

## RICINOLEIC ACID AS A REAGENT IN THE SYNTHESIS OF IONOMERIC COPOLYESTER AMIDES FOR COATING APPLICATIONS

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### Abstract

In this study, water soluble poly(ester amides) with ricinoleic acid units were prepared. The water solubility is imparted by adding a proper amount of sulfonate groups, randomly distributed along the polymeric chains. The ricinoleic acid has been chosen in reason of its antimicrobial properties, which can be conferred to the final materials. The ionomeric polymers prepared were coated on PET films. The tensile properties showed higher values of tensile strength and elongation at break, besides Young's Modulus, compared to the neat PET film, indicating that the coatings adhered well to the PET surface film. The cytotoxicity analysis revealed the non-cytotoxic nature of the materials (24h and 168h tests).

**Keywords:** ricinoleic acid, castor oil, ionomers, poly(ester amides), coatings

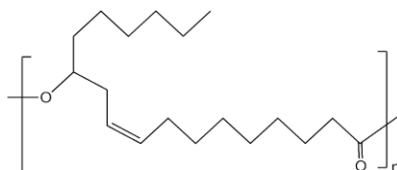
### Introduction

Polymers obtained from renewable raw materials are alternatives to conventional materials such as synthetic polymers derived from fossil sources [1] and vegetable oils are among the most promising alternatives as renewable sources for the production of bio-based polymers because, e.g., they are not expensive and can be chemically modified targeting diverse applications [2].

Castor oil, obtained from castor seeds, *Ricinus Communis*, is a relevant raw material because it contains about 90% of ricinoleic acid (12-hydroxy-9-octadecenoic acid) in its composition. The ricinoleic acid has three reaction sites: carboxyl group, unsaturation, and hydroxyl group and has a wide possibility of modifying its structure, making it very attractive [3].

Castor oil can be used to disperse reagents, in addition to act as a polyol in the synthesis of polyurethanes with simultaneous composite [4] or film [5] formation.

From the ricinoleic acid, it is possible to synthesize the poly(ricinoleic acid) (Fig. 1) through an auto-polycondensation reaction using titanium tetrabutoxide (TBT) as a catalyst, producing a viscous liquid oligomer, at room temperature, with an average molar mass of 8000 g/mol [6] or higher [7].



**Figure 1.** Structure of poly(ricinoleic acid).

Polyamides can be used in textile applications [8] and in cotton fabrics [9].

Poly(ester amide)s (PEAs) can combine the stiffness and the excellent thermal and mechanical properties of polyamides with the biocompatibility and biodegradability of polyesters [10].

In particular, in this study poly(hexamethylene isophthalamide) (PA6I) was synthesized starting from the monomers 1,6-hexamethylenediamine and isophthalic acid. When a proper amount of 5-sulfoisophthalic acid was added to the reaction mixture, the ionic poly(hexamethylene isophthalamide-co-5-sulfoisophthalamide) was obtained. Ionic groups were randomly distributed along the chain, which led to new intermolecular interactions and modified the properties of the poly(hexamethylene isophthalamide). The results showed that the ionic groups made the sulfonated polyamides soluble in water, being able to be used in specific applications such as coatings and adhesives with good barrier properties [11]. Then, the poly(ester amide) poly(hexamethylene isophthalamide-co-5-sulfoisophthalamide-co-ricinoleic acid) was prepared by adding a proper amount of ricinoleic acid in order to confer additional antimicrobial activity to the final material.

**The objective of this study was to prepare water soluble poly(ester amides) for coating application.**

## Experimental

Isophthalic acid (IPA), 5-sulfoisophthalic acid sodium salt (5-SIPA), 1,6-hexamethylenediamine (HMDA), sodium hypophosphite, ricinoleic acid (RA, purity around 80%), and titanium tetrabutoxide (TBT) were purchased from Sigma-Aldrich, while sodium acetate was supplied by Carlo Erba. All materials are of high purity and were used as received.

### 1. Syntheses of polymers and copolymers

#### 1.1. Synthesis of poly(hexamethylene isophthalamide) (PA6I) and poly(hexamethylene isophthalamide-co-5-sulfoisophthalamide) (PA6I/PA6ISO<sub>3</sub>) (80/20) [11]

PA6I was synthesized from 1,6 hexamethylenediamine (HMDA), isophthalic acid, sodium hypophosphite as a catalyst and acetate sodium as an anti-crosslinker. The reagents were placed in a round bottom flask, HMDA water-solution was slowly dripped into the reactor and, at the conclusion of HMDA addition, it was immersed in a salt bath, the temperature was then increased to 300 °C and a yellow color polymeric product was formed.

In the synthesis of PA6I/PA6ISO<sub>3</sub> the procedure was the same as that performed for the synthesis of PA6I, but isophthalic acid (IPA) and sodium salt of 5-sulfoisophthalic acid (5-SIPA) were added in the proportion of 80/20 (mol%), respectively.

#### Synthesis of the copolymer PA6I/PA6ISO<sub>3</sub>/PRA (64/16/20)

In the synthesis of PA6I/PA6ISO<sub>3</sub>/PRA, hexamethylenediamine (HMDA), sodium acetate isophthalic acid, sodium salt of 5-sulfoisophthalic acid (5-SIPA), ricinoleic acid, maintaining the ratio of 64/16/20 (mol%) and TBT. It started at a temperature of 190°C and, after the catalyst is added, the temperature was increased to 250°C and the vacuum was switched on. An ivory color polymeric product was formed.

### 2. Coating of PET films

Coated PET films were prepared by coating the polymeric materials prior synthesized on bioriented films (23 µm thick). PA6I/PA6ISO<sub>3</sub> or PA6I/PA6ISO<sub>3</sub>/PRA was added to distilled water and placed in an oven at 90°C, obtaining an opalescent solution in both cases. The solutions were spread on the PET films using a ZAA 2300 Zehntner Automatic film applicator equipped with a cylindrical bar to prepare coatings with a nominal depth of 13.7 µm.

## 2.1. Physical and Chemical Characterization

<sup>1</sup>H Nuclear Magnetic Resonance (NMR) characterization: the samples were dissolved in a mixture of 1,1,1,3,3,3-hexafluoro-2-propanol/deuterated chloroform 50/50 (v/v) and were recorded at 600 MHz with a Varian Inova 600 spectrometer.

Differential Scanning Calorimetry (DSC): was performed using Perkin-Elmer DSC6 under nitrogen flow (40 mL.min<sup>-1</sup>). The samples (PA6I and PA6I/PA6ISO<sub>3</sub>) (ca. 10 mg) were first heated at 20 °C.min<sup>-1</sup> from 20 to 280 °C, kept at this temperature for 1 min, and then cooled to 20 °C at 10 °C min<sup>-1</sup>. After this, the samples were heated from 20 °C to 280 °C at 10 °C.min<sup>-1</sup> (2nd scan). For the copolymer (PA6I/PA6ISO<sub>3</sub>/PRA) the same conditions were used, but the minimum temperature reached in the cooling scan was -70 °C.

Thermogravimetric analysis (TGA): was performed using a Perkin-Elmer TGA 4000 in a nitrogen atmosphere (40 mL.min<sup>-1</sup>) from 50 to 800°C at a heating rate of 10°C.min<sup>-1</sup>.

Tensile properties: performed in a TA Instruments DMA Q800 equipment, with Tension film type claws and dimensions of approximately 5.2 mm x 6.3 mm x 0.75 mm, with a frequency of 1 Hz, method of 1 N.min<sup>-1</sup> – 18 N, mode: force control and pre-load of 0.001 N.

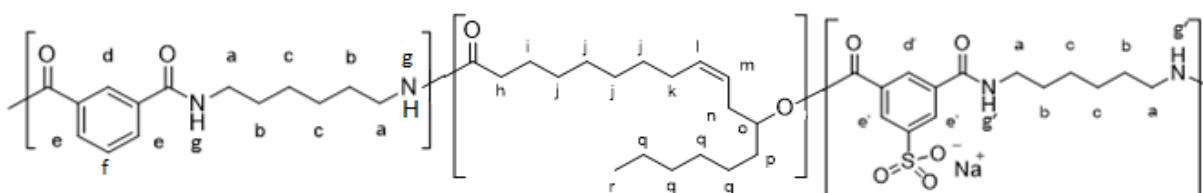
Cytotoxicity analysis: the films were previously sterilized in an autoclave at 121°C for 15 min. The viability of the cells was carried out at the Biophotonics Group, São Carlos Institute of Physics, University of Sao Paulo. The cells were evaluated by means of a colorimetric assay using MTT 3- (4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide and using a fibroblast culture (HDFn) through the material extract method in cell culture medium. For the control of the reaction, wells were used where there was no cell culture (white).

## Results and Discussion

### 1. Characterization of PA6I, PA6I/PA6ISO<sub>3</sub> (80/20), PA6I/PA6ISO<sub>3</sub>/PRA (64/16/20) and PRA

#### 1.1. Chemical characterization

Fig. 2 shows the structure of the obtained ionomeric copolymer (PA6I/PA6ISO<sub>3</sub>/PRA).



**Figure 2.** Poly(hexamethylene isophthalamide-co-5-sulfoisophthalamide-co-ricinoleic acid).

The <sup>1</sup>H NMR spectra (not shown) of PRA, PA6I, and the copolymer PA6I/PA6ISO<sub>3</sub>/PRA confirmed the chemical structures. In particular, PA6I/PA6ISO<sub>3</sub>/PRA showed chemical shifts referring to PA6I/PA6ISO<sub>3</sub> and PRA in proper molar ratio (64/16/20) confirming the chemical structures expected.

#### 1.2. Thermal properties

**Table 1.** Thermal characterization of PA6I, PA6I/PA6ISO<sub>3</sub> (80/20), PA6I/PA6ISO<sub>3</sub>/PRA (64/16/20) and PRA.

Sample	T <sub>onset</sub> (°C) <sup>a</sup>	T <sub>max</sub> (°C) <sup>a</sup> first loss	T <sub>max</sub> (°C) <sup>a</sup> second loss	T <sub>g</sub> (°C) <sup>b</sup>
<b>PRA</b>	339	365	475	-67
<b>PA6I</b>	463	481	-	122
<b>PA6I/PA6ISO<sub>3</sub> (80/20)</b>	457	475	-	163

<b>PA6I/PA6ISO<sub>3</sub>/PRA (64/16/20)</b>	445	469	-	155
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$T_{\text{onset}}$ : initial thermal decomposition temperature;  $T_{\text{max}}$ : maximum thermal decomposition rate temperature.

<sup>a</sup> Determined by TGA at 10 °C.min<sup>-1</sup> under nitrogen flow.

<sup>b</sup> Determined by DSC during the 2nd heating scan at 10 °C.min<sup>-1</sup>.

Table 1 shows that PRA begins its degradation process at 339 °C and its weight loss occurs in two main processes. PA6I on the other hand starts to degrade at 463 °C and lose weight in one main decomposition process. The sulfonate group led to a slight decrease in the thermal stability of the polyamide (PA6I/PA6ISO<sub>3</sub>) in relation to PA6I. In the copolymer PA6I/PA6ISO<sub>3</sub>/PRA, in addition to the sulfonated group, there is the contribution of the ricinoleic acid units, making the product even less thermally stable. In general, the materials showed high thermal stability.

Through the curves obtained from the DSC analyses, it was possible to determine the glass transition temperature ( $T_g$ ) of PA6I, PA6I/PA6ISO<sub>3</sub> (80/20), PA6I/PA6ISO<sub>3</sub>/PRA (64/16/20) and PRA, reported in the table 1. All materials resulted amorphous. The incorporation of the sulfonate group in the polyamide PA6I/PA6ISO<sub>3</sub> increased the  $T_g$  value (163 vs 122 °C in PA6I). This increase is due to intermolecular ionic interactions involving the sulfonate groups, reducing the mobility of the segments. The presence of ricinoleic acid units in the copolymer PA6I/PA6ISO<sub>3</sub>/PRA led to a slight decrease in the glass transition temperature of the sulfonated polyamide, due to the presence of cis double bonds and six methylene groups in the RA molecule, making it flexible, justifying the decrease in the  $T_g$  of the copolymer.  $T_g$  of PRA was indeed -67 °C. The data are coherent with literature [6,9,11].

## 2. Characterization of coated PET films

### 2.1. Tensile properties

**Table 2.** Tensile strength at break, elongation at break, and Young's Modulus for PET, PET<sub>PA6I/PA6ISO<sub>3</sub></sub>, and PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub>.

Film	Tensile strength at break (MPa)	Elongation at break (%)	Young's Modulus (MPa)
<b>PET</b>	78±4	222±29	925±114
<b>PET<sub>PA6I/PA6ISO<sub>3</sub></sub></b>	116±3	269±11	1288±131
<b>PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub></b>	116±5	274±4	1203±164

The tensile properties of PET, PET<sub>PA6I/PA6ISO<sub>3</sub></sub> and PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub> films (Table 2) indicated that the presence of the coatings increased the tensile strength, the elongation at break compared to the neat PET film. The Young's Modulus values showed that PET<sub>PA6I/PA6ISO<sub>3</sub></sub> was stiffer than the neat PET film. This indicated that the coatings adhered well to the PET surface film, increasing the force necessary for the material to rupture, in addition to increasing its flexibility without the use of a plasticizer.

### 2.2. Cytotoxicity analysis

**Table 3.** Cell viability evaluated by MTT of PET, PET<sub>PA6I/PA6ISO<sub>3</sub></sub> and PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub>, after 24 and 168 hours.

Film	Cell viability 24 h	Cell viability 168 h
<b>Control</b>	100±5	100±7
<b>PET</b>	103±4	103±4
<b>PET<sub>PA6I/PA6ISO<sub>3</sub></sub></b>	97±7	95±5
<b>PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub></b>	101±6	94±4

The data of cytotoxicity analysis through the cell viability test (Table 3) showed that the coatings on PET films (PET<sub>PA6I/PA6ISO<sub>3</sub></sub> and PET<sub>PA6I/PA6ISO<sub>3</sub>/PRA</sub>) were non-cytotoxic to the cells, as the neat PET, and led to cell viability above 90% [12]. This means that the materials are biocompatible and suitable for tissue engineering applications.

## Conclusions

In this study, water soluble poly(ester amides) with ricinoleic acid unit were prepared. The water solubility is conferred by adding a proper amount of sulfonate groups, randomly distributed along the polymeric chains. Ricinoleic acid, known as antimicrobial agent, can confer such activity to the final materials. The ionic groups caused an increase in the  $T_g$  value respect to pristine PA6I, due to the intermolecular ionic interactions, which reduce the mobility of the chains, while ricinoleic acid units led to a slight decrease in  $T_g$  of the sulfonated poly(ester amide). PA6I/PA6ISO<sub>3</sub> and PA6I/PA6ISO<sub>3</sub>/PRA were coated on PET films. Their tensile properties were greater than that of the neat PET film, which indicated that there was a good adhesion. All prepared films were non-cytotoxic and favored cell viability both in the 24 h and 168 h tests, therefore the materials resulted biocompatible. Additional characterizations such as barrier properties of the coated PET films will be evaluated, as well as antimicrobial activity.

## Acknowledgements

The Authors acknowledge the Coordination of Improvement of Higher Level for the financial support (Financing Code 001).

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