# Antimicrobial modification of polyethylene based on plasma assisted grafting

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**Abstract:** Polyethylene (PE) is a polymer with outstanding mechanical properties and therefore it is widely used in many biomedical applications. However, PE has a limitation in case of a biofilm formation responsible for many infections. To avoid the biofilm formation on the PE substrate, a suitable antimicrobial modification can be applied. In this research, sorbic acid (S), commonly used antimicrobial agent, was used for modification of the PE surface using plasma assisted grafting with subsequent immobilization of chitosan.

**Keywords:** radio-frequency plasma, polyethylene, sorbic acid, chitosan.

## 1. Introduction

Many polymeric materials are used in a bio-science paralleling with a development in technology sectors [1]. However, infections associated with these materials represent serious problems for their use in biomedical applications. A biofilm formation is mainly responsible for these infections, whereby microorganisms are attached to the polymeric surface forming strong attached multicellular communities [2]. The suitable antimicrobial modification of polymeric materials can be used to prevent a proliferation of any type of microbial organisms, such as fungal or bacteria strains. The antimicrobial modification of the polymer surface by plasma assisted grafting of antimicrobial agent seems to be preferred technique because of the bulk properties remain unchanged and antimicrobial agent are not released from the bulk. Moreover, this technique is very simple and effective [3]. This research was focused on the preparation of functional coatings on the low-density polyethylene (LDPE) substrate in terms of antimicrobial activity. For this purpose, plasma assisted grafting of sorbic acid (SA) with subsequent immobilization of chitosan was carried out. Surface properties and chemical composition was analysed by various analytical and microscopy techniques, such as contact angle measurements, atomic force microscopy (AFM), Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR).

## 2. Experimental

The material used for this research was pellets of LDPE FE8000 (QAPCO, Qatar). The chemicals used were Acetone (99.9% pure, VWR Chemicals), Sorbic Acid (≥99.0%, Sigma-Aldrich), Ethanol (99.9%, Scharlau), Chitosan (High purity, Sigma-Aldrich), Acetic acid (99.8%, Scharlau), N-(3-diethylaminopropyl)-N'-ethylcarodiimide hydrochloride (EDAC, pure powder, Sigma-Aldrich), Ethylene glycol (98.0%, Fluka), Formamide (>98.0%, Fluka), and ultra-pure water (prepared by Purification System Direct Q3, France).

Equipment and methods used for the modification of LDPE are summarized below.

Plasma treatment of LDPE films (prepared by mounting hot press, Carver, USA) was performed using an enclosed low-temperature plasma generating system Venus75-HF (Plasma Etch Inc, Carson, USA).

Antibacterial modification of LDPE was carried out by an immediately immersion of the plasma treated LDPE samples into 5 %(w/v) SA ethanol solution for 24 h at 30 °C to allowing grafting process (Fig. 1). Unreacted SA was thoroughly washed by pure ethanol to remove any residues. LDPE grafted by SA were subsequently immersed into 0.1% (w/v) EDAC aqueous solution at 4 °C for 6 h allowing an activation of the carboxyl groups present in SA. Finally, chitosan 1% (w/v) in 2% (v/v) acetic acid aqueous solution was immobilized on SA grafted on LDPE for 24 h at 30 °C.

Wettability investigation of modified LDPE samples was performed by static contact angle measurements using the sessile drop method. An optical contact angle analysis system OCA35 (DataPhysics, Germany) equipped with CCD camera was used for this purpose.

The grafting yield (GY) was calculated for each step of the process by the following equation:

GY%= $((W_2-W_1)/W_1)*100$, where $W_1$ refers to the weight of the samples before surface modification and $W_2$ represents weight after the modification process.

Surface topography analyses were performed by AFM (MFP-3D, Asylum Research, USA) to confirm plasma treatment effect on LDPE surface and the resulted structures of grafted SA and immobilized chitosan. Moreover, surface roughness parameter Ra was evaluated using this technique.

Chemical composition was evaluated by FTIR-ATR technique using Spectrometer Frontier (PerkinElmer, USA) equipped with a ZnSe crystal.

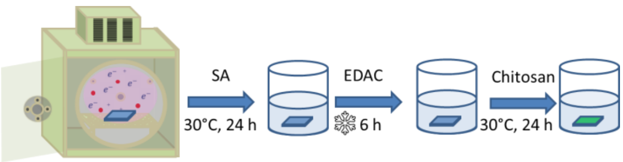



Fig. 1. Scheme of antimicrobial modification of LDPE.

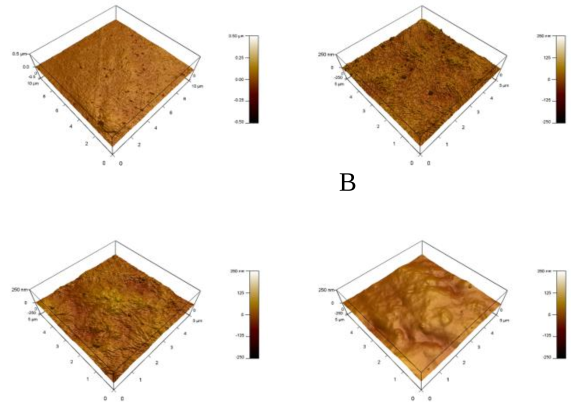
## 3. Results and Discussion

Wettability analyses by contact angle measurements were performed due to optimization of the plasma treatment process for subsequent grafting reactions. Due to the hydrophobicity character of LDPE polymer, contact angles of testing liquids on untreated LDPE achieved relatively high values (95.7° for water, 67.7° for ethylene glycol and 76.5° for formamide (Table 1). Those values were changed dramatically after the plasma treatment process and therefore contact angles were significantly decreased (50.0° for water, 16.6 for ethylene glycol and 11.1 for formamide). The contact angle values slightly increased after LDPE grafting by SA and immobilization by chitosan based on the polarity of used antimicrobial agent. Graft yield analyses confirmed grafting of SA acid on plasma treated LDPE and immobilization of chitosan by increasing weight after these sequences.

Table 1. Wettability of LDPE by process sequence.

| LDPE sample | Θ Water (°) | Θ Ehtylene glycol (°) | Θ Formamide (°) | GY (%) |
|---|---|---|---|---|
| Untreated | 95.7 (±3.0) | 67.7 (±1.2) | 76.5 (±1.8) | - |
| Plasma treated (A) | 50.0 (±1.6) | 16.6 (±1.7) | 11.1 (±1.8) | 0.00 |
| (A)+SA grafted→(B) | 57.1 (±0.8) | 28.6 (±0.8) | 29.2 (±1.1) | 0.14 |
| (B)+chitosan immobilized | 71.5 (±1.2) | 46.9 (±2.9) | 58.4 (±3.5) | 0.20 |

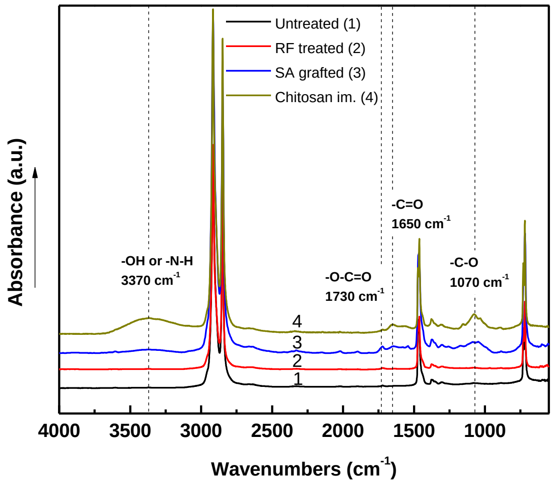
The untreated LDPE sample excelled specific textures in the surface area with Ra=7.7 nm. Plasma treatment of LDPE was responsible for slightly increase of Ra to the value 8.2 nm. SA grafting led to the more increase in Ra parameter achieving value 12.0 nm. The immobilization of chitosan led to smoother structures in compare with the SA grafted layer and Ra achieved value 8.9 nm.



A B C D

Fig. 2. AFM images of LDPE: A - untreated (Ra=7.7 nm), B - plasma treated (Ra=8.2 nm), C - SA grafted (12.0 nm), D - Chitosan immobilized (Ra= 8.9 nm).

The FTIR-ATR measurements proved the presence of functional groups of SA and chitosan on the LDPE samples after modification process. The FTIR-ATR spectrum of untreated LDPE is characterized by presence of vibrations, mainly -CH stretching, bending and rocking (2900-2800, 1500, 730 $cm^{-1}$, respectively) as it contains only hydrocarbon bonds. Plasma generated alkyl radicals on the LDPE are responsible for surface functionalization and covalent bonding between these radicals and new polar functional groups. These groups can be consisted of oxygen containing groups (-OH, -C-O, -C=O, -COO). However, their detection by the FTIR-ATR is quite difficult because of very thin layer (only few nm). Decomposition of plasma created hydroperoxides and grafting of SA on the LDPE surface was responsible for appearing of new absorbance bands in the FTIR-ATR spectrum. These could be associated with polar functional groups, such as -OH, -O-C=O, -C=O or -C-O. Moreover, chitosan immobilization led to the intensity increase of absorbance bands with maximum wavelength at 3370 $cm^{-1}$ ($-NH_2$), 1650 $cm^{-1}$ and 1070 $cm^{-1}$ (-C-O), while intensity of -O-C=O decreased (SA).




## 4. Conclusions

The LDPE surface was modified by plasma assisted grafting of SA and subsequent chitosan immobilization in order to improve its antimicrobial effect. The plasma treatment of LDPE led to the significant increase in the surface wettability as result of functionalization processes. The plasma assisted SA grafting led to the creation only very thin layer such was confirmed from graft yield and AFM analyses. The immobilization of chitosan on grafted SA on the LDPE surface was proven by AFM and FTIR-ATR techniques.

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