

Surface Functionalization of Poly(lactic acid) Film by UV-Photografting of *N*-Vinylpyrrolidone

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ABSTRACT: The photoinitiated grafting of *N*-vinylpyrrolidone (NVP) onto poly(lactic acid) (PLA) film with the use of benzophenone (BP) as the initiator, modified the natural hydrophobic PLA behavior to an hydrophilic film with desirable wettability. The surface photografting parameters-percent conversion of monomer to overall photopolymerization (Cp), percent conversion of monomer to the photograft polymerization (Cg), and grafting efficiency (Eg) were calculated. The resulting film surface was ana-

lyzed using ATR-FTIR and UV spectroscopy, derivative spectroscopy and water contact angle. Besides, we demonstrated that the grafted polyvinylpyrrolidone chains could easily react with iodine to form a complex as the homopolymer does with antibacterial activity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 163–169, 2008

Key words: *N*-vinylpyrrolidone; differential UV spectroscopy; photografting; surface modification; contact angle

INTRODUCTION

In recent years, modification of polymer surfaces have been widely investigated because their surfaces play an important roll on different applications such as coating, dyeing, adhesion, printability, antifogging, and biocompatibility.

Poly(lactic acid) (PLA) is a natural polyester with biodegradable and bioabsorbable properties, has been applied at industrial level as a packaging material and in the medical and pharmaceutical fields. However, PLA has some application limitations because: (1) it is highly crystalline, (2) it does not have side-chain groups which could be chemically modified, and (3) it is not suitable to have contact with hydrophilic or polar materials because of its hydrophobic nature.

It is expected that modification of its surface, by grafting introduction of polar groups or hydrophilic materials, could open the opportunity to make this polymer a versatile material for new applications by increasing its biological compatibility and accelerating its biodegradation. Different methods have been used for this purpose such as X-ray¹ plasma and co-

rona discharge,^{2–4} treatment with ozone,⁵ chemical oxidation,⁶ and UV photopolymerization process.⁷

For this study we have chosen the photoinduced grafting process for its low operation cost, the weak penetration of absorbed UV light, and the required mild reaction conditions which does not affect the bulk polymer.

N-vinylpyrrolidone (NVP) has seldom been used in surface photografting, although some researchers have used γ -ray or other initiation methods to graft it onto different substrates.^{8–10} Recently, Chang-Min et al. have functionalized polypropylene film with NVP by UV-induced photografting process¹¹ and Albertsson and coworkers, grafted NVP over PLA surface on a single-step under solvent free conditions.¹² Polyvinylpyrrolidone (PVP) is a versatile synthetic polymer which is soluble in water, and has different applications depending on its molecular weight. It can form different complexes with different substances such as iodine, metal ions, and some pharmaceutical molecules,^{13–15} but to our knowledge, investigation of surface grafted PVP on complexing reactions has had little attention.

To modify commercial porous polypropylene membranes, Bowman and coworkers,¹⁶ used a sequential two-steps photoinduced living graft polymerization method. As shown in Figure 1, under UV irradiation the excited benzophenone (BP) abstracts hydrogen from the polymer surface to generate a surface free radical and semipinacol radicals, which combine to form surface initiators and the subsequent graft reaction in the presence of vinyl mono-

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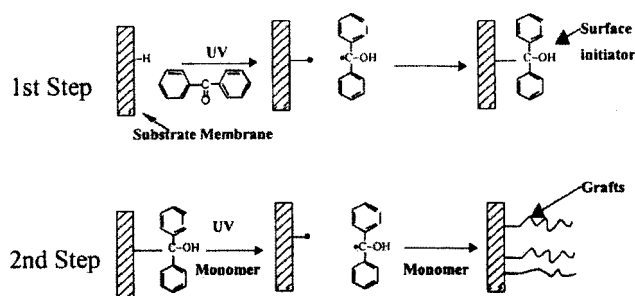
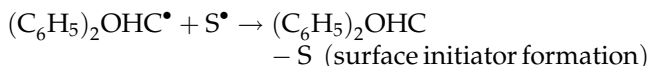
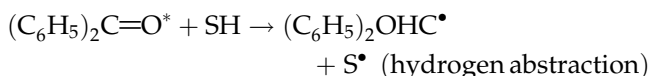
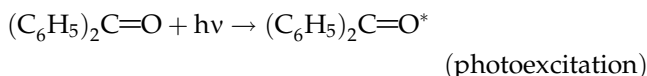


Figure 1 Process steps for the photoinduced graft polymerization with monomers onto a polymer surface and post photopolymerization. (Reprinted with permission from Ma et al.¹⁶ Copyright 2000 American Chemical Society.).

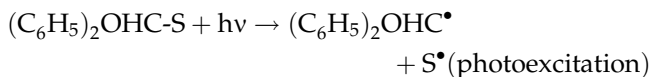
mers. These two steps described by Bowman as (1) synthesis of surface initiator and (2) graft polymerization of monomers are represented on the following equations:

For the first step it was proposed:

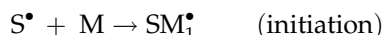


SH represents the polymer film with hydrogen on the surface, (*) represents the excited state, and (•) for radical.

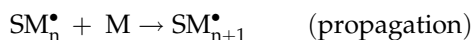
For the second step (graft polymerization of monomers), the proposed equations are:



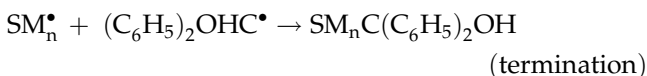
where a surface radical is formed



here the monomer (M) radical is grafted



in this step a grafted polymer radical is formed



The main purpose of our research was to modify PLA film surfaces by grafting NVP molecules with an ultimate aim of making the surface wettable, reactive and bioactive.

EXPERIMENTAL

Materials

PLA pellets 3001D were supplied by Cargill Dow LLC, 1-vinyl-2-pyrrolidinone (Aldrich) was purified by vacuum distillation before using. The photoinitiator BP was analytical grade used without further purification, anhydrous heptane, and iodine (Aldrich) were used as received.

Sample preparation

Preparation of PLA film was carried out by melt extrusion process in absence of additives, having a nominal film thickness of 30 μm . A sample ($5 \times 5 \text{ cm}^2$) was prepared for UV irradiation, where a UV processor (Model No. 60000; Oriel Corp.) was used. The processor was equipped with a 100-W mercury arc lamp (Model No. 8261; Oriel) having a wavelength range of 232–500 nm and intensity of $\sim 25 \text{ mW/cm}^2$ at 365 nm.

Grafting polymerization procedure

Photografting procedure was carried out using the method followed by Deng et al.,¹⁷ in our work a 10 μL sample of water solution (75 wt % of monomer and 3 wt % of BP) prepurged with nitrogen, was deposited between two PLA films with a microsyringe and pressed into a thin and even liquid layer. A piece of quartz plate was used to cover the films. The system was laid on the holder under nitrogen atmosphere and irradiated with UV radiation, keeping a distance from the UV lamp to the films of 30 cm. The irradiation time was varied to control the degree of polymerization. A control film was prepared following the same procedure without UV irradiation.

Separation of the substrates was carried out after irradiation, and sonicated in water for 10 min at 10 Htz, to remove any unreacted BP, monomer, and ungrafted polymer. Films were dried under vacuum for 24 h to a constant weight. The grafted films were analyzed by contact angle goniometry, ATR-FTIR, and UV spectroscopy.

Conversion percent (Cp), grafting percent (Gp), and grafting efficiency (Ge) were obtained by gravimetric method according to the following definitions

$$Cp = (Wp/Wm) \times 100\% \quad (1)$$

$$Gp = (Wg/Wm) \times 100\% \quad (2)$$

$$Ge = (Wg/Wp) \times 100\% \quad (3)$$

where Wm is the weight of monomer added, Wp the weight of total polymer formed including grafted and ungrafted polymer, Wg the weight of grafted polymer after sonication and drying.

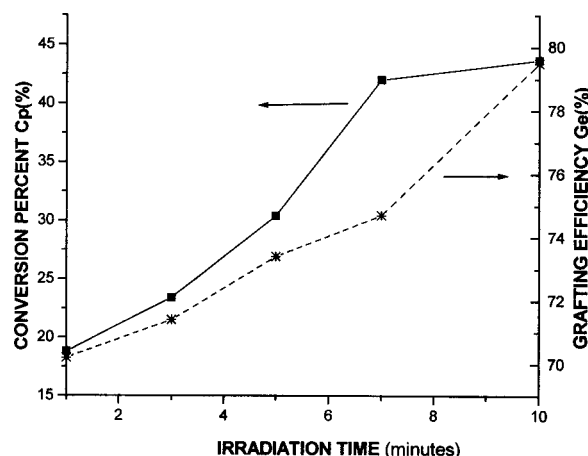


Figure 2 Evolution of photopolymerization process and surface photograft polymerization of NVP versus irradiation time at room temperature.

Postreaction of the grafted surface

The grafted films, irradiated at different times, were impregnated in a 10 wt % iodine ethanol solution at room temperature for 24 h, and then thoroughly rinsed with anhydrous heptane to remove the free iodine, (iodine complex attached to the surface is not affected). The films were dried in air at room temperature.

The antibacterial activity of the PLA film with the PVP-I complex immobilized on its surface, was evaluated placing small disc samples of the neat and modified film onto a dish of nutrient agar previously inoculated with two types of microorganisms; *S. aureus* (gram-positive bacterium) and *E. coli* (gram-negative bacterium). The culture dishes were incubated at 37°C for 24 h.¹⁸

Characterization

FTIR spectroscopy

Neat and modified films were characterized by a Fourier transform infrared (FTIR) spectrometer (Nicolet Nexus 470), equipped with a variable-angle attenuated total reflection (ATR) accessory with a crystal of ZnSe as the internal reflection element wafer, using the transmission mode with a resolution of 4 cm⁻¹ and 100 scans at three different incidence angles: 45°, 50°, and 60°.

UV spectroscopy

Neat, modified, and iodine-treated grafted films were carried out using a UV spectrophotometer (Shimadzu model MultiSpec 1501) from 200 to 400 nm.

In our work we have introduced the first-derivative curves of electronic spectra as a tool for qualitative analysis. With this method, we can solve the problem of band overlapping and facilitate the

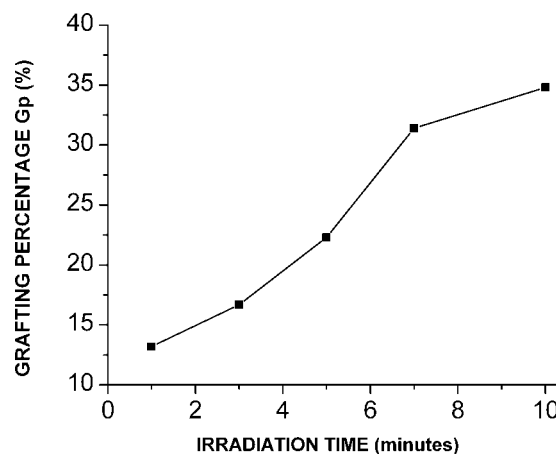


Figure 3 Evolution of grafting percent at different irradiation time.

detection of grafting process of NVP onto PLA surface.

Derivative spectroscopy concept¹⁹ is related with a spectral technique where the slope of the spectrum, (that is the rate of change of absorbance per nanometer of wavelength versus wavelength) is measured. The zero-crossing of the first derivative, corresponds to the maximum of the normal spectrum, and the minimum peak of the first-derivative spectrum corresponds to the inflection point (point of greatest slope) of the normal spectrum.

Static contact angle measurements

Grafted films were analyzed using a contact angle apparatus Rame-Hart, model 100, with 2 μL of deionized water deposited onto the film surface at room temperature. An average of at least 10 droplets were measured for each sample and the data was handle with a ±95% confidence intervals.

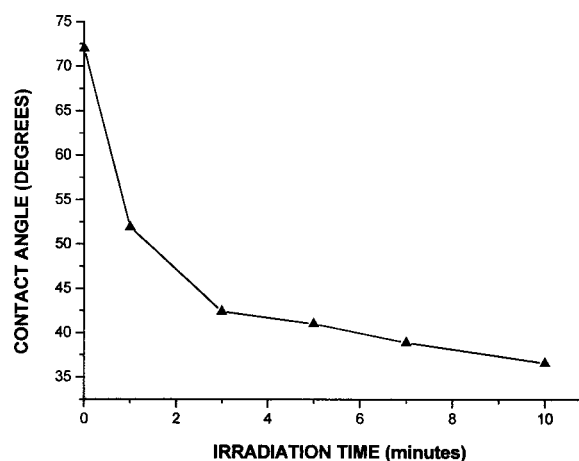


Figure 4 Water contact angles measured for the PLA film surface grafted with NVP at different irradiation times.

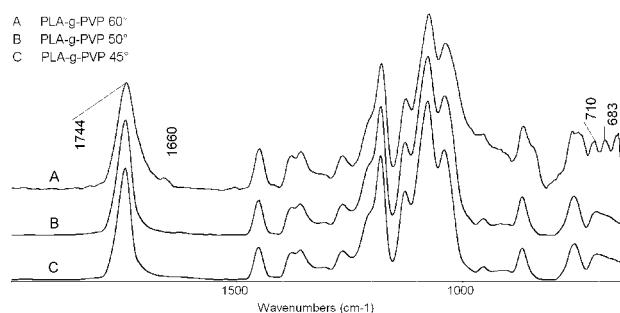


Figure 5 ATR-FTIR spectra of PLA grafted film at different incidence angles.

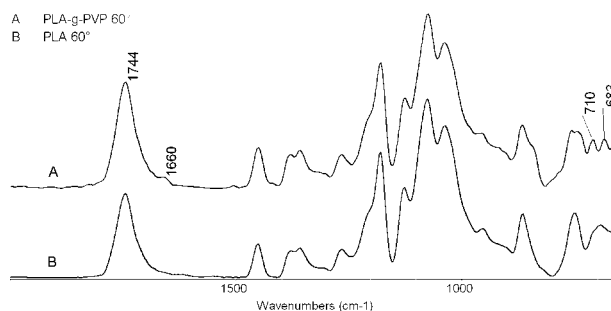


Figure 6 ATR-FTIR spectra of (A) grafted and (B) untreated PLA film at 60° angle of incidence.

Gel permeation chromatography

Pure and irradiated NVP monomer with photoinitiator in absence of PLA, were carried out on a system consisting of a Waters Model 2695, equipped with a three PLgel 5 μm columns, 300 \times 7.5 mm (HP) and a UV detector model 996.

Gel permeation chromatography

To evaluate the extension of the homopolymerization of the NVP under irradiation in absence of PLA film, a blank sample with BP as initiator, was irradiated for 10 min with UV light, a GPC analysis of this sample was carried out to determine its molecular weight. The NVP polymerized under these conditions, reaches a molecular weight lower than 500 Da, according with a PS standard used as reference. The low molecular weight of the NVP polymer formed during irradiation guarantees an easy elimination by washing and sonication of the homopolymer formed during the grafting process.

RESULTS AND DISCUSSION

Grafting studies of NVP

The results using PLA film as substrate and BP as photoinitiator, the evolution of overall photopolymerization (C_p) and surface photograft polymerization efficiency (G_e) of NVP monomer are shown in Figure 2 as a function of irradiation time. Within 10 min, 45% of the total monomer participated in photopolymerization (C_p), and the polymer was grafted onto the surface (G_e) with near 80% of efficiency.

Figure 3 shows grafting percent (G_p), (defined as the percentage of grafted polymer relative to the total amount of polymer) getting a value around 36% after 10 min of irradiation.

Contact angle

The variation of contact angle versus irradiation time for grafted surfaces with NVP monomer water solution is shown in Figure 4. Pure extruded PLA film exhibits a water contact angle of $72^\circ \pm 1^\circ$ and with irradiation, at $36.6^\circ \pm 1^\circ$ after 10 min which indicates a substantial modification of the PLA surface during the irradiation process. A reduction of $\sim 25\%$ from the original value after the first minute clearly shows

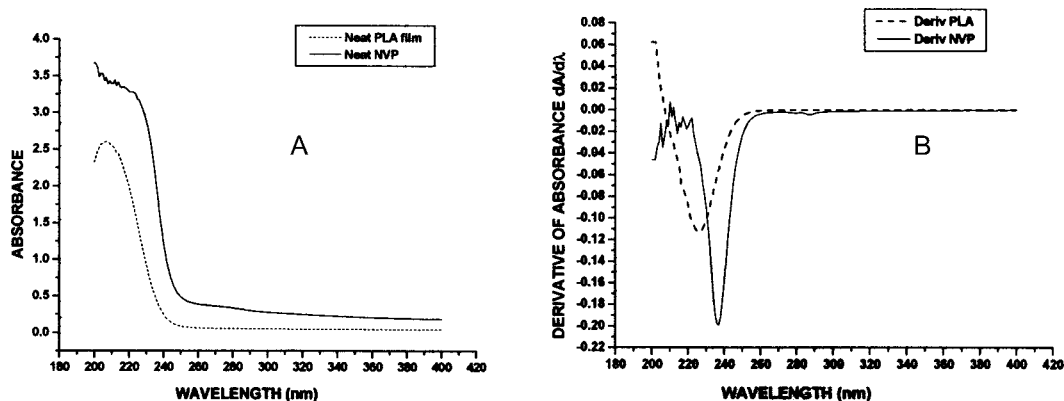


Figure 7 Normal (A) and first derivative (B) UV spectra of PLA film and neat NVP.

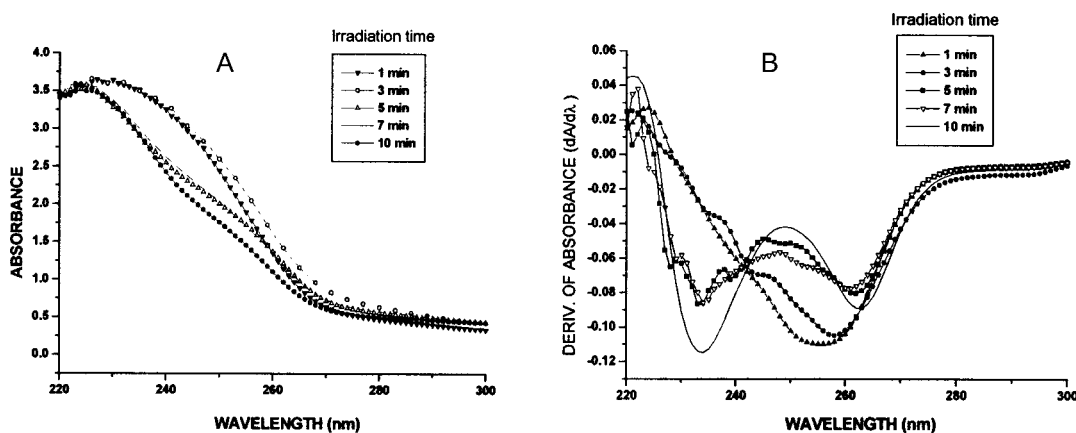


Figure 8 Normal (A) and first derivative (B) UV spectra of grafted PLA film with NVP monomer at different irradiation times.

that NVP grafting occurred immediately after UV exposure.

Infrared spectroscopy

A grafted film sample which was irradiated for 10 min was characterized by ATR-FTIR spectra at various incidence angles, as shown in Figure 5. According to the principle of ATR technique^{20,21} the sampling depth decreases with the increase of incidence angle. This figure shows an absorbance at 1660 cm^{-1} assigned to a mixing band of the C—O and C—N stretching vibration of PVP which is expected on the $1660\text{--}1630\text{ cm}^{-1}$ region.²² Such a pick can be seen in our sample at an angle of 60° , but not at 45° and 50° , which is indicative of low depth grafting; even to the low absorbance, this band can be easily distinguished from the strong absorption band at 1744 cm^{-1} assigned to the carbonyl stretching vibration of the L-PLA as is shown in Figure 6.

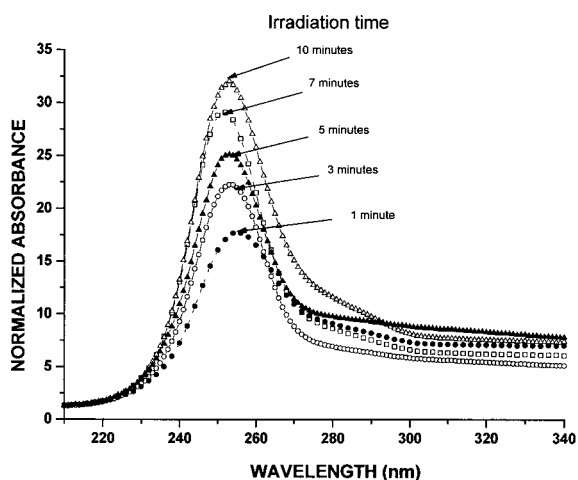


Figure 9 Normalized spectra of grafted PLA film at different irradiation times.

Transmission-UV spectroscopy

The zeroth and first-derivative UV spectra for neat PLA extruded film and pure vinylpyrrolidone are shown in Figure 7. Negative values of the derivative curves reflect the negative slope toward longer wavelengths, and the gradual tendency toward zero at longer wave lengths reflects slight curvature in the plot.²³ Figure 8 shows the spectral changes of normal and first-derivative UV spectra of the grafted PLA film at different irradiation times. First derivative spectra offer substantial advantages against zeroth derivative if the slope of the absorbance versus wavelength for the blank is not too large, as compared with the slopes of the spectra for the component (s) of interest. The first derivative method is a reliable and sensitive tool to study the grafting time-induced changes onto the polymer surface; in the spectral region displayed, the changes observed reflect the grafting process taking place. These spectral changes indicate a structural transition involving an increase on intensity with grafting time.

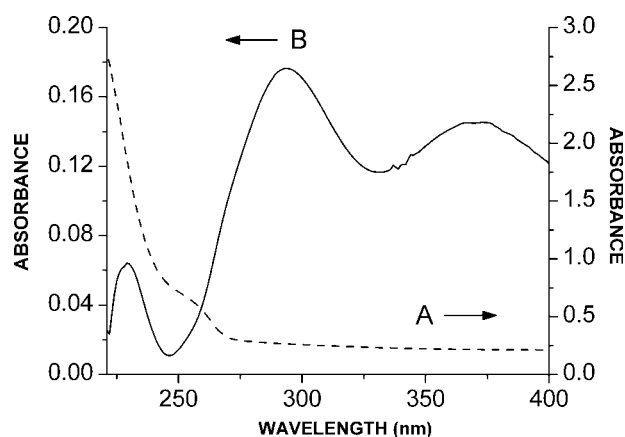


Figure 10 UV spectra of (A) PLA-NVP grafted film and (B) PLA-NVP-I complex film.

In addition to the changes in the intensity of the first derivative, another important feature observed in this spectra is the presence of an isobestic point at 242 nm. The presence of this point indicates a transformation involving two components.²⁴

Normalized spectra are shown in Figure 9, these are characterized by a band centered at 253 nm, where intensity increases as irradiation time increases, indicative of the grafting process.

Postreactions of grafted surface

Iodine complexation of surface grafted pyrrolidone groups, were carried out by immersing the grafted PLA films in 10 wt % ethanol iodine solution at room temperature for 24 h, forming a reddish-brown color surface, which suggest a chemical bonding of iodine onto the grafted PVP. A UV spectroscopy technique was used to determine the change of chemical structure after the formation of the NVP-I complex, Figure 10 shows the UV spectra film, where an absorbance band at 295 nm is assigned to the pyrrolidone units grafted to the PLA surface. Further, at ~ 365 nm, an absorption maximum is present which corresponds to the formation of PVP-I complex as it was previously analyzed by Chang-Min et al.²⁵ and Siggia and Cournoyer²⁶ The ¹H-NMR spectrum of the complex obtained by Mazumdar and coworkers²⁷ suggest a bridge structure between two NVP units with their pyrrolidone carbonyl groups interacting specifically with iodine.

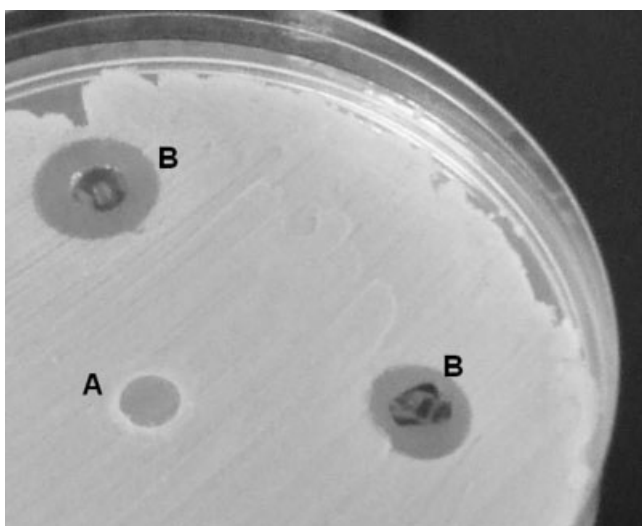


Figure 11 Antibacterial activity of PLA film with NVP-I complex over *S. aureus* (gram-positive). (A) Neat film, (B) Grafted complex film.

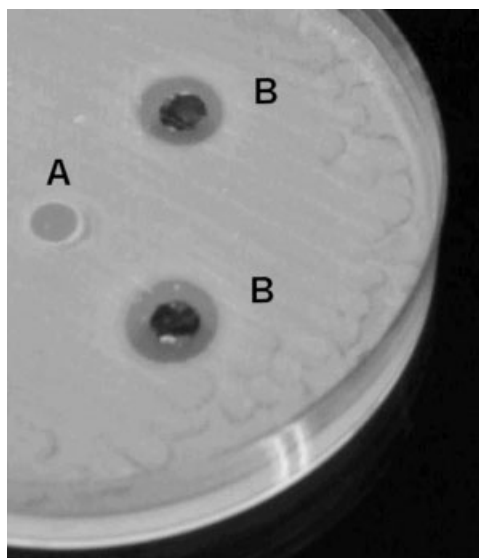


Figure 12 Antibacterial activity of PLA film with NVP-I complex over *E. coli* (gram-negative). (A) Neat film, (B) Grafted complex film.

Antibacterial activities of grafted PLA

The antibacterial activity of the PLA film with the PVP-I complex immobilized on its surface, was evaluated placing small disc samples of the modified film onto a dish of nutrient agar previously inoculated with two types of microorganisms; *S. aureus* (gram-positive bacterium) and *E. coli* (gram-negative bacterium). The culture dishes were incubated at 37°C for 24 h, the results are shown in Figures 11 and 12.

It can be seen that the film with immobilized complex inhibit the growth of both microorganisms, as indicated by the clear inhibitory zone around the modified films, while the virgin sample at the center of the dish does not show this inhibition.

SUMMARY

NVP was easily photografted onto PLA film surfaces using BP as a photoinitiator, the wettability of the PLA surface was improved and it can be manipulated by changing the irradiation time. UV photografting process is an effective technique for rapid surface modification of polymeric materials. Differential UV spectroscopy is shown as an easy analytical tool to follow the grafting process. The grafted films treated with iodine solution reacted easily forming a NVP-I complex, which was confirmed by UV spectroscopy and the antibacterial activity of the modified films was demonstrated by a clear growth inhibition of the two microorganisms *S. aureus* and *E. coli*.

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