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A novel SiO_2/Polyetherimide (PEI) Composite Synthesized by Sol-Gel Route: Characterization and Antibacterial Activity

*Giovanni Dal Poggetto, Marika Fiorentino, Antonio D'angelo, and Michelina Catauro**

Polyetherimide (PEI), an amorphous thermoplastic material, is a promising candidate for wide applications due to its high heat stability and its biocompatibility in human tissues. In the present paper, PEI (4 wt%) is added to SiO_2 inorganic matrix in order to obtain a novel composite biomaterial through sol-gel route. Structural characterization by means of *Fourier Transform Infrared Spectroscopy* (FTIR) confirmed, through hydrogen bond interactions, the presence of both organic and inorganic components in the structure. Concerning the compatibility in the biological systems, a study of antibacterial properties is carried out, analyzing the effect of SiO_2/PEI composite on *Escherichia coli* (gram-negative) and *Enterococcus faecalis* (gram-positive).

1. Introduction

Thermoplastic Polyetherimide (PEI), as a biomaterial, has an increased importance in the medical industry. In fact, its high chemical and thermal resistance allow to employ it for many sterilization methods as autoclaving and chemical treatments.[1–3] The Polyetherimide properties depend on its structure consisting of the aromatic imide ring units, which confer the heat resistance and stiffness, and the ether groups which allow obtaining a more flexible chain improving its processability compared to other poly-imides (PIs) polymers.[4]

Due to its features, by adding this organic polymer to an inorganic matrix it is possible improve mechanical, thermal and anti-corrosive properties, that are useful for medical devices. An attractive route to produce an organic/inorganic composite material is the sol-gel technique. This method is based on hydrolysis and polycondensation reactions of metal alkoxide M(OR)x, where M = Si, Sn, Ti, Zr, Mo, V, W, Ce, Al, and several other.[2] The process leads to the transition from "sol" to "gel." Sol-gel reactions depend on many parameters[5] such as concentration of reactant, solvent used, process temperature, and presence of a catalyst (for instance, nitric acid is able to faster sol-gel synthesis when silicon alkoxides are used as precursors).

G. D. Poggetto
Ecoricerche srl Via Principi
Normanni 36, Capua 81043, Italy
M. Fiorentino, A. D'angelo, M. Catauro
Department of Engineering
University of Campania "Luigi Vanvitelli,"
Via Roma 29, Aversa I-81031, Italy
E-mail: michelina.catauro@unicampania.it

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In a previous work, we synthesized a TiO_2/PEI hybrid via sol-gel route and observed the formation of a biomaterial with a high superficial homogeneity and an excellent bioactivity for both 6 wt% and 12 wt% PEI compositions.[6] In this work, we prepared a novel composite with the addition of PEI at 4 wt% to a silica matrix to evaluate the inorganic/organic structure and its antibacterial properties.

2. Experimental Section

2.1. Synthesis

SiO_2/PEI composite containing 4 wt% of organic polymer was synthetized via sol-gel technique (**Figure 1**). Reagents comprised analytical reagent grade tetraethylortosilicate (TEOS), $Si(OC_2H_5)_4$ (Sigma-Aldrich) as metal alkoxide precursor, ethanol 99.8% (Sigma- Aldrich), HNO_3 (≥ 65%, Sigma-Aldrich) as catalyst and distilled water. Molar ratio used for silicate gel is: EtOH/TEOS = 6.2, TEOS/HNO_3 = 1.7, TEOS/H_2O = 2.

2.2. Characterization

The structural analysis of SiO_2/PEI composite has been studied through the FTIR. The powder of synthesized material was analyzed with a Prestige 21 Shimadzu Spectrophotometer (Tokyo, Japan) recording spectra in the 400–4000 cm^{-1} range with a resolution of 4 cm^{-1} (45 scans). For the analysis, a tablet with 1:100 weight ratio between sample and KBr was made. The FTIR spectra have been processed by IR solution software.

In order to estimate the antibacterial properties of the SiO_2/PEI composite, *Escherichia Coli* (ATCC 25922) and *Enterococcus faecalis* (ATCC 29212) were growth in the absence and presence of the synthetized biomaterial. Samples used for analysis were grounded, obtaining the powders that were radiated by UV light for 1 h in order to sterilized them.

The bacterial suspension of 10^5 CFU mL^{-1} was obtained by diluting the strains in distilled sterilized water. After plating *E.coli* in TBX Medium (Tryptone Bile X-Gluc) (Liofilchem, Italy) and *E. faecalis* in Slanetz Bartley agar base (Liofilchem, Italy), a proper amount of composite material was placed in the middle of Petri Plate. *E.coli* and *E. faecalis* plates were incubated at 44°C for 24 h and 36°C for 48 h, respectively. The diameter of inhibition halo was calculated by four measures for each sample, determining also the mean Standard Deviation.[7]

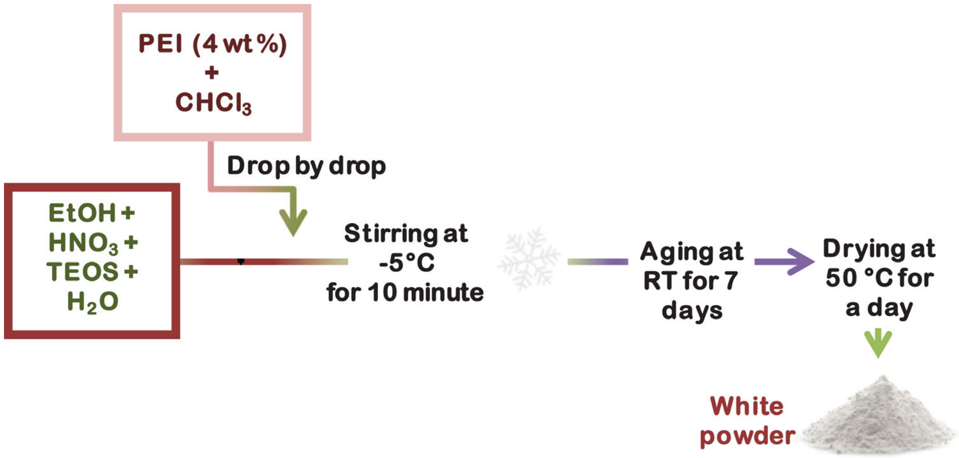

Figure 1. Flow-chart of the SiO_2/PEI composite sol-gel synthesis.

3. Results and Discussion

3.1. FTIR Analysis

Figure 2 shows the infrared spectra of the SiO_2 gel (Figure 2A), the SiO_2/PEI gel (Figure 2B), and PEI (**Figure 3**C). The SiO_2 spectrum (Figure 2A) is characterized by a strong band at 1080 cm^{-1} (with a shoulder at 1200 cm^{-1}), together with bands at 800 and 460 cm^{-1} ascribed to the symmetric and asymmetric stretching and bending modes of SiO_4 tetrahedra, respectively.[8] The bands at 3600-3200 and 1641 cm^{-1} are attributed to the stretching and bending of the water,[9] and the sharp N–O stretching band of residual nitrate anions at 1382 cm^{-1} caused by the presence of residual HNO_3, which was used as a catalyst in the synthesis procedure. In Figures 2B, PEI spectrum, the bands at 1778 and 1726 cm^{-1} are attributed to the asymmetric and symmetric C = O stretching vibration (imide band I). The bands at 1356 and 744 cm^{-1} correspond to the characteristic C-N stretching and bending vibrations (imide band II), while the peak at 2968 cm^{-1} is assigned to CH_3 groups present in PEI backbone. In addition, the peak at 1236 cm^{-1} is due to the presence of the ether group C-O-C.[10,11] FTIR measurements prove that the structure of the composite network was realized by hydrogen bonds between the inorganic matrix and the carboxylic group in the repeating units of the polyetherimide (Figure 2C). In fact, in Figure 2C, the presence of the peaks at 3600-3200, 1637, 1774, and 1726 cm^{-1} clearly show the interaction described between the Si-OH and carboxylic group mediated by stretching and bending of water O-H.

3.2. Antibacterial activity

In order to solve the hospital-acquired infection problems, the production of medical devices with antibacterial activity has became prominent.[9,12,13] For this reason, we evaluated the antibacterial properties of PEI/SiO_2 composite through the study of the inhibition halos of two pathogenic strains: *E. coli* and *E. faecalis*. A comparison of the composite material effects respect to organic polymer and SiO_2 samples was reported in Figures 3 and 4.

It is possible to notice the visible inhibition halos for both SiO_2 and PEI/SiO_2 composite material for *E.coli* while the organic

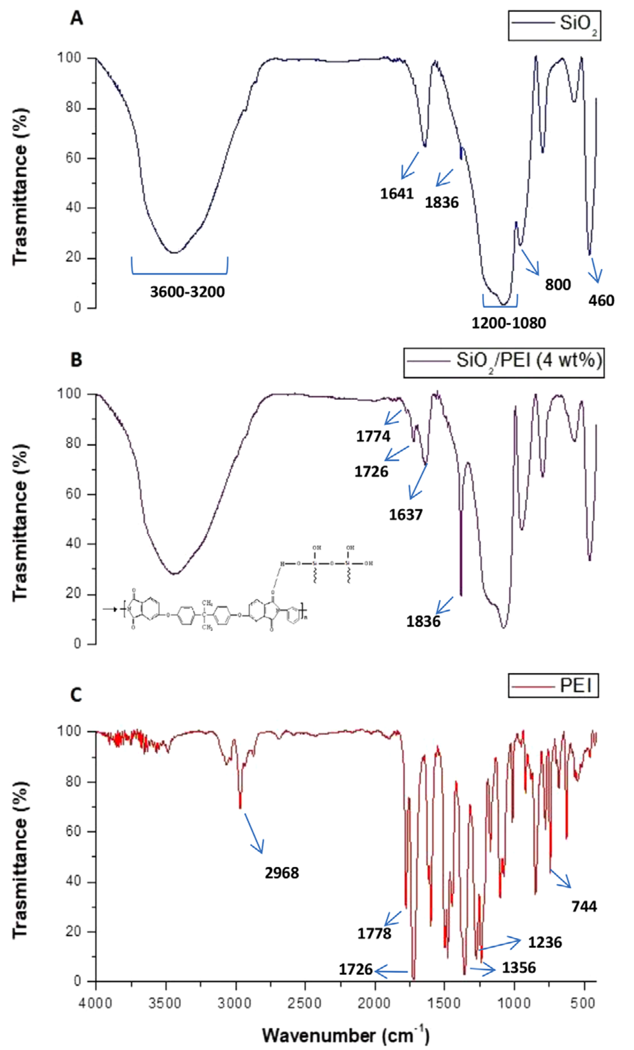

Figure 2. FTIR spectra of A) pure SiO_2, B) SiO_2/PEI 4 wt% composite (with the hydrogen interaction), and C) pure PEI.

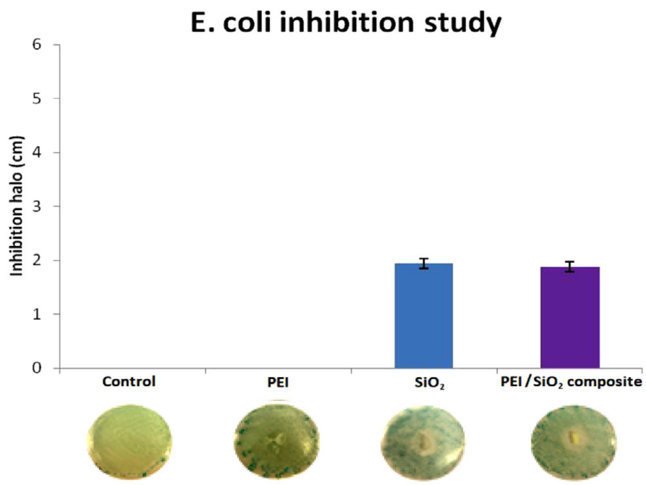

Figure 3. *E. coli* inhibition halo study for PEI, SiO_2, and PEI/SiO_2 composite.

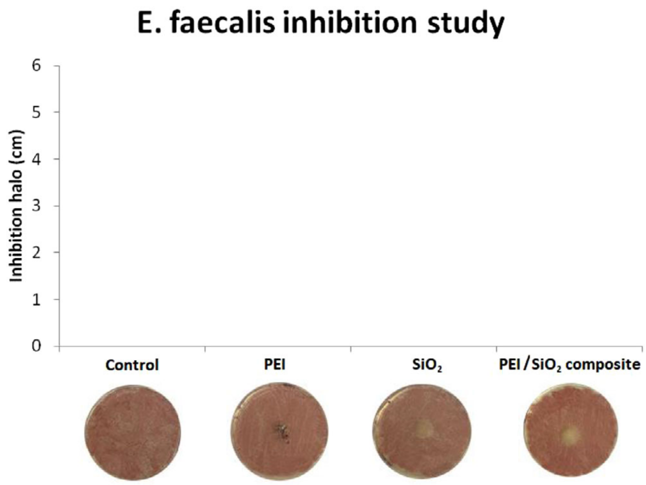

Figure 4. *E. faecalis* inhibition halo study for PEI, SiO_2, and PEI/SiO_2 composite.

polymer seems to be not toxic for this strain (Figure 3). The study of inhibition halos for *E. faecalis* (**Figure 4**) reveals that all the materials do not inhibit the bacterium growth. The results suggest that the mean antibacterial activity of the composite depends on the presence of silica for only the *E.coli* strain.

4. Conclusion

In this work, it was demonstrated that a novel SiO_2/PEI (4 wt%) composite was synthesized by Sol-gel route. Moreover, the structural analysis, by the FTIR spectrum of this biomaterial, proved the interaction between the inorganic matrix and the organic polymer. In the end antibacterial activity confirmed that the novel composite was able to inhibit *E. coli* growth, principally due to the silica bioactivity, while no inhibition halos were present on the Petri plate of *E. faecalis* growth. Therefore, the results show that the materials do not have toxic effects against gram-positive and gram-negative bacterial strains.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

antibacterial properties., composite, FTIR, polyetherimide, sol-gel

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