

SYNTHESIS AND THERMAL STUDIES OF NEW SOYBEAN AND GRAPE SEED OIL-BASED POLYMERS: CLEAN AND EFFICIENT PATHWAY USING GREEN CHEMISTRY PRINCIPLESMarcos Vinícius de Almeida¹, Rafael Turra Alarcon¹, Gilbert Bannach^{*1}¹ College of Sciences, UNESP – Sao Paulo State University, Department of Chemistry, SP - Brazil;

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ABSTRACT

This paper describes the synthesis of polymers from glycerol and vegetable oils as soybean and grape seed, synthesized following the principles of Green Chemistry. Simultaneous Thermogravimetric Analysis – Differential Thermal Analysis (TG-DTA) and Differential Scanning Calorimetry (DSC) were employed to evaluate the thermal decomposition, thermal stability, oxidation, glass transition and crystallization processes. Hence it was possible to verify that they have glass transition near to room temperature. Therefore these polymers may be used such as chemical slow release agents triggered by temperature and thermal security tags.

Introduction

The using of polymers in the modern society is evident and has a huge importance nowadays, however the benefit of these materials and their negatives effects are connected [1]. The irregular and bad disposal, production using raw material of no renewable resources as petroleum; and high time of degradation are just some of the problems associated to these materials. Thus, the polymers are one of the biggest environmental polluters in this century [1-3]. Against these damaging tissues, some alternatives are arising, as development of products using cleaner technologies and products that have more degradability. Due to these products are environmentally friendly and sustainable, thus this type of development follows some purposes and requirements reported in articles and assumptions around the whole world [3].

In this point of view, the Green Chemistry, as well as reuse of industrial by products or products of

natural resources, has been gaining importance as a sustainable alternative against the traditional unsustainable method [4-8].

The thermal analysis may provide some data as thermal decomposition, thermal stability, oxidation, glass transition and crystallization processes, therefore a more accurate understanding of characteristics of these polymers [9-11].

Glycerol, vegetable oils and compounds of natural resources, has been reported in literature as substitutes of petroleum compounds. They are inexpensive, plentiful, renewable and show high degradability, then they are good choice for the polymer production [12].

Materials and methods

The reagents used were glycerol 99.0 % (Merck), maleic anhydride (Aldrich), and soybean and grape seed oil (Aldrich).

Synthesis

The polymers syntheses were performed following the patent BR 10 2016 01805-6 [13].

Thermogravimetric analysis – simultaneous differential thermal analysis (TG-DTA) and Differential scanning calorimetry (DSC)

The TG-DTA curves were obtained using a Netzsch equipment, model STA 449 F3, using 70 μL α -alumina open crucibles with samples of about 10.0 mg and a heating rate of 20 $^{\circ}\text{C min}^{-1}$ in a dry air atmosphere at flow rate of 50 mL min^{-1} and a temperature range of 30.0-800.0 $^{\circ}\text{C}$.

The DSC analyses were obtained on Mettler-Toledo equipment, model DSC 1 Stare System, using 40 μL closed aluminum crucibles with perforated lids, samples of about 11.0 mg without previous thermal treatment, a heating rate of 20 $^{\circ}\text{C min}^{-1}$ in dry air atmosphere and a 50 mL min^{-1} flow rate. The heating/cooling procedures were performed between -35.0 and 160.0 $^{\circ}\text{C}$ for PSOB and -35.0 and 200.0 $^{\circ}\text{C}$ for PGRS.

Middle Infrared Spectroscopy (MIR)

A Nicolet IS10 FTIR spectrophotometer, operating in the range of 4000-600 cm^{-1} with a Ge crystal, was used to collect the spectroscopic data of the polymers.

Results and Discussion

Thermogravimetric analysis – simultaneous differential thermal analysis (TG-DTA) and Differential scanning calorimetry (DSC)

The TG-DTA curves of the oil-based polymers are shown in Figure 1. The PSOB was stable up to 160.0 $^{\circ}\text{C}$, were observed dehydration that occurred at 30.0-160.0 $^{\circ}\text{C}$ interval ($\Delta m = 2.00\%$) due to humidity and condensation water, and two decomposition steps. The first decomposition step

occurred at 160.0-432.0 $^{\circ}\text{C}$ interval ($\Delta m = 77.76\%$), this event is accompanied by an exothermic peak in the DTA curve (351.7 $^{\circ}\text{C}$), proving the polymers decomposition. The second decomposition step occurred at 432.0-675.0 $^{\circ}\text{C}$ interval ($\Delta m = 20.24\%$) together with exothermic peak at 574.0 $^{\circ}\text{C}$ in the DTA curve.

The PGRS was stable up to 200.0 $^{\circ}\text{C}$. Were observed dehydration step like in PSOB, due to humidity and condensation water, but that occurred at 30.0-190.0 $^{\circ}\text{C}$ interval ($\Delta m = 2.00\%$). The first decomposition step occurred at 200.0-454.0 $^{\circ}\text{C}$ interval ($\Delta m = 81.09\%$) together with two exothermic peaks at 343.0 $^{\circ}\text{C}$ and 415.0 $^{\circ}\text{C}$ observed in the DTA curves. The second decomposition step occurred at 454.0-664.0 $^{\circ}\text{C}$ interval ($\Delta m = 16.10\%$), in the DTA curves was observed a peak at 577.0 $^{\circ}\text{C}$ that was attributed to oxidation of the remaining organic matter. The TG curves of soybean oil and grape seed oil can be found in article [14, 15]; thereby they are not showed in this article.

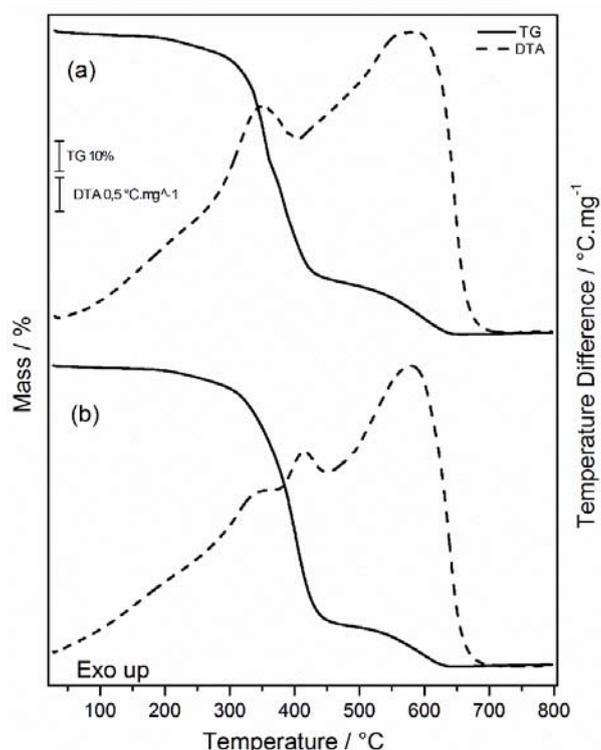


Figure 1. TG-DTA curves (a) PSOB (mass= 10,44 mg) and (b) PGRS(mass= 10,20 mg)

The DSC curve of PSOB and PGRS are shown in Figure 2. No thermal events were observed in all cooling stages to both polymers. However in the first heat stage of the PSOB was observed dehydration that occurred at the 50.0-160.0 °C interval. During second heat step was observed a glass transition with onset at 28.2 °C and middle point at 39.0 °C.

In the first heat stage of the PGRS was observed dehydration between 40.0-190.0 °C, also was

observed two peaks at 85.0 °C and 88.5 °C, then regarding the polymers cure, due to a liberation and evaporation of small molecules, whereas all the polymers in this study are synthesized by condensation reactions in the first synthesis step. In the second heat step it was no longer observed the polymer cure, just a glass transition with onset at 27.3 °C and middle point at 36.3 °C.

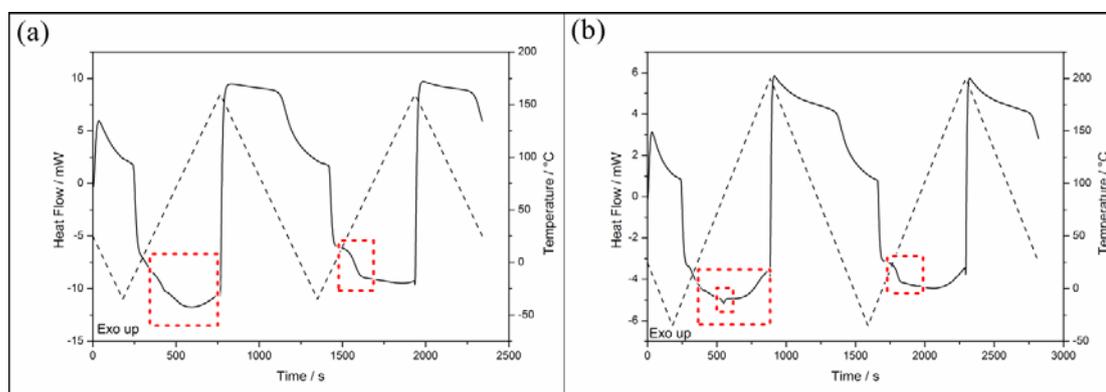


Figure 2. DSC curves (a) PSOB (mass= 11,39 mg) and (b) PGRS (mass= 11,36 mg)

Middle Infrared Spectroscopy (MIR)

The infrared absorption of the soybean oil, glycerol/maleic anhydride and PSOB are shown in Figure 3. The IR spectrum of the soybean oil shown characteristic peaks at 1746 cm^{-1} attributed to stretching vibrations of C=O that refer the ester group and peaks at 2854, 2925 and 3008 cm^{-1} attributed to stretching vibrations of C-H.

The IR spectrum of glycerol/anhydride mixture (first reaction step) shown characteristic region at 3500 cm^{-1} attributed to stretching vibrations of O-H which is associated to glycerol or water. The peak at 1719 cm^{-1} is attributed to stretching vibrations of C=O that refer the carboxylic acid group, and peak at 1645 cm^{-1} attributed to stretching vibrations of C=C in the maleic anhydride.

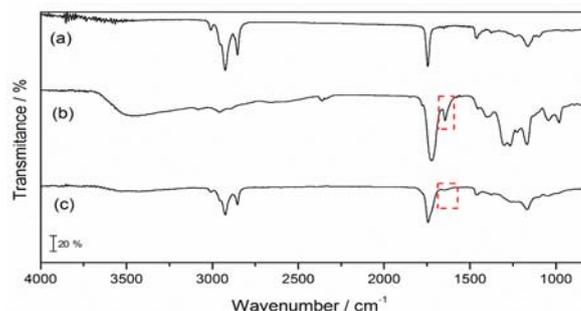


Figure 3. Infrared spectra (a) soybean oil, (b) glycerol/maleic anhydride mixture and (c) PSOB

The IR spectrum of PSOB shown characteristic peaks at 2854, 2952 and 2924 cm^{-1} attributed to stretching vibrations of C-H in the oil structure and the stretching vibration peak at 1745 cm^{-1} is attributed to C=O. The peak that refer the C=C stretching vibration (Highlighted in the spectrum)

decreases, thus providing that the π bonds was cleaved, which it is a possible to indication about "Ene" reaction.

Similar IR spectrum data about PGRS were obtained and shown in Figure 4

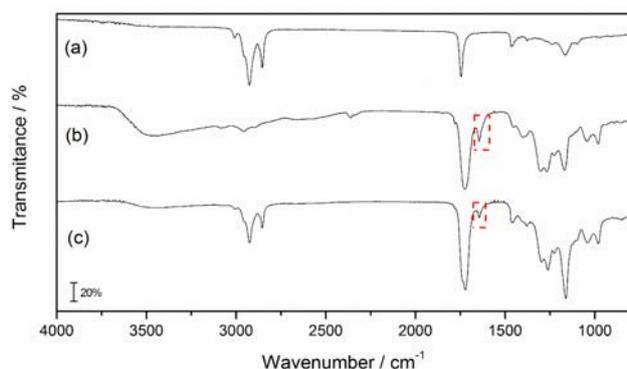


Figure 4. Infrared spectra (a) grape seed oil, (b) glycerol/ maleic anhydride mixture and (c) PGRS

Polymer's characteristic

The polymers are shown in Figure 5. They are solids and have a yellowed color. The PSOB is rigid while the PGRS is rubbery, both are insoluble in methanol and ethanol, but are slightly soluble in acetone, however they are not resistant to alkaline solutions.

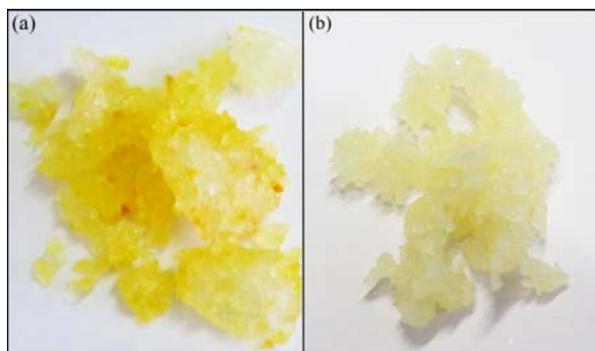


Figure 5. Photographic images of (a) PSOB and (b) PGRS

Conclusion

The new synthesis pathway proved to be fast and efficient. All the synthesized polymers were solids which soybean oil-based polymer is rigid and grape seed oil-based polymer is rubbery.

The infrared absorption spectra presented a decrease in the C=C vibrational stretching of maleic anhydride, indicating that the π bonds was cleaved during polymerization, which may indicate about the "Ene" reaction.

The TG-DTA curves showed thermal stability for these polymers and their decomposition steps, thus it was possible verify that the soybean oil-based polymer had thermal stability at 160.0 °C and the grape seed oil-based polymers had thermal stability at 200.0 °C. The first mass loss step is referent a dehydration of humidity and condensation water.

The DSC analysis showed polymer cure, glass transition and dehydration in this range of temperature studied. Furthermore both polymers did show glass transition with onset near at 27.0 °C and middle point at 36.5 °C, therefore these polymers may be used such as chemical slow release agents triggered by temperature and thermal security tags.

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