



# Synthesis and characterization of a conductive and self-healing composite

Marcela Mantese Sander\*, Carlos Arthur Ferreira

LAPOL –PPGE3M – Universidade Federal do Rio Grande do Sul (UFRGS), Brazil



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## ABSTRACT

An electrically conductive composite of poly(glycerol sebacate) (PGS) and polypyrrole (PPy) was prepared by solvent free synthesis. The PGS matrix was obtained with a 1:1 proportion of sebacic acid and glycerol. The PPy was prepared by chemical synthesis, using iron chloride as oxidant. Films containing 1, 3 and 5% PPy were prepared by adding the conductive polymer, as a finely dispersed powder, into the PGS pre-polymer matrix. PGS polymerization was confirmed by GPC, ATR-FTIR and NMR. Preparation time of the crosslinked film was decreased by 50% via the addition of PPy. The films were characterized by thermal and dynamic mechanical analysis, indicating a thermally stable composite. The matrix behaved as an elastomer at room temperature. The electrical conductivity of the composite films was in the order of  $5 \times 10^{-5}$  S/cm. Based on the chemical characteristics of the matrix, the self-healing properties of PGS and its composites with PPy were investigated. The results showed that the films can fully recover their mechanical strength after being cut and repaired at 130 °C for 24 h, retaining the electrical conductivity.

## 1. Introduction

Materials which possess several useful characteristics have proven to be the most promising path in the development of lighter, more sensitive and functional devices. So called “smart materials” are being studied because they have multiple properties, are sensitive to external stimuli and can be tailored as needed. Conductive polymer composites (CPCs) are a type of smart material which combines the mechanical properties of a host polymer matrix, with the electrical properties of a conductive filler [1]. CPCs have been studied for many applications, such as biomaterials [2,3], biosensors [4,5], gas sensors [6], as anti-static covers for electronic devices [7], self-heating materials [8] and coatings [9]. Most recently, Larimi et al [10] described a low-cost ultra-stretchable CPC made into a commercial rubber-like adhesive patch. This piezo-resistive strain sensor demonstrated great potential for monitoring bio-signals and human motion. CPCs could be also obtained in special forms, as demonstrated by Shu Ying et al [11], that obtained an elastic conducting polypyrrole nanotube aerogel.

Both matrix and conductive filler can bestow special characteristics to the CPC. They could be obtained from renewable feedstock, for example, or enhance biodegradability and biocompatibility. Poly (glycerol sebacate) (PGS) is a non-expansive biodegradable polyester prepared by polycondensation of sebacic acid and glycerol, both obtained from castor oil [12]. PGS alone has poor mechanical properties [13] but using this polymer as a matrix in composites expands its range of useful application. For example, a composite of PGS and Bioglass, proposed by

Liang et al [14], presented improved mechanical properties, like Young's modulus and tensile strength, without compromised extensibility.

In this paper, we describe a new CPC, prepared by using a PGS matrix and a polypyrrole (PPy) functionalisation component. PPy is an electrically conductive and biocompatible polymer [15], even in small amounts [16,17], used in several CPCs [18–20]. However, it is not fusible and has poor solubility [21]. The combination of the rubber-like characteristics of PGS and the electrically conductive properties of PPy, makes this composite a potentially very interesting CPC. The physico-chemical characteristics, thermal and conductive behaviour and morphological aspects of the composite were studied. Additionally, based on the chemical characteristics of PGS, it was hypothesized that this polymer can exhibit self-healing properties [22]. Self-healing materials are able to recover themselves after mechanical damage. Therefore, the PGS as well as the composite polymer were tested for its self-healing capability by evaluating their properties against some criteria, suggesting a new method to identify potential intrinsic self-healing polymers.

## 2. Experimental

### 2.1. Materials

Glycerol (Neon, purity 99.7%) and sebacic acid (Sigma-Aldrich, purity 99%) were used as received. Pyrrole (Sigma-Aldrich, purity 98%)

\* Corresponding author at: Bento Gonçalves Av, 9500, Building 43426, PO Box 15010 Zip Code: 91501-970, Porto Alegre, Brasil.  
E-mail address: [marcela.sander@ufrgs.br](mailto:marcela.sander@ufrgs.br) (M.M. Sander).

was distilled and stored under refrigeration prior to use. Ferric chloride (Sigma-Aldrich, purity 99,9%) was used without further purification.

## 2.2. Synthesis of polymers

An equimolar mixture of glycerol and sebacic acid was reacted for 24 h at 130 °C, in a three-neck flask with a magnetic stirrer, under nitrogen flux in the first 5 h, to form the PGS prepolymer (a low molecular weight polymer). The PGS film used as control was obtained by similar synthesis, but the prepolymer was reacted for 48 h, and vacuum was fitted in the last 4 h of reaction.

The PPy was synthesized at 0 °C in a jacketed vessel. An aqueous solution of 0.06 mol of pyrrole and 0.11 mol of ferric chloride was stirred for 6 h. The polymer was washed with water until it reached pH 6, filtered and dried in an oven for 24 h [23].

## 2.3. PGS/PPy film preparation

The films were prepared by adding the finely dispersed PPy powder to the PGS prepolymer, at 130 °C, and stirring for 2 h. At this temperature, the PGS prepolymer is a viscous liquid and the mixture viscosity increased with successive PPy addition. The amount of PPy added was 1, 3 and 5% w/w. The polymer mixtures, and PGS control, were cast in silicon molds and the films were obtained by thermal-curing, in a vacuum oven at 130 °C for 48 h.

## 3. Characterization

### 3.1. PGS synthesis

PGS synthesis was confirmed by gel permeation chromatography (GPC) and NMR (nuclear magnetic resonance) of the prepolymer. For GPC analysis a 1 wt% PGS prepolymer solution was prepared in tetrahydrofuran (THF). The elution rate of the mobile phase (also THF) was adjusted to 1 mL/min, and 1  $\mu$ L of solution was injected in a chromatograph (Viscotek model VE2001) with a Viscotek TDA 302 detector. The proton NMR spectra was obtained in a Varian 400 MHz. The sample was prepared with 50 mg of prepolymer in 5 mL of deuterated chloroform ( $\text{CDCl}_3$ ) with trimethylsilane (TMS).

### 3.2. Composite characterization

The crosslinked polymer and composites were characterized for chemical bonds with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Spectral images were acquired in ATR mode using a Perkin-Elmer Frontier. Data were collected in 64 scans in the wavenumber range between 400–4000  $\text{cm}^{-1}$  and spectral resolution of 4  $\text{cm}^{-1}$ .

Scanning electron microscopy (SEM) of cryogenically fractured cross-sections was performed on a scanning electron microscope (Phenom World, model Pro X (Phenom, Netherlands)). The samples were sputtered with gold in a Balzers model Sputter Coater SCD 050, for 100 s, under vacuum and at a deposition current of 40 mA.

The thermal properties of the films were evaluated with a differential scanning calorimeter (DSC) (TA instrument, model Q20), using heating/cooling rates of 10 °C/min and 50 mL/min nitrogen flow. The samples weighed approximately 6 mg.

The thermal stability of the films was measured using a thermogravimetric analyzer (TGA) (TA Instruments, model TGA-50). The temperature was increased from 30 °C to 800 °C at a rate of 20 °C/min, under nitrogen flow of 90 mL/min.

The electrical conductivity of the PGS/PPy films was measured at room temperature using the four-point probe technique (Cascade Microtech model CS 4–64). A current source (Keithley model 2040) was used for the supply of constant current through the two outer probes, and the current was measured in the inner probes. The films were cut in

1  $\text{cm}^2$  squares. Using the values of current, voltage and thicknesses of the films, the resistivity was calculated using the following formula.

$$\rho = (V/I) t \quad (1)$$

where  $\rho$  = electrical resistivity, V = voltage, I = current and t = thickness (cm). The electrical conductivity ( $\sigma$ ) was then calculated using the following equation:

$$\sigma = 1/\rho \quad (2)$$

Tensile tests were performed in an Instron model Emic 23-5D, equipped with a 50 N cell load, at room temperature, at a rate of 50 mm/min. The specimens (n = 4) were cut in a dog bone shape, with dimensions 35 × 2 × t mm (total length x width in the neck section x film thickness, measured individually). The ultimate tensile strength (UTS) and elongation at break were measured at the highest stress that the material could reach. Blue Hill 3 software was used for data analysis.

### 3.3. Self-healing evaluation

As there are no standard methods to evaluate the self-healing properties of polymers, it was decided to investigate the novel materials both quantitatively and pure PGS qualitatively. Hence, UTS and elongation at break data from tensile tests and photographs of self-healed and undamaged samples were compared.

For the quantitative tests, specimens cut in a dog bone shape were tested as described above, in tensile test. Samples were cut in half with a blade and put together by closely fitting the two halves again after 30 s. The specimens were kept at four temperatures, 25, 37, 60 and 130 °C, for 2 and 24 h. Three samples for each condition were prepared.

For the qualitative evaluation specimens of pure PGS with dimensions of 8 × 30 × 5 mm (width, length and thickness, respectively) were kept at 25 and 130 °C, for 2 and 24 h. Each was photographed while being manually stretched in axial direction, with tweezers. Differently for the quantitative test, and in order to best visualize the healed interface, one half of pure PGS specimen was colored with 1 drop of green pigment (Food Green 3) before thermal curing.

## 4. Results and discussion

### 4.1. Polymer synthesis

The PGS prepolymer was successfully prepared by equimolar polycondensation of glycerol and sebacic acid. A schematic diagram of the fabrication process of PGS control and PGS/PPy composites is shown in Fig. 1. The partly cross-linked PGS prepolymer had an average molecular weight (Mw) of 15,900 and a number average molecular weight (Mn) of 2,603, with a polydispersity index (PDI) of 6.1, as measured by GPC. These results are similar to those previously reported [24]. The FTIR spectra of the PGS control, after being cured, (and the composite with PPy) can be seen in Fig. 2.

Characteristic spectra were obtained for PGS, showing the ester bond formation. The main peaks are located at 3400  $\text{cm}^{-1}$  (O–H stretching), two peaks at 2926 and 2853  $\text{cm}^{-1}$  (alkane groups) and 1734  $\text{cm}^{-1}$  (C=O stretching). In the proton NMR spectra of the PGS prepolymer (Fig. 3) the peaks at 1.31, 1.62, and 2.35 ppm were assigned to the methylene protons of sebacic acid; peaks from 4.05 to 4.35 ppm and 5.05–5.30 ppm were observed due to protons in the glycerol [25]. The composition ratio of glycerol to sebacate (0.93:1) in the PGS prepolymer was estimated by the integral area ratio of described peaks. This slight decrease in glycerol amount, when compared to initial 1:1 M ratio, was described in previous studies [26] and is attributed to unreacted glycerol molecules evaporating and being carried away by nitrogen flux in the first 5 h of reaction.

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