm wavelengths. The laser beam was focused using lenses with different focal length for each laser source: 211, 365, and 235 mm, respectively. In consequence, the laser spot diameter on the surface of the sample was approximately 30 μm, 25 μm and 11 μm for the 1064 nm, 532 and 355 nm wavelengths, respectively. Galvanometric mirrors were used to scan the laser beam across the polymeric samples. In all cases, treatments were performed in air and at atmospheric pressure.

First set of experiments were devoted to determine the transparency of the base material to the laser radiation. These experiments were performed using a laser power meter (Thorlabs PM213), and measuring the laser power transmitted ($P_T(z)$) through the sample as compared to the initial laser power (P_0). Then, the transmittance of the sample was determined using the expression:

$$T(z) = \frac{P_T(z)}{P_0} \quad (1)$$

The observed large transparency of this material to these laser wavelengths, imposed the requirement of using an absorbing coating prior to all laser treatments. The selected coating consisted of a thin layer of carbon particles applied onto the surface of the PP samples. The deposition of these particles onto the test pieces was carried out by using a low velocity gas jet.

After determining the optical response of PP samples, a 2^4 full factorial design (FFD) experiment was developed to screen out the key variables (irradiance, pulse frequency, scanning speed, and overlapping between pulses) which significantly influence on the response variables: average roughness, contact angle, and microhardness of treated areas under the three studied laser wavelengths. Two levels (designated "+" and "−") for each of the four processing parameters were investigated, as summarized in Table 1. The irradiance (I), pulse frequency (f), scanning speed (v), and spot overlapping (OL) were selected as processing parameters. Overlapping represents the overlap between two consecutive pulses (an overlap of 0% indicates that successive spots are tangent). This experimental strategy allows the determination of the influence of a reduced number of different laser parameter combinations without decreasing the accuracy of the results. In a full factorial experiment, all factors (in the present case four) at the two levels (i.e. only a high and low value for each experimental factor is considered) are combined with each other, resulting in 2^4 combinations; then, responses are measured for all these combinations of experimental factor levels. To improve statistical reliability, each factor combination was tested twice. Factorial experiments enables to investigate both individual effects of each factor, and determine whether the factors interact (i.e. if the response to one processing parameter depends on the value of other/s). Mathematical details relative to this experimental strategy are provided in Ref. [18].

Furthermore, using an analysis of variance (ANOVA) scheme, those factors having a significant effect on the response variables are identified. Only factors with $p < 0.05$ are considered statistically significant. Finally, a regression model is used to estimate the response values as a function of the effects.

2.3. Sample characterization

Selected samples were inspected in frontal view to the laser treated area using an optical microscope (Nikon SMZ-10A) and a SEM microscope (Philips XL 30) after surface metallization with gold.

ATR-FTIR measurements of the as received, and laser treated PP samples were carried using an ATR-FTIR spectrometer (Nicolet i510, ThermoScientific) to determine possible chemical modifications.

Average roughness was measured using a Veeco Dektak 3ST surface profiler in several locations of the treated areas an average value was extracted. Measurements were made in accordance with the recommendations specified in the International Standard ISO 4288:1996.

Measurements of the contact angle (θ) with bidistilled water were performed using the sessile drop technique to determine the wettability of the treated and untreated areas using a goniometer measuring system (FIBRO System).

Vickers microhardness was measured for all samples before and after laser treatment by using a microhardness tester (Shimadzu HMV-G21), with an applied load of 98.07 mN during a time of 10 s.

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