POLYURETHANES BASED ON POLYOLS FROM CASTOR OIL, STARCH GRANULES AND STARCH-DERIVED GLYCOL AND GLYCEROL GLYCOSIDES: MORPHOLOGY, SYNTHESIS, CHEMICAL, MECHANICAL, AND THERMAL PROPERTIES

Alvaro Ramírez[a*], Manuel F. Valero[a], Jorge E. Pulido[a], Zhengdong Cheng[b]

[a]Polymers Research Group, School of Chemical Engineering, Universidad Industrial de Santander A.A. 678, Bucaramanga, Colombia.

[b]Chemical Engineering Department, Texas A&M University, College Station, 77840, TX, USA.

*Corresponding author. Telephone: 57-7-6344000 ext. 2434, Fax: 57-7-6344684.
E-mail: argarcia@uis.edu.co. Address: Cra 27 calle 9 Campus Universitario, Escuela de Ingeniería Química, U.I.S, Bucaramanga, Colombia.

Abstract

A series of polyols were prepared from castor oil (CO) and cassava starch (S) by two routes in order to obtain products with high hydroxyl content: a) Incorporation of starch granules into the original castor oil and pentaerythritol- modified castor oil and b) Modification of starch by glycosylation and transesterification with castor oil and castor oil modified. The resultant polyols were characterized by hydroxyl value, *Fourier* transform infrared spectroscopy (FTIR) and Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectroscopy (MALDI TOF MS). MALDI TOF MS was used to detect and characterize the components of castor oil and to determine the products of the transesterification reaction. Several polyurethanes (PU) were synthesized by reacting the different polyols derived from castor oil and cassava starch with 4,4-diphenyl methane diisocyanate (MDI) and isophorone diisocyanate (IPDI). The crosslink density of polyurethanes was determined by swelling tests using the Flory-Rehner's equation. The variation of the crosslink density of polyurethanes was studied based on the hydroxyl value of the polyol utilized in the synthesis. The effect of polyol modification on the mechanical, chemical and thermal properties of the resulting polyurethanes was evaluated as a function of the percent of modifier agent (pentaerythritol, starch or starch-derived glycosides). The properties of the elastomeric polyurethanes were studied related to their chemical structure and morphology.

Introduction

Castor oil is a renewable recourse and a natural polyol and has been a successful candidate in the formation of industrially useful materials like cost-effective polyurethane elastomers, it is yet to be exploited for the modification of polymers [1, 2, 3]. The polyurethanes obtained from castor oil are typically water resistant and flexible due the presence of a long fatty acid chain and lend themselves to thermosetting-type structures due to their tri-functional nature. The long pendant chains of the fatty acids impart flexibility and hydrolysis resistance to the network and the double bond present in the castor oil serves as a grafting center. The properties of material obtained from castor oil include low hydroxyl number leading to inherently low modulus materials, a sluggish rate of curing of secondary hydroxyl groups and structural irregularity due to steric hindrances caused by the long pendant fatty acid chains during polyurethane formation, resulting in low tear strength [4, 5, 13].

To modify these properties, oil-based polyurethanes are mixed in the form of interpenetrating networks with others monomers like styrene, methacrylate, formaldehyde, etc. They are also transesterified or alcoholized with alcohols thereby introducing reactive hydroxyl groups. Most of the literature published has illustrated the use of glycerol for transesterification [4, 12]. However, glycerol (a component of the triglyceride molecule) is readily destructible at high temperatures. This disadvantageous property stems from the presence of hydrogen atoms in position β relative to the hydroxyl group in the glycerol molecule. This structural feature is conductive to the partial defragmentation of the molecule and the formation of unsaturated compounds. The problem can be solved by replacing glycerol with another polyhydric alcohol that does not contain β-hydrogen atoms, i.e pentaerythritol.

Other route evaluated to increase the hydroxyl functionality of the castor oil was glycosylation of starch, followed by transesterification with the castor oil [6, 7]). Starch was reacted with ethylene glycol to form glycol glycoside. Polyols were synthesized by reacting castor oil with glycol glycoside.

The goal of this work was to study the effect of polyol modification on the mechanical, chemical and thermal properties of the resulting polyurethanes was evaluated as a function of the percent of modifier agent (pentaerythritol, starch or starch-derived glycosides). The properties of the elastomeric polyurethanes were studied related to their chemical structure and morphology. There were also evaluated the effects due to the structure of the soft segments, consisting on the polyol, and the hard segments, consisting on the polyfunctional isocyanate and crosslinker. The morphology of polyurethane was investigated as related to compatibility and microphase segregation between the two segments. The change in the crosslink density and physical interactions in the polyurethane were studied in function of the chemical modification of castor oil and starch.

Experimental

Materials

Castor oil and yucca starch were obtained from the local market. Pentaerythritol (Fisher, USA) and catalyst litharge (Merck, USA) were used for transesterification. Glycerol and ethylene glycol along with sulfuric acid were reactants for glycosylation of the starch. Isophorone diisocyanate (IPDI) (Aldrich, USA) was employed to obtain polyurethanes.

Transesterificacion castor oil using Pentaerythritol

The castor oil transesterification was carried out in a flask with four openings equipped with agitator, reflux condenser, nitrogen gas entry and a thermo regulated warming blanket. 400 g of castor oil and the transesterification modifier were charged in a previously established proportion, along with a 0.05% of PbO catalyst, based on the oil weight. The reaction took place at 200ºC for 2.5 hours

Preparation of Glycosides

Starch was reacted with ethylene glycol and catalyst sulfuric acid (0.5%), in a 1 L reactor connected to a constant temperature system, under nitrogen atmosphere. The glycosylation reaction was carried out for 2 h at 1108C. Glycerol was also used in place of glycol for some experiments that look for variation in the glycoside structure. After reaction, the residual sulfuric acid was precipitated with barium hydroxide. The residual ethylene glycol or glycerol after reaction was also separated by vacuum distillation [10, 11].

Preparation of Polyols and Polyol-glycosides

Polyols were synthesized from castor oil by transesterification reactions with pentaerythritol at different proportions, under nitrogen atmosphere with catalyst litharge (0.05%) [12]. The time of reaction was 2.5 h at 2008C in a 1 L reactor equipped with agitator, reflux condenser, and a thermo regulated warming blanket. Two types of these polyols were obtained: P0 and P1 with increasing hydroxyl values of 186 and 233mg KOH/g, respectively. Original castor oil had hydroxyl value of 160mg KOH/g. Either glycol glycosides or glycerol glycosides were mixed with the castor oil polyols in amounts of 5 and 10% along with catalyst litharge (0.05%) and reacted at 2108C for 2 h under nitrogen atmosphere, in a reactor of similar characteristics as the one used for transesterification. Thus, two kinds of products were obtained: polyol-ethylene glycol glycosides (PEG) and polyol-glycerol glycosides (PGG). As a point of reference, original castor oil was also reacted with glycol glycoside and glycerol glycoside to obtain, respectively, a castor oil-glycol glycoside (CO-EG) and a castor oil-glycerol glycoside (CO-GG).

Characterization

Castor oil polyols, glycosides, and polyol-glycosides were characterized by measuring the hydroxyl value (ASTM D1957-86), specific gravity (ASTM D792-86), viscosity on a Brookfield DV-III rheometer at 200 rpm and 268C and Fourier Transform Infrared spectroscopy (FTIR) on a Nicolet Avatar 360 spectrometer. FTIR spectra for polyurethanes were also obtained. Glycosides and polyol-glycosides were analyzed using MALDI TOF mass spectroscopy; iodometric tests were also used to check the presence of any traces of starch not converted to glycoside.

Chemical and solvent resistances were measured according to ASTM D543-67 method. Each polymer specimen of known dimensions was immersed in solvents with increasing order of solubility parameter δ from 8.2 to 14.5 $(\mathrm{cal/cm}^3)^{1/2}$. This procedure was continued till equilibrium swelling was achieved. The swelling behavior of the polyurethanes in various solvents was investigated and the solubility parameter was determined based on the average structure of each polyurethane repeating unit, as determined by the method of matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI TOF MS). The crosslink density of polyurethanes was determined by swelling tests using the Flory-Rehner's equation. The variation of the crosslink density of polyurethanes was studied based on the hydroxyl value of the polyol utilized in the synthesis. The stress-strain properties were determined using an Instron universal testing machine according to ASTM D-527 procedure and hardness measurements were made on a Shore-A hardness test apparatus using ASTM-785 method. Dynamic mechanical thermal analyses (DMTA) of the selected polyurethanes were carried out on a Rheometrics DMTA V. The storage modulus (E'), the loss modulus (E'') and loss factor (tanδ) were measured. The temperature corresponding of the maximum of the tanδ peak position was taken as glass transition temperature (Tg). Scanning electron micrographs were obtained on a JEOL JSM-6400 electron microscope. The samples were previously coated with a gold layer and the morphology of the materials was studied through their fractures after immersion into liquid nitrogen.

Results and discussion

Figure 1 shows the relation between the hydroxyl value of the polyol and the concentration of modifier agent for the polyols obtained from castor oil since a. starch incorporating without modification, b. oil transesterification with ethylene glycol and c. oil transesterification with glycerol glycoside. It can be seen that the hydroxyl value of polyols obtained from castor oil modified with glycosides is higher than the polyols obtained from incorporating starch without prior modification.

Figure 1. Relation between the hydroxyl value of the polyol and the concentration of modified agent.

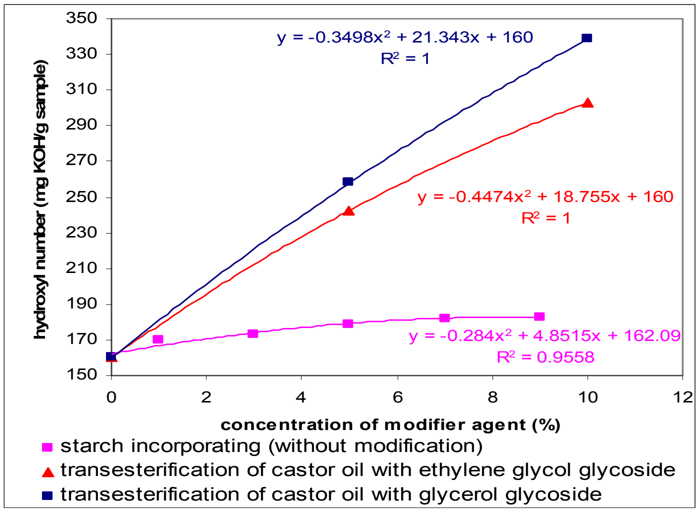
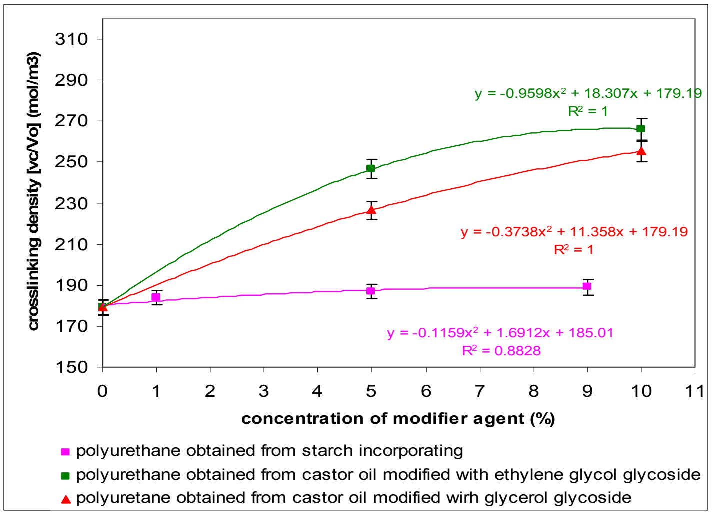


Figure 2 shows the relation between crosslinking density and the concentration of modifier agent. It is observed that crosslinking density of polyurethanes obtained from starch incorporating is almost constant. Without prior modification, starch cannot be reacted with the diisocyanate to obtain polyurethane. In contrast, polyurethanes obtained from transesterification of castor oil with glycosides exhibited an increment of crosslinking density in function of the modifier agent due to the hydroxyl groups of the glycosides participating in the formation of urethane bonding. The data suggests that The modification of starch also affects the physical crosslinking by hydrogen bonding between polar groups.

Figure 2. Relation between crosslinking density of the polyurethane and the concentration of the modifier agent.



The data of tensile strength and shore A hardness of polyurethanes obtained from castor oil original and modified are shown in Figure 3. It is observed that polyurethane obtained from castor oil modified with glycosides showed higher tensile strength and shore A hardness compared to polyurethane obtained from original castor oil and starch incorporating. Polyurethane prepared by castor oil modified with glycosides improved properties over unmodified castor oil due to more crosslinking density due to an increase in hydroxyl content. The incorporation of starch without modification results in a increase in stiffness due to starch acts as a rigid filler.

Figure 3. Tensile strength and shore A hardness results of polyurethanes obtained from castor oil (original and modified)

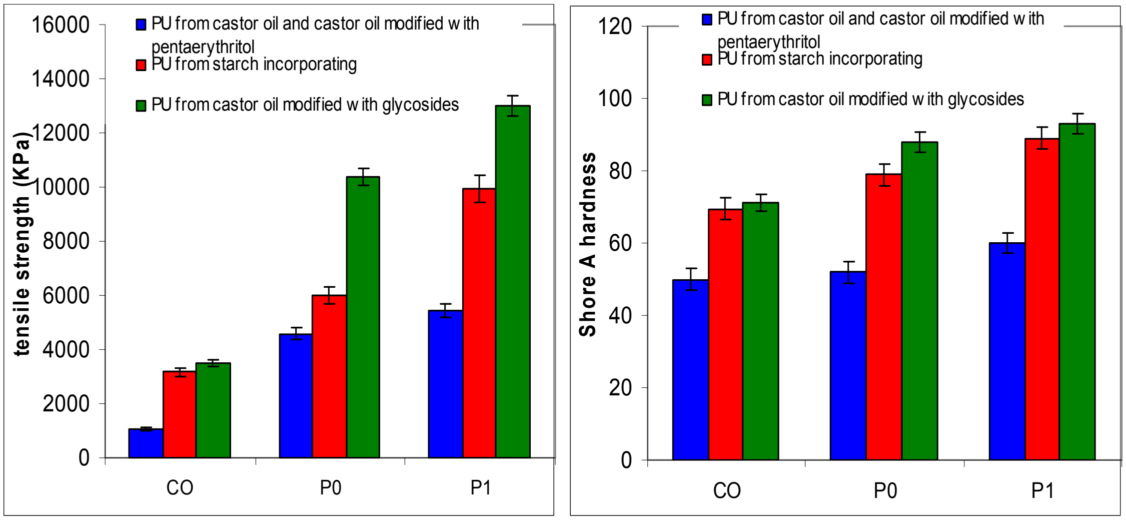
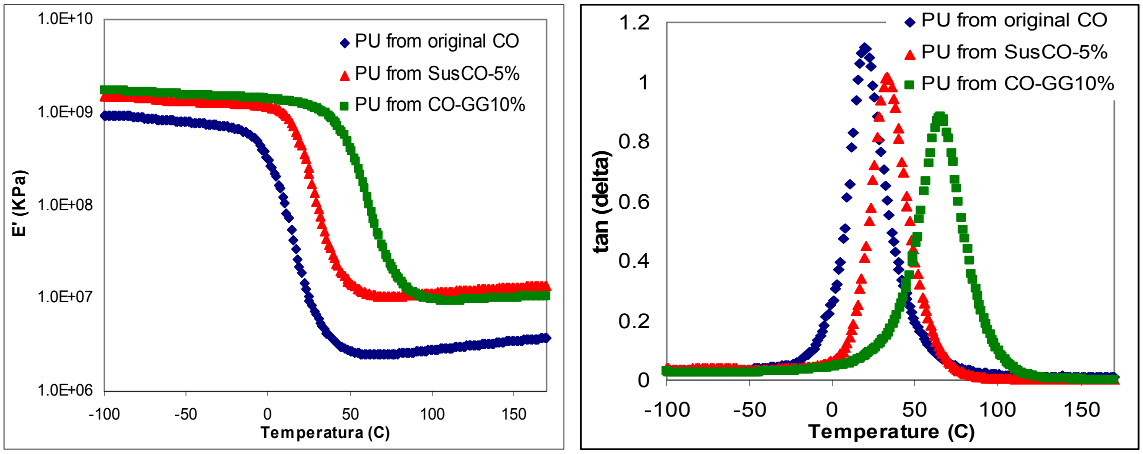


Figure 4.a shows the storage modulus, *E'*, versus the temperature for the studied polyurethanes. It can be seen that the storage modulus of polyurethane obtained from castor oil modified with glycosides is higher than the polyurethane from starch

incorporating and original castor oil, indicating increased rigidity in these materials. In the Figure 4.b, it is observed that the glass transition temperature (Tg) is greater for the PU obtained from castor oil modified with glycosides; it is also observed that the intensity of the peak of tanδ for this polyurethane decreases (the restriction in the mobility of the chains increases as a consequence of the higher density of crosslinking). These results demonstrate the greater degree of crosslinking of polyurethane obtained from castor oil modified with glycosides due to the high hydroxyl functionality of this polyol.

Figure 4. a. Storage modulus and b. tanδ versus temperature for the polyurethanes obtained from castor oil (original and modified)

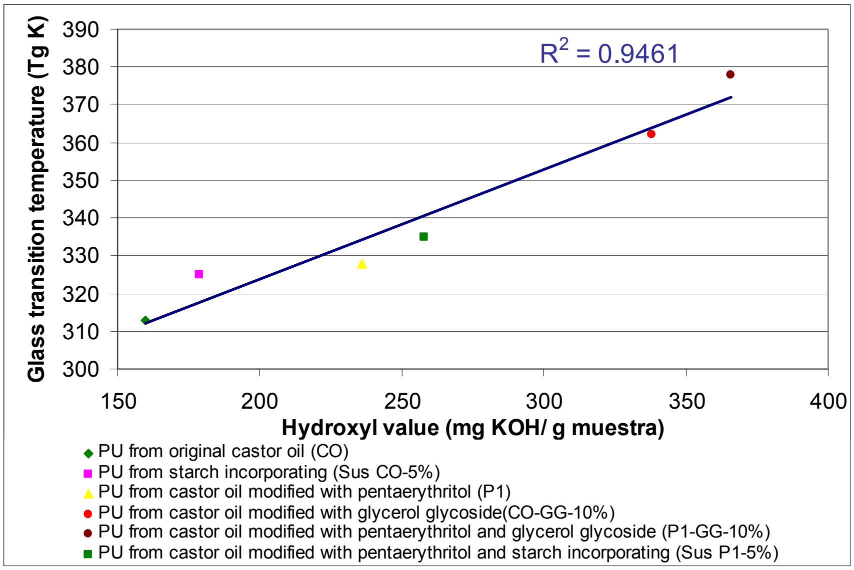


The Figure 5 shows the dependence between the glass transition temperature determined by DMTA and the number of hydroxyl groups of polyol, for polyurethanes obtained from the original castor oil and castor oil modified by the routes raised. We found a linear relationship between the hydroxyl value of the polyols and the glass transition temperature, with a correlation parameter of 0,946. By increasing the crosslinking density increases Tg due to increasing restrictions on the movements of the chains. Petrovic and colleagues reported a similar result for different polyols derived from vegetable oils [5]. Polyurethanes with high crosslinking density are obtained from polyols with high functionality. For the other hand, soft and elastic polyurethanes are obtained from polyols with low hydroxyl value [6]. Using the results of Figure 5, its possible predicts the values of the crosslinking density of the PU with the hydroxyl value of the polyol (for a given relationship NCO / OH).

Conclusions

Polyurethane networks prepared from IPDI and castor oil modified by transesterification with pentaerythritol and by reaction with starch glycosides showed excellent chemical resistance, hardness and tensile strength properties compared to the ones synthesized from unmodified castor oil. All materials prepared showed a uniform polyurethane phase without any presence of starch particles which indicates that polyol-glycosides of high hydroxyl content have been effectively reached and reacted to obtain a network formation in which starch glycosides are chemically incorporated. The degree of crosslinking in these networks can be controlled according to the type of polyol-glycoside used, which gives higher levels when glycerol is employed instead of ethylene glycol.

Figure 5. Dependence between the glass transition temperature determined by DMTA and the number of hydroxyl groups of polyol



References

1. Ho¨ffer, P., Daute, P., Gru¨tzmacher, R. and Westfechtel, A. **(1997).** *Journal Coatings and Technology*, 69(869): 65–72.
2. Carraher Jr, C.E. and Sperling, L.H. **(1981).** p. 304, Plenum Press, New York.
3. Yenwo, G.M., Manson, J.A., Pulido, J., Sperling, L.H., Conde, A. and Devia, N. **(1977).** *Journal of Applied Polymer Science*, 21(6): 1531–1541.
4. Athawale, V. and Kolekar, S. **(1998).** *European Polymer Journal,* 34: 1447–1451.
5. Petrovic´, Z.S. and Fajnik, D.J. **(1984).** *Journal of Applied Polymer Science,* 29: 1031–1040.
6. Sonal, D., Thakore, I.M., Sarawade, B.D. and Devi, S. **(2000).** *Polymer Engineering and Science,* 40(5): 1200.
7. Seung Kyu, H. and Broecker, H. **(2003).** *Macromolecular Materials and Engineering,* 288(7): 569–577.
8. Siddaramaiah, J. and Kendaganna, B. **(2003).** *Journal Applied Polymer Science*, 90: 2945–2954.
9. Cao, X. and Zhang, L. **(2005).** *Biomacromolecules,* 6: 671–677.
10. Otey, F.H., Bennet, F.L., Zagoren, B.L. and Mehltretter, C.L. **(1965).** *Product Research and Development*, 4: 224–227.
11. Carr, M.E. **(1991).** *Journal of Applied Polymer Science,* 42: 45–53.
12. Prashantha, P., Vasanth Kumar Pai, K., Sherigara, B.S. and Prasannakumar, S. **(2001).** *Bulletin of Materials Science,* 24(5): 535–538.
13. Kaushik, A. and Paramjit, S. **(2005).** *International Journal of Polymer Analysis and Characterization,* 10: 373.
14. Alvaro Ramírez, Manuel F. Valero, Jorge E. Pulido, Zhengdong Cheng **(2008).** *Journal of Elastomers and Plastics.* DOI: 10.1177/0095244308091785.