Modulation of the hydrophilic character and influence on the biocompatibility of polyurethane-siloxane based hybrids

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Organic-inorganic hybrid materials are known for their outstanding chemical and physical properties. Although some studies have been published regarding the use of hybrids for biomedical applications, relationship between hydrophilic character and biodegradation, bioactivity and biocompatibility has not been studied yet. The sol-gel method has been chosen for the manufacturing of siloxane-polyurethane hybrids for the exceptional potential of the method to obtain nanostructured materials. The effect of the amount of the urethane oligomer (OPU) on the structure, hydrophilic character, degradability, bioactivity and cytotoxicity was investigated. Gelling time of these hybrids increases linearly with the decrease on the Siloxane/OPU ratio up to an 80/20 value. Hydrophilic character of the hybrids can be modulated and affects dramatically the degradation rate of the specimens. A hybrid with a 50/50 Siloxane/OPU ratio displayed an appropriate degradation rate, bioactivity and lack of cell toxicity that makes this material a candidate for further studies for applications in bone regeneration.

Keywords: Sol-gel process; Biomedical applications; Hybrid Materials; Bioactivity; Polyurethane.

Modulación del carácter hidrofílico e influencia sobre la biocompatibilidad de híbridos base poliuretano-siloxano

Los materiales híbridos Orgánico-Inorgánico son conocidos por sus excepcionales propiedades químicas y físicas. Aunque se han publicado algunos estudios respecto al uso de híbridos para aplicaciones biomédicas, aun faltan estudios que determinen la relación que existe entre el carácter hidrofílico de estos materiales y las propiedades que les permiten ser utilizados como biomateriales: degradación, bioactividad y biocompatibilidad. El método sol-gel se ha escogido para la fabricación de híbridos debido a la posibilidad de obtener materiales nanoestructurados que comprenden un componente orgánico y un inorgánico. Se investigó el efecto de la cantidad del oligómero de uretano (OPU) sobre la estructura, el carácter hidrofílico, la degradabilidad, la bioactividad y la citotoxicidad. El tiempo de gelificación de estos híbridos incrementa linealmente con la disminución en la relación Siloxano/OPU hasta un valor de 80/20. El carácter hidrofílico de los híbridos se puede modular y afectar considerablemente la velocidad de degradación de las muestras. Un híbrido con una relación 50/50 Siloxane/OPU muestra una velocidad de degradación, una bioactividad y falta de toxicidad que hacen a este material un candidato para futuros estudios para aplicaciones en regeneración ósea.

Palabras claves: Proceso sol-gel; Aplicaciones biomédicas; Materiales Híbridos; Bioactividad; Poliuretano

1. INTRODUCTION

Organic-inorganic hybrid materials are known for their outstanding chemical and physical properties. The ionic-covalent bonds of these compounds provide them with unique properties capable of surpassing those of the inorganic and organic materials themselves [1-3]. Their extraordinary physical and chemical properties are due to good degree of homogeneity and purity at a molecular level that open the possibility of tailoring properties for applications in optics, electronics, medicine, pharmacology and biotechnology [4-7]. Although some studies have been published regarding the use of hybrids for biomedical applications, studies that relate hydrophilic character with degradation properties, bioactivity and biocompatibility are still lacking.

The principal hybrid materials used are those composed of polydimethylsiloxane (PDMS), tetraethoxysilane (TEOS)

and a load of calcium ions (Ca^{2+}) in order to combine the best mechanical properties with bioactivity [8, 9]. Also, the use of other organic compounds such as polytetramethylene oxide (PTMO), polyethylene oxide (PEO) and poly(ϵ -caprolactone) [10-12] combined with tetraisopropyltitanate (TiTP) as the inorganic component have been tested [13-16]. Apparently the incorporation of calcium ions is necessary to obtain an apatite-forming ability on the surfaces and hence bioactivity. The mechanical properties and the changes in element concentrations of SBF during the soaking of the samples have been studied, but studies that relate bioactivity with the degradation of the materials assayed are lacking.

Polyurethane-silica hybrid materials have been studied recently in applications such as membranes [17], abrasion-resistant layers with high optical transparency [18] or shape memory effect [19]. However they have not been tested as

bioactive materials. The only exception is as support for bioactive glass-ceramics [20, 21].

The development of polyurethanes-siloxane hybrids materials and their potential application in the field of calcified tissues repairing is proposed in this work. The degradation rate in relation to the bioactivity of the materials and the cell viability is examined.

2. MATERIALS AND METHODS

2.1 Materials

Materials used as precursor of the hybrids were: A commercial oligomeric-polyurethane diol (OPU, Mn 320, 88% purity, OH number = 350 mg, KOH per g), tetraethoxysilane (TEOS, 98% purity), silanol terminated polydimethylsiloxane (PDMS, 550 g·mol⁻¹), and 2-Propanol (IPA, 99% purity) were supplied by Sigma-Aldrich. Hydrochloric acid (32% purity) was purchased from J. T. Baker and deionized water from the local market. All chemicals were used without further purification.

2.2 Synthesis of hybrid materials

The hybrid materials were prepared keeping a 70/30 inorganic/organic mass ratio. Several PDMS/OPU ratios were used from 30/0 to 0/30. The synthesis was performed by dropping a TEOS solution on IPA on a PDMS or/and OPU solution (on IPA). After homogenization of the mixture a water/HCl solution was dropwise added. The mixture was, then, stirred for 60 minutes at room temperature before being poured into a polypropylene bottle and sealed hermetically for further gelation. The gels were dried at room temperature for two months to avoid decomposition of the urethane oligomer.

2.3 Materials characterization

The gelling time was determined by observing that the sol does not flow passing to gel. The structural groups in the hybrid materials before and after soaking in Simulated Body Fluid (SBF) were analyzed by Fourier transformed infrared spectroscopy (FTIR) with a Nicolet Instruments model Nexus 470 spectrometer using the KBr pellet method. The FTIR spectra were recorded in the range of 4000-400 cm⁻¹ using a 2 cm⁻¹ resolution and 16 scans per measurement. X-ray diffraction patterns were taken before and after soaking in SBF, and were obtained in a Siemens D5000 diffractometer, using CuK_α radiation. The patterns were registered in the 2θ range 1 - 30° with a rate of 0.02 °/min. Glazing angle mode was used for the examination of the bioactivity using an incident angle of 0.5 between 2θ 15 and 40 with a step of 0.02 A ° and 10 second per step. The morphology of materials before and after soaking in SBF, was observed by SEM using a JEOL 6300 CFX scanning electron microscope at 15 KV and 25 mA. Samples were covered with a layer of Au/Pd to make them conductive. Thermal analysis were carried out in a SETARAM instrument, the samples were heated from 40 °C to 850 °C at 5 °C per min under nitrogen atmosphere. Differential scanning calorimetry analysis was carried out in a Perkin-Elmer DSC-7 instrument, the samples were heated

from -60 °C up to 160 °C using a scanning rate of 10 °C per min under nitrogen purge.

The degradability of samples was evaluated measuring the pH change of a phosphate buffer solution at 37°C, and the change of weight of the samples at certain time intervals (1, 3, 4 and 28 days) after washed with abundant distilled water.

Bioactivity of materials was tested by soaking the specimens in simulated body fluid (SBF) as proposed by Kokubo et al. [22] for 1, 3, and 7 days at 37.5 °C. The materials were analyzed by XRD in glazing angle mode, FTIR and SEM after soaking in SBF.

The biological response of the materials was tested with a primary cell culture of Human Osteoblasts (HOB) of the European Collection of Cell Culture (ECACC). The culture medium was Dulbecco's modified Eagle's medium enriched with 4500 mg/ml of glucose (DMEM, Sigma) supplemented with 10% foetal bovine serum, 200 mM L-glutamine, 100 units/ml penicillin and 100 mg/ml streptomycin, modified with 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) for human fibroblasts and supplemented with 110 mg/ml sodium pyruvate for glioblastoma line. Toxicity of extracts eluted from hybrid materials was determined with the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay according to [23]. Thermanox® (TMX) control disc and discs coated of hybrid materials were placed in 5 mL of modified eagle's medium (MEM), fetal calf serum-free (FSC), supplemented with esterase (15 units/ml). They were put on a roller mixer at 37 °C and the medium was removed at different time periods (1, 2 and 7 days) and replaced with other 5 mL of fresh medium. Analysis of variance (ANOVA) of the results was performed with respect to TMX at a significance level $\alpha < 0.05$.

Fig. 1. Preparation scheme of hybrid materials by sol-gel process.

3. RESULTS AND DISCUSSION

The flow chart used for the synthesis of the intended hybrids materials is shown in Figure 1. Gelling time depends on the ratio siloxane/OPU as showed in figure 2. The gelling time is greater, increasing the amount of OPU. It goes from 8 hours for a OPU free reaction up to 18 hours for a 80/20 ratio with a 0.84 increasing rate.

OPU may act as a chelating agent that interfere the alcoxide hydrolysis-condensation reaction, thus retarding the gelling process [2, 24] as is displayed in figure 3. A competition between the OH terminated OPU and the polycondensation reaction of silanol may explain this phenomenon. The reaction terminates forming the hybrids as reported previously by Guglielmi et al. [24]. Another explanation is that the OPU form hydrogen bonds with the alcoxide and slows the hydrolysis and subsequent condensation, when the TEOS and PDMS react to each other, the hydrogen bonds are broken and the OPU is trapped in the clusters of siloxane.

All prepared gels turn up to be monolithic. No phase segregation could be observed. The starting compositions and sample codes of the obtained materials are given on Table 1. OPU free specimens are opaque and became translucent when they contain OPU. Translucency is accentuated for larger amounts of OPU. SEM photographs are shown on figure 4.

3.1 Structure of the hybrids

Figure 5 shows the IR spectra registered in transmission mode for the obtained samples. FT-IR spectrum of TP1 sample shows a wide band centered at around 3460 cm⁻¹ due to the OH vibration contained in Si-OH groups as well as in water. There are two absorption bands located at 2960 and 2905 cm⁻¹ attributed to the ν_a and ν_s of C-H in the -CH₃ group of PDMS, respectively. [25, 26]. The absorption bands due to ν_a and ν_s of Si-O in Si-O-Si bonding of inorganic network appears as a shoulder at 1190 cm⁻¹ and as an intense

Fig. 2. Gelling time as function of amount of OPU.

Fig. 3. Scheme of chelation of TEOS.

TABLE 1. CHEMICAL COMPOSITION USED FOR PREPARED HYBRID MATERIALS

Samples	Weight composition (wt %)			Molar ratio		
	TEOS	PDMS	OPU	H ₂ O/TEOS	HCl/TEOS	iPrOH/TEOS
TP1		30	0			
TPP1		25	5			
TPP2		20	10			
TPP3	70	15	15	3	0.3	4.5
TPP4		10	20			
TPP5		5	25			
TP2		0	30			

wide band at 1080 cm^{-1} , respectively. At around 1040 cm^{-1} appears a shoulder assigned to PDMS and the intense sharp band at 805 cm^{-1} is assigned to ν_s in SiO_4 and ν_s of Si-C in PDMS. The effective incorporation of PDMS (organic part) into the inorganic network can be seen at 1263 cm^{-1} which corresponds to the deforming band of C-H and Si-CH₃ bonds. The band located at 850 cm^{-1} is attributed to the copolymerization reaction between TEOS and PDMS in D-Q units ($-\text{O}-\text{Si}-(\text{CH}_3)_2-\text{O}-\text{Si}-(\text{O}-)_3$) [27]. At lower frequencies arises a shoulder located at 565 cm^{-1} assigned to the structural defects in silica glasses and a slight band at 440 cm^{-1} indicating the deformed vibration of O-Si bond in O-Si-O network [28].

The same bands plus bands due to carboxyl group ($-\text{C}=\text{O}$) and $-\text{NH}-$ from polyurethane, at 1700 cm^{-1} and 1540 cm^{-1} , respectively, can be observed for the spectra of samples TPP1-TPP5. The effect of PDMS/OPU mass ratio can be noted in the greater relative intensity of $-\text{C}=\text{O}$ and $-\text{NH}-$ bands for greater amounts of OPU. TPP3-TPP5 also shows a new band at 950 cm^{-1} which is stronger for greater OPU content. This band may be attributed to the Si-OH group indicating a greater hydrophilic character. For a greater OPU content, the PDMS content is lower, thus the quantity of methyl groups (hydrophobic) in the surface decreases allowing the hydroxylation of the inorganic component [29, 30].

Fig. 4. SEM micrographs of hybrid materials.

Fig. 5. FTIR spectra of hybrid materials.

Last, the spectrum of TP2 sample shows only the bands from the inorganic network described above, and the bands proceeding from the OPU (1700 and 1540 cm^{-1}). Thus, FTIR spectroscopy confirms that there is not bonding between the polyurethane and the siloxane matrix.

X-Ray Diffraction patterns are shown in Figure 6. All the prepared hybrids are amorphous as shown by the broad maxima observed for all the compositions. TP1-TPP4 display a maximum at $2\theta\ 6^\circ$, that shifts to greater d-spacing when the OPU content increases up to $2\theta\ 2.5^\circ$ for TP2. The maximum at $2\theta\ 6^\circ$ may be associated to the spacing between silicon attached to methyl groups and it seems to indicate the presence of channels surrounded by methyl groups in the siloxane structure [31].

An alternative explanation is that this spacing proceeds from discrete structural units in a matrix based on an octameric silicon arrangement where the methyl groups tend to replace hydroxyl groups as the terminal group [31]. When the quantity of methyl groups diminishes due to the decrease of the PDMS content in the hybrid material, the disposition of these groups in the surface disappears.

The peak at $2\theta\ 2.5^\circ$ has to be related to the OPU component. Peaks below $2\theta\ \sim 4.5^\circ$ are related with arrangement of soft segment of the polyurethane [32, 33]. Depending on the length and arrangement of soft segment, the d-spacing increases with the number of ethylene groups in the soft segment.

3.2 Thermal stability

Figure 7 shows the TGA analysis of hybrid materials. As it can be seen, weight lost on sample TP1 is 30%. Weight losses of TPP1-TPP5 go from 33 to 42 wt. %. The greater the OPU content the weight loss increases. The thermal decomposition of hybrids takes place in various steps depending on the OPU content. The first step goes from room temperature up to around 360°C with a 2 wt. % loss for samples that contains less than 15 % of polyurethane and it is due to the evaporation of solvent, residual monomers and water. The second step goes from 360°C up to 450°C

Fig. 6. XRD spectra of hybrid materials.

Fig. 7. TGA analysis of hybrid materials.

Fig. 8. DSC analysis of TP1, TPP3, and TP2 hybrid materials.

with a 10 wt. % loss and it might be due to the elimination of either lineal or cyclic chains from PDMS and OPU dispersed in the silica matrix [34]. The weight loss from 450 °C up to 630 °C (30 wt. %) may be attributed to elimination of methyl groups in PDMS [35, 36].

On the other hand, materials with more than 15 % of OPU suffer a weight loss greater than 30%. A 5% weight loss can be observed from room temperature to 140 °C that can be explained due to the elimination of solvent and water. From 140 up to 380 °C a 15 % weight loss is ascribed to the decomposition of the hard segment of the polyurethane [37] and residual monomers. A weight loss between 32 and 51 % is observed for samples with a 20 to 30 % of OPU content in the interval 380-540 °C and it can be assigned to the decomposition of both, the soft segment of the polyurethane and the PDMS chain [38, 39]. Over 540 °C, no weight loss is observed, indicating that all the organic part has been eliminated from the silica matrix. The total weight loss of these hybrids was 52 %, which shows the influence of the OPU content. The thermal stability decreases and the weight loss increases as the OPU content is higher.

DSC analysis of TP1, TPP3, and TP2 hybrid materials (30/0/, 15/15 and /0/30 mass ratio of OPU/PDMS, respectively) are showed in Figure 8. For sample TP1 (OPU free) no change is observed in the temperature range studied (-50 to 160 °C). On the other hand, an endothermic peak is observed at 136 °C for TPP3 and at 131 °C for TP2. Both peaks can be related to the decomposition of the hard segment of the polyurethane.

3.3 Evaluation of degradability

Figure 9a, shows the pH change for TP1, TPP3 and TP2 samples soaked in a Phosphate Buffer Solution (PBS) for 1, 3, 7, 14 and 28 days. The pH decreases for 7 days, and start to rise for the rest of the experiment period for all the compositions tested. The decay is lower than 0.2 pH units for TP1 and it can be attributed to the elimination of trapped acid catalyst (HCl) that did not react during the synthesis. On the other hand, the dramatic drop of pH observed for TPP3 and TP2 samples may be related to the degradation of polyurethane by hydrolysis giving amines and carbon

Fig. 9. a) Evaluation of pH of PBS and b) Weight loss of TP1, TPP3 and TP2 samples in PBS.

Fig. 10. a) FTIR spectra, b) DRX and c) SEM for TPP3 sample before and after soaking in SBF.

dioxide [40] and subsequent dissolution of these products. After 7 days, OPU containing specimens showed a similar behaviour to that of TP1, since only the Si-O-Si matrix is remaining. The evolution of the weight of the specimens during immersion in PBS is presented in figure 9b. The TP1 sample does not show any weight loss whereas the TPP3 and TP2 suffer a considerable weight loss during all the soaking period. Eventually, the TP2 sample was completely dissolved after 7 days of soaking. In consequence, the presence of the OPU units affects the chemical stability of the prepared materials. Whether the faster degradation rates are required a greater amount of OPU should be introduced in the structure.

3.4 In vitro bioactivity

TPP3 composition was selected for the “in vitro” bioactivity tests. Compositions with more than a 50% PDMS should be hydrophobic enough, as discussed above, to prevent the ionic exchange described for bioactive materials [41]. Compositions with a greater content in OPU result in an unsuitable fast degradation.

FTIR spectra, XRD patterns and micrographs of TPP3 specimens soaked in SBF for different periods are shown in figure 10.

The characteristic band for $(\text{PO}_4)^{3-}$ at 1035 cm^{-1} in an apatite environment can be observed after only three days of soaking [9, 42]. Broad maxima characteristic of an apatite like material are also observed at 2θ 25° and 32° in the XRD patterns.

Fig. 11. Scheme of pH increase of SBF by (a) OPU release and (b) Ca^{2+} release.

Fig. 12. MTT assay for TP1 and TP2 samples.

A micrograph of TPP3 soaked for 7 days in SBF is shown in Figure 10c. The growing of a layer of globular apatite can be observed as already detected with the FTIR and XRD techniques.

The pH of the SBF increases due to the ion exchange that occurred between the SBF and the hybrid materials and is compatible with the mechanism described for the growing of an apatite layer on bioactive materials [43, 44]. In this mechanism, OPU and calcium are released to the media and yield an increase in the pH according to the sequence displayed in figures 11 a and b

3.5. Cytotoxicity

Cell viability is comparable to the positive control TMX employed. No significant differences could be observed for any of the assayed compositions. A viability over 85% ($\alpha < 0.05$) could be observed as displayed in figure 12. The cytotoxicity is independent of the polyurethane content. The degradation of polyurethane by hydrolysis discussed above seems not to have any deleterious effect on the viability of the osteoblastic cells employed.

4. CONCLUSIONS

Hybrid monolithic materials based on siloxane-polyurethane have been manufactured. Gelling time of these hybrids depends on Siloxane/OPU ratio. Hydrophilic character of the hybrids can be modulated with the Siloxane/OPU ratio. Degradation rate can be designed adjusting the relative content of OPU. A hybrid with a 50/50 Siloxane/OPU ratio displayed an appropriate degradation rate, bioactivity and lack of cell toxicity that makes this material a candidate for further studies for applications in bone repairing.

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