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Controlled Modification of the Structure of Polymer Surfaces by Chemically Grafting Inorganic Species

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Many chemical and physical methods, such as plasma, e-beam, sputtering, CVD and others, have been used to modify the structure of polymer surfaces by depositing thin inorganic films. Most of these techniques are based upon the use of high energy sources that ultimately can damage either chemically or physically polymer surfaces. Moreover, these methods are usually not versatile enough to allow the design of structurally and chemically tailored surfaces through the control of the distribution of chemical functionalities throughout the surface. In this work, inorganic species were introduced onto polymer substrates in a controlled manner by performing a sequence of chemical reactions at the surface. Sulfonation followed by silanization reactions were used to graft alkoxysilane species at the surface of poly(aryl sulfones). The heterogeneous chemical modification of poly(aryl sulfones) was monitored by FTIR-ATR (Attenuated Total Reflection - FTIR). Model compounds were used to study the chemical reactions occurring during the grafting procedure. The results showed that the developed procedure can allow a controlled introduction of inorganic species onto polymer surfaces. Furthermore, in order to prove that this procedure enables the deposition of specific chemical functionalities onto polymer surfaces that can be used to create chemically and structurally tailored surfaces, silicate films were deposited on previously silanated PAS bioactive glass composites. *In vitro* tests showed that the surface modified composite can enhance the rates of hydroxy-carbonate-apatite precipitation.

Keywords: *silane, heterogeneous modification, inorganic films, surface engineering*

1. Introduction

Deposition of inorganic films on polymer substrates is a crucial step in the production and development of many devices for optoelectronical, mechanical and biomedical applications[1]. Some examples of important processes that involve the deposition of inorganic films on polymers are: (a) metalization of polymers to produce electrical connections; (b) deposition of ceramic films to enhance hardness of polymers and wear resistance; (c) deposition of magnetic films to enhance magnetic properties of polymer substrates; among others.

Methods of deposition of inorganic films, usually involve chemical vapor (CVD), thermal spray, sol-gel or sputtering processes. The performance of the films deposited by these processes is usually determined by the level of adhesion between film and substrate. Polymers and ceramic or metallic materials have often very distinct surface energies that ends up leading to poor wetting between the surfaces and low levels of interfacial strength. Moreover, some of the processes mentioned above, such as thermal spray and sputtering, require high levels of energy to perform the deposition. These high-energy processes can damage polymer surfaces and are also not flexible enough to allow the manipulation of the chemical and physical structure of the films.

On the other hand, surface modification of polymers has been explored in depth for the last fifteen years, motivated mainly by biomedical needs[2]. Some of the most important polymers are hydrophobic in nature, due to the absence of polar groups. However, hydrophilicity is necessary in many applications where the interactions between polymer and a polar media should be maximized. Thus, surface modification of polymers is commonly employed to increase hydro-

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philicity of polymer surfaces. Surface modification of polymers is also used in many other applications, such as to improve chemical resistance (fluoridization of polyethylene), enhance wear resistance and others.

The goal of this work is to modify the structure of polymer surfaces by chemically attaching special functionalities onto it. These novel surfaces will then be able to support the growth of a variety of structurally tailored films, such as inorganic films.

1.1. Growth of silicate films on polymer substrates as a method to enhance bioactivity of polymer composites

In order to explore the proposed process involving the chemical alteration of polymer surfaces for a specific application, the hypothesis that surfaces of bioactive composites can be designed to enhance the bioactivity of the composites will also be tested in this work.

The "bioactivity" of some particular glasses has been defined as their ability to bond to bone[3]. It was also demonstrated that the bioactivity of those glasses are related to surface phenomena that occur when these materials are introduced into body environments, such as the evolution of ions (calcium, phosphates and silicates) from the glasses and capability of inducing the precipitation of hydroxy-carbonate-apatite (HCA). More recently[4], polymer composites reinforced by bioactive glasses have been proposed as a novel class of bioactive materials. It was demonstrated that this type of composite having 40% in volume of the bioactive phase has an ionic evolution coming from the composite that can reach levels similar to bulk bioactive glasses. However, the precipitation of HCA occurs only on the surface of exposed particles of the composite (instead of the whole surface), when these materials are tested *in vitro* in a buffer solution (37 °C) at pH 7.2 for 20 h. Even after 7 days under the same test conditions, only the surface of the particles remains covered with HCA It was hypothesized that this behavior is due to the fact that the percent of the surface covered by the polymer does not have the characteristics that can lead to heterogeneous precipitation of HCA (such as silanol groups, high surface area and negative surface charge).

In this work, the incorporation of calcium-silicate species on the polymeric fraction of the surface of a bioactive composite will be used as a way to enhance the rates of HCA precipitation.

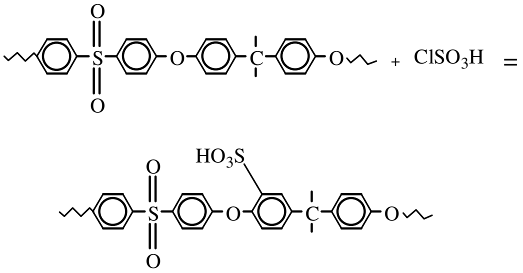
2. Experimental Procedure

2.1. Heterogeneous modification of poly(aryl sulfones) (PAS)

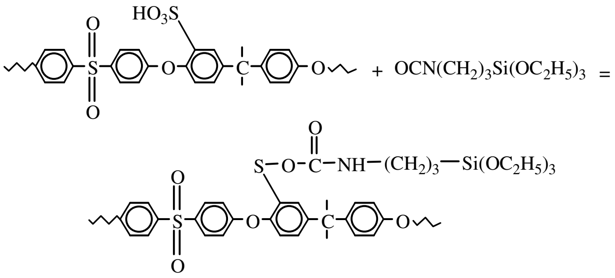
Poly(aryl sulfones) are commonly used in many applications including medical and structural ones due to basically their high mechanical properties and great stability at body environment. Chemical modification of poly(aryl sulfones) (PAS) has been studied by several authors[5,6].

Poly(aryl sulfones) (Udel®) samples were prepared by compression molding pellets at 200 °C. Samples were cut using a diamond saw and the surfaces were cleaned with methanol followed by drying at 90 °C.

Heterogeneous sulfonation of poly(aryl sulfones) was performed by reacting the samples with chlorosulfonic acid in 1 vol.% carbon tetrachloride solution for 15 min. Many variables of the process can be used to control the thickness of the modified layer, such as time and temperature of reaction, concentration of chlorosulfonic acid in solution and type of solution that can swell the sample in different extents.



Surface Silanation of Poly(aryl sulfones). Surface sulfonated poly(aryl sulfones) samples were treated with a silane agent (1 vol.%) in ethanol for 15 min and washed extensively with ethanol after the reaction. Isocyanatepropyl triethoxysilane (ICS) was used as the active agent to introduce alkoxysilane groups on the polymer.



Growth of Silicate Species on Poly(aryl sulfones)-Bioactive Glass Composites. The methodology applied for attaching alkoxysilane groups on pure poly(aryl sulfones) samples was extended to poly(aryl sulfones) composites having 40 vol.% of bioactive glass particulate. Poly(aryl sulfones) composites were prepared by dissolving the polymer in a suitable solvent (chloroform) and adding bioactive glass particles (size: 125-106 mm) into the solution. The solvent was then removed by adding a non-solvent (ethanol) to the solution, resulting in the production of homogeneous polymer-reinforcing agent blends. The blends were subsequently hot-pressed at 220 °C. The obtained composites had their surfaces polished with sand paper (#1200) and cleaned with methanol.

Sulfonation and silanation of the fraction of the composite surface covered with poly(aryl sulfones) (60%) were performed as previously described for pure polymer samples. Surface silanated composites were then dipped into a silica sol containing calcium nitrate for 15 min followed by washing the samples with ethanol. The silica sol was prepared by introducing tetramethoxy silane (TMOS) into a water/ethanol solution (pH = 1.5, regulated by HCl and molar ratios between water/ethanol = 0.5 and water/TMOS = 20). The molar ratio between TMOS and $Ca(NO_3)_2$ used was calculated to yield a 60/40 ratio between silica and calcium oxide.

Infrared spectroscopy (FTIR) in ATR mode (Attenuated Total Reflection) mode was used to monitor changes on the surface of the samples. FTIR spectroscopy was performed using a Nicolet 20SXB spectrometer with a triglyceride sulfate detector. Samples were pressed against a KRS-5 crystal and FTIR spectra was collected with a 4 cm^{-1} resolution. ATR can usually give information of surface thicknesses from 0.5 to 1 µm. A DRIFT (DRIFT: Diffuse Reflection FT-IR Spectroscopy) accessory from Spectra Tech, Inc. was used to perform diffuse reflectance.

Molecular weight analysis was accomplished by using Gel Permeation Chromatography (GPC) from Waters Corporation. A solution of polymer in tetrahydrofuran (THF) was passed through chromatographic columns filled with polystyrene beads. The volume of solution (retention volume) was monitored as a function of time and the concentration of solution that comes out of the columns was analyzed by measuring its refractive index and comparing it to the pure solvent. The raw data (retention volume *vs.* time) was converted to a molecular weight basis by making use of a calibration curve produced by running monodisperse polystyrene samples through GPC columns. The final molecular weight distribution was then reported in terms of polystyrene molecular weight.

3. Results and Discussion

3.1. Surface silanation of poly(aryl sulfones)

The sulfonation process of poly(aryl sulfones) (PAS) was studied using infrared spectroscopy. FTIR/ATR spectra of PAS's samples before (Fig. 1-a) and after (Fig. 1-b) the sulfonation reaction are depicted in Fig. 1. The hydroxy bands at frequencies between 3200 and 3400 cm^{-1} and the presence of the sulfonate peak around 1028 cm^{-1} in the ATR spectrum of a surface sulfonated poly(aryl sulfone) are clear indications that the sulfonation reaction had indeed occurred, with the incorporation of sulfonic acid groups onto the backbone structure of PAS.

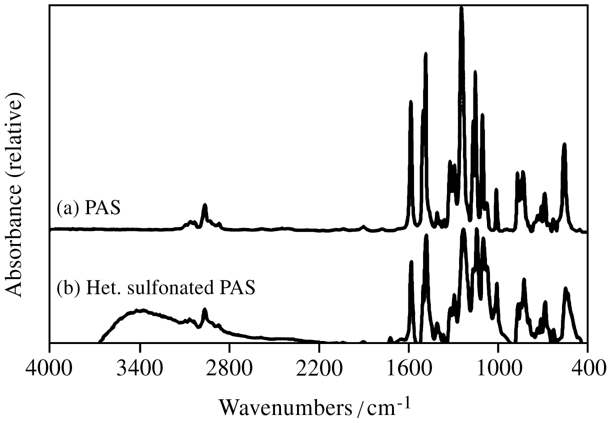


Figure 1. FTIR-ATR spectra of poly(aryl sulfones) and heterogeneous sulfonated poly(aryl sulfones).

In Fig. 2-a, the FTIR/ATR spectrum of a surface sulfonated poly(aryl sulfones) reacted with isocyanatepropyl triethoxysilane is exhibited. The result of a spectral subtraction between the spectra of silanated and non-silanated PAS is also revealed in this figure (Fig. 2-b). It can be seen that the subtracted spectrum is very similar to the spectrum of pure isocyanatepropyl triethoxysilane (Fig. 2-c), with the exception of the isocyanate peak at 2300 cm^{-1}. Siloxane peaks are seen at frequencies around 1100-1000 cm^{-1}. It was demonstrated therefore that surface silanation of poly(aryl sulfones) can be accomplished by treating surface sulfonated poly(aryl sulfones) with specific silanes, such as ICS. In the case of isocyanatepropyl triethoxysilane, the results indicate that the isocyanate group was consumed in a reaction with sulfonic acid groups.

A simulated reaction using model compounds was performed to prove the hypothesis that isocyanate groups can react with sulfonic acid groups. Instead of sulfonated poly(aryl sulfones), methane sulfonic acid was treated with isocyanatepropyl triethoxysilane in a 1/1 molar ratio and the reaction was monitored by FTIR in transmission mode. In Fig. 3-a, the "artificial" FTIR spectrum of a 1/1 molar mixture of isocyanatepropyl triethoxysilane and methane sulfonic acid, obtained by the summation of the spectra of pure compounds, is exhibited. The FTIR spectrum of the

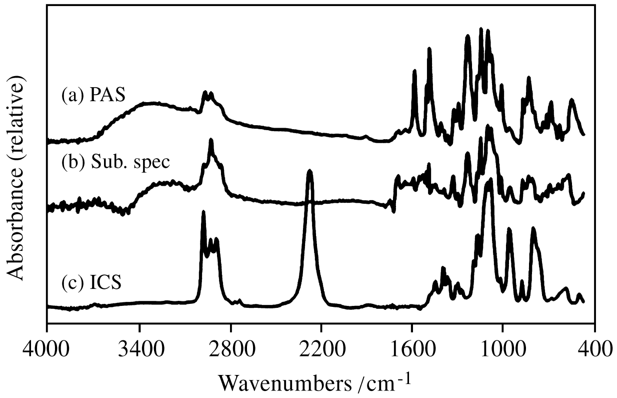


Figure 2. FTIR-ATR spectra of heterogeneous silanated poly(aryl sulfones).

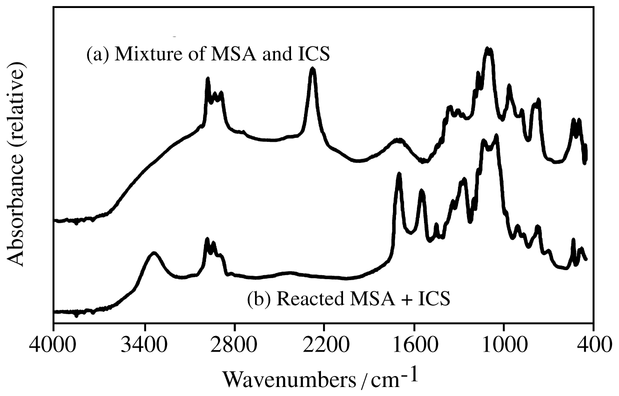


Figure 3. FTIR spectra of a model reaction involving methane sulfonic acid and isocyanatepropyl triethoxysilane.

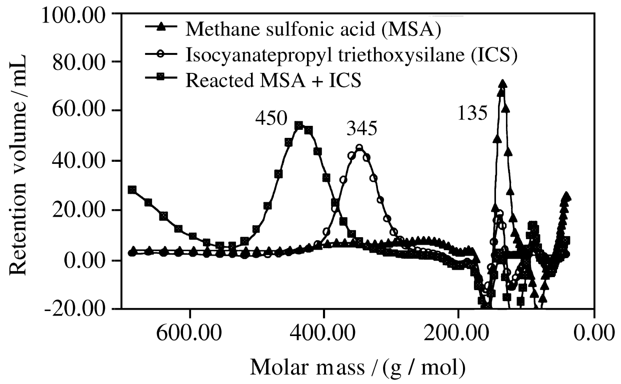


Figure 4. Molar mass analysis (GPC) of a model reaction involving methane sulfonic acid and isocyanatepropyl triethoxysilane.

reaction products is illustrated in Fig. 3-b. In this spectrum, the elimination of the isocyanate peak (2300 cm^{-1}) with the proportional growth of amide peaks (3300, 1650 and 1500 cm^{-1}) is observed. Moreover, the large absorption band between 3400 and 2800 cm^{-1}, due to the sulfonic acid, is not present in the spectrum of the products, indicating that the chemical bond must have been formed by the reaction between sulfonic acid and isocyanate functionalities. A diisocyanate butane was also used instead of the isocyanatepropyl triethoxysilane and the results were very similar, meaning that the nature of the alkoxysilane groups do not affect the overall reaction.

The model reaction was studied by gel permeation chromatography (GPC) (Fig. 4). Methane sulfonic acid (MW = 96.1 g/mol), isocyanatepropyl triethoxysilane (MW = 247 g/mol) and the product of 1/1 mol reaction were dissolved in THF (0.5%) and submitted to the GPC analysis. The analysis was calibrated using monodisperse polystyrene, and therefore the results expressed in Fig. 4 are relative to polystyrene. Due to the calibration procedure, the values of molar mass measured were shifted to higher values. However, it is still possible to note that the molar mass of the product of the model reaction was close to the sum of the molar mass of the reactants. Therefore, it was demonstrated that isocyanate functionality can react with sulfonic acid groups.

3.2. Poly(aryl sulfones)-bioactive glass composites with silicated surfaces

The methodology applied for introducing alkoxysilane species on pure PAS samples was extended to PAS composites having 40 vol.% of bioactive glass particulate. Silicate groups were attached to a silanated surface by dipping the samples into a silica sol with $Ca(NO_3)_2$. This silicate film can have ideal characteristics for enhancing the deposition of HCA in body fluids, *i.e.* high surface area, negative surface charge and high silanol concentration. Furthermore, the presence of calcium ions can also favor a local supersaturation in ions needed for the HCA precipitation.

FTIR spectra (diffuse reflectance mode) of PAS composites before (Fig. 5-a) and after (Fig. 5-b) the growth of the silicate film are shown in Fig. 5. Broad siloxane peaks (1100-1000 cm^{-1}) can be observed in the spectrum of the silicated surface. Moreover, polymer peaks are not seen in the spectrum of the silicated composite, indicating the presence of a thick silicate film covering the majority of the composite surface. Sharp peaks between 700 and 640 cm^{-1} may be related to calcium hydrates. It was then demonstrated the success of the procedure developed to grow silicate species on the surface of silanated PAS composites. In this case, the presence of alkoxy groups at the silanated surface allows the formation of siloxane bonds between these groups and silanol groups produced from the hydrolysis of the silica sol precursor (TMOS).

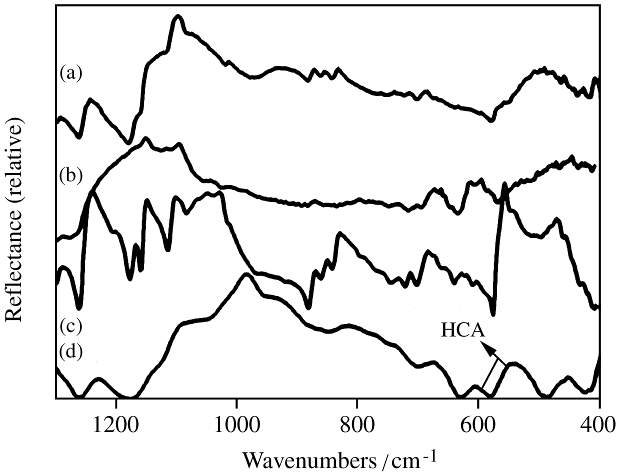


Figure 5. FTIR (diffuse reflectance) spectra of poly(aryl sulfone)-40 vol.% bioactive glass composites: (a) original composite; (b) composite with silicated surfaces; (c) original composite after *in vitro* test; (d) surface modified composite after *in vitro* test.

3.3. *In vitro test on silicated pas-bioactive glass composites*

Surface silicated PAS-40 vol.% bioactive glass composites were submitted to a 20 h *in vitro* test in a buffered solution at pH 7.2 and 37 °C. The FTIR (diffuse reflectance) spectra of the silicated composite (Fig. 5-d) and non-treated composite (Fig. 5-c) after 20 h *in vitro* are also revealed in Fig. 5. The peaks due to the deposition of a thick HCA layer covering the whole composite surface are observed in the spectrum of the surface modified composite (600 and 550 cm^{-1}), while no HCA peaks are evident in the spectrum of the original PAS composite. As commented before, deposition of HCA occurs only on the exposed bioactive particles in conventional PAS composites submitted to a *in vitro* test in a buffered solution for 20 h. Thus, peaks due to the HCA overlap those due to the polymer matrix and the presence of HCA peaks can only be seen after a spectral subtraction or by using FTIR microscopy[4]. Otherwise, the presence of HCA peaks and absence of both silicate and polymer peaks in the spectrum of the treated composite (Fig. 5-d) indicate that the deposition of the HCA had occurred throughout the composite surface.

Since an untreated PAS 40 vol.% bioactive glass composite is not able to induce the precipitation of a HCA layer covering the whole surface of the sample after 20 h, the growth of silicate species on the PAS fraction of the composite surface shifted the onset of HCA precipitation (on the whole composite surface) to shorter times.

4. Conclusion

In this work, the structure of the surface of polymers was chemically modified by introducing new alkoxysilane groups via a series of sequential reactions. The processed reactions involved first the introduction of very reactive functionalities (sulfonic acid) on the surface of originally inert polymers. These chemically active surfaces were then further modified by the reaction with alkoxysilane species. This novel polymer with silanated surfaces has ideal characteristics for allowing the growth of inorganic films, such as silicate species.

Structural features of the modified surfaces (thickness of the modified layer, for example) can be easily controlled by manipulating the variables of the process, such as the concentration of reactants and temperature of the reaction. The developed process has also high levels of versatility in creating structurally tailored surfaces, where chemical functionalities can be incorporated onto surfaces to more promptly activate them towards interfacial processes, such as the growth of inorganic films.

In order to emphasize the capability of the process to specifically design the structure of polymer surfaces to act in well defined applications, silicate species were grown from the partial surface of bioactive particulate composites covered by the polymer.

It was demonstrated that bioactive composites composed of poly(aryl sulfones)-40 vol.% bioactive glass having highly silicated surfaces were able to develop a thick and uniform HCA layer throughout the composite surface within 20 h, when tested in a buffered solution. Otherwise, PAS composites with “conventional surfaces” did not have their surfaces fully covered with HCA after 20 h under the same test conditions.

5. Acknowledgment

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