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Characterization of Plasma-Polymerized 4-vinyl Pyridine with Silver Nanoparticles on Poly(ethylene terephthalate) Film for Anti-Microbial Properties

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Summary: 4-vinyl pyridine was polymerized on poly(ethylene terephthalate) (PET) film by using lower energy pulsed AC plasma under low pressure in Ar atmosphere. The plasma polymerized coating was characterized by ATR Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Different thicknesses of poly(4-vinyl pyridine) coating under different plasma polymerization conditions were studied. Silver nanoparticles with diameter around 50nm deposit were precipitated on the poly(4-vinyl pyridine) coating by UV irradiation in Silver nitride water solution, in order to enhance the anti-microbial properties. Different kinds of modified PET films were tested for anti-microbial properties against yeast (*Debaryomyces hansenii*) by using microbiological analyser μ-4200 and direct microscopic count method.

Keywords: anti-microbial; morphology; nanoparticles; plasma polymerization

Introduction

The common polymers that we use daily, such as poly(ethylene terephthalate) (PET) (Cola bottle), polyethylene (PE) (food bags), do not have anti-microbial properties. Most of the polymers even have tendency of absorbing proteins on the surfaces,[1–3] which will provide environment for the micro-organisms to grow on. This leads to some contamination on some medical devices and food packaging. Therefore it is necessary to modify the polymer surfaces in order to inhibit the growth of the micro-organisms.

Vinyl-*N*-hexylpyridinium and other *N*-alkylated vinyl pyridine derivatives are used for modification of the polymer surfaces to have anti-microbial properties.[4–6] Poly(4-vinyl pyridine) (P4VP) is a rather interested material because of its stable basic pyridine group and ability to form charge transfer complexes with acidic dopants.[7] As monomer, 4-vinyl pyridine (4VP) is easy to be polymerized and, in additional, the pyridine functional group gives possibility of bonding metal ions or particles on the surface.[8]

In our earlier work, we have used pulsed AC plasma to polymerize monomers on the polymer surfaces, and still preserved the function group in the coating.[9,10] In present paper, 4VP was polymerized by pulsed AC and the modified films were tested for anti-microbial properties. Silver nanoparticles were precipitated on the P4VP coating by UV irradiation to enhance the anti-microbial properties.

Materials

Melinex polyester film (PET) film, 125 μm in thickness from ICI; 4-vinyl pyridine (>90%) stabilized monomer from Fluka Chemie AG; Silver Nitrate (>99.8%), pro-analysis grade from MERCK & Co. All

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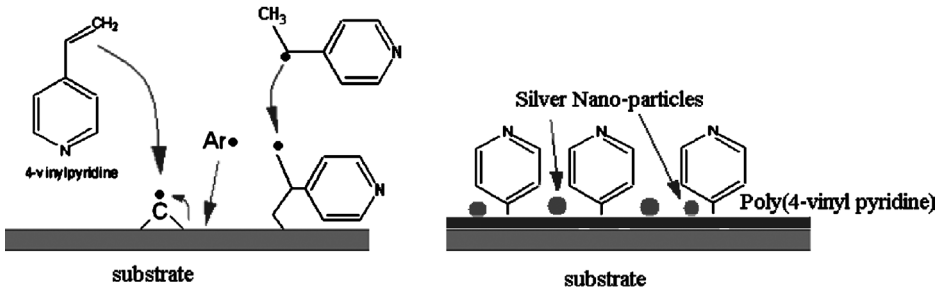


Figure 1.
Scheme of polymerization of 4-vinyl pyridine and silver deposition.

other chemicals used were purchased from Aldrich. Chemicals were used as received.

Plasma Polymerization of 4-Vinyl Pyridine

4VP was plasma-polymerized, using a low-power plasma system,[10] on PE and PET films as well as on glass slides. Substrates were placed in the vacuum chamber purged with Ar. Then a standard procedure with pre-treatment, polymerization followed.[9,10] Two series plasma conditions experiments were made: 1. same polymerization time (10 minutes), varying plasma reaction power (in current, from 3 to 20 mA); 2. same plasma reaction power (10 mA), varying polymerization time (in minutes, from 5 to 20 minutes).

Silver Deposit on Poly(4-Vinyl Pyridine) Coating

Silver nitrate ($AgNO_3$) solution was made at a concentration of 200 mg/L using Millipore water (purified water in a high-grade Milli-Q Plus De-ionizer system). For each experiment 20 mL solution was used.

Table 1.
(a). same plasma power (10 mA), different reaction time; (b). same reaction time (10 min), different plasma power

Time (min)	5	10	15	20		
Thickness (Å)	416	1500	1695	2370		
		(a).				
Power (mA)	3	5	8	12	15	20
Thickness (Å)	226	218	348	1214	1375	2105
		(b).				

P4VP coated film was cut into 5 cm × 5 cm and put in a glass container with $AgNO_3$ solution. The solution was degassed with Ar for 20 minutes before it was sealed under argon atmosphere. UV irradiation was carried out by using 1 kW UV lamp for 15 min or 30 min.

Bio-test Against Microorganisms

The test for anti-microbial properties of the modified surfaces was carried out by using Microbiological Analyser μ-Trac 4200 (SY-LAB, Austria) and also direct microscopic count (Thoma counting chamber (Marienfeld) with the area 0.025 mm^2 and depth 0.05 mm). The chosen microorganism was: yeast (*Debaryomyces hansenii*) from IBT culture collection at the Bio-centre, Technical University of Denmark.

For Microbiological Analyser μ-Trac 4200 test, indirect measurement was applied.[11] For each experiment, 100 μL, 10^3 colony forming unit (cfu) per mL yeast spore suspension was put into 5 mL tryptone soya broth (TSB) media in the μ-Trac inner container. Then the inner container was put into μ-Trac outer container (with 2 short electrodes), together with 2 mL, 0.2% potassium hydroxide (KOH). The outer container was then put into the measuring chamber, and kept at 30°C during the growth period (120 h). The impendence of the KOH solution was measured and the signal curve was collected by the computer. Then the concen-

Table 2.
XPS analyse result of coating composition comparing to the P4VP composition.

Composition	Carbon (C) (%)	Nitrogen (N) (%)	Ration of C:N
poly(4-vinyl pyridine)	85.7	14.28	6:1
XPS analyze result	81.2	9,8	8.28:1

tration of the media was measured by direct microscopic count.

Analysis

The thickness of the coating was measured by DekTak 3030 profilometer (Veeco Instruments Inc., Santa Barbara) on coated glass slides. FT-IR spectra were made by 1600 series FTIR spectrometer (Perkin Elmer, Inc.) with coated PE films. SEM (ISI, SX-40A), FE-SEM (SUPRA™ 40 FESEM, Carl Zeiss SMT AG.) and AFM (XE-150, PSIA Corporation) were carried out to observe the morphology on coated PET films. XPS analyse were performed on a Sage 100 (Specs, Berlin, Germany) using a non-monochromated $Mg_{K\alpha}$.

Thickness Measurement

For each batch of the two series of plasma-polymerization□two glass slides sample were made and at least 12 measurements were made at different positions on the glass. The average thickness value is shown in below.

FT-IR

Pyridine ring peak can be seen in the FT-IR spectrum at 1600 cm^{-1}. (Figure 2.)

The ring peak area of two series samples was calculated, and the profile of the peak area had the same trend as thickness measurement. (Figure 3.) The thickness of the coating increases approximately linearly according to varying reaction time. Same kinds and amount radical are created at the same plasma power, which build up the coating. Therefore the thickness depends on the reaction time. While different plasma energy level also creates different kinds and amount radicals. For the same polymerization time, the higher the

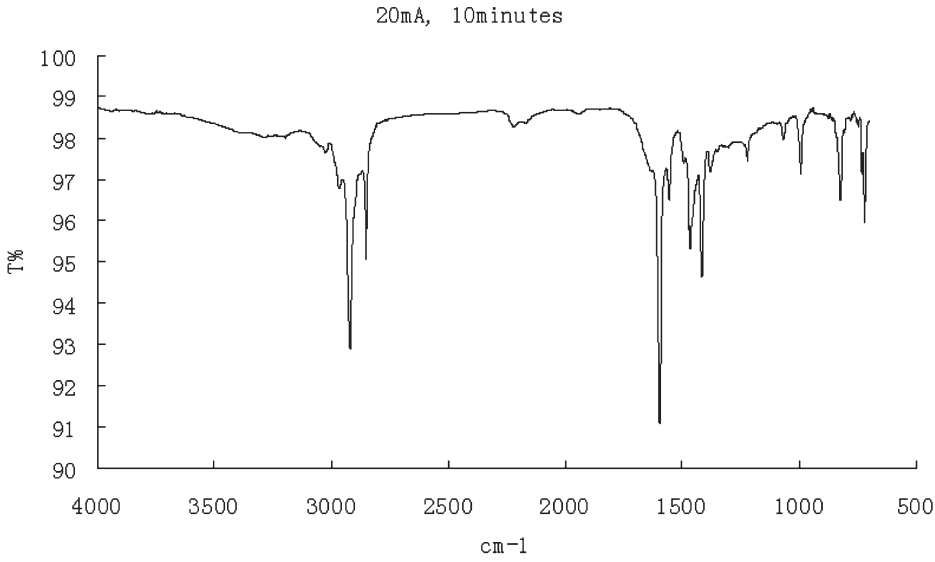


Figure 1. IR spectrum of P4VP on PE film, polymerization condition is 20mA, 10min

Figure 2.
FT-IR spectrum of P4VP on PE film, polymerization condition: 20 mA, 10 min.

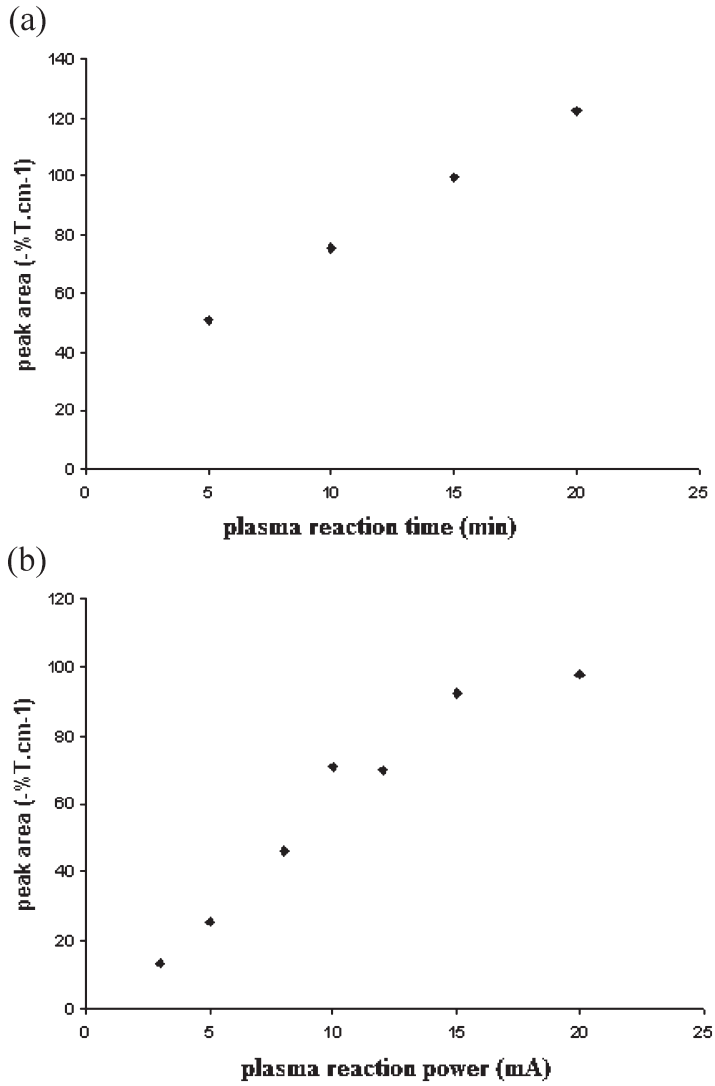


Figure 3.
1600 cm^{-1} peak profile for two series samples: (a).same reaction power (10 mA), different reaction time (5 min, 10 min, 15 min, 20 min); (b).same reaction time (10 min), different reaction power (3 mA, 5 mA, 8 mA, 10 mA, 12 mA, 15 mA, 18 mA, 20 mA).

plasma energy is, the more radical can be created and thicker the coating is.

SEM

Microstructure of the P4VP coating can be observed from SEM picture. (Figure 4.)

FE-SEM

FE-SEM observed the P4VP coating on the polymer surfaces and existence of the silver deposit. The element analyser on the FE-SEM identified the bright particles on the surface was silver and the dimension of the particle was around 50 nm.

AFM

Microstructure can be clearly seen on the surfaces of the coated PET films, same as the observation in SEM pictures. From the peaks measurement, it can be ascertained

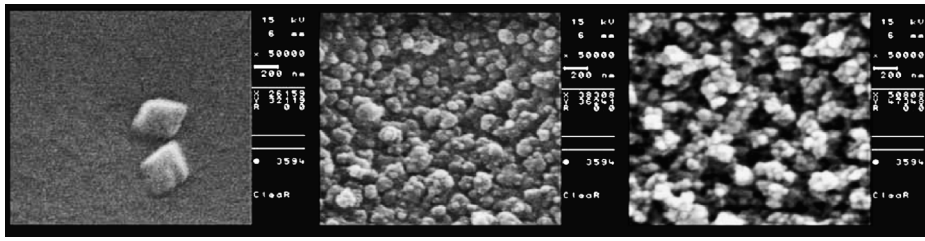


Figure 4.
SEM pictures at magnifying ×50000: original PET film (left); P4VP coated PET film, reaction condition: 20 mA, 10 min (middle); P4VP coated PET film with silver nanoparticles, reaction condition: 20 mA, 10 min, UV irradiation in $AgNO_3$ solution for 30 min (right).

that P4VP coating covers the whole substrate. The topography differs with the varying reaction conditions: the higher the reaction energy level is, the higher the microstructure peak is.

XPS

XPS analytic depth normally is ~10 nm and the information depth is 5nm, which are less than the thickness of the coating, therefore analyses were carried out within the P4VP coating. The existence of silver and Nitrogen on the surface coating could be seen from the overview spectrum. (Figure 7.) The composition of the elements in the coating was calculated by the program "The XI Spectrum Data Processor v2.3" (XPS international Inc.). (Figure 7.) The

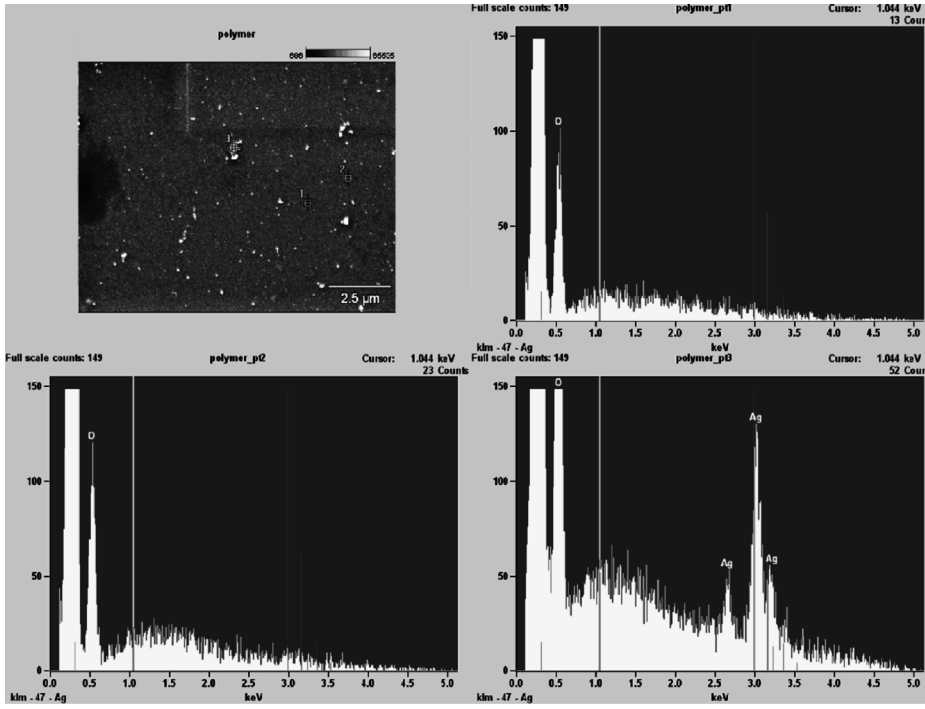
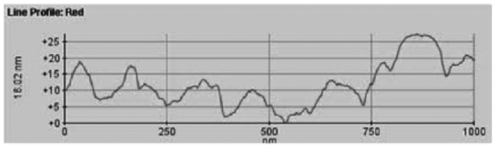
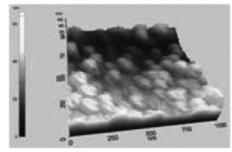


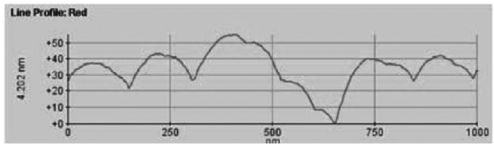
Figure 5.
FE-SEM picture and element analyse of P4VP coated PET film with reaction condition: 10 mA, 10 min, with UV irradiation in $AgNO_3$ solution for 30 min.



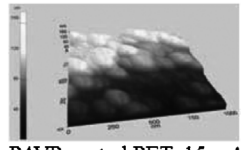
10mA, 10min; peak average height ~13.1nm, thickness of the coating ~150nm



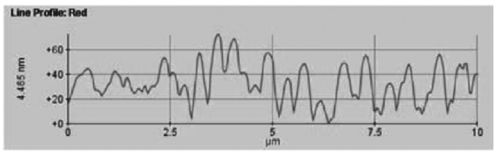
P4VP coated PET, 10 mA, 10 min



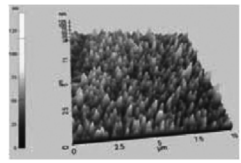
15mA, 10min: peak average height ~36.1nm, thickness of the coating ~170nm



P4VP coated PET, 15 mA, 10 min



20mA, 10min: peak average height ~47.4nm, thickness of the coating ~237nm



P4VP coated PET, 20 mA, 10 min

Figure 6.
Line profile on the coated surfaces and the average height of the microstructures with different reaction condition coatings. (All the result data was processed by software XEI.1.5: Image Processing Program for SPM data (PSIA Corporation))

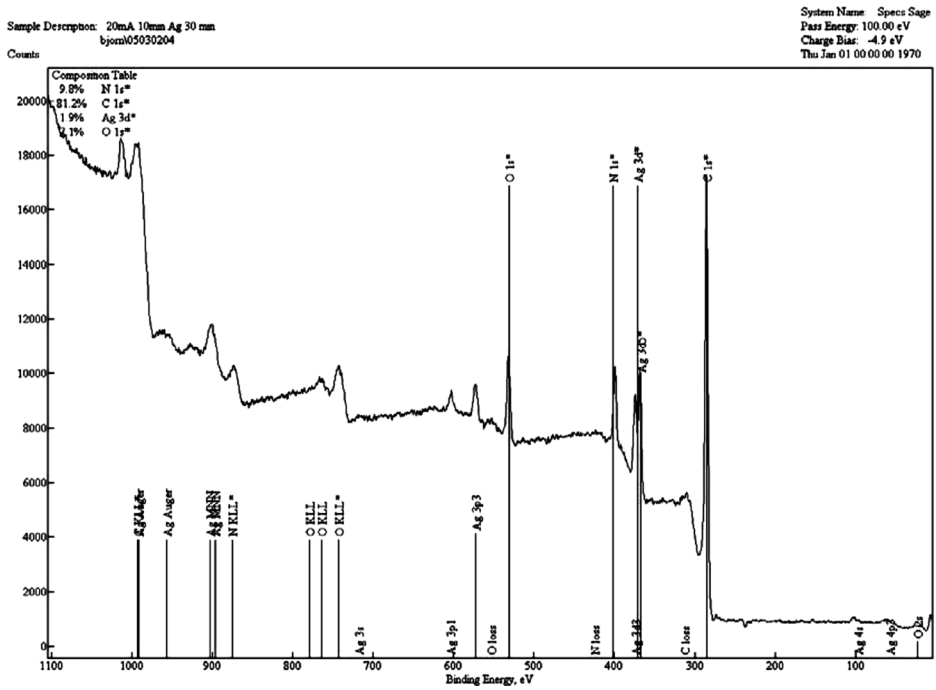


Figure 7.
XPS overview spectrum of P4VP coated PET film with reaction condition: 20 mA, 10 min, UV irradiation in $AgNO_3$ solution 30 min.

Table 3.
Yeast concentration before and after growth with different polymer films by direct microscopic count (To correct the inaccuracy by direct microscopic count, the concentration is calculated as: when there is no yeast in the whole chamber the concentration is $<2.5 \times 10^4$, otherwise the concentration is calculated by the counting number(n): $n \times 10^5 \pm \sqrt{n} \times 10^5$.)

Substrate condition	Concentration before growth (cfu/mL)	Concentration after growth (cfu/mL)
Reference PET	20	$82 \times 10^5 \pm 9 \times 10^5$
No film	20	$70 \times 10^5 \pm 8 \times 10^5$
20 min, 10 mA P4VP on PET;	20	$68 \times 10^5 \pm 8 \times 10^5$
20 min, 10 mA P4VP on PET;UV 30 min	20	$<2.5 \times 10^4$
10 min, 10 mA P4VP on PET;UV 30 min	20	$28 \times 10^5 \pm 5 \times 10^5$
10 min, 20 mA P4VP on PET;UV 30 min	20	$<2.5 \times 10^4$
10 min, 20 mA P4VP on PET;UV 15 min	20	$35 \times 10^5 \pm 6 \times 10^5$

oxygen is always unavoidable in the XPS analyses, especially when P4VP is hydrophilic. Oxygen should mainly be water that bonded to the surface.

Some of the pyridine rings open during the reaction, and the cross-linking with in the coating increase the carbon content.

Bio-test

The silver deposit exits stronger anti-microbial properties than films only coated with P4VP. (Table 3) The longer the UV irradiation of silver deposit time is, or the thicker the PVP coating is, the better the anti-microbial properties are. The anti-microbial properties of the coating are depending on the amount of the silver deposit.

Conclusion

4VP was successfully polymerized on PET film by pulsed AC plasma polymerization in different thickness. The pyridine functional group was well preserved in the coating. The microstructure of P4VP coating on the modified polymer surface was observed. The silver nanoparticles were also able to be precipitated on P4VP coating by UV irradiation. The modified films exhibit anti-microbial properties against yeast (*Debaryomyces hansenii*).

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